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Life Cycle Assessment of nano-TiO_2 functionalized building materials extended to historical buildings

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A Emma

Sarà difficile lasciarti al mondo e tenere un pezzetto per me
e nel bel mezzo del tuo girotondo non poterti proteggere.
Sarà difficile ma sarà fin troppo semplice mentre ti giri
e continui a ridere.

& Giovanni

Because I don't want you to forgive me,
You'll follow me down, you'll follow me down,
You'll follow me down
Survive tonight, I see you're head's exposed
So we shall kill constructive might, s' right
As your emotion fool you, my strong will rule.

Abstract

Industry is rapidly developing engineered nanoparticles (ENPs) that are applied in a more and more wide variety of consumer and industrial products. Thanks to the unique physical and chemical properties of nanoparticles it is possible to obtain innovative applications. Nanoparticles gain novel properties (self-cleaning, antibacterial, anti-fogging, lightness, mechanical strength, durability, fire resistance and etc.) compared to the corresponding bulk material, thanks to their small dimensions, which range approximately from 1 to 100 nm. Thereby, ENPs have been recently used in a wide number of construction uses, such as inclusion of or coating with specific nanoparticles into building materials in order to obtain glazing, ceramic, resin, paint, glaze, concrete etc. with additional and superior properties.

This uncontrolled growth of ENPs employment is leading to an inevitable release of these materials into the environment. This rises the necessity to assess the potential risks that these new materials provoke to human health and environment. Life Cycle Assessment (LCA) methodology has been recognized as a key tool for assessing the environmental performance of nanoproducts. Release of ENPs into the environment can potentially occur throughout their entire life cycle: from the ENPs manufacture to the use and end of life phases. However, there are currently no indicators to evaluate the potential damage on human health and on the environment generated by the nanoparticles emissions during all their critical life cycle steps (e.g. nanoparticle application, installation, use and end of life). Therefore, a clear toxicological characterization is a prerequisite in order to establish trustworthy characterization factor (CFs) for the assessment of releases of nanoparticles in the LCA methodology. One of the aims of this thesis is to provide a methodological framework to identify human health CFs and to show its application for one of ENPs commonly used in construction field, namely titanium dioxide nanoparticles (nano-TiO_2). These indicators have been validated on four LCA case studies of the ecodesign of nano-TiO_2 functionalized building materials, in particular float glass, polyurea resin, ceramic glaze, porcelain stoneware tile. Furthermore, the LCA study of the nano-TiO_2 production have been performed. Considering a bottom-up hydrolytic synthesis. Finally, the environmental performance of these nano-TiO_2 functionalized building materials embedded, during a restoration process, into an historical building has been assessed. Nowadays, building materials functionalized with ENPs are largely used in both new and historical building restoration, due to their additional properties they enable the reduction of many hot spots that characterize the use phase of a building that is mainly affected by the energy and environmental loads, namely the use phase. Regarding historical buildings, nowadays, the sustainability assessment in the cultural heritage field has not yet been investigated. In particular social, cultural and historical aspects are not still taken into account in the LCA studies. At the present, there are also no indicators which enable to model the social sustainability of historical buildings. For this reason, another goal of this thesis is to fill up this gap integrating social, cultural and historical issues into the LCIA (Life Cycle Impact Assessment) phase. In this way it is possible to have an holistic view of all benefits and impacts generated by the restoration/retrofit activities of an historical building. The final purpose of this thesis is to assess, using LCA methodology, the environmental burdens of the restoration of an historical building considering both nanotoxicological, social, cultural and historical indicators.

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Summary

1 Buildings and their environmental impacts

Finding an appropriate compromise between the anthropological human activities, that however lead to technological advantages, and the environmental protection is nowadays one of the great problem that humanity have to face. Over the two past century, the world has undergone very significant changes due to human activities, economic contingency and social processes. Humanity's use of natural resources (Ecological Footprint) has been exceeding the regenerative capacity of the Earth since the 1980s, causing so an overshoot which prevents the biocapacity to regenerate natural resources that at the same time are consumed. For this reason, in recent years, the Ecological Debt Day (Global Footprint Network, 2011) has been established in order to monitor the humanity's resource consumption that exceeds Earth's capacity that can regenerate those resources in one year. Energy production to satisfy the present demand, urbanization processes affecting even concentration always more increasing of population ratio (global human population may attain 9.6 billion by 2050 (UN, 2013), agriculture development which is essential to meet the growing food needs, standard of living increasing and many other factors related to the population growth and technological development lead to several environmental and energy problems to our planet. These are some examples of the causes that determinate the environmental impacts.

In addition, the construction sector increasingly affects the energy consumptions and the quality and/or quantity of materials used, and consequently the environmental impacts resulted. In this sector a reduction of energy consumption and a regulation of non-renewable resources exploitation are important points on which it is necessary to face. The design systems implementation, which take into account both energy and materials (amount and typology) used during the building lifetime, together with the construction systems optimization, which allows to obtain the largest energy savings and minimize the environmental loads, become essential aspects of eco-design for both building material components and for the whole building. The characteristic elements of an eco-sustainable design should moreover be extended to a sustainability assessment over the time. Therefore, the environmental impacts should be analyzed in the previous steps such as gathering and manufacturing of raw materials, which are necessary for the technological elements production, and at the end of life cycle as demolition, disposal and/or recycling steps of materials and components (Callegari, 2008). Hence, the construction process must be reviewed adopting new basis and new scenarios that take into account a complete vision over the time able to evaluate the whole life of building. The prospective must change moving from the solely construction design to the assessment of the entire life cycle of building, in which the temporal dimension plays a fundamental role in the decision making and in the design phase. Indeed, the duration and the maintenance program play a decisive role on the building life cycle from earlier life cycle stages. Life Cycle Thinking (LCT) can be a suitable approach in support of this way of analyzing the construction design process, by means of which it is possible consciously perform actions or make decisions in respect to the whole building lifetime. LCT considers all building life cycle aspects that are connected with the surrounding environment or adjacent systems and assess the interaction with social, cultural, economic and environmental spheres (Monticelli, 2013). In this context, in order to address the environmental considerations and to improve the sustainability in the construction sector, it is growing the need of a tool to assess the environmental performance of a building materials component or of the entire building and also to facilitate the decision making process. There are many methods available to achieve these aims within the building sector. The LCA (Life Cycle Assessment) methodology is a reference point for the detailed quantification of the environmental

impacts related to a product and to a building along their entire life cycle. The assessment includes the determination of input (materials and energy) and output (emissions and waste materials) flows; extraction and processing of raw materials; manufacturing, transportation and distribution; building construction; use, reuse, maintenance and final treatment (recycling or waste disposal). LCA methodology consists of four distinct analytical steps: defining the goal and scope; creating a detailed life-cycle inventory, quantifying all input and output flows, which are translated in environmental impacts by the characterization phase (global warming, ozone depletion, etc.) and successively are turned into a score that considers the damage severity in a specific geographic area; and finally interpreting the results (Monticelli, 2013). Figure 1.1 shows the application of LCA to the construction industry reported in Ortiz et al. study (Ortiz, et al., 2009), in particular for the Whole Process of the Construction (WPC), for example in urban constructions of dwellings, commercial buildings and other civil engineering constructions and for the Building Materials Component Combinations (BMCC).

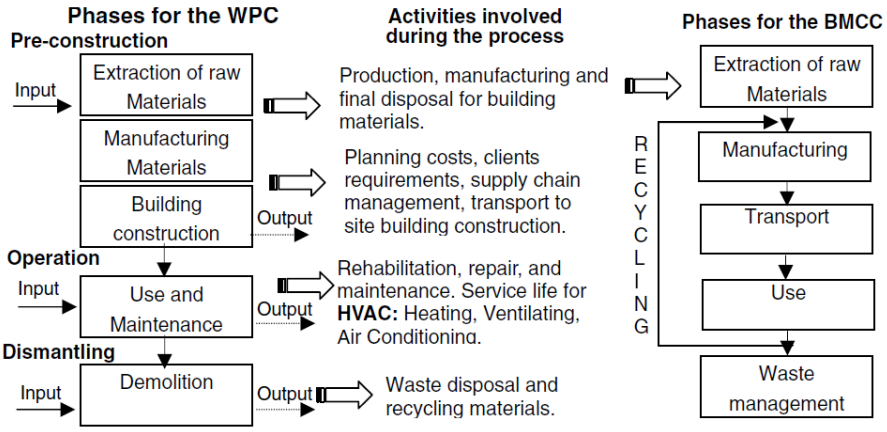

Figure 1-1 Schematic representation of the building life cycle (Ortiz et al., 2009)

The first approach assesses the entire life cycle of a build going from extraction of raw materials to demolition step and further waste treatment of all building components. Alternatively, the second methodology based on building materials components, which examines the reuse and/or recycling of construction materials and the implementation of eco-materials, has been gaining the attention of academics and researchers. The choice of the materials to be employed and of the industrial building processes to be adopted in the construction phase, is becoming essential to limit the associated environmental impacts. Hence, it would be worth evaluating, in a predictive way, the environmental convenience adopting materials derived from recycling, reusing and recovering of building materials and industrial building processes to better ensure an environmental performance. Moreover, the increasing attention on eco-materials has led to the development of new materials with low environmental loads during their entire life cycle. Smart building materials such as titanium dioxide in nanoparticle form. Nanotechnology can enable the construction industry to produce new building materials, with higher technological properties. Due to the increasing use of nanoparticles in the construction sector, it would be important to examine the life cycle, effects and risk assessment that nanoparticles have on humans and on the built environment (Ortiz et al., 2009), thus allowing to balance the benefits of using advanced technology materials and the environmental risk provoked by nanoparticles to human and the environment.

2 Nanoparticles in the construction sector

Nanomaterials with unique physical and chemical properties are increasingly being used by the construction industry to enable novel applications. In fact, nanomaterials gain novel properties compared to the corresponding bulk material, thanks to their small dimensions, which ranges approximately from 1 to 100 nm. Therefore, nanotechnology permits to develop new building materials with higher and advanced technology properties, such as self-cleaning, anti-purifying, anti-fogging, lightness, mechanical strength, more durable, fire-resistant and the main consumption sources. Moreover, nanoparticles application allows energy saving, as they reduce heating, lighting, and air conditioning. Table 1 summarizes some nanoparticle applications in the construction industry, including high performance structural materials, multifunctional coatings and paintings, sensing/actuating devices (Lee et al., 2009 and 2010).

Table 1 Selected Nanomaterial Applications in the Construction Industry (Lee et al., 2009 and 2010).

Construction Materials	*Nanomaterials*	*Expected benefit*	*References*
Concrete	Carbon Nanotubes SiO_2 Fe_2O_3	Reinforcement Crack Hindrance	(Li, 2004) (Sobolev et al., 2005)
Steel	Copper nanoparticles	Weld Ability Corrosion Resistance	(Ge & Gao, 2008)
Window	TiO_2 SiO_2	Self-Cleaning Anti-Fogging Self-sterilizing UV and Heat Blockings Fire-Protective	(Kontos et al., 2007) (Mann, 2006) (Paz et al., 1995)
Coatings/ Paintings	TiO_2 Silver Nanoparticles	Anti-Fouling Self-Cleaning Self-Sterilizing Anti-Fogging Biocidal Activity	(Irie et al., 2004) (Kumar et al., 2008)
Solar Cells	Dye/TiO_2 C60 and Carbon Nanotubes CdSe Quantum Dots	Solar Energy Utilization	(Brown et al., 2008) (Girishkumar et al., 2005) (Zhu et al., 2004)
Cement	Carbon Nanotubes Polypropylene Nanofiber	Strength Fire Resistance	(Mann, 2006)
Sensor	Carbon Nanotubes	Real-Time Monitoring of Structures	(Zhang et al., 2006)
Ceramics	Carbon Nanotubes SiO_2	Enhance mechanical and thermal properties Fire Resistance Light transmission	(Luo et al., 2004) (Becher, 1991) (Pishch et al., 2007) (Gerasimov et al., 2004)

The main nanomaterials used in construction sector and the expected benefits are (NanoWerk, 2014):

- Carbon nanotubes: mechanical durability and crack prevention; enhanced mechanical and thermal properties; real-time structural health monitoring; and effective electron mediation.

- Silicon dioxide (SiO_2) nanoparticles: reinforcement in mechanical strength; coolant, light transmission, and fire resistance (in ceramics); flame-proofing and anti-reflection.
- Titanium dioxide (TiO_2) nanoparticles: rapid hydration, increased degree of hydration, and self-cleaning; superhydrophilicity, anti-fogging, and fouling-resistance; non-utility electricity generation.
- Iron oxide (Fe_2O_3) nanoparticles: increasing compressive strength and abrasion-resistant.
- Copper nanoparticles: weldability, corrosion resistance, and formability.
- Silver nanoparticles: biocidal activity.
- Quantum dots: effective electron mediation.

Some representative application of nanoparticles used in the building sector and reported by Lee J. et al. (Le et al., 2009) are:

- Concrete: undergoes strong enhancement in mechanical properties by the addition of carbon nanotubes or SiO_2 or Fe_2O_3 nanoparticles to the concrete mixtures consisting of binding phase and aggregates. Addition of 1 wt% carbon nanotubes efficiently prevents crack propagation in concrete composites by functioning as nucleating agents. Addition of 3 to 10 wt% SiO_2 and Fe_2O_3 nanoparticles function as filling agents to reinforce concrete.
- Steel: the introduction of metal nanoparticles enable the metal to improve strength, formability, and corrosion resistance. Particularly, nanosized copper particles reduce the surface roughness of steel to impart higher weldability and anti-corrosion activity.
- Glazing: can accomplish various additional functions by incorporation of TiO_2 and SiO_2 nanoparticles. TiO_2 coated on glass photochemically generates reactive oxygen species (ROS) with sunlight or indoor light, effectively removing dirt and bacterial films attached on window. Light-excited superhydrophilic properties of TiO_2 make glass anti-fogging, self-sterilizing and self-cleaning by decreasing contact angle between water droplet and the glass surface. The insertion of SiO_2 nanoparticles between two glass panels can make windows highly fireproofing.

Furthermore, one of the major nanomaterials application in the construction sector are coatings:

- Coatings: nanocoatings typically make use of one nanomaterial to introduce specific and advance functionality and then change the coating base to allow for the application on a large variety of substrates. TiO_2 and silver are the main nanoparticle types that are applied on a surface to create the nanofilm. TiO_2 in nanoparticle form optimizes its photocatalytic and superhydrophilic properties and confer to the surface self-cleaning, anti-fogging, and self-sterilizing. Silver nanoparticles have unique properties of high antimicrobial activity.

3 Nanomaterials

3.1 Definition

The concept of nanotechnology was born theoretically in 1959, by Feynman during his speech at the annual meeting of the American Physical Society on December 29, 1959 (Drexler, 2009). He received the Nobel Prize in Physics in 1965 for his contributions to the development of quantum electrodynamics, together with Julian Schwinger and Sin-Itiro Tomonaga. Feynman considered the possibility of direct manipulation of individual atoms as a more powerful form of synthetic chemistry than those used at the time. The talk is considered to be a seminal event in the history of nanotechnology, as it inspired the conceptual beginnings of the field decades later (Feynman, 1960 and Wikipedia, 2014a). Over the past decade, the focus of nanotechnology has extended beyond physics and precision engineering to include "almost any materials or devices which are structured on the nanometre scale in order to perform functions or obtain characteristics which could not otherwise be achieve" (Whatmore, R. W. and Sweeney, 1995).

Over the last years, several international committees and organisations provided definitions, working definitions, guidance and other documents addressing the issue of nanomaterial definition and nanotechnology terminologies. Many of these documents are opinions or recommendations on a definition of nanomaterial and are therefore non-normative documents. Although many of the documents referred to below use the same term 'nanomaterial' it should be kept in mind when comparing those documents that these definitions and criteria used to describe certain materials have been developed for different purposes (Rauscher et al., 2014). For example, ISO/TS 80004-1 defined a "nanomaterials" as the material with any external dimension in the nanoscale (size range from approximately 1 nm to 100 nm) or having internal structure or surface structure in the nanoscale. OECD (Organisation for Economic Co-operation and Development) states "a nanomaterial or a nanoparticle is usually considered to be a structure between 0.1 and 100 nm". SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks) of European Commission (EC) declared in this issue that the definition of "nanomaterial" should use the number based particle size distribution and not the mass fraction, as a minimal fraction of the mass could contain large numbers in the low size range, while a low number of large sized particles would represent most of the mass. Moreover, the Committee concluded that it is important to consider the "whole nanoscale metric: 1 nm to 999 nm" when deciding for an approach for the risk assessment of nanomaterials. The Nanotechnology Panel of the American Chemistry Council (ACC) presented a comparative assessment of regulatory definitions of nanomaterials and made recommendations on the key aspects that should be included in all regulatory definitions. The panel directed the following core elements in a regulatory definition of "nanomaterial": solid, particulate substances; distributional threshold of 10 wt% by weight; continued use of 1-100 nm to define nanoscale; exclude naturally occurring and incidentally produced nanomaterials; describe the characteristics of solubility that make it biologically relevant; focus on materials with novel properties not present in non-nano forms; and differentiate between aggregates and agglomerates, and consider the potential for these structures to break down into nanoscale particles. Lastly, the European Commission defined "nanomaterials" as "a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 wt% or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm -

100 nm". Within this thesis, the terms Engineered Nanoparticles (ENPs) and/or Engineered Nanomaterials (ENMs) are used following ISO/TS 80004-1 definition.

Nanoparticles can be classified, depending on the origin, into three types (Tiwari, A. and Turner, 2014): natural, incidental and engineered. *Natural* nanoparticles have existed from the beginning of the earth's history and still occur in the environment, such as volcanic dust, dust storms, forest fires, mineral composites, ocean and water evaporation, etc. *Incidental* nanoparticles are formed as result of anthropogenic activities (industrial processes), such as diesel and engine exhaust, coal combustion, welding fume, cigarette smoke, building demolition, etc. *Engineered* nanoparticles can be classified into the following classes (Tiwari, A. and Turner, 2014 and Salieri, 2013):

1) Carbon based materials, which includ Fullerene (C_{60}) and carbon nanotubes (CNTs). Two types of CTNs can be distinguished single-walled: carbon nanotubes (SWNTs) and multi-walled carbon nanotubes (MWNTs). SWCNTs are structurally single-layered graphene sheets rolled up in cylindrical shapes of approximately 1 nm diameter and several micrometers of length, whereas MWCNTs possess two or more concentric layers with varying length and diameters.
2) Metal-based materials, such as quantum dots, nanogold, nanozinc, nanoaluminium and nanosilver.
3) Dendrimers which are multifunctional and nanosized polymers built from branched units and capable of being tailored to perform specific chemical reaction.
4) Composites which combine nanoparticles with other nanoparticles and present different morphologies such as sphere, tubes, rods and prims.
5) Quantum dots, which are a closely packed semiconductor crystal comprised of hundreds or thousands of atoms, and whose size is on the order of a few nanometers to a few hundred nanometers. Usually they are nanoparticles made of semiconductor materials with fluorescent properties, crucial for biological applications.
6) Zerovalent metals, usually prepared by reduction of metal salts, e.g. zerovalent iron is made through the reduction of ferric (Fe^{3+}) or ferrous (Fe^{2+}) salts with a sodium borohydride. Similarly, the chemical synthesis of gold and silver ENPs involves dissolution of the metal salt in an appropriate solvent and its subsequent reduction to the zero valency.

Nanoparticles can be found in three different dimensions (Figure 3.1) (Schodek et al., 2009 and Gusev, 2014):

- Zero-dimensional nanomaterials are materials wherein all the dimensions are measured within the nanoscale and include nanocluster materials and nanodispersions, i.e. materials in which nanoparticles are isolated from each other.
- One-dimensional (1D) nanomaterials are materials with one dimension that is outside the nanoscale nanofibre (nanorod) and nanotubular materials with fibre (rod, tube) length from 100 nm to tens of microns.
- Two-dimensional (2D) nanomaterials are materials with two dimensions in the nanometer scale and are nanofilms, nanolayer and nanocoatings.
- Three-dimensional (3D) nanomaterials are bulk nanomaterials namely materials that are not confined to the nanoscale in any dimension. They include powders, fibrous, multilayer and polycrystalline materials. An important type of three-dimensional nanostructured materials is a compact or consolidated (bulk) polycrystal with nanosize grains, whose entire volume is filled with those nanograins, free surface of the grains is practically absent, and there are only grain interfaces.

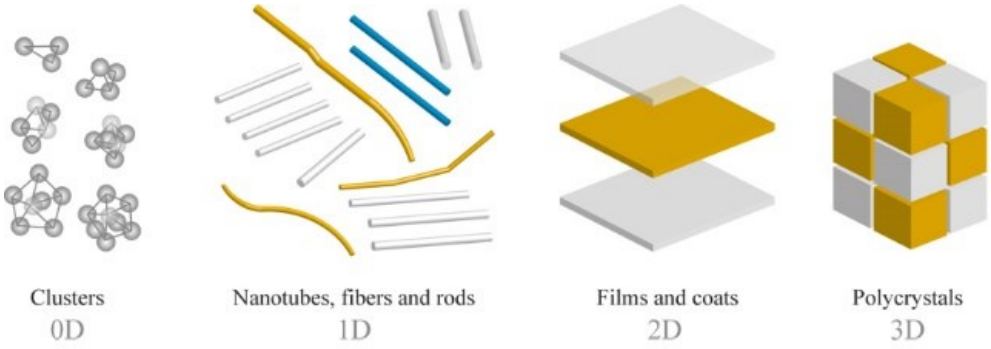

Figure 3-1 Different dimensions of nanoparticles (Gusev, 2014)

The revolutionary perspectives associated to nanotechnology is due to the fact that at these dimension levels, the behaviours and characteristics of material can change drastically. Therefore, nanotechnologies represent a fundamentally new manufacturing way that aims at obtaining materials, structures and devices with new and advantage properties and functionalities.

3.2 Physical and chemical properties

Nanoparticles often have unique physical and chemical properties. For example, the electronic, optical, and chemical properties of nanoparticles may be very different from those of each component in the bulk. At the nanoscale, materials behave very differently compared to larger scales and it is still very difficult to predict the physical and chemical properties of particles of such a very small size. The principal parameters of nanoparticles are their shape, size, surface characteristics and inner structure. Nanoparticles can be encountered as aerosols (solids or liquids in air), suspensions (solids in liquids) or as emulsions (liquids in liquids). In the presence of certain chemicals, properties of nanoparticles may be modified. The composition of a specific nanoparticle can be very complex, depending on what interactions it has had with other chemicals or particles and on its lifetime. The chemical processes taking place on the surfaces of nanoparticles are also very complicated and remain largely unknown.
Table 2 shows the unique physical and chemical properties which enable NMs to be used for various applications.

Table 2 Properties and Common Uses of NMs (EPA, 2010)

Types of NMs (Occurrence)	Example	Physical Properties	Chemical Properties	Uses
Carbon-based (Natural or Engineered)	Fullerenes/Buckyballs (Carbon 60, Carbon 20, Carbon 70); carbon nanotubes; nanodiamonds; nanowires.	They exist as hollow spheres (buckyballs), ellipsoids, tubes (nanotubes); 1nm wires (nanowires) or hexagonal structures (nanodiamonds). Excellent thermal and electrical conductivity;	Carbon-based NMs are stable, have limited reactivity, are composed entirely of carbon, and are strong antioxidants.	Biomedical applications, super-capacitors, sensors, and photovoltaics.
Metal Oxides (Natural or Engineered)	Titanium dioxide (TiO_2); zinc oxide (ZnO); cerium oxide (CeO_2).	Some have photocatalytic properties, and some have ultraviolet (UV) blocking ability. When used in sunscreen, nano-TiO_2 and nano-	High reactivity; photolytic properties.	Photocatalysts, pigments, drug release, medical diagnostics, UV blockers in sunscreen, diesel fuel

		ZnO appear transparent when applied on skin.		additive, and remediation.
Zero-Valent Metals (Engineered)	Nanoscale zero-valent iron (nZVI), emulsified zero-valent iron (EZVI), and bimetallic nanoscale particles (BNPs). BNPs include elemental iron and a metal catalyst (such as gold, nickel, palladium, or platinum)	Between 1 to 100 nm or greater, depending on the NM-type containing the zero-valent metal. Properties can be controlled by varying the reductant type and the reduction conditions.	High surface reactivity. Popular starting materials used in production include: ferric (Fe [III]) or ferrous (Fe [II]) salts with sodium borohydride.	Remediation of waters, sediments, and soils to reduce contaminants such as nitrates, trichloroethene, and tetrachloroethene.
Quantum Dots (Engineered)	Quantum dots made from cadmium selenide (CdSe), cadmium telluride (CdTe), and zinc selenide (ZnSe).	Size: 10 to 50 nm. Reactive core controls the material's optical properties. The larger the dot, the redder (lower energy) its fluorescence spectrum.	Closely packed semiconductor whose excitons (bound electron-hole pairs) are confined in all three spatial dimensions. Possible metal structures include: CdSe, CdTe, CdSeTe, ZnSe, InAs, or PbSe, for the core; CdS or ZnS for the shell.	Medical imaging, photovoltaics, telecommunication, and sensors.
Dendrimers (Engineered)	Hyperbranched polymers, dendrigraft polymers, and dendrons.	Size: 2 to 20 nm. Highly branched polymers. Common shapes include cones, spheres, and disc-like structures.	Highly branched; multi-functional polymers.	Drug delivery, chemical sensors, modified electrodes, and DNA transferring agents.
Composite NMs (Engineered)	Made with two different NMs or NMs combined with nanosized clay. They can also be made with NMs combined with synthetic polymers or resins.	Composite NMs have novel electrical, magnetic, mechanical, thermal, or imaging features.	Multifunctional components; catalytic features.	Potential applications in drug delivery and cancer detection. Also used in auto parts and packaging materials to enhance mechanical and flame-retardant properties.
Nanosilver (Engineered)	Forms include colloidal silver, spun silver, nanosilver powder, and polymeric silver.	Size: 10 to 200 nm. Made up of many atoms of silver in the form of silver ions.	High surface reactivity; strong antimicrobial properties.	Medicine applications, water purification, and antimicrobial uses. They are used for a wide variety of commercial products.

Different in *vivo* or in *vitro* studies highlighted the possibility to obtain potential adverse effects (nephrotoxic, genotoxic and reproductive effects, granulomas and tumoural reactions in lungs and translocation to other tissues or organs depending on the different physical and chemical nanoparticles properties (INAIL, 2010). These is enable an appropriate assessment of the potential exposure risk and the definition of prevention and protection measures for minimizing the human health and the environmental impacts.

3.3 Environmental exposure

The essence of nanotechnology is the synthesis of ENMs that exhibit characteristics, such as small size, large surface area to mass ratio, shape, crystallinity, surface charge, reactive surface groups, dissolution rate, state of agglomeration, or dispersal that confer them properties substantially different from those of the bulk particles of the same composition (Iavicoli et al., 2011). These properties offer great opportunities for the development of new ENMs industrial applications increasing their worldwide distribution and use. This has increased the probability of ENMs (accidental or incidental) release into the environment and thereby human exposure at different stages of their life cycle. ENMs have been highlighted as a group of materials that may have potentially adverse effects on human health and environment. However, research on human and environmental toxicity (i.e. ecotoxicity) of this group of materials has only recently started, drawing

upon existing knowledge in toxicology, ecotoxicology and environmental sciences in an attempt to predict potential future problems related to spreading of engineered nanoparticles in the environment (Klaine et al., 2012 and Kahru et al., 2013). Release of ENMs into the environment can potentially occur throughout their entire life cycle (Figure 3.2): from the fabrication of ENMs, to the use and end of life phases (Som et al., 2010). Risks from releases of nanoparticles may emerge if both exposure (due to the presence of nanoparticles in the environment) and hazard (in the form of toxic effects) are observed (Gottschalk et al., 2013).

Once in the environment, ENMs may undergo diverse physical, chemical, and biological transformations that change their properties, impact, and fate. Thus, a holistic ENMs lifecycle exposure profiling is essential to evaluate potential impacts to human and ecosystem health, as well as to mitigate unnecessary risks. This underscores the need for predictive models for multimedia fate and transport of ENMs and analytical methodologies to quantify ENMs (and their form) in environmental matrices. Currently, quantitative information on ENMs sources dynamics and exposure pathways remain relatively scarce, and there is concern that the current headlong rush into nanotechnology applications in construction may impede proactive exposure assessment (Lee, 2009). Therefore, understanding the environmental exposure and toxicity of ENMs provides the basis for assessing the environmental risks posed by these compounds (Sun et al., 2014). To address the potential influence of nanomaterials on the environment, assessment of their physiochemical properties is needed to determine their fate, mobility, degradation, persistence, and bioavailability. The biological effects and the detection of nanomaterials in nature and in any environmentally exposed species, including humans, are also essential elements to consider. Nanomaterial risk assessment must evaluate the following: the toxicity of particular nanomaterials, the extent of their dispersion in the environment, environmental fate and transport, transformations and modifications in the environment that may affect bioavailability, absorption, and toxicity upon exposure to biological systems, biological and ecological relevance of exposure, acute versus low level chronic exposure, and the ability to determine and measure exposure to the environment and to biological systems. In humans, the extent of exposure in several settings has to be considered. These include exposure from occupational, commercial, and environmental sources. Given the bulk of knowledge needed for a proper assessment of the growth of nanoparticle use and manufacture, it seems that there is always a lag in research as the properties of these nanoparticles are identified (Grassien, 2008).

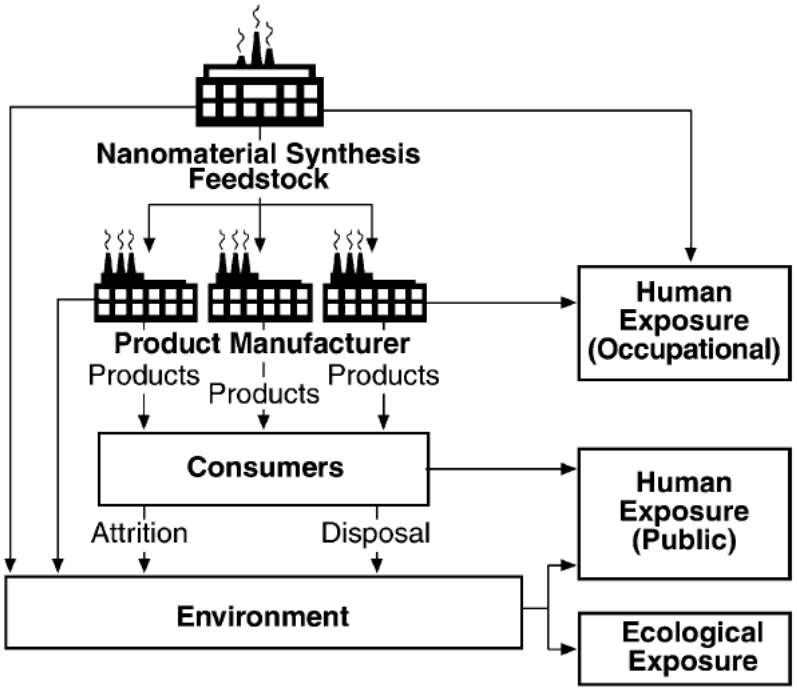

Figure 3-2 Potential for release and exposure to nanoscale substances (Tsuji et al., 2006)

3.3.1 Routes of exposure to nanoparticles

To better understand the toxicological effects associated with human exposure of nanoparticle releases, it is also necessary examine the possible route of human exposure to nanoparticles. The U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a brief summary of nanoparticles as emerging contaminants, including these potential routes (EPA, 2010):

- Human exposure to NPs may occur through ingestion, inhalation, injection, and dermal exposure depending on the source and activities of the person. In the workplace, inhalation is a widely recognized route of human exposure.
- The small size, solubility, and large surface area of NPs may enable them to translocate from their deposition site (typically in the lungs) and interact with biological systems. Circulation time increases drastically when the NPs are water-soluble. With smaller NP sizes, the likelihood of greater pulmonary deposition and potential toxicity exists.
- Studies have shown that NPs, due to their small size, have the potential to pass through both the blood-brain barrier (BBB) and the placenta. For example, a recent study showed that nano-anatase TiO_2 may pass the BBB of mice when injected with high doses.
- Some types of NPs that translocate into systematic circulation may reach the liver and spleen, the two major organs for detoxification and further circulatory distribution. Various cardiovascular and other extra pulmonary effects may occur. In humans, although most inhaled carbon NPs remain in the lung, less than 1 wt% of the inhaled dose may reach the circulatory system.
- Use of sunscreen products may lead to dermal exposure of NPs (TiO_2 and ZnO) depending on the properties of the sunscreen and the condition of the skin. In healthy skin, the epidermis may

prevent NP migration to the dermis. However, damaged skin may allow NPs to penetrate the dermis and access regional lymph nodes, as suggested by quantum dots and nano-Ag.

- Ingestion exposure may occur from consuming NPs contained in drinking water or food (e.g., fish, vegetables, fruit, dairy products).

3.4 Fate and transport

Nanoparticles are generally incorporated in a substrate since it is expected that the substrate with time can be broken down and release nanomaterials in some form, possibly as free particles, into the environment. The production, use, and disposal of nanomaterials is inevitably lead to their entrance and travel through the natural environment (air, water, soil) potentially in different ways than larger particles. Once in the environment, a number of factors may sequester, modify, mobilize, or degrade nanomaterials, thereby influencing their bioavailability and potential toxicity. In order to determine the extent of human and environmental exposure to ENMs, knowledge on their environmental behavior is required, however until now, only a limited number of environmental fate studies with ENMs have been reported (Garner & Keller, 2014). So far, only few multimedia models that account for nano-specific fate processes in order to assess the predicted environmental concentration and with that, the potential human and environmental exposure, have been published (Meesters et al., 2014; Liu & Cohen, 2014; Praetorius et al., 2012; Arvidsson et al., 2011) the latter two referring to the aquatic compartment only.

Modifications greatly influence the behavior of nanomaterials, including their interaction with fauna and flora, accumulation in biological systems, and toxicity (Grassien, 2008). The main characteristics that affect environmental fate and behavior and that should be known are chemical composition, mass concentration, surface area, charge, and chemistry as well as reactivity, particle number concentration, shape, structure, solubility, state of aggregation/agglomeration, size distribution as well as dissolution, stabilization, bioavailability, reactivity, sorption and mobility of nanoparticles. The environmental and health consequences of these materials, their production, and the life-cycle implications of the products have to be carefully considered during the early stages of development. The largely unknown risks to human health and ecosystems presented by nanomaterials have been the subject of considerable speculation. Since sometime may pass before the risks of nanomaterials have to be accurately assessed, an urgent need exists to consider the possible impacts of nanomaterial fabrication and the manner in which conventional chemical feedstocks and wastes are handled (Wiesner et al., 2006). In addition, more knowledge on the fate of the released nanoparticles indoors and outdoors has to be collected, e.g. potential nanoparticle emissions from indoors to outdoors. Accordingly, the fate of the nanoparticles released during the entire life cycle has to be known, including transformation and accumulation patterns (Hischier & Walser, 2012).

Figure 3.3 reports nanoparticles releases to the environment that can be emanated from point sources, such as factories or landfills, and from nonpoint sources, which include wet deposition from the atmosphere, storm-water runoff, and attrition from products containing nanomaterials. As result of biogeochemical weathering nanomaterials can be subjected to a variety of transport and removal processes and physical-chemical transformation, such as aggregation; or uptake, attachment; accumulation, transformation, and degradation in organisms. Nanomaterials in groundwater and surface water used for drinking water is subjected to conventional treatment

methods, such as flocculation, sedimentation, and sand or membrane filtration. Air filters and respirators is used to remove nanomaterials from air (Nancy et al., 2007 and Wiesner et al., 2006).

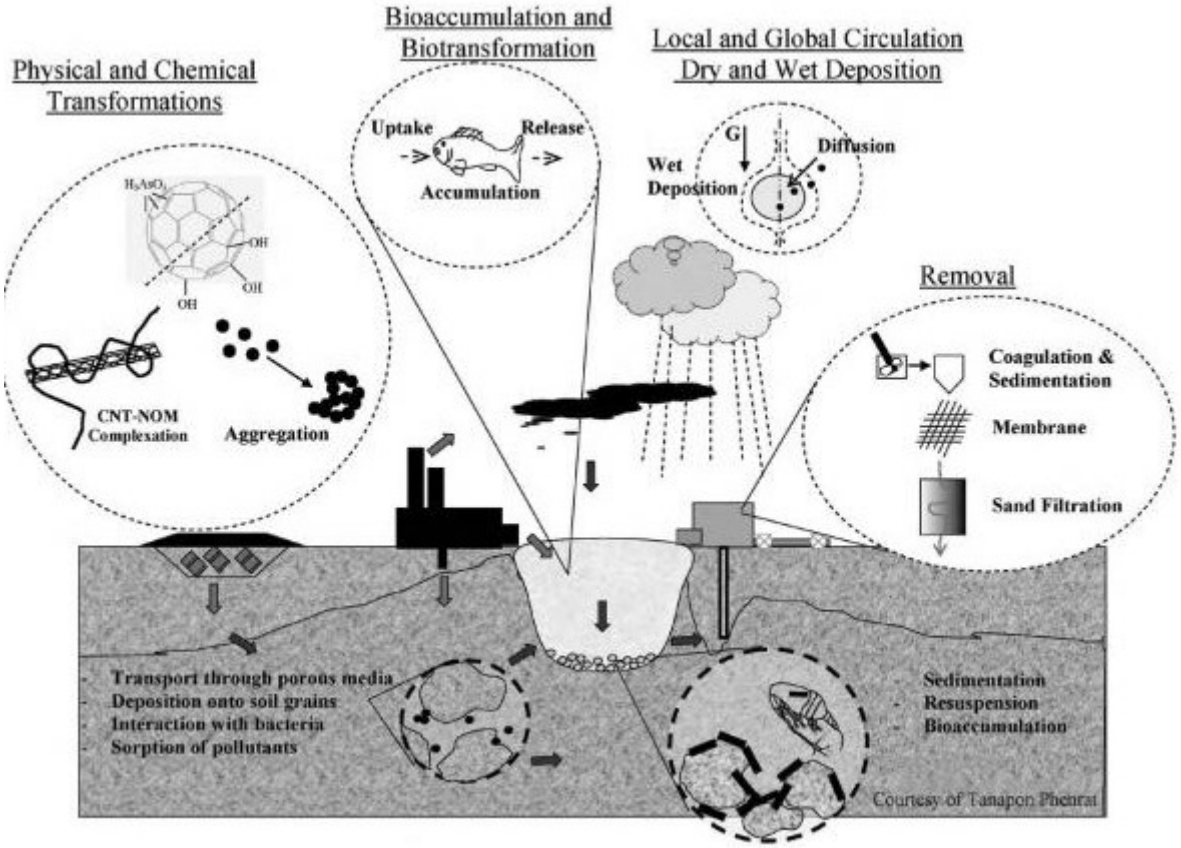

Figure 3-3 Nanoparticles release to the environment (Nancy et al., 2007)

Life Cycle Assessment methodology has been recognized as a key tool for assessing the environmental performance of nanoproducts (Klöpffer et al., 2006), assessing the ENMs releases into the environment that can potentially occur throughout their entire life cycle.

4 Life Cycle Assessment methodology

With the growing of consciousness of the importance of environmental protection in order to reduce the environmental pollutant and saving energy and resources, it has been increasing the interest toward tools and methodology able to better understand and address these impacts. One of the techniques being developed for this purpose is Life Cycle Assessment (LCA). The International Organization for Standardization (ISO), provides guidelines for conducting a Life Cycle Assessment within the series ISO 14040 and 14044.

ISO states that LCA methodology is able to *i*) identify opportunities to improve the environmental performance of products at various points in their life cycle, *ii*) inform decision-makers in industry, government or non-government organizations (e.g. for the purpose of strategic planning, priority setting, product or process design or redesign), *iii*) the selection of relevant indicators of environmental performance, including measurement techniques, and *iv*) marketing (e.g. implementing an ecolabelling scheme, making an environmental claim, or producing an environmental product declaration).

LCA methodology assesses the environmental loads, caused by use of resources, energy and environmental consequences of pollutants released into the environmental compartments, throughout the entire life cycle of a product, service, process. LCA covers all life cycle steps of analyzed system ranging from raw material supply, to manufacturing, use, end of life treatment, recycling and final disposal, considering a *cradle to grave* perspective.

LCA is structured in four phases (Figure 4.1):

1. goal and scope definition
2. inventory analysis
3. impact assessment
4. interpretation

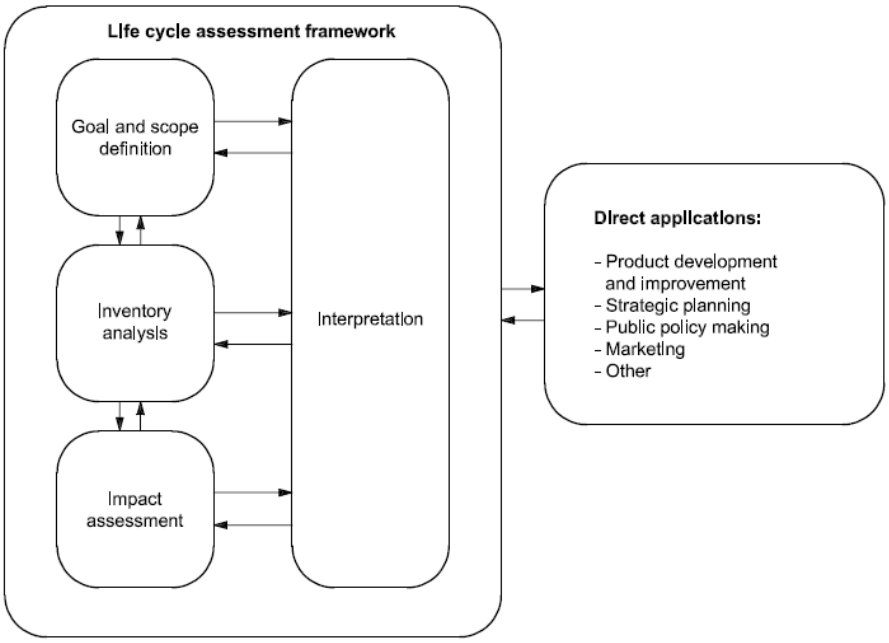

Figure 4-1 Stage of a Life Cycle Assessment (ISO 14040, 2006 and ISO 14044, 2006)

4.1 Goal and scope definition

The definition of the goal and scope of an LCA depends on the analyzed system and the intended use of the study. The depth and the breadth of LCA can differ considerably depending on the goal of a particular LCA. In defining the goal of an LCA, the following items shall be unambiguously stated: the intended application, the reasons for carrying out the study, the intended audience, whether the results are intended to be used in comparative assertions intended to be disclosed to the public. The scope of the study must clearly describe the analyzed system (product, process, service), the function of the product system, the functional unit, the system boundary, the allocation procedure, the data quality, the methodology applied, and finally, the necessary assumptions, and restrictions.

The *functional unit* defines what is studied and plays a reference role to which the input and output data must be normalized in a mathematical sense. The functional unit must be clearly defined and measurable. The *system boundaries* determine which life cycle steps and processes are included and which are excluded within the LCA. Here, the level of detail to which the LCA shall be performed is explained. The system boundaries definition can be helped from a flow diagram use, which specifies the typologies and amounts of input (materials, resources, energies) and output (emissions, waste materials).

The *allocation procedure* carries out the allocation of all inputs and outputs to the different products according to clearly stated procedures that shall be documented and explained together with the allocation procedure. The *data quality* shows its ability to satisfy stated requirements, such as time-related coverage, geographical coverage, technology coverage, measure of the variability of the data, completeness, representativeness, consistency, reproducibility, sources of the data, uncertainty of the information. The *methodology applied* indicates the LCIA methods shall be adopted to perform the impacts assessment. The *assumptions and restrictions* made shall be clearly stated and explained in the first LCA phase.

4.2 Life cycle inventory

Life Cycle Inventory (LCI) is the second phase of LCA and is an inventory of input/output data with regard to the system being studied. It involves the collection of the data necessary to meet the goals of the defined study. The LCI represents the core of LCA, the collection and use of complete and reliable data and the availability of clear explanations of applied assumptions, advantages and disadvantages, as well as caveats to satisfy transparency, acceptability and credibility criteria for such analyses. The qualitative and quantitative data for inclusion in the inventory shall be collected for each process represented in the analyzed LCA and included within the system boundary. The collected data, acquired from several reporting locations and published references, shall be measured in order to reach uniform and consistent understanding of the product systems to be modelled. ISO 14044:2006 suggests that the measures to take into consideration are:

- drawing unspecific process flow diagrams that outline all the unit processes to be modelled, including their interrelationships;
- describing each unit process in detail with respect to factors influencing inputs and outputs;
- listing of flows and relevant data for operating conditions associated with each unit process;
- developing a list that specifies the units used;
- describing the data collection and calculation techniques needed for all data;

- providing instructions to document clearly any special cases, irregularities or other items associated with the data provided.

4.3 Life cycle impact assessment

The third phase of LCA is the life cycle impact assessment (LCIA). LCIA aim at providing additional information to help assess a product system's LCI results so as to better understand their environmental significance. It shall be determined some parameters such as impact categories, damage categories and characterization models are included within the LCA study. LCIA is different from other techniques, such as environmental performance evaluation, environmental impact assessment and risk assessment, since it is a relative approach based on a functional unit. The LCIA phase shall be carefully planned to achieve the goal and scope of an LCA study. The LCIA and all others LCA phases shall be coordinated with each other in order to take into account possible shortcomings, such as the quality of the LCI data; the system boundary and data cut-off decisions have been sufficiently reviewed to ensure the availability of LCI results necessary to calculate indicator results for the LCIA and the environmental relevance of the LCIA results is decreased due to the LCI functional unit calculation, system wide averaging, aggregation and allocation (ISO 14044, 2006).
Hence, the LCIA phase is a collection of environmental effect indicators which come out from different impact categories, which together represent the LCIA profile for the analyzed system. Traditionally, as in many other environmental assessments, LCIA uses linear modeling and takes the effects of the substances into account, but not their background concentrations and the geographical dependency on fate. The method aggregates the environmental consequences over release points in time, release locations and substances (chemicals). This allows calculating potential impact scores, which reflect contributions to environmental burdens (Klöpffer et al., 2006).
There is consensus (ISO 14044, 2006) in distinguishing the four stages of the impact assessment: classification, characterization, normalization and weighting. The first two stages are mandatory elements, whereas the latter two are optional ones.

4.3.1 Mandatory elements of LCIA

The LCIA phase shall include the following mandatory elements:

- **Classification**: assignment of LCI results to impact categories should consider the following: a) assignment of LCI results that are exclusive to one impact category; b) identification of LCI results that relate to more than one impact category, including: distinction between parallel mechanisms (e.g. SO_2 is apportioned between the impact categories of human health and acidification), and assignment to serial mechanisms (e.g. NOx can be classified to contribute to both ground-level ozone formation and acidification).
- **Characterization**: the calculation of indicator results involves the conversion of LCI results to common units and the aggregation of the converted results within the same impact category. This conversion uses characterization factors. The outcome of the calculation is a numerical indicator result. The method of calculating indicator results shall be identified and documented, including the value-choices and assumptions used.

4.3.2 Optional elements of LCIA

Normalization and weighting are optional steps under ISO 14044:2006 to support the interpretation of the impact profile and are steps towards a fully aggregated result. These phases may also be used to define the quantitative cut-off rules and to check the achieved degree of completeness of the data set inventory (JRC-IES, 2010b)

- **Normalization**: calculation of the magnitude of indicator resulted from characterization phase; the indicator results for the different midpoint level impact categories or endpoint level damages are expressed relative to a common reference, by dividing the indicator results by the respective reference value. As reference values typically the impact or damage results of the total annual territorial elementary flows in a country, region, or continent, or globally (or per average citizen, i.e. per capita) are used. For midpoint level results the normalization basis is the overall potential impact, calculated from the annual inventory of elementary flows. For endpoint level results the normalization basis is the overall damage to the areas of protection (JRC-IES, 2010a).
- **Weighting**: adapting and aggregating indicator results across impact categories using numerical factors based on value-choices; data prior to weighting should remain available; In weighting, the indicator results for the different impact categories or damages are each multiplied by a specific weighting factor, that is intended to reflect the relative relevance of the different impact categories (midpoint) and damage category (endpoints) among each other. The identification of a suitable weighting set shall be done, justified, and documented during the initial scope phase of the study and in line with its goal, especially the intended applications and target audience.

A general framework for the impact assessment can be seen in Figure 4.2.

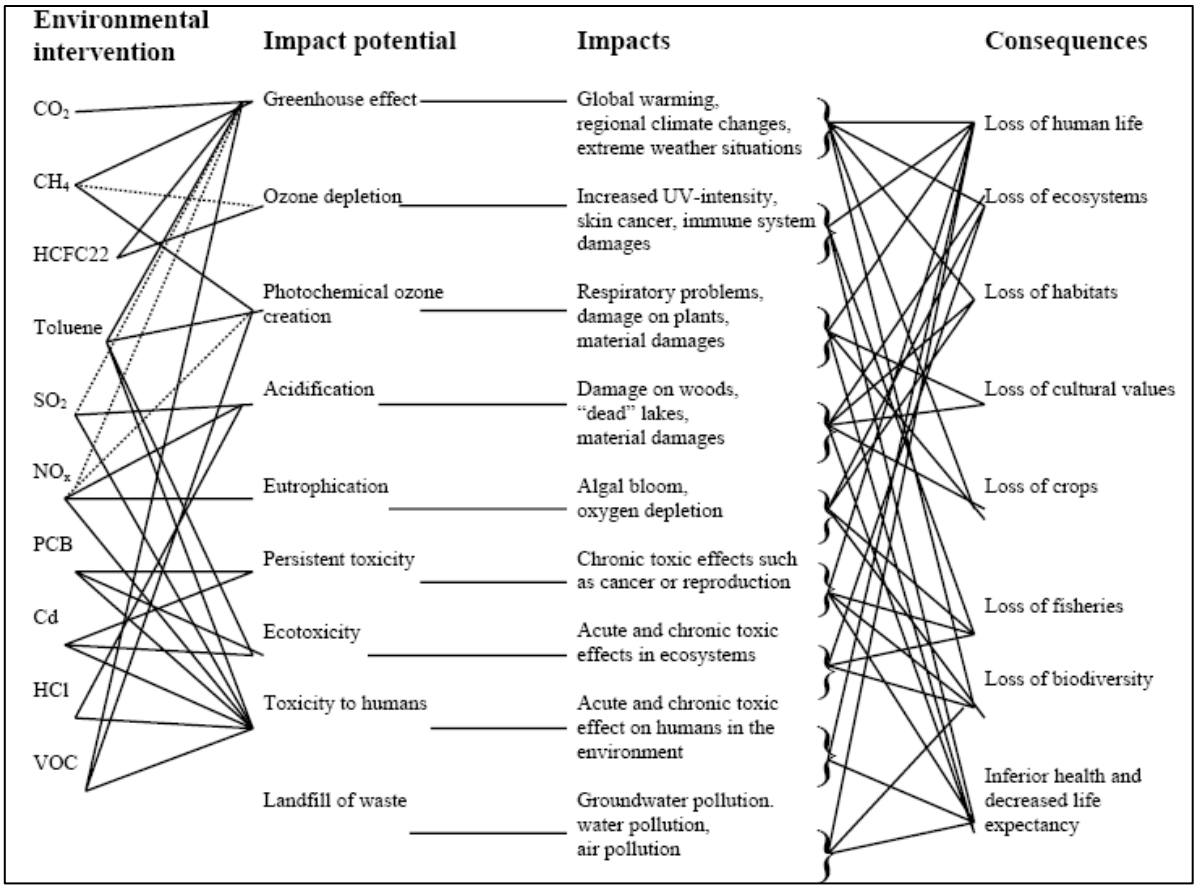

Figure 4-2 The concept of impact assessment: relationship between the life cycle inventory results (environmental interventions) impact potentials (midpoints) and their consequences (endpoints) (Klöpffer et al., 2006).

The LCIA covers both toxic and non-toxic impact categories. Some example of non-toxic impact categories are climate change, acidification, resource depletion. In contrast, carcinogens, human toxicity and ecotoxicity represent the toxic impact categories. Furthermore, the impact categories are distinguished in midpoint or endpoint. The distinction among *midpoint* or *endpoint* categories is based on the point in which the indicator is chosen along the impact pathway. Characterization at *midpoint level* models the impact using an indicator located somewhere along (but before the end of) the environmental impact pathway of a substance. Characterization at the *endpoint level* requires modelling all the way to the impact on the entities described by the Area of Protection i.e. on Human Health, on the Natural Environment and on Natural Resources (JRC-IES, 2010a) (Figure 4.3).

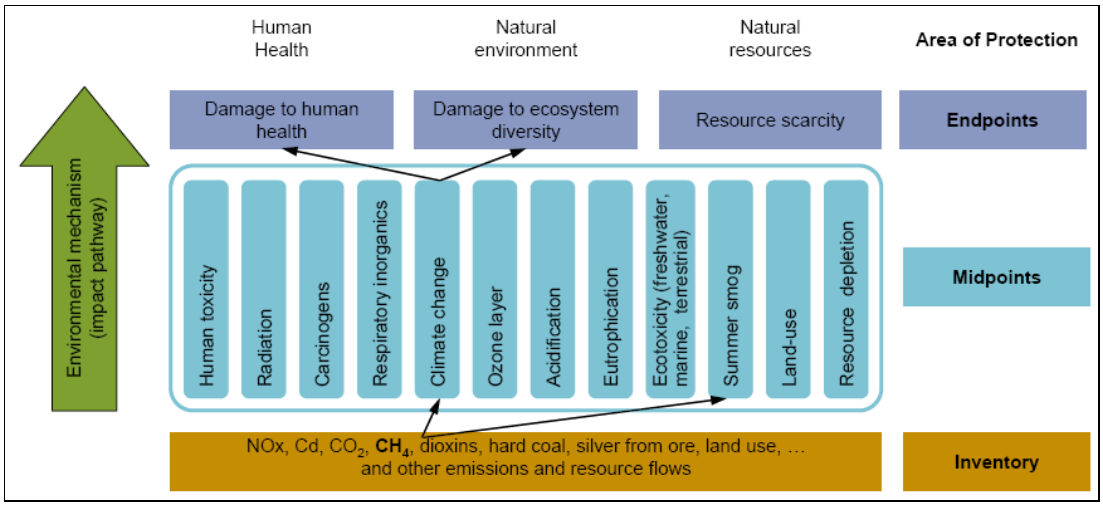

Figure 4-3 Life cycle impact assessment - Schematic steps from inventory to category endpoints (JRC-IES, 2010a).

4.4 Interpretation

The life cycle interpretation phase comprises several elements as follows (ISO 14044, 2006) (see Figure 4.4):

- identification of the significant issues based on the results of the LCI and LCIA phases of LCA;
- an evaluation that considers completeness, sensitivity and consistency checks;
- conclusions, limitations, and recommendations.

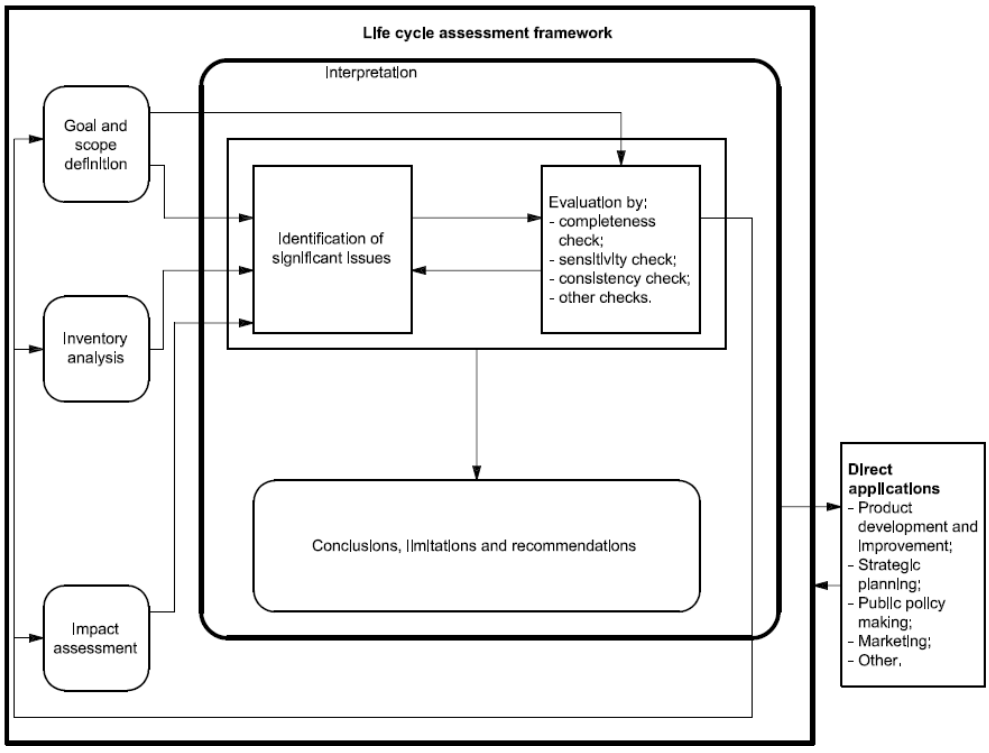

Figure 4-4 Relationships between elements within the interpretation phase

The interpretation should reflect the fact that LCIA results *i*) are based on a relative approach, *ii*) indicate potential environmental effects, *iii*) do not predict actual impacts on category endpoints, the exceeding of thresholds or safety margins or risks. The findings of this interpretation may take the form of conclusions and recommendations to decision-makers, consistent with the goal and scope of the study (ISO 14040, 2006). Life cycle interpretation is also intended to provide a readily understandable, complete and consistent presentation of the results of an LCA and can involve the iterative process of reviewing and revising the scope of the LCA, as well as the nature and quality of the data collected in a way which is consistent with the defined goal. Finally, the findings of the life cycle interpretation should reflect the results of the evaluation element (ISO 14040, 2006).

5 LCA and nanomaterials

5.1 Introduction

Until now, numerous uncertainties regarding the potential NPs impact on the environment and human health are still existing. Therefore, holistic and comprehensive assessment tools such LCA methodology are essential to analyze, evaluate, understand and manage the environmental and health effects of nanotechnology (Klöpffer et al., 2006). However, some issues relating the application of ISO-framework for LCA to nanotechnology field have to take into consideration and needed further precision for their application in this area. In particular, these issues can be summarized in an appropriate definition of functional unit, access to comprehensive and adequate LCI data and the development and embedded in LCIA of characterization factors for nanoparticles impacts on both human health and environment. Despite its uncertain environmental, health and safety impacts, nanotechnology has shown a great potential for "smart" multifunctional and high-performance products for innumerable commercial and industrial applications (Klöpffer et al., 2006), this thanks to the unique NPs properties that make the materials to which are applied quite different than the corresponding bulk counterparts (Gavankar, Suh, & Keller, 2012). However, some tensions between the potential environmental and human health impacts caused by the nanoparticles use and the potential benefits gained from their application may surface. This has been leading to still ongoing controversy on the implications of nanotechnology. Currently, there is significant debate concerning whether nanotechnology or nanotechnology-based products merit special government regulation. This mainly relates to when to assess new substances prior to their release into the market, community and environment (Wikipedia, 2014b). Until now, no recommendations and regulations exist of a proper and safe *i*) production, *ii*) employment and *iii*) final treatment (end of life) of nanoparticles or product containing nanoparticles; neither labelling which may identify that such material contains nanoparticles in order to make, at least, the consumer aware of the contents of the purchased product. Currently, the regulation in nanotechnologies field is obtained through the adaptation (with technical specifications, guidelines etc.) and integration of the existing regulatory framework for the production, use and marketing of chemical substances (REACH[1]) and/or related to occupational safety and health and environmental protection (INAIL, 2010). Therefore, neither engineered nanoparticles nor the products and materials that contain them are subject to any special regulation regarding production, handling or labelling. This results in the fact that the consumers are still not fully aware of the use of nanotechnology in a number of products on the market and neither of the potential risk to which are exposed.

5.2 Goal and scope definition

According to ISO (ISO 14040, 2006), the "scope should be sufficiently well defined to ensure that the breadth, depth and detail of the study are compatible and sufficient to address the stated goal". ENPs feature many specific functions and material properties, resulting in additional gains compared to the traditional material when used as substitute for a traditional material. Hence, when evaluating the environmental benefits, these specific functions and properties have to be taken into

[1] Registration, Evaluation, Authorization and Restriction of Chemicals (REACH) is a European Union regulation. REACH addresses the production and use of chemical substances, and their potential impacts on both human health and the environment.

account as part of the scope. The choice of functional unit is an especially important consideration in order to perform a meaningful LCA of ENPs. The definition of the functional unit becomes more difficult when dealing with ENPs due to the plenty of function and materials properties which can be achieved at the nanoscale (Lazarevic & Finnveden, 2013). Therefore, the ENPs properties or the properties of the matrix within of which ENPs are embedded should be taken into account during the functional unit delineation. Theoretically, the system boundaries determine what processes should be included in an LCA. ISO (ISO 14044, 2006) states that "ideally, the product system should be modelled in such a manner that inputs and outputs at its boundary are elementary flows". Decisions regarding what processes should be included or excluded from a study will ultimately have an influence on the result of the study. Hence, it is important that the models, assumptions and choices made should be transparent (Lazarevic & Finnveden, 2013). The system boundaries can be parted in two typologies: "cradle-to-grave" studies where the LCA covers all life cycle stages from the extraction of raw materials and energy until the end-of-life treatment and "cradle-to-gate" studies which have the gate either on the level of the factory gate of the production site of the engineered nanomaterials or on the level of the factory gate of the nano-enabled product. Hence, the system boundary should include all life cycle processes required to achieve the system function. In nanotechnology field, the system boundaries as well have to take into account the ENPs in an appropriate way and should cover the same functional reality in all scenarios.

5.3 Life Cycle Inventory data of nanomaterials

From the point of view of an impact assessment the more important issue is to have adequate LCI data on a material in order to take the material into account in a more appropriate manner for the support of the decision making of the LCA practitioner (Hischier & Walser, 2012). A critical problem in the gathering of all data necessary to compile the inventory analysis, guaranteeing in this way the use of complete and reliable information and the availability of clear explanations of applied assumptions, advantages and disadvantages, as well as caveats to satisfy transparency, acceptability and credibility criteria for such analyses. In this novel nanotechnology field the main problem is that many of these process data may be subject to confidentiality constraints. Data should be specified according to the goal and scope of the study. For instance, an LCA for a producer of nanomaterials should use company-specific data whenever possible, but an LCA for governmental-strategy determination could be based on sector-wide averages and possibly take into account the future consequences of a decision study (Klöpffer et al., 2006). It remains a problematic task to collect proprietary information from companies, and it is really important that the nanomaterial producers have a comprehensive knowledge of it. It is strongly need the definition of an approach to estimate data which will be implemented in LCA. Therefore, an inventory datasets with a high level of representativeness of a certain engineered nanomaterial would be required.

5.4 Life Cycle Impact Assessment of nanomaterials

The ISO framework for LCA (ISO 14040-44) is fully suitable to nanomaterials and nanoproducts, since environmental impacts of nanoproducts can occur in any life cycle stage (depending on the specific product category and even the specific product), hence the environmental performance of all stages of the life cycle of nanoproducts should be assessed, even if data regarding the elementary flows and impacts might be uncertain and scarce. The production, use and disposal of nanoproducts are associated with the standard impact categories, either at the midpoint level (e.g., climate change,

human toxicity, eco-toxicity and acidification) or at the endpoint level (e.g., human health, ecosystem health and resource depletion) (Klöpffer et al., 2006).
In order to evaluate the human and environmental impacts along the life cycle of a nanoproduct, it is necessary to increase the efforts to determine toxicity factors – indicators to identify and quantify the impacts on human health and ecosystems due to emissions of toxic substances into the environment (Rosenbaum et al., 2011) – for LCIA phase. For the impact categories most frequently used in LCIA, no special difficulties can be foreseen in applying these for the assessment of nanomaterials and nanoproducts. However, for toxicological impacts, the current understanding of effect mechanisms, dose-response relationships, as well as transport and transformations in the environment may not be sufficient to ascertain a representative characterization of nanomaterials. Currently, there is a lack of homogeneity among ENMs toxicological and ecotoxicological studies, so conflicting results regarding potential hazard impede an adequate evaluation of the risks of the respective ENM. For this reason, there is an urgent need in obtaining a database composed of the results of toxicological and ecotoxicological tests in order to achieve a comprehensive set of information useful for ENMs to study potential risk associated to the respective material (Iavicoli et al., 2011).
LCA allows the quantification of potential human and environmental impacts of a product or a system over its entire life cycle (ISO 14040-44). Until now, only 36 LCA case studies of ENMs have been published so far (see chapter 5.5). Currently such LCA studies on ENMs are limited by the still on-going investigations from toxicologists. However, a clear toxicological characterization is in the end a prerequisite in order to establish trustworthy characterization factors[2] (CFs) for the assessment of releases of nanoparticles in the LCA framework (Hischier, 2014). The CF of a substance is developed on the basis of 1) "fate and exposure model" (e.g. USEtox™ 2014; Goedkoop & Spriensma, 2001; Rosenbaum et al., 2008) which calculates the environmental concentration at which the organisms are exposed and 2) its toxicity potential (e.g. concentration of toxic effect).
Used in the impact assessment step within an LCA study, such a CF is a substance-specific factor that accounts for the cause–effect chain linking emissions to impacts through three steps: environmental fate, exposure and effects (JRC-IES, 2010a; Rosenbaum et al., 2007). To date in LCA studies focusing on ENMs, the toxic impact categories are not properly assessed in the sense of ISO 140040-44 (Hischier & Walser, 2012). This is due partly to *i*) the lack of inventory information about the release of nanoparticles into environmental compartments, but *ii*) especially also due to the lack of CF for releases of ENMs to the environment (Hischier & Walser, 2012). Until now, only two aquatic ecotoxicity CFs for carbon nanotubes (Eckelman et al., 2012) and for titanium dioxide nanoparticles (Salieri et al., 2015) have been published, while in the area of human toxicity no such factors at all have been published so far. This leads to the need to investigate the environmental fate and toxicity of nanoparticles in order to identify factors for assessing the potential human health and environment effects caused by the nanoparticles emissions in the environment.
In order to develop such toxicity factors, the initial questions are which environmental compartments and organisms are actually affected, to what magnitude, by which characteristics of nanoparticles. Therefore, one has to know which characteristics of nanoparticle emissions are key

[2] The characterisation factor is a quantitative representation of the hazardousness or impact potential related to the emission of pollutant on human health and on environment.

for these impacts, and how such emissions should be adequately measured, e.g. based on number concentrations with additional information on size distribution, (biologically active) surface area, etc. Strongly linked to the above core question of the second phase is the question dealing with the degree of detail – especially concerning the release of nanoparticles – that has to be collected in the third phase to allow for an adequate evaluation of nanoparticle emissions in the impact assessment (Hischier & Walser, 2012).

5.5 State of the art: LCA and ENMs

A comprehensive systematic literature review of the state-of-the-art of LCA research on ENMs shall be necessary to investigate the LCA methodology limitations when it is applied on nanoproducts. Until now few meta-analysis of the LCA of ENMs can be found in the peer-reviewed: Hischier & Walser 2012; Gavankar et al. 2012; Upadhyayula et al. 2012; Lazarevic & Finnveden 2013; Miseljic and Olsen 2014. They addressed some of the observed barriers that need to be overcome in order to strengthen LCAs of ENMs (in particular, adequate and comprehensive life-cycle inventory data, especially for manufacturing and use, and the lack of data for nanospecific fate, transport and toxicity effects). Upadhyayula et al. specifically focused the attention on carbon nanotubes (CNTs) and carbon nanofibres (CNFs), whilst all others authors reviewed LCA case studies of ENMs. These latter LCA studies have covered the "classical" ENMs such as carbon nanotube (CNT) single-walled carbon nanotube (SWCNT), multi-walled carbon nanotubes (MWCNT), Nano-TiO_2, nanosilver, quantum dot, nanoclay, nanocomposite, or carbon nanofibers (CNF) as well as applications of several of these ENMs. Lazarevic and Finnveden gathered the first three mate-analysis together and described it in a report.
Within this thesis a cross-check between the latest review performed by Miseljic and Olsen and Lazarevic and Finnveden report has been done. In this way, a complete literature review of the state-of-the-art of LCA research on ENMs has been here considered and reported in Table 3.

Table 3 State-of-the-art of published LCA case studies of ENMs (Miseljic & Olsen, 2014 and Lazarevic & Finnveden, 2013)

	Author	ENM	Focus of study	Assessed Life cycle phases	Impacts assessment
1	Dahlben et al. 2013	CNT	Evaluate the life cycle hot spots of the carbon nanotube semi-conductor production for cellular phone flash memory	Cradle to gate	Two upstream processes are mainly responsible for the impacts, namely the electricity generation and the mining and refining of gold. One of the concerns with LCA of CNTs is the shortage of consistent data for estimation of toxicity impacts of CNTs.
2	Griffiths et al. 2013	MWCNT	Identification and quantification of the environmental impact of MWCNT formation via catalytic chemical vapour deposition.	Cradle to gate	The high embodied energy of MWNT synthesis is often quoted as the major embodied impact in CNT growth. Previously unmeasured contributions of the embodied impacts of the equipment infrastructure have been shown to be in the same order of magnitude in terms of environmental damage during the growth period of the MWNTs. The production of the chemical reactants used have a very minimal effect on the overall environmental impact due to the small quantities involved in MWNT synthesis.
3	Babaizadeh and Hassan 2013	nsno-TiO_2	Comparison of TiO_2 coated class with float glass	Cradle to grave (excluding End-of-Life)	The LCA combined with economic score for the construction materials shows that the most cost-efficient and environmentally friendly material for use in the building is the TiO_2 nano-coated glass, according to most of the impact categories. Likewise, in the weighted environmental and economic

					impacts, the TiO_2 nano-coated windows perform better when considering the raw material extraction to recycling boundary.
4	de Figueirêdo et al. 2012	Cellulose nanowhiskers	The comparison of two alternative processes for the production of cellulose nanowhiskers: nanowhiskers extracted from unripe coconut fibers (EUC) and from white cotton fibers (EC)	Cradle to gate	The comparison between the EUC and EC systems showed that nanowhiskers produced in the EC system required less energy and water, emitted less pollutants, and contributed less to climate change, human toxicity, and eutrophication than those produced in the EUC system.
5	Deorsola et al. 2012	Molybdenum Sulphide (MoS_2)	Evaluation of Molybdenum sulphide (MoS_2) production for lubricant applications.	Cradle to gate	55% of the CED is due to electricity use (IT) during the synthesis of molybdenum sulphide nanopowder and to that 63% of global warming impact during production is associated to the electricity consumption. The impacts during production are dominated by electricity use and the rest of the energy/impacts are due to use of reactants as ammonium molybdate, citric acid and ammonium sulphide.
6	LeCorre et al. 2012	Nanocrystals Nanoclay	Comparison of starch nanocrystals production and organically modified clay production.	Production process	The production of starch nanocrystals requires less energy to produce than organically modified nanoclay. Nonetheless, starch nanocrytals have a higher impact in global warming and acidification impact categories. The other benefit of starch nanocrystals is that they have a better score in nonrenewable energy and mineral depletion, as starch nanocrystals are renewable and biodegradable.
7	Manda et al. 2012	nsno-TiO_2	Comparison of printing and writing paper production with new coatings (micro or nano TiO_2) and different pulp types with conventional approaches.	Cradle to grave	Nanoparticle based paper shows the highest savings, e.g. in recovered paper fibre, and the lowest environmental impacts. The consequential LCA modelling approach yields the highest savings for nano and secondly for the micro-sized TiO_2 paper, compared to the conventional paper.
8	Weil et al. 2012	SWCNT & MWCNT	Comparison of black carbon and activated carbon with single and multi-wall carbon nanotubes (SWCNT & MWCNT through CVD or laser ablation) for supercapacitor based electric energy storage in hybrid and full electric car	Cradle to gate	The production of an SWNT electrode for supercapacitors is by far worst through a laser ablation compared to CVD, as the energy required is approximately twice as high. Far less energy is needed to produce MWCNT (through CVD, fluidized bed or floating catalyst approach) and activated and black carbon. Hereby it is underlined that the production of nano-scale carbon is highly energy demanding, even though the technology is promising in the use for supercapacitor based electric energy storage in vehicles.
9	Şengül and Theis 2011	QD photovoltaics	LCA of a proposed type of nanophotovoltaic, quantum dot photovoltaic module	Cradle-to-gate	The study shows that Cadmium selenide (CdSe) QDPV modules would exhibit energy return and environmental emission levels better than the other types of PV solar systems (existing and novel PV types), with exception of heavy metals emissions. It should be noted that the study compares relatively mature technologies with emerging ones like CdSe QDPV, which in reality are apt to change. In general QDPV modules are performing better in all impact categories than carbon based energy sources, but have a longer energy payback time than wind- and hydropower and also a higher global warming potential.
10	Walser et al. 2011	nsno-Ag	Comparison of the environmental benefits and impacts of nanosilver T-shirts with conventional T-	Cradle to grave	The annual climate footprint for T-shirt use in Switzerland is lower in the nano than in the non-nano scenarios (including triclosan treated polyester T-shirts). Because the additional burden of the nanosilver T-shirt

			shirts and T-shirts treated with triclosan		production process is compensated with lower washing frequency. Additional analyses indicate that a nanosilver T-shirt produced with commercial plasma polymerisation with silver co-sputtering process will never perform better than regular T-shirts in terms of climate footprint, even if consumers decrease the impact of the use phase by reducing washing temperature, or washing and tumbling frequencies.
11	Wender et al. 2011	SWCNT	Quantification of energy use during manufacturing of SWCNT anode for a lithium-ion battery. Further the material inputs and outputs are also quantified for the entire battery.	Cradle to gate	To produce SWCNT anodes in Li ion batteries 45-130 MWh of electricity is needed per kWh of battery storage capacity. The material need, for the entire lithium-ion battery, is mainly represented by DI water, graphite $CaCO_3$ and the material inputs become waste in almost equal quantities.
12	Merugula et al. 2010	CNF	Quantification of energy requirement for glass fibre-reinforced plastics (GFRP) and the vapour-grown CNFs production to reinforce the interface of a glass fibre/epoxy matrix aimed for reinforcing large wind turbine blades.	Cradle-to-grave (use and disposal assumed to be the same for the CNF based product as for the commonly used)	Cradle-to-gate processing energy of the new CNF added material is 1.4-1.7 times greater than for the original GFRP material on a MJ/kg basis and implicit assumption of weight savings of 20 %. Effects on energetic return on investment (EROI) vary from insignificant to substantial based on the upstream production processes of CNF manufacturing and solvent handling. The choices of solvent application and CNF production are dominant in the potential for energy benefits; ergo it is not substantiated whether CNF introduction is advantageous mechanically and energetically.
13	Meyer et al. 2010	nsno-Ag	Comparison of production process of socks with and without Ag nanoparticles	Cradle-to-gate	Nano-Ag socks cause higher environmental impact across all categories, due to the energy required for production of nano-Ag. The liquid flame spray production method for producing the particles has the highest impact due to its use of hydrogen and oxygen as fuel gases.
14	Moign et al. 2010	Zirconium nanopowder	Comparison of spraying technologies for the manufacture ofyttria-stabilised-zirconia nanostructured coating	Cradle-to-gate	From the three used plasma spray technologies, each using powder, suspension or solution as feedstock to manufacture zirconia coating. It was showed that the solution precursor technology had the lowest environmental impacts. The thermal spray process (coating deposition on products) is the impact hotspot and 70–80 % of impacts derive from the use of electricity for spraying.
15	Roes et al. 2010	SiO_2, $CaCo_3$, CNTs WMCNTS, organophilic montmorillonite	Comparison of the non-renewable energy use of 23 nanocomposite materials with 3 conventional composite materials.	Cradle-to-grave	For 17 of the different nanocomposites materials analyzed a decrease of the functionality-based non-renewable energy use with increasing filler content has been observed.
16	Steinfeldt et al. 2010	CNT	Comparison of carbon nanotube composite materials (carrier tray e.g. for toner cartridge) and films (for wind power plant) production.	Cradle-to-grave	The first case study (CNT composite material as carrier tray) shows that an increase in the production efficiency plays an important role in the environmental impact. This also resembles in the second case study (CNT films for wind power applications), where a small increase in energy production efficiency of 0.25% can result in an environmental impact improvement between 3.7–11%
17	Dahlben and Isaacs 2009	CNT	Manufacturing of two CNTs containing applications of a switch and a polymer mesh	Cradle-to-gate	Results indicate significant environmental impact contribution to airborne inorganics, climate change and fossil fuels due to materials used in cleansing processes and electricity consumption. In every impact category the CNT polymer mesh manufacture has a slightly greater environmental burden than the CNT switch.

18	Fthenakis et al. 2009	nano-CdTe, nanocrystalline-Si and nano-Ag PV system	Comparison of the cumulative energy demand for the production of PV systems using nanomaterials	Cradle-to-gate	Preliminary estimates indicate that nanotechnology-based PV designs use substantially more energy in producing the material and fabricating the device than do the current methodologies, particularly when coupled with the current immature, laboratory-scale processes. In addition, using nano-size forms of cadmium telluride and silver may introduce new hazards.
19	Ganter et al. 2009	SWNCT	Quantification of energy requirement for manufacturing of single wall carbon nanotubes (SWNCT) through laser vaporisation.	Production process	To produce 1 kg SWCNTs at the laboratory scale, through laser vaporisation, 0.13-0.19 GWh energy is needed. From that, 0.114 GWh electrical energy is used. The energy consumed is mainly related to thermal and resistive losses of the laser and single zone use in the production.
20	Khanna and Bakshi 2009	CNFs reinforced polymer nanocomposites (PNCs).	Environmental burden and quantification of energy demand of CNF synthesis	Cradle-to-gate	A comparison suggests that for equal stiffness design, CNF reinforced PNCs are 1.6-12 times more energy intensive than steel. The product use phase influence whether any net savings in life cycle energy consumption can be realized. Factors such as cost, toxicity impact of CNF, and end-of-life issues specific to CNFs need to be considered to evaluate the final economic and environmental performance of CNF reinforced PNC materials.
21	Köhler et al. 2008	CNT	Potential release of carbon nanotubes throughout the life cycle of textiles and lithium-ion batteries	Manufacturing, use and End-of-Life	Release of nanotubes can occur not only in the production phase, but also in the usage and disposal phases of nanotube applications. The likelihood and form of release is determined by the way CNT are incorporated into the material. A considerable part of all CNT used may finally be dispersed somewhere in the technosphere or the environment, e.g. by cross-product contamination during recycling. As long as potential adverse effects of CNT cannot be ruled out, we recommend implementing precautionary measures along the value chain in order to reduce the release and possible negative environmental or human health effects of CNT.
22	Bauer et al. 2008	TiN, TiAlN, Ti^{+}, TiAlN	Examine the implications of life cycle thinking on nanotechnology (and nanoproduct) evaluation; 2 case studies	Manufacturing	The (Cumulative energy demand (CED) increases with the energy consumption of each PVD process and can be related like this: TiN\TiAlN\Ti^{+}\TiAlN. Metal production of titanium and aluminium accounts for more than 75 wt% of the total amount of the global warming potential - the consumption of metals is of essential importance. As Ti^{+}, TiAlN coating needs explicitly less metal than TiAlN coating, the potential environmental impacts are lower in the categories, climate change, resource depletion and acidification compared to TiAlN coating.
		CNT		Cradle-to-grave	The use phase is dominating the overall impacts due to the electricity consumption during operation and these impacts account approximately from 60-75%. Secondly, 15-30% of the impacts can be associated to the back glass coating and more precisely to the cathode and thus also to the CNT layer coating (applied by a CVD process).
23	Grubb and Bakshi 2008	nsno-TiO_2	Evaluation of the hydrochloride process for producing nano-TiO_2	Cradle to gate	The Altair hydrochloride process for producing Nano-TiO2 has lower energy requirements than the traditional materials, such as steel and aluminum. The main impacts from producing TiO_2 comes from ilmenite mining and steam generation, while in terms of normalization the fossil fuel category has the largest normalised damage impact due to steam generation and methane combustion.

24	Healy et al. 2008	SWCNT	Environmental assessment of manufacturing of SWNT by arc, CVD HiPco processes	Cradle-to-grave	Nearly all emissions resulted from the generation of electricity for all three production methods. The CVD production process contributed with the largest quantity of other emissions (beside the ones from electricity), which were an order of magnitude larger than those of the arc and HiPco production processes. In order to perform a more representative LCA, e.g. SWNT worker exposure will also have to be considered.
25	Joshi 2008	nano-clay	Comparison of production process of fibre-biopolymers and organically modified montmorillonite (OMMT) nanoclaybiopolymer composites	Cradle-to-gate	The comparison of the nanoclaybiopolymer composites with the fibrebiopolymer composites shows that the environmental burdens from nano-clays are worse than those from the fibrebiopolymers. Except from the phosphate and nitrate emissions. Though in term of GHG emissions and the energy use the nano-clays are performing environmentally better than the glass fibres. These conclusions are based on a kg basis comparison, and the conclusion is that a product specific LCA is recommended in order to better describe the potential environmental impacts.
26	Khanna et al. 2008	CNF	Production of polymer Nanocomposites (PNC): Carbon nanofibre (CNF) and carbon nanofibreglass fibre (CNF-GF) hybrid nanocomposites - also compared with steel	Extraction and manufacturing	Cradle-to-gate PNC is 1.3-10 times more energy intensive than steel, but in the case of automotive body panels the PNC life energy savings are realized through the automobile use phase. In cases where PNC is applied in a structural function the energy intensive production overshadows the environmental profile compared to conventional materials as steel. The release and exposure of nanoparticles is unknown, but is more likely to occur in the disposal stage and the knowledge of this impact is currently severely lacking.
27	Krishnan et al. 2008	nanoscale semiconductor	Life-cycle inventory and quantification of energy demand of nanoscale semiconductor manufacturing	Manufacturing	Total primary energy requirement associated with upstream (chemicals and infrastructure) and semiconductor manufacturing is at 14100 MJ/wafer with 7100 MJ/wafer used for device fabrication and 2900 MJ/wafer used for silicon wafer production. The results indicate that it may be Important to further investigate the energy consumption of nanofabrication, as this study considers the specific processing energy within the manufacturing facility.
28	Kushnir and Sandén 2008	Fullerenes and CNT	Impl ications for industrial scale carbon nanoparticle production	Cradle-to-gate	Carbon nano particle production is found to be potentially 2-100 times more energy intensive than aluminum production. The higher energy requirement in the cradle-to-gate system can be counterbalanced in the use phase, with savings in energy.
29	Singh et al. 2008	Single-wall carbon nanotubes (SWCNT)	Environmental Impact Assessment (EIA), via LCA method, of two methods for producing SWCNTs	Extraction and manufacturing	It was observed that from the base design to the new design, the emission of carbon dioxide, carbon monoxide and hydrogen is reduced as we treat them as by-products in new design. Another important observation is that the performance of these processes has switched from base design to the new design in terms of its contribution towards smog formation. This shows that a comprehensive environmental impact assessment may produce vital data about the performance of each process in terms of various environmental impact categories.
30	Khannaa et al. 2007	CNF	Environmental burden and quantification of energy demand of CNF synthesis	Cradle-to-gate	The preliminary energy analysis indicates a 6-60 times higher life cycle energy requirement for carbon nanofibres than aluminium, steel and polypropylene. Carbon nanofibres may have a higher environmental burden than conventional materials, when compared on an equal mass basis. The human and ecotoxicological impacts are not

					fully accounted as this lacks knowledge and information on potential release and related impacts.
31	Roes et al. 2007	Polymer nanocomposite	Compare environmental impacts ad costs with nanocomposi te products vis-a-vis those with conventional products	Cradle-to-grave	The production and incorporation of nanoclays may be compensated by the weight reduction provided to the endproduct. The polypropylene nanocomposite use for agricultural film has clear environmental benefits, but on the other side the use of these nanocomposites in packaging film and automotive panels has no obvious environmental benefits. In terms of economy the use of nanocomposites is advantageous if the nanoclay is not higher than € 5,000/ton. Depending on which material and energy prices are assumed the life cycle costs for agricultural film with a polypropylene nanocomposite can be reduced by 26–39%. The economic advantage for using nanocomposites in automotive applications can be reduced with 3–6%
32	Isaacs et al. 2006	SWNCT	Environmental assessment of SWNCT production	Manufacturing	HiPco is economy-wise the cheapest method, approximately 4 times cheaper than the other two production methods. In terms of environmental potential attributes the data background is not proper, but the CDV has the greatest and arc ablation the least environmental burden. Based on the process comparison of resources used and emissions generated the electricity consumption during synthesis is the major contributor to the environmental burden.
33	Osterwalder et al. 2006	Various oxide nanoparticles	Energy comparison of wet and dry synthesis methods for oxide nanoparticle production	Cradle-to-gate	Clear differences are seen in the energy requirements in the production of oxide nanoparticles (TiO_2, ZrO_2) using electricity-intensive plasma processes or chloride derived flame synthesis and liquid precipitation processes. The short process dry synthesis in general requires a larger amount of energy than the multi-step wet processes. The choice between these two processes is often determined by the product composition.
34	Lloyd et al. 2005	Nanoscale platinum group (PGM) metal particles	Evaluating reduction in non-renewable resources like PGM via greater process control offered by nanotech	Cradle-to-grave	The nanofabrication technique that enables precise control of the metal particles in catalysts should result in reduced loading levels of platinum group metal. These reductions would then decrease energy consumption, improve environmental quality and contribute to sustainable resource usage. By application of this nanofabrication technique the environmental impacts would be lowered due to reduced mining and refining, as a function of less use of platinum in the manufacturing stage.
35	Lloyd and Lave 2003 Lloyd et al. 2005	Polymer nanocomposite (based on nanoclay)	Replacing auto-body panels made of steel or aluminium with clay-polypropylene nanocomposite.	Cradle-to-grave	Despite being more expensive and having a higher environmental production impact than steel and aluminium, claypolypropylene nanocomposite has a reducing energy and environmental impact advantage by improving car fuel-economy. This, along with the design possibilities of this material, could entice consumers to purchase lower weight vehicles and thereby reduce the environmental impact in the use-phase of the car.
36	Greijer et al. 2001	nano-crystalline dye	Identify the significant environmental aspects of nano-crystalline dye sensitive solar cell (ncDSC) system.	Cradle to grave	The most significant activity contributing to environmental impact over the life cycle of the ncDSC system is the process energy for producing the solar cell module. Secondly comes the components: glass substrate, frame and junction box.

5.6 Conclusions: limitations and future challenges of LCA methodology in the nanotechnology field

On the basis of the LCA studies applied in the nanotechnology field and above reported, several limitations can be identified, in particular, they reflect the current state of knowledge regarding LCA of ENMs and consequently highlight the future challenges that it is necessary to overcome:

- Cradle-to-gate or manufacturing system boundaries have been generally taken into account.
- Use and End-of-Life (EOL) steps are inadequately covered.
- The common use of generic life cycle inventory (LCI) data and assumptions cannot be classified as comprehensive due to the lack of emission data.
- Release of ENMs (e.g. in the manufacture, use or EOL steps) and the potential toxic impacts of these (fate, exposure and effect consideration) have not been considered. Walser et al. (2011) study is the only exception, the author evaluated the release of nano-Ag from T-shirt throughout its entire life cycle, even though the nanospecific environmental effects of potentially released nanomaterials and therefore also a specific characterisation factor of studied ENM have been not calculated. Release of ENMs and assessment of their impacts contain a degree of complexity that makes them difficult to grasp scientifically and to include in a LCA approach (Miseljic & Olsen, 2014).
- the toxic impact categories are not properly assessed in the sense of ISO 140040-44 (Hischier & Walser, 2012). This is due partly to:
    i. the lack of inventory information about the release of nanoparticles into environmental compartments;
    ii. the lack of CF for releases of ENMs to the environment.

Until now, only two aquatic ecotoxicity CFs for carbon nanotubes (Eckelman et al., 2012) and for titanium dioxide nanoparticles (Salieri et al., 2015) have been published, while in the area of human toxicity no such factors at all have been published so far.

In order to perform an LCA of ENMs, certain aspects need to be considered and some are more important than others. The potential toxicological impact of ENMs is one of these and it depends on the possible release of ENPs during an ENM products life, on their environmental fate and their potential effect when penetrating into living organisms. There is currently a lack in understanding of fate, exposure and effect of released ENPs in the environment (Miseljic & Olsen, 2014).

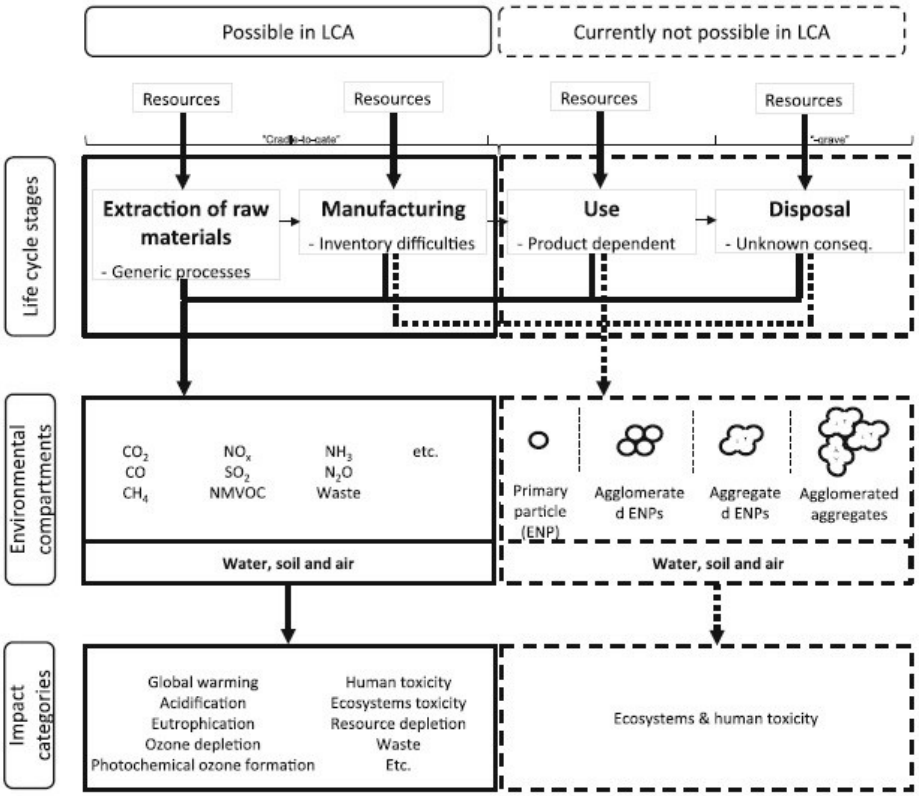

Figure 5-1 Possibilities and limitations of LCA - what currently can be assessed of ENMs (Miseljic M. and Olsen, 2014).

Figure 5.1 shows the LCA limitations regarding the impact assessment of ENMs, which are connected to the limited knowledge on fate and effects of released ENPs. Currently, the LCA case studies of ENMs previously mentioned neglect the potential toxicity impacts of ENM release to environmental compartments. Moreover, ENMs toxicity is linked to a series of properties typical of these materials, such as the crystal form, size, shape, surface area and chemical structure as well as on aggregation status and impurities. Unfortunately, these parameters have not been fully characterized in most published reports. But, surface area and reactivity and particle number should be carefully characterized in order to determine relationships between nanoparticle properties and consequent biological activities (Iavicoli et al., 2012). To make LCA more robust when assessing ENMs the factors controlling transport, transformation, fate (e.g. aggregation and deposition) and effect of released ENMs must be uncovered and corresponding LCA environmental impact characterisation factors should be developed. For these reasons, one of the aim of this thesis is the determination of human health characterization factor of one of the ENMs commonly used in several manufacturing fields (e.g. building sector), namely titanium dioxide nanoparticles.

The LCIA phase is based on a global, continental geographic scale, but for ENMs can be not appropriate, as site-specific conditions strongly affect their fate, behavior and bioavailability (Salieri, 2013). A growing interest towards introducing spatial differentiation in regional impact categories emerged. Different indicators and characterization models have been proposed to calculate the site-dependent CFs for a variable number of interventions and for the following impact categories: acidification, photo-oxidant formation, terrestrial eutrophication and toxicological impacts. However, spatial differentiation requires collecting local-specific data and calculating spatially specific characterisation factors (CF). Local-specific data are rarely available for all

processes within a product life cycle, but at least for processes that appear to predominate in the overall impact of a product life cycle, additional effort to collect location-specific data is advisable (Zamagni et al., 2008).

6 Titanium dioxide nanoparticles

Titanium is widely distributed and is the ninth most abundant element in the earth's crust. Although it was discovered in 1791, in Cornwall, England, commercial exploitation did not take place until 1913 when titanium dioxide (TiO_2) pigment was manufactured by a fusion process. This was soon superseded by the sulphate process which was developed by Farup and Jebsen in Norway, and commercial production started in 1918. An alternative method, the chloride process, was introduced commercially in 1958. Nano-TiO_2 dioxide is currently used in many products. Depending on the type of particle, it may be found in sunscreens, cosmetics, food additives and building materials (e.g. paints, coatings, glass, concreate). It is also being investigated for use in removing contaminants from drinking water. The physical and chemical properties that make TiO_2 attractive as a component of various consumer products and applications are outlined along with their uses and applications.

6.1 Physical and Chemical Properties

Basic chemistry and physical properties of TiO_2 have been understood and used by man for centuries. This knowledge is outlined in the following paragraphs.

6.1.1 Crystalline Phases

Pure titanium dioxide (TiO_2) is a colourless, crystalline solid. As with other dioxides of d-block elements in its group in the periodic table TiO_2 is stable, non-volatile, insoluble and is rendered refractory by ignition. It is amphoteric but has more acidic than basic characteristics. TiO_2 naturally occurs as crystalline phases: anatase, rutile, and brookite (Figure 6.1) and is the most widely used photocatalyst for decomposition of organic pollutants because it is chemically stable and biologically benign. The band gap of TiO_2 is larger than 3 eV (~3.0 for rutile and ~3.2 for anatase), thus making pure TiO_2 primarily active for UV light. Pure TiO_2 phases it is generally accepted that anatase exhibits a higher photocatalytic activity compared to rutile TiO_2 (Liu et al., 2012).

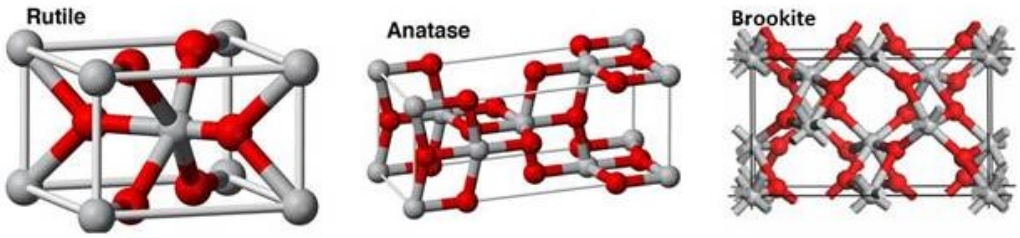

Figure 6-1 Crystal structures of rutile, anatase and brookite titanium dioxide (Shannon, 2015)

Anatase and rutile phases are the most commonly encountered. Rutile is the thermodynamically stable form of TiO_2 at all temperatures and at normal pressures. It is the most stable form and is thus the most abundant, it has a more compact structure than anatase and this gives rise to important differences in properties between the two modifications, it has a higher refractive index, higher specific gravity and greater chemical stability than anatase. It melts at 1825°C.

Instead, anatase has no specific melting point as it is irreversibly transformed to rutile before a melting point is reached. Anatase phase is always found as small, isolated and sharply developed crystals, and like rutile, a more commonly occurring modification of titanium dioxide, it crystallizes in the tetragonal system; but, although the degree of symmetry is the same for both, there is no

relation between the interfacial angles of the two minerals, except in the prism-zone of 45° and 90°. Crystals of anatase can be prepared in laboratories by chemical methods such as sol-gel method. Examples include controlled hydrolysis of titanium tetrachloride ($TiCl_4$) or titanium alkoxides (Wikipedia, 2015a).
Finally, brookite is rare compared to anatase and rutile and like these forms it exhibits photocatalytic activity. Brookite has a larger cell volume than either anatase or rutile, with 8 TiO_2 groups per unit cell, compared with 4 for anatase and 2 for rutile. Iron, tantalum and niobium are its common impurities. At temperatures above about 750 °C, brookite reverts to the rutile structure (Wikipedia, 2015b).

6.2 Synthesis routes

Any synthetic method for nanomaterials aim to yield a material owns properties that are characteristic length scale in the nanometer range (1 ÷ 100 nm). Accordingly, the synthetic method should exhibits control of size in this range so that one property or another can be achieved. Often the methods are divided into two main types *Bottom Up* and *Top Down*. *Bottom up* methods involve the assembly of atoms or molecules into nanostructured arrays. In these methods the raw material sources can be in the form of gases, liquids or solids. The latter requiring some sort of disassembly prior to their incorporation onto a nanostructure (Wikipedia, 2014b). *Top Down* approach uses macroscopic initial material and then it is broken into smaller pieces and transformed into uniform size by a mechanic process as milling. Similarly, methods to manufacture nano-TiO_2 are generally adopted. In general, two commercial processes are used to produce pigment grade TiO_2: the sulfate process and the chloride process. Industries produced nano-TiO_2 by two top-down methods: chloride or sulfate processes; due to economic and environmental concerns industries, commonly, prefer the first approach than the latter one. Moreover, a more green and bottom up synthesis process is now used to produce nano-TiO_2, namely sol-gel synthesis.

6.2.1 Raw materials

Titanium occurs naturally in the minerals rutile (TiO_2) and ilmenite ($FeTiO_3$) and to a lesser degree in other minerals. Ilmenite ($FeTiO_3$) and mineral rutile (TiO_2) are the most important naturally occurring ores. Rutile ore from Australia and South Africa typically contains approximately 95 wt% of TiO_2. The amount of TiO_2 in ilmenite content of ranges from 44 wt% in Norway, to 55 wt% in Australia, and 65 wt% in Florida, U.S. (the only identified domestic location). In 2011, about 47 wt% of TiO_2 produced worldwide belongs to ilmenite. Ilmenite must be processed to remove iron before the TiO_2 may be chlorinated to produce titanium tetrachloride. This processing of ilmenite produces synthetic rutile. Synthetic rutile typically contains approximately 94 wt% of TiO_2. Ilmenite supplies approximately 92 wt% of the global demand for titanium minerals. The remaining 8 wt% of this demand is supplied by rutile ore. Australia accounted for the greatest ilmenite and rutile mine production per country with approximately 25 wt% of the global mine production of ilmenite and rutile combined. Australia was followed by South Africa with approximately 17 wt% of the global mine production of ilmenite and rutile combined (USGS, 2007).

6.2.2 Sulfate Process

The most common method for the production of titanium dioxide utilizes the mineral ilmenite. Ilmenite is mixed with sulfuric acid. This reacts to remove the iron oxide group in the ilmenite. The by-product iron(II) sulfate is crystallized and filtered-off to yield only the titanium salt in the

digestion solution. This product is called synthetic rutile. This is further processed in a similar way to rutile to give the titanium dioxide product. Synthetic rutile and titanium slags are made especially for titanium dioxide production. The use of ilmenite ore usually only produces pigment grade titanium dioxide (Wikipedia, 2014d). The iron sulfate wastes produced by the sulfate process present an environmental concern. Therefore, the chloride process is currently favored over the sulfate process.

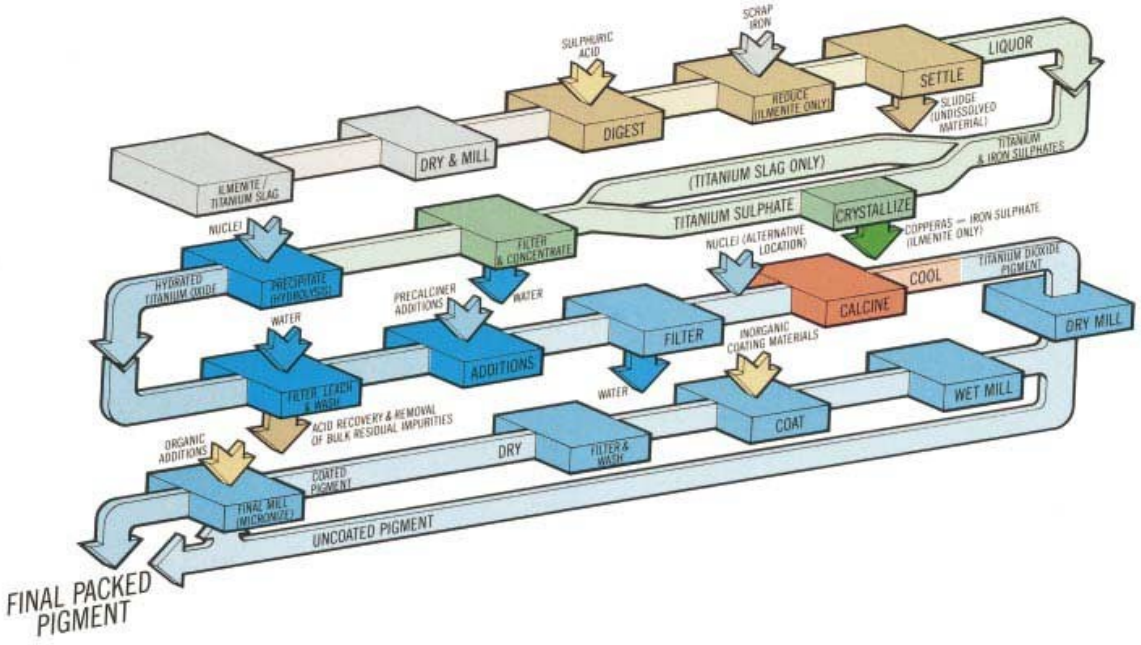

Figure 6-2 Sulfate process

Though complex in operation the sulphate process depends on a series of simple chemical reactions.

$$FeTiO_3 + 2H_2SO_4 \rightarrow TiOSO_4 + FeSO_4 + 2H_2O \quad \text{(eq. 1)}$$

$$TiOSO_4 \rightarrow TiO_2 \cdot nH_2O + H_2SO_4 \quad \text{(eq. 2)}$$

$$TiO_2 \cdot nH_2O \rightarrow TiO_2 + nH_2O \quad \text{(eq. 3)}$$

The sulfate process is a batch or discontinuous process (Figure 6.2). The ore, previously dried and ground is digested with sulphuric acid. The strength of the acid is usually 85-92% but is adjusted according to the composition of the ore. The mixture of ground ore and sulphuric acid is agitated by compressed air and superheated steam is blown in. When the temperature reaches about 100°C a vigorous exothermic reaction starts and the mixture is converted to a porous cake which may contain ferrous, ferric and titanium sulphates. This cake is dissolved in water or dilute acid to form a black liquor. Ferrous iron sulphate is much more soluble than ferric. Later in the process, the iron needs to be washed out of the TiO_2 precipitated so it must be kept in the ferrous state. This is achieved by the addition of scrap iron which reduces ferric to ferrous. A small amount of over-reduction of the liquor is necessary to allow for re-oxidation by the air. The over-reduction produces a small amount of trivalent titanium. The liquor is then clarified by sedimentation to remove insoluble residues such as silica, zircon and residual unreacted ore. Much of the iron present is then removed by crystallization as $FeSO_4 \cdot H_2O$ (copperas), the solution being cooled to about 10°C for

this purpose. It may be possible to omit this crystallization if a raw material of sufficiently low iron content, such as titanium slag, has been used. The last traces of sludge are removed by filtration and the solution is concentrated. Hydrolysis of the liquor to produce a precipitate of hydrous titanium dioxide follows, and is a particularly critical state in the process. Ideally, no ferric iron should be present and conditions must be controlled so that the precipitate can be easily filtered and washed. Also, it must produce crystals of the correct type and size when it is subsequently calcined. Precipitation is achieved by boiling for some hours. Nuclei may be introduced at this stage, or just prior to calcination. These are prepared from pure titanium tetrachloride and may be produced in the anatase or the rutile form, depending on the method of preparation. Although precipitates from sulphate liquors are invariably in the anatase form, the type of nuclei added determines whether calcination gives anatase or rutile pigment. Optimum precipitation depends on the condition of the initial solution, quality of the added nuclei and duration of hydrolysis. Yield of hydrous titanium dioxide can be improved if the solution is diluted when precipitation is nearing completion but excessive dilution can impair the quality. The precipitate is then filtered and washed with water. The acid filtrate is recovered and some of it is recycled. The precipitated pulp is leached under reducing conditions to reduce any last traces of ferric iron to ferrous. After a final wash minor additions of materials which help to control crystallite growth are made. The pulp is then calcined. Calcination is carried out in internally fired, inclined rotary kilns through which the pulp moves slowly, under gravity. As it progresses through the kiln the wet pulp is first dried, then strongly adsorbed water, SO_2 and SO_3 are driven off. The acidic, gaseous effluent is washed to remove the SO_3 and then passed through a bed of activated carbon where the SO_2 is converted to sulphuric acid. The sulphuric acid is recycled to earlier stages of the process. Crystallite growth and, where relevant, conversion to rutile occurs in the last few meters of the kiln. The temperature, which is carefully controlled according to the type of pigment being made, is usually in the region of 1000°C. After calcination the pigment is fed directly into a cooler. Cooling must be relatively slow to prevent the formation of trivalent titanium which would adversely affect the colour. The unrefined pigment may then be dry milled to break down aggregates and packed for sale as untreated pigment. However, most pigment is wet milled and further treated to coat the particles with selected inorganic oxides before it is finally milled and packed.

6.2.3 Chloride Process

The chloride process depends on the following chemical reactions:

$$TiO_2\,(\text{impure}) + 2Cl_2 + C \rightarrow TiCl_4 + CO_2 \qquad \text{(eq. 4)}$$

$$TiCl_4 + O_2 \rightarrow TiO_2\,(\text{pure}) + 2Cl_2 \qquad \text{(eq. 5)}$$

The chloride process is illustrated in Figure 6.3. The dry ore is fed into a chlorinator in which it forms a bed, fluidized by an air stream. Heat is applied and the temperature is increased to 650°C approx. Crushed coke is fed in on top of the ore, where it ignites, increasing the temperature and enabling the initial heat source to be removed. When the required temperature is attained the air stream is replaced by chlorine and reaction occurs to form titanium tetrachloride vapour. As the reaction proceeds the bed is continuously charged with ore and coke to keep its height constant. The gas stream is cooled as it leaves the chlorinator and solid matter is precipitated. After further cooling and cleaning, the crude titanium tetrachloride is distilled to produce a pure product, suitable for oxidation to titanium dioxide. For successful oxidation it is necessary to bring the reacting gases

together at a suitable temperature and to provide suitable nuclei on which the pigment particles may form.

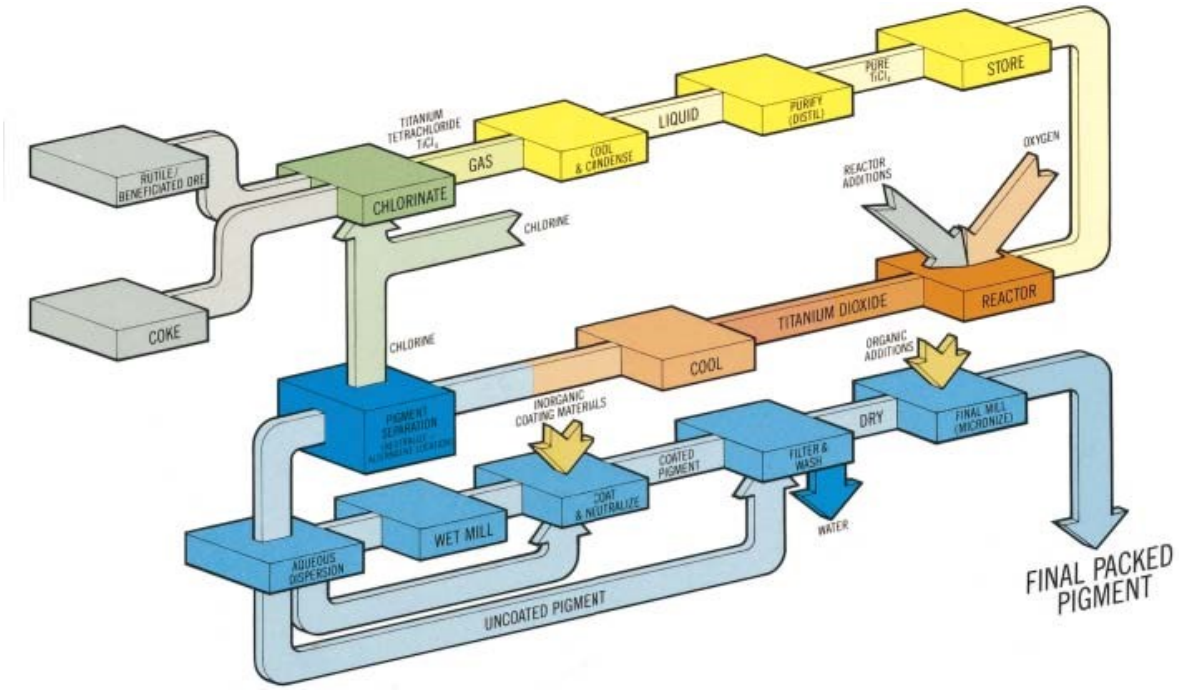

Figure 6-3 Chloride process

The heat evolved when $TiCl_4$ is burned in oxygen is not sufficient to raise the temperature of the reactants to reaction temperature and to maintain that temperature. Consequently additional heat must be supplied, which may be hydrocarbon combustion or by electrically heating oxygen in a plasma torch. Design of the reactors is complicated and there are several variants. It is important to keep the inlet nozzles cool enough to prevent growth of massive TiO_2 on them, thereby preventing their operating characteristics from becoming impaired. Nucleation of the reacting gases is necessary to promote the formation of pigmentary particles. This may be affected by means of a small concentration of water vapour introduced in the oxygen stream or produced by the hydrocarbon combustion. Another method is the addition of a small amount of anhydrous $AlCl_3$ to the $TiCl_4$ feed, when particles of Al_2O_3, formed by oxidation, act as centres for the growth of TiO_2. Whatever the design of the reactor, the gases carrying the fine pigment must be cooled rapidly to below reaction temperatures so that further growth does not occur. This may be done by an admixture of spent gases recycled from a later stage or by liquid chlorine. Separation of the pigment then follows by bag filters, for example. Finally chlorine is directly recycled to the chlorinator or compressed and condensed to liquid for storage and reuse. Pigment made by oxidation of $TiCl_4$ is liable to contain adsorbed chlorine. This must be removed and the pigment neutralized and washed. The reactor product usually requires milling to break down oversize particles and to break up aggregates. Although the pigment can be used in this untreated state it is more usual for it to go forward to be coated.

6.2.4 Sol-Gel Process

The sol-gel process is used as a specialty nano-TiO_2 production process. The recent rewiev of Gupta and Tripathi (Gupta & Tripathi, 2012) described the typical sol-gel process. The sol-gel method is based on inorganic polymerization reactions. It includes four steps: hydrolysis, polycondensation,

drying and thermal decomposition. Hydrolysis of the precursors of the metal or non-metal alkoxides takes place with water or alcohols. The schematic of the preparation process has been shown in Figure 6.4.

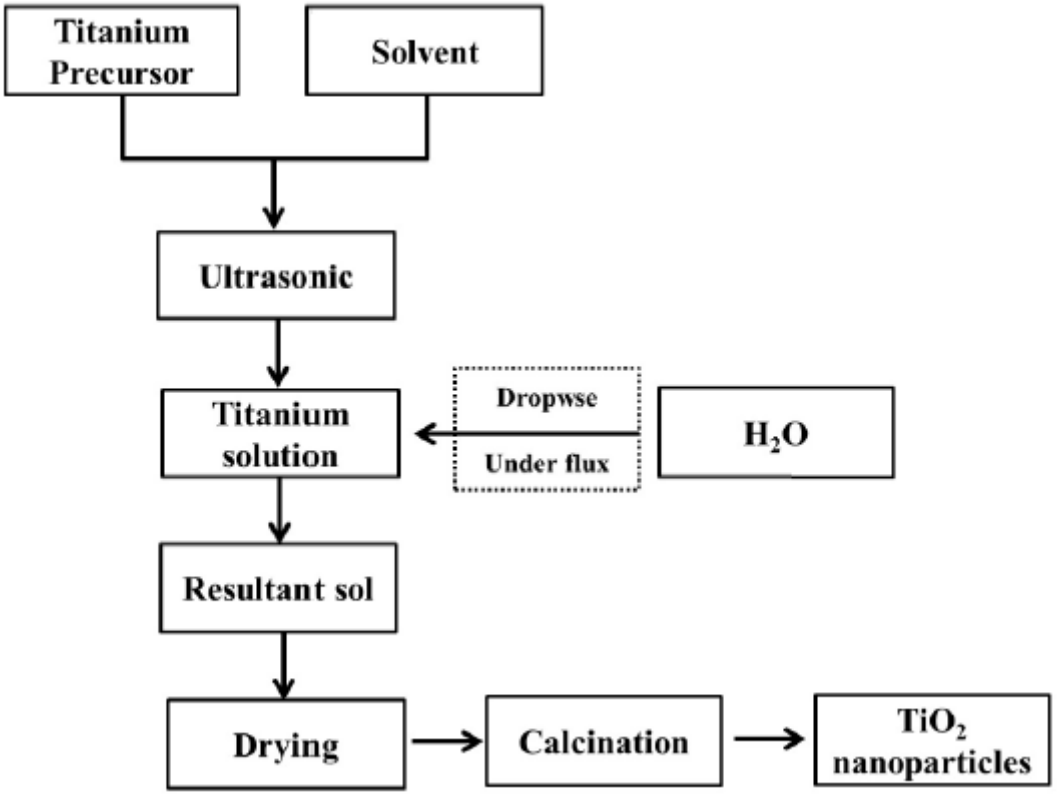

Figure 6-4 Scheme of the preparation of nano-TiO_2 sol-gel (Gupta & Tripathi, 2012)

Hydrolysis reaction:

$Ti(OR)_4 + 4H_2O \rightarrow Ti(OH)_4 + 4ROH$, where R = alkylgroup

In addition to water and alcohol, an acid or a base also helps in the hydrolysis of the precursor. After condensation of the solution to a gel, the solvent is removed.

Condensation reaction:

$Ti(OH)_4 \rightarrow TiO_2 + 2H_2O$

Calcination at higher temperature is needed to decompose the organic precursor. The size of the sol particles depends on the solution composition, pH and temperature. By controlling these factors, one can tune the size of the particles. The major advantages of sol-gel processing for optical and electronic applications are: *i*) ambient temperature of sol preparation and gel processing; *ii*) product homogeneity; *iii*) low temperature of sintering; *iv*) ease of making multi-component materials and *v*) good control over powder particle size and shape as well as size distribution (Gupta & Tripathi, 2012). Solution sol-gel processing of titanium alkoxides and supercritical drying techniques have

been used to prepare TiO_2 aerogels with much higher specific surface areas and tailored pore-size distributions. Some solution routes of the sol-gel synthesis process of nano-TiO_2 are following reported (Gupta & Tripathi, 2012):

- Heller and co-workers (Sitkiewitz & Heller, 1996) (Jackson et al., 1991) (Paz et al., 1995) and others (Watanabe et al., 1993), (Negishi et al., 1995), have developed several methods for the creation of such nano-TiO_2 films, *via* a sol-gel process. In their method, a titanium alkoxide (*e.g.* titanium isopropoxide) is hydrolyzed, coated onto a glass substrate, previously treated with sulphuric acid to produce a sodium-depleted layer, and calcined at a high temperature (usually 500°C) for a short time (approximately 20 min). Layers of nano-TiO_2 can be built up using the sol-gel procedure to produce films approximately 60-100 nm thick.
- Chau et al. (Chau et al., 2009) prepared well-dispersed surface-modified such nano-TiO_2 by a modified sol-gel process and incorporated them into epoxy matrix to form hybrid nanocomposites with higher refractive index than pure epoxy system. The nano-TiO_2 solid content in the epoxy matrix could be more than 70 wt% without affecting the optical transparency of the hybrid film.
- Loryuenyong et al.(Loryuenyong et al., 2012) prepared nano-TiO_2 by a sol-gel process, employing titanium tetraisopropoxide as a starting precursor and ethanol/sopropanol as an alcoholic solvent. The synthesized mesoporous TiO_2 was calcined at 300–700°C. It was found that pore collapsing, crystallite growth, and anatase-rutile phase transformation occurred with an increase in calcination temperatures. The use of isopropanol solvent was likely to inhibit the anatase–rutile transformation through the control of hydrolysis rate. The photocatalytic property of TiO_2 consisting predominantly of anatase crystallites improved the degradation of methylene blue under UVC light. Compared to ethanol, enhanced photocatalytic activity was obtained with isopropanol solvent through the thermal stability of anatase phase.

6.3 Photocatalytic and superhydrophilic properties

6.3.1 Photocatalytic property

Titanium dioxide (TiO_2) is one of the most widely used and promising materials in photocatalytic application due to strong oxidizing power of its holes, its redox selectivity, high photostability, redox selectivity and easy preparation. An important requirement for high TiO_2 photocatalytic efficiency is a large surface area which increases both amount of photongenerated electron hole pairs and surface-adsorbatesm (Karkare, 2014). If has been pointed out by Heller, all of the extensive knowledge that was gained during the development of semiconductor photoelectrochemistry during the 1970 and 1980s has greatly assisted the development of photocatalysis (Heller, 1981). In particular, it turned out that TiO_2 is excellent for photocatalytically breaking down organic compounds (Fujishima et al., 2000) and pollutants.

The word photocatalysis is a composite word which is composed of two parts, “photo” and “catalysis”. The prefix “photo” means pertaining to light. Catalysis is the process where a substance participates in modifying the rate of a chemical transformation of the reactants without being altered or consumed in the end. This substance is known as the catalyst which increases the rate of a reaction by reducing the activation energy. Generally speaking, photocatalysis is a reaction which uses light to activate a substance which modifies the rate of a chemical reaction without being involved itself (Kathirvelu et al., 2008) .

When a given photosemiconductor (e.g. titanium dioxide) absorbs Ultraviolet (UV) radiation from sunlight or illuminated light source (fluorescent lamps), with light of energy greater than the band gap energy of the photosemiconductor, charge separation occurs. Then, utilizing the formation of electron–hole pairs generated by the charge separation, the photocatalyst triggers an oxidation-reduction reaction (Mori, 2005). The electron–hole (e^- and h^+) charge carriers react with chemical species such as H_2O, OH^-, and O_2 to produce hydroxyl radicals ($^{\bullet}OH$), superoxide radical anions ($O2^{\bullet-}$), and H_2O_2 which contribute to decomposition of organics at the surface where TiO_2 is applied (Nakata & Fujishima, 2012).

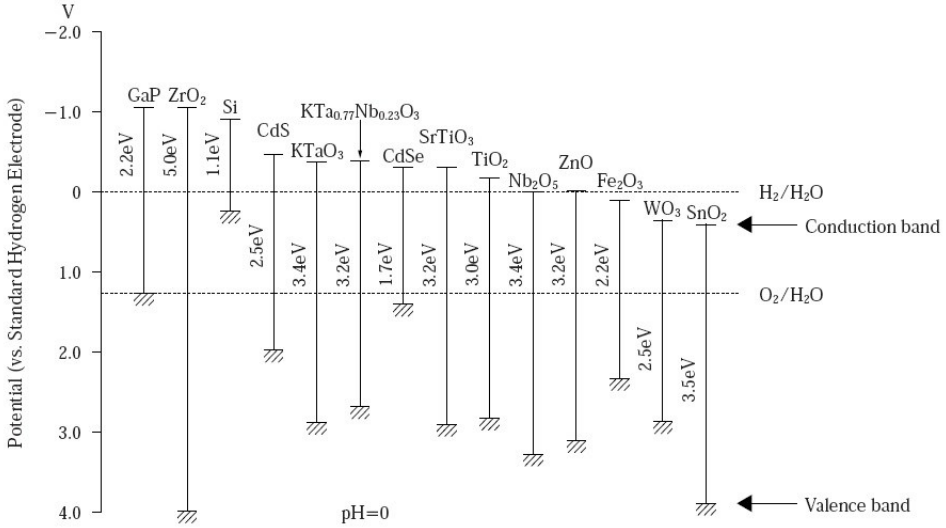

Figure 6-5 Energy structures of various photosemiconductors (Mori, 2005)

As show in Figure 6.5, TiO_2, with a relatively large band gap energy of 3.0 eV for the rutile type to 3.2 eV for the anatase type, can achieve a powerful oxidation reduction reaction with the ultraviolet rays present in the living environment (sunlight or illuminated light source).

The mechanism of photocatalysis TiO_2 can be easily understood from Figure 6.6 which describe the actions of a manmade photocatalyst (e.g. nano-TiO_2) on exposure to light. It is known that the conduction band in the anatase type is closer to the negative position than in the rutile type; therefore, the reducing power of the anatase type is stronger than that of the rutile type. Due to the difference in the position of the conduction band, the anatase type exhibits higher overall photocatalytic activity than the rutile type (Bozzi, Yuranova, & Kiwi, 2005).

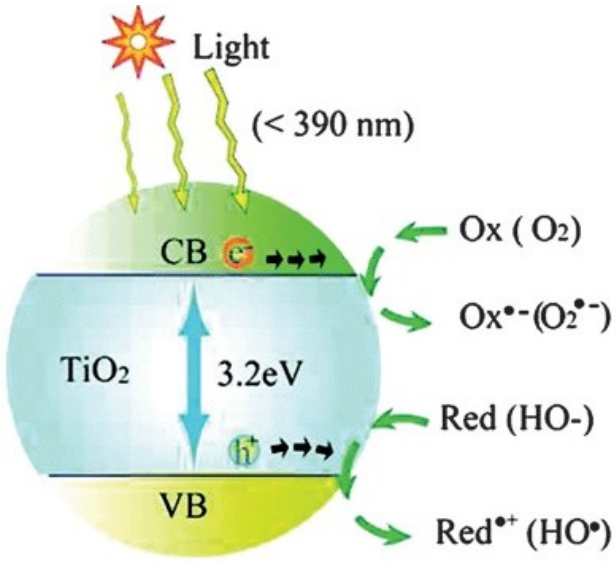

Figure 6-6 Photoexcitation of a semiconductor (e.g., TiO_2) and the subsequent generation of an e^- and h^+, which are trapped by an oxidant (Ox) and a reductant (Red), respectively. For TiO^2 photocatalysis, the ''Ox'' is a surface-adsorbed oxygen molecule and the ''Red'' is a surface-bound hydroxyl group (Li, C., Wang, F. and Yu, Ji. C., 2011).

6.3.2 Superhydrophilic property

When the surface of a photocatalytic TiO_2 coating is exposed to light, the contact angle of the photocatalyst surface with water is reduced gradually. When it reaches less than 5°, the TiO_2 surfaces become superhydrophilic (Figure 6.7).

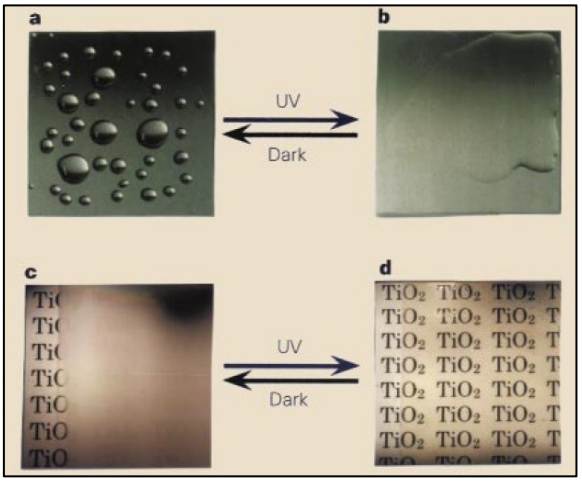

Figure 6-7 a: A hydrophobic surface before ultraviolet irradiation. b: A highly hydrophilic surface on ultraviolet irradiation. c: Exposure of a hydrophobic TiO_2-coated glass to water vapour. The formation of fog (small water droplets) hindered the view of the text on paper placed behind the glass. d: Creation by ultraviolet irradiation of an antifogging surface. The high hydrophilicity prevents the formation of water droplets, making the text clearly visible (Wang & Hashimoto, 1997).

The superhydrophilicity is originated from chemical conformation changes of a surface (Ikeda et al., 1997). The majority of the holes are subsequently consumed by reacting directly with adsorbed organic species or adsorbed water, producing •OH radicals as previous mentioned. However, a small proportion of the holes is trapped at lattice oxygen sites and may react with TiO_2 itself, which

weakens the bonds between the lattice titanium and oxygen ions. Water molecules can then interrupt these bonds, forming new hydroxyl groups. The singly coordinated OH groups produced by UV-light irradiation are thermodynamically less stable and have high surface energy, which leads to the formation of a superhydrophilic surface (Nakata & Fujishima, 2012). For this type of surface water cannot exist in the shape of a drop, but spreads flatly on the surface where TiO_2 is applied and water takes the form of a highly uniform thin film, which behaves optically like a clear sheet of glass (Fig 6.6 a, b). The photogenerated hole weakens the binding energy between Ti atom and the lattice oxygen, thus the adsorbed water molecules breaks the Ti-O-Ti bond to form 2 new Ti-OH bonds making them superhydrophilic. When the water is rinsed over the surface, the pollutants, oil, dust etc. are washed away (Kumar, 2011).

6.3.3 Self-cleaning and antibacterial features

The general concept of the self-cleaning capacity of TiO_2 is well known and the application of TiO_2 coatings to buildings for self-cleaning purposes is of considerable interest (Gupta & Tripathi, 2010). In fact, the deposition of pollutants, soiled, soot, vehicular exhaust and other particulates results in the necessity of cleaning the surfaces of buildings. The growth of organisms, such as bacteria, algae and fungi disfigures the facades of buildings and results in mechanical weakening and eventual destruction. To prevent this, buildings can be coated with a layer of photocatalyst. As above reported, photocatalyst is able to decompose common organic matter in the air, such as molecules causing odour, volatile organic compound (VOC) (e.g. Toluene), bacteria and viruses or organic stain, dirt and inorganic compounds (e.g. NOx, SOx). Furthermore, when photocatalytic TiO_2 is exposed to sunlight, it exhibits super-hydrophilic behavior, which allows partially decomposed stain/dirt residues on the surface to be washed away easily. Photocatalysis occurs in the presence of light and contact angle of water is increased, making the surface superhydrophobic which would allow dirt to be washed away easily (Kathirvelu et al., 2008). For these reasons, TiO_2 is used to create coating materials installed in an outdoor environment, when the TiO_2-coating is exposed to rainwater, organic contaminants laying on the surface are decomposed by UV-light irradiation and the residual inorganic particles are readily washed away by the rainwater. The coated surface exhibits the expected self-cleaning effect. Figure 6.8 schematically illustrates a self-cleaning model with an outdoor application (Mori, 2005).

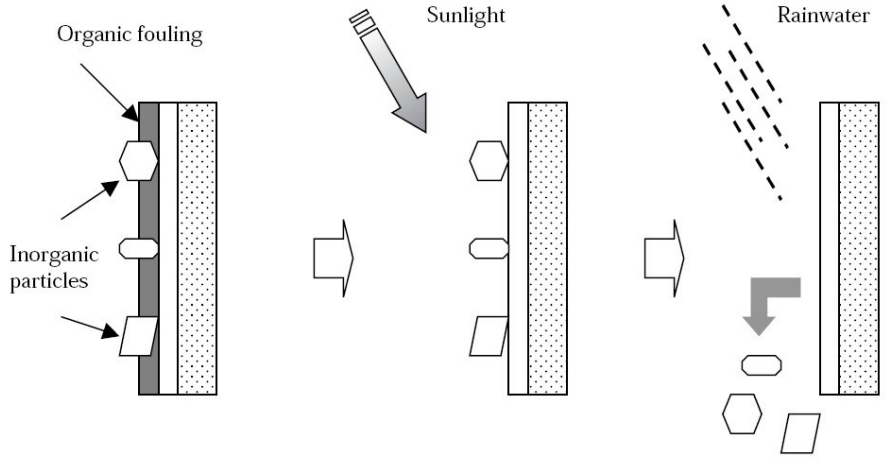

Figure 6-8 Model of pollutants removal by self-cleaning effect (outdoor environment) (Mori, 2005).

6.4 Toxicity

Fine TiO_2 form (micro-sized) is generally regarded as moderately toxicologically inert, with a low toxic potential. However, in several studies there is clear evidence that nano-sized TiO_2 is more toxic than micro-sized TiO_2. Nano-sized TiO_2 is absorbed from the gastrointestinal tract and distributed to secondary target organs, whereas micro-sized TiO_2 is not absorbed via this exposure route. It has been consistent within a wide range of investigations that the acute toxicity increases as particle size decreases. In addition the toxicity is dependent on the structure of the particles, being the anatase form the most toxic. The toxicity of TiO_2 nanoparticles has been demonstrated to be inflammation, induction of oxidative stress, and histological changes in the target organs. Lung is primary target organ after inhalation (Mikkelsen et al., 2011). Oberdorster et al. (Osterwalder et al., 2006) reported that nano-TiO_2 (21 nm) caused a greater pulmonary inflammatory response than TiO_2 at same mass burden, with greater amounts of nano-TiO_2 entering the alveolar interstitium in the lungs. Sager et al. (Sager et al., 2008) have reported similar results after intra-tracheal instillation of well-dispersed suspensions of nano-TiO_2 (80/20 anatase/ rutile; 21 nm, P-25) and fine TiO_2 (100% rutile; 1μm) in rats. On an equal mass burden, nano-TiO_2 was 40 fold more potent in inducing lung inflammation and damage at 1 and 42 days post-exposure than fine TiO_2 (Shi et al., 2013). A few studies indicate the liver is the primary target organ after oral exposure, and that TiO_2 exposure also may be related to cardiac damage. There is indication from in vitro studies that nano-sized TiO_2 but not microsized TiO_2 is genotoxic, and that the genotoxic response is caused by oxidative stress, assuming a thresholded mechanism. The genotoxic effect of in vitro of TiO_2 has been confirmed in two in vivo studies, which also indicate that genotoxicity is due to inflammation and oxidative stress. Although the genotoxic effect observed after oral exposure might be thresholded, concern is raised due to its carcinogenic potential following chronic exposure (Heinrich et al., 1995), and because of the potential to induce genetic disorders in the offspring as indicated by Trouiller et al. 2009 (Mikkelsen et al., 2011).

Human exposure to nano-TiO_2 may occur during both manufacturing and use. Nano-TiO_2 can be encountered as aerosols, suspensions or emulsions. The major routes of nano-TiO_2 exposure that have toxicological relevance in the workplace are inhalation and dermal exposure.

The most common nanomaterials found in consumer products for dermal application are nano-TiO_2. Nano-TiO_2 are also widely used for toothpaste, food colorants and nutritional supplements. Therefore, oral exposure may occur during use of such products. Worker exposure could occurs during handling, transferring, bagging, mixing, and equipment cleaning.

7 Determination of the potential damage of nano-TiO_2 and their implementation in LCIA.

7.1 Introduction

As mentioned in chapter 5.4, there are currently a number of major uncertainties and knowledge gaps in regard to behavior, chemical and biological interactions and toxicological properties of engineered nanomaterials. Nano-TiO_2 toxicity is linked to a series of properties typical of nanoparticles, such as the crystal form, size, shape, surface area and chemical structure as well as on aggregation status and impurities. Unfortunately, these parameters have not been fully characterized in most published reports. This is a critical issue since dose metric parameters that go beyond traditional mass may better reflect the nanoparticle biologically effective dose in the nano-toxicological field. In fact, surface area, reactivity, morpholgy and particle number should be carefully characterized in order to determine relationships between nanoparticle properties and consequent biological activities (Iavicoli et al., 2012).

7.2 Preliminary definition of the potential damage to human health following Eco-indicator99 framework and implementation in *IMPACT 2002+* method.

In order to identify a preliminary definition of human health characterization factors NIOSH recommendations (NIOSH, 2011) and IARC classification (IARC, 2010) have been considered:

- NIOSH (*National Institute for Occupational Safety and Health*) recommended an occupational exposure limits (REL) of 0.3 mg/m^3 for ultrafine (including engineered nanoscale) TiO_2 as a TWA concentration for up to 10 hrs/day during a 40-hour work week and it suggested a lower level in order to reduce the risks of lung cancer of 1/1000.
- IARC (*International Agency for Research on Cancer*) reviewed TiO_2 and concluded that it is a "possibly carcinogenic to humans".

Eco-indicator99 method calculates the damage to Human Health caused by carcinogenic substance through three main steps (Goedkoop & Spriensma, 2001):

1. Fate analysis: from emission to concentration. Fate factor is calculated from the concentration in air, the concentration in drinking water and the dose by food resulting from EUSES (European Union System for the Evaluation of Substances) output, based on an emission of 10000kg/d and an emission area of 3.6E6 square kilometers.

2. Fate factors are used to transform an emission into a concentration:
   F,air → air: Emission (mg*y^{-1})/m^2 * Fate factor (m^2*y)/m^3 = Concentration in air (mg/m^3)
   F,air → drinking water: Emission (mg*y^{-1})/m^2 * Fate factor (m^2*y)/l = Concentration in drinking water (mg/l)
   F,air → food: Emission (mg*y^{-1})/m^2 * Fate factor (m^2*y)/(kg*d) = Dose by food (mg/kg/d)

3. Effect analysis: from concentration to cancer cases per kg emission. For the effect analysis the list of unit risk (UR) factors compiled by Hofstetter (Hofstetter, 1998) is used. The unit-risk concept (WHO 1987) is used for estimation of the dose response relationship.
   The definition of the unit risk factor is:

Unit risk factor for inhalation is an estimate of the probability that an average individual will develop cancer when exposed to a pollution at an ambient concentration of one microgram per cubic meter for the individual's life (70 years) [UR in cases per μg/m^3].
Effect factor (E)= Unit Risk (per year) * population density
E (cases*μg*m^3/(m^2*y))= UR (cases*μg^{-1}*m^3) / lifetime (70 years) * population density (persons/m^2)
The incidence factors in cancer cases per kg emission in Europe can be calculated by multiplying the Effect factor with Fate factor:
Incidence (cases/kg) = Effect (cases*μg*m^3/(m^2*y)) * 10^9 * Fate (m^2*y)/m^3

4. Damage analysis: from cancer cases per kg to DALYs per kg emission. The estimation of DALYs per incidence case is copied from Hofstetter (Hofstetter, 1998). DALY stands for "disability-adjusted life years" and characterizes the severity by taking into account both mortality (Years of Life Lost - YLL - due to a premature death) and morbidity (Years of Life Lived with Disability -YLD). It is calculated as DALY= YLL+YLD. For this estimation information on the seriousness of the illness, the duration, the death rate and age of the people affected are used. The total DALYs are per kg emission to a specific compartment are calculated by adding the different exposure pathways. In formula:
DALYs per kg emission to air = Incidence, air-air (cases/kg) * DALYs (inhalation) + Incidence, air-drw (cases/kg) * DALYs (oral uptake) + Incidence, air-food (cases/kg) * DALYs (oral uptake).

This framework has been here taken into account to determine the potential damage to Human Health caused by nano-TiO_2 emissions releases to outdoor environment and also to freshwater compartment.

7.2.1 Nano-TiO_2 emissions release to outdoor environment

1. Fate analysis:
The nano-TiO_2 fate factor has been assumed to be equal to the Particulates, < 2.5μm fate factor (Goedkoop & Spriensma, 2001).
Fate Factor (F) = 1.70E-5 m^{2}yr/m^3 This means considering the same long term (steady state) concentration for Particulates, < 2.5μm and nano-TiO_2.

2. Effect analysis:
A concentration limit at the chimney of nano-TiO_2 has been considered equal to 0.3 mg/m^3 (REL of nano-TiO_2 for occupational exposure define by NIOSH). NIOSH calculates the REL values considering a pulmonary particle surface area dose associated with a 1/1000 increase in rat lung cancer and to extrapolate that dose to humans on the basis of particle surface area per unit of lung surface area.
Unit risk factor (UR): 1/1000 cases / 0.3 mg/m^3 = 3.333E-6 cases/μg/m^3 per year.
European population density (PD): 9.44E-5 persons/m^2
Effect factor (E): **UR**(per year)***PD** = 3.333E-6 cases*μg^{-1}*m^3/70 years (average life)* 9.44E-5-persons/m^2 = 4.49E-12 cases*μg^{-1}*m^3/y*persons/m^2.

Only the inhalation route "Incidence, air-air (cases/kg)" (see chapter 7.2) has been taken into account.

Incidence factor (I): **E*F** = 4.49E-12 cases*μg^{-1}*m^3/y*persons/m^2*1.70E-5m^2y/m^3 = 7.633E-17 cases/μg = 7.633 E-8 cases/kg

3. Damage analysis:
   A life expectancy of 80 years, an individual's age of 40 years and the years of life lost (YLL) for nano-TiO_2 inhalation of 40 have been assumed.
   DALYs per kg emission to air = Incidence, air-air (cases/kg) * DALYs (inhalation).
   DALYs = I*YLL = 40yrs*7.633E-8 cases/kg = 3.052E-6 DALY/kg.
   The damage assessment factor of **Human Health** damage category, which included **Carcinogens** impact category, of *IMPACT 2002+* method (Jolliet et al., 2003) has been considered. In particular this value is equal to 2.8E-6 DALY/kg_{C2H3Cl}.
   Characterization factor: 3.052E-6DALY/kg / 2.8E-6DALY/kg_{C2H3Cl} = **1.0904kg_{C2H3Cl}/kg**

Modification of *IMPACT 2002+* method:
IMPACT 2002+ method has been modified by adding in **Carcinogens** impact category a new substance ***Particulates, < 100 nm in air***, that represents the Nano-TiO_2 emission in air with the calculated characterization factor (1.0904 kg_{C2H3Cl}/kg).
Damage, normalization and weighting factors remain unchanged (damage factor: 2.8E-6 DALY/kg_{C2H3Cl}; normalization factor: 141; weighting factor: 1).

7.2.2 Nano-TiO_2 emissions release to freshwater compartment

In order to evaluate the potential damage caused by nano-TiO_2 emissions release into freshwater Anandanl and Kumar study (Anandan and Kumar, 2011) has been considered. The authors evaluated the target organ toxicity dose (TTD) value for human liver cell toxicity in stream water of 8.33μg/L for nano-TiO_2. In addition, the following assumptions have been made.

- Local damage: area of Reggio (Emilia Romagna region – Northern Italy).
- Annual nano-TiO_2 emissions released by industrial plants during the purification of water contaminated with nano-TiO_2: 1kg/y.
- Water bodies volume studied area: 9E6m^3.
- Nanoparticles Concentration into studied water bodies volume (C): 1kg/9E6m^3 = 1.1111E-7 kg/m^3.
- Emitting area (sewage treatment): 10000 m^2.
- Emissions per m^2 (E): 1kg/y/10000m^2 = 1E-4 kg/(m^2*y).
- Limit concentration = Target organ toxicity dose (TTD) value for human liver cell toxicity in stream water of 8.33μg/L for the nano-TiO_2 over this value the concentration of nanoparticles cause cancer with 1/1000 as probability.
- Life expectancy: 80 years.
- population density of Reggio Emilia area (PD) = 2.3429E-4 (pers/m^2).

1. Fate analysis:
   Fate Factor (F) = C/E = 1.1111E-7kg/m^3/1E-4 kg/(m^2*y) = 1.1111E-3 m^2*y/m^3

2. Effect analysis:
   TTD value for human liver cell toxicity in stream water: 8.33μg/L
   Unit Risk (UR): 1/1000cases/(8.33*1E3)μg/m^3 = 1.2E-7casi/μg/m^3
   Effect Factor (E): UR(per year)*PD = 1.2E-7 cases*μg^{-1}*m^3/70yrs*2.3429E-4 (pers/m^2) = 4.018E-13cases/μg/m^3/(m^2*y).
   Only the ingestion of water route "Incidence, drw-drw (cases/kg) * DALYs (oral uptake)" has been taken into account.
   Incidence Factor (I): E*F = 4.018E-13cases*μg^{-1}*m^3/(m^2*y)*1E9 μg/kg*1.1111E-3 m^2*y/m^3 = 4.4644E-7cases/kg

3. Damage analysis:
   YLL (*years of life lost*) = 30 years, YLD (*years lived disability*) = 2 years.
   Cancer survival probability: 50%
   DALYs = I*YLL = (30+2)/2= 16 DALY/cases
   Damage assessment factor (DF): I*DALY = 4.4644E-7cases/kg*16DALY/cases = 7.14E-6 DALY/kg.

Modification of *IMPACT 2002+* method

IMPACT 2002+ has been modified adding a new substance: *Nano-TiO_2 Human Toxicity,* in water and a new impact category: **Nano-TiO_2 carcinogens in freshwater** (kg) with a characterization factor of 1 kg/kg, and also a new damage category, with the same name: **Nano-TiO_2 carcinogens in freshwater** (DALY) with the calculated damage assessment factor of **7.14E-6 DALY/kg**
Normalization and weighting factors remain unchanged (normalization factor: 141; weighting factor: 1).

7.2.3 Nano-TiO_2 emissions inhaled by worker

In order to evaluate the potential damage caused by nano-TiO_2 emissions released to air and directly intaken by workers which apply/use TiO_2 nanoparticles or handle/carry nano-TiO_2 functionalized materials the following assumptions have been done:

- Permissible concentration limit at the chimney of nano-TiO_2 emissions: 0.3 mg/m^3 (over this value the concentration of nanoparticles cause lung cancer with probability of 1/1000).
- 1% of emissions released into the production room during the production process (p); the 99% of these emissions are captured by a vacuum system (E) and the remaining 1% are directly released into the production room.
- Installation of HEPA (High-efficiency particulate absorption) filter with an efficiency of 99.97% (H).
- PPE (Personal Protective Equipment) with mask face filter efficiency of 95% (M).
- Average volume of industrial production area: 1200 m^3.
- Life expectancy: 80 years.
- YLL (years of life lost): 40 years.
- Number of workers in the production room: 5.

Calculation of hourly production limit of nano-TiO_2 emissions:
Hourly production limit: P
C (concentration limit) = (P*p)/V*(1-H)*E
An average flow rate of industrial vacuum system has been considered, V = 2700 m^3/h.
P = (C*V*(1-H)*E)/p = 272.73 kg/h.
Quantity of nano-TiO_2 emissions release into the production room (indoor environment) = p*(1-E)*P = 1%*1%*272.73kg/h = 0.027273 kg/h.
Real concentration limit which has to be taken into consideration for nano-TiO_2 emissions release in the production room: 0.027273kg/h/1200m^3 = 0.227 mg/m^3/h (< 0.3 mg/m^3/h NIOSH concentration limit).
Probability to develop the lung cancer with 0.227 mg/m^3 concentration= 1/1000*0.227mg/m^3/0.3 mg/m^3 = 7.57E-4.
Damage factor = 5workers*40YLL/workers*7.57E-4/0.027573kg/h = 5.5557 DALY/kg.

Modification of *IMPACT 2002+* method
IMPACT 2002+ method has been modified, adding a new substance: ***Particulates, < 100 nm inhaled*** and new impact category: **Carcinogens inhaled** with a characterization factor of 1kg and a new damage category with the calculated damage factor (5.5557 DALY/kg).
Normalization and weighting factors remain unchanged (normalization factor: 141, weighting factor: 1).

7.3 Damage to Aquatic Organism caused by titanium dioxide nanoparticles released in freshwater ecosystem

Salieri identified a freshwater ecotoxicity characterization factor for nano-TiO_2 of 0.28 PAF*m^3*day/kg (Salieri et al., 2015). Since the *Aquatic ecotoxicity* impact category and the respective *Ecosystem quality* damage category of *IMPACT 2002+* method are expressed in kg TEG water (TEG = triethylene glycol) and PAF*m^2*yr respectively, it has been necessary to modify the method adding two new impact and damage categories with the same name. These new categories consider a new substance that represents nano-TiO_2 emissions released in freshwater using the characterization factor calculated by Salieri as damage factor.

Modification of *IMPACT 2002+* method
IMPACT 2002+ has been modified adding a new substance: ***Particulates, < 100 nm in water***, and new impact category: **Nano-TiO_2 ecotoxicity in freshwater** (kg) with a characterization factor of 1 kg and a new damage category, with the same name: **Nano-TiO_2 ecotoxicity in freshwater** (PAF*day*m^3/kg) with a damage assessment factor of 0.28 PAF*day*m^3/kg.
The inverse of *Toluene* characterization factor in water undefined (55.9 CTUe/kg = PAF*m^3*day) of USEtox™ method (USEtox Manual, 2014) has been considered as reference point to calculate the normalization factor, which results of 1/55.9 = 0.0178891.
The weighting factors remains unchanged, namely equal to 1.

7.4 Identification of characterization factor for Human Health indoor and outdoor exposure to nano-TiO_2 emissions following the USEtox™ model

The framework developed in this chapter has been performed in collaboration with EMPA - Swiss Federal Laboratories for Materials Science and Technology, Technology and Society Laboratory and submitted to International Journal of Life Cycle Assessment (Pini et al., 2015).
USEtox™ represents a consensus amongst LCA model developers for the calculation of human and ecotoxicity characterization factors amongst associated multimedia models (Sala et al., 2011a). The ILCD Handbook (JRC-IES, 2010b) recommends the used USEtox™ to model impacts related to ecotoxicity and human toxicity at the midpoint level. USEtox™ is not spatially regionalized and thus does not reflect the influence of landscape parameters variability on ecotoxicity and human toxicity impact scores for different geographical units (Sala et al., 2011b).

7.4.1 Framework for human health impact assessment

Figure 7.1 shows the USEtox™ framework to model human exposure and related toxicological effects of releases into air, starting from the emitted amount.

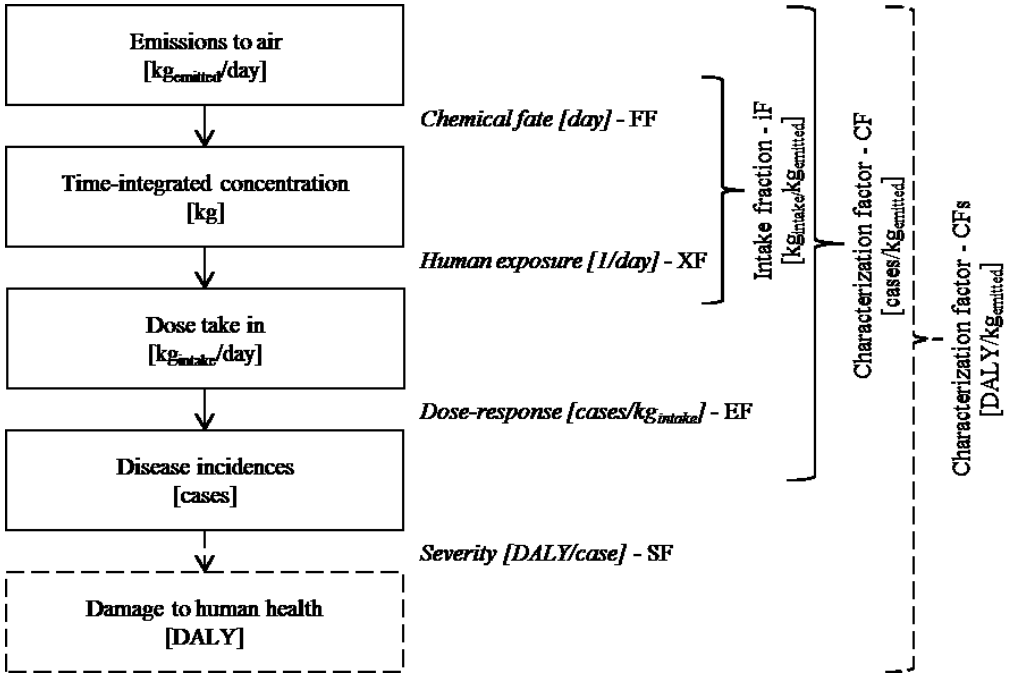

Figure 7-1 USEtox™ Framework for human health impacts assessment (Rosenbaum et al., 2011)

USEtox™ framework for human health impact takes into account the fate factor (FF), the exposure factor (XF), and the effect factor (EF) of the emitted substance (Rosenbaum et al., 2008 and 2011) together with the severity factor (SF) to obtain the endpoint characterization factor (Huijbregts et al., 2005). Thereof, the first two factors, i.e. FF and XF, are aggregated into the so-called intake fraction (iF) [$kg_{intake}/kg_{emitted}$], defined as the integrated incremental intake of a pollutant, summed over all exposed individuals, and occurring over a given exposure time, per unit of pollutant emitted (Bennett et al., 2002 and Humbert et al., 2011):

$$iF = \frac{\sum_{people,time} \text{intake of pollutant by an individual (mass)}}{\text{mass released into the environment (mass)}} \quad \text{(eq. 8)}$$

The iF is thereby defined as the ratio of the mass intake by an individual over the mass released to the environment (Ilacqua et al., 2007). Hence, the iF expresses the marginal increase in exposure due to an increase in emission. The XF, relates the amount of a chemical in an environmental compartment to the chemical intake by humans. The latter is separated into direct intake (e.g. by breathing air and drinking water, etc.), and indirect intake (through bioaccumulation processes in animal tissues such as meat, milk and fish). The EF can be interpreted as the increase in the number of cases of a given morbidity (e.g. cancer or non-cancer diseases) risk, in the exposed population, per unit mass ingested or inhaled [cases/$kg_{emitted}$] (Rosenbaum, R. K., Margni, M., Jolliet, 2007).
The CF is a quantitative representation of the hazardousness or impact potential related to the emission of a mass unit of a pollutant (Henderson, A.D., Hauschild, M.Z., van de Meent, D., Huijbregts, M.A.J., Larsen, H.F. Margni, M., McKone, T.E., Payet, J., Rosenbaum & Jolliet, 2011) and can be estimated, on the level of cases, through fate, exposure and effect steps (equation 9).

CF = FF * XF * EF (eq. 9)

The characterization factor (CF) can then be measured either in (disease) cases/$kg_{emitted}$, or as damage in DALY/$kg_{emitted}$. DALY stands for "disability-adjusted life years" (Hofstetter, 1998) and characterizes the severity by taking into account both mortality (Years of Life Lost -YLL- due to a premature death) and morbidity (Years of Life Lived with Disability -YLD). It is calculated as DALY= YLL+YLD. For the damage in DALY/kg, the severity factor SF – factor representing an increase in adversely affected life years as a consequence of an emission in the environment (Rosenbaum et al., 2007) – has to be added to this equation (equation 10).

CF = FF * XF * EF * SF (eq. 10)

SF distinguishes between differences in the severity of disabilities caused by a disease (e.g. cancer, non-cancer) in terms of affected life years. Included in this study are both human toxicity effects, i.e. the carcinogens and the non-carcinogens effects. Based on the benchmark dose (defined as "*a dose or concentration that produces a predetermined change in response rate of an adverse effect compared to background*") used by NIOSH to identify the recommended occupational exposure limit (REL), the effect factor for carcinogens effects can be determined (NIOSH, 2011). Regarding non-carcinogens health effect NOAEL (no-observed adverse effect level) and LOAEL (lowest observed adverse effect level) values have been considered in the calculation (SCCS, 2013).

7.4.2 Methodological approach

The general USEtox^{TM} framework is here adapted and applied on releases of ENMs, in particular on releases of nano-TiO_2. Only direct exposure as route of exposure is considered, since to date the calculation of bioaccumulation and biomagnification factors, in order to evaluate indirect human exposure, it is not possible for ENMs due to a lack of respective data (SCENIHR, 2009). For the indoor environment a single-compartment box model is recommended as default in LCA, as this is enabling to screen occupational and household exposures consistent with the existing models to assess outdoor emission in a multimedia environment (Hellweg et al., 2009). Instead, for outdoor

iF, the FF calculation is required in order to assess the environmental behavior of ENM considering all the transport and removal processes occurring in and across the environmental media. For this, the SimpleBox4Nano (SB4N) multimedia model, developed by Meesters and co-authors (Meesters, et al., 2014) has been used here.

7.4.2.1 *Intake Fraction*

Indoor intake fraction

So far, health effects due to *indoor* exposure are generally neglected in LCA. However, such an omission is an important shortcoming, as it may result in product or process optimizations at the expense of workers' or consumers' health (Hellweg et al., 2009). Therefore, in this work the human occupational indoor exposure has been assessed as corresponding intake fraction (iF_i). The iF_i has been calculated following the formula proposed by (Hellweg et al., 2009):

$$iF_i = \frac{INH * POP_i}{V_i * m * k_{ex}} \quad \text{(eq. 11)}$$

Within equation 11, *i* is the index for indoor (environment); INH is the daily inhalation rate of a person (being a constant volume of 13 m^3/person/day) (Rosenbaum, R.K., Huijbregts, M.A.J., Henderson, A. D., Margni, M., McKone et al., 2011); POP_i is the number of workers exposed, V_i is the indoor building volume (m^3), k_{ex} is the air exchange rate of the building volume in the exposure area and *m* (unitless) is the mixing rate (defined as the abundance of one component of a mixture relative to that of all other components). For an occupational setting with a mechanical system, the air exchange rate value of 3 h^{-1} (Hellweg et al., 2009 and Humbert et al., 2011), represents the number of air changes per hour (in this case is 3 changes per hour). Moreover, assuming a complete mixing of the indoor volume, *m* is set to 1 [1] (Hellweg et al., 2009 and Humbert et al., 2011). Hence, evaluating the occupational exposure, equation 11 can be rewritten considering an industry building volume per person as reported in equation 12.

$$iF_i = \frac{INH}{V_{i\,person} * m * k_{ex}} \quad \text{(eq. 12)}$$

Where $V_{i\ person}$ is the ratio between V_i an POP_i (equation 11). Hellweg estimated an average building volume per worker for chemical industry in Switzerland of 440 m^3/worker (Hellweg et al., 2009).

Outdoor intake fraction

The human outdoor intake fraction is calculated in principle as described in the USEtox™ model, i.e. out of the chemical fate, termed fate factor (FF), and the human exposure (XF) (Figure1). The fate factor describes thereby how a chemical substance behaves in the environment. In USEtox™ the principles of the multimedia box model and the environmental fate are quantified on the basis of portioning coefficients (Rosenbaum et al., 2007; USEtox™, 2014). However, concerning ENMs there is evidence that portioning coefficients calculated like this are no valid to describe and quantify the fate and the behaviour (Praetorius et al., 2014). Instead, for modelling the behaviour of ENMs in environmental compartments colloidal science is currently applied (Liu & Cohen, 2014;

Meesters et al., 2014; Praetorius et al., 2012). The SB4N model (J. a J. Meesters et al., 2014) used in this work is a multimedia media box model where the transport and removal processes of ENMs in the environmental media are accounted e.g.:

- the transport between compartments,
- the removal by transport outside the system,
- the uptake in aggregates or the attachment to the surfaces of larger particles,
- the removal via processes such as degradation and dissolution.

With this, the model expresses transport and removal rates in and across air, rain, surface water, soil and sediment by accounting for nano-specific processes such as aggregation, attachment, and dissolution for ENMs. Furthermore, the model accounts that an ENMs (like nano-TiO_2 in our case) can occur in different physical-chemical forms – e.g. as free dispersive species, as heteroagglomerate with natural colloids, or attached to larger natural particles. Since the fate of airborne ENMs is also influenced by wet deposition, the atmospheric compartment is further divided in the two sub-compartments "rain" and "dry air". In this way the model allows to evaluate both wet and dry deposition. Outputs of the application of the SB4N model are in the end mass concentrations of an ENM (here nano-TiO_2) as free dispersive species, as heteroagglomerate with natural colloids, and as larger particles in each compartment in time and at a steady-state conditions. In their publication, Meesters and co-authors calculated first-order rate constants (k, day^{-1}) for all above mentioned transport and removal processes for the nano-TiO_2 in Switzerland (Table 4 reports the Meesters and co-authors's rate constants), based on the flow data reported in Mueller and Nowack (Nowack & Mueller, 2008).

Table 4 First-order rate constant values that SB4N model calculates for environmental transport and removal processes for the Mueller and Nowack nano-TiO_2 scenario (J. a J. Meesters et al., 2014).

Rates	Transport / Removal Process	Value	Unit
k_{aggA}	Aggregation rate for ENPs with aerosol particles in dry air (A)	1.36E-01	day^{-1}
k_{attA}	Attachment rate for ENPs with coarse particles in dry air (A)	1.14E-03	day^{-1}
$k_{\Lambda ARfree}$	Rain drop collection rate for free ENP species	5.20E-01	day^{-1}
$k_{\Lambda ARagg}$	Rain drop collection rate for aggregated ENP species	1.56E-01	day^{-1}
$k_{\Lambda ARatt}$	Rain drop collection rate for attached ENP species	3.84E-01	day^{-1}
$k_{depASfree}$	First-order rate constant for dry deposition from dry air (A) to soil (S) for free ENP species	1.37E-01	day^{-1}
$k_{depASagg}$	First-order rate constant for dry deposition from dry air (A) to soil (S) for aggregated ENP species	2.17E-02	day^{-1}
$k_{depASatt}$	First-order rate constant for dry deposition from dry air (A) to soil (S) for attached ENP species	8.13E-02	day^{-1}
$k_{depAWfree}$	First-order rate constant for dry deposition from dry air (A) to soil (W) for free ENP species	2.07E-03	day^{-1}
$k_{depAWagg}$	First-order rate constant for dry deposition from dry air (A) to water (W) for aggregated ENP species	2.42E-03	day^{-1}
$k_{depAWatt}$	First-order rate constant for dry deposition from dry air (A) to soil (W) for attached ENP species	2.59E-03	day^{-1}
$k_{depRSfree,agg,att}$	First-order rate constant for wet deposition from rain (R) to soil (S) for free, aggregated or attached ENP species	2.06E+02	day^{-1}
$k_{depRWfree,agg,att}$	First-order rate constant for wet deposition from rain (R) to water (W) for free, aggregated or attached ENP species	6.58E+00	day^{-1}
k_{aggS}, k_{aggSE}	Aggregation rate for ENPs with natural colloids to soil (S) and to sediments (SE) pore water	7.27E-02	day^{-1}

$k_{attS,}$ k_{attSE}	Attachment rate for ENPs with solid grains to soil (S) and to sediments (SE)	3.15E+02	day^{-1}
$k_{runSWfree,agg}$	First-order rate constant for run-off from soil (S) to water (W) for free or aggregated ENP species	2.53E-02	day^{-1}
$k_{erosionSWatt}$	First-order rate constant for run-off from soil (S) to water (W) for attached ENP species	1.45E-06	day^{-1}
$k_{leachSagg,free}$	First-order rate constant for run-off from soil (S) to water (W) for free ENP species	2.53E-02	day^{-1}
k_{aggW}	Aggregation rate for ENPs with natural colloids in surface water (W)	7.27E-02	day^{-1}
k_{attW}	Attachment rate for ENPs with suspended particles in surface water (W)	5.27E-05	day^{-1}
$k_{depWSEfree}$	First-order rate constant for deposition from water (W) to sediments (SE) for free ENP species	2.02E-05	day^{-1}
$k_{depWSEatt}$	First-order rate constant for deposition from water (W) to sediments (SE) for attached ENP species	2.04	day^{-1}
$k_{depWSEagg}$	First-order rate constant for deposition from water (W) to sediments (SE) for aggregated ENP species	1.42E-03	day^{-1}
$k_{rsSEWfree,agg}$	First-order rate constant for resuspension from sediments (SE) to water (W) for free or aggregated ENP species	6.57E-02	day^{-1}
$k_{rsSEWatt}$	First-order rate constant for resuspension from sediments (SE) to water (W) for attached ENP species	2.63E-01	day^{-1}

For this, they quantified the rate coefficient values (k, s^{-1}) through SB4N using Switzerland as geographical unit and assuming nano-TiO_2 particles with a radius of 10 nm and a density of 4230 kg/m^3. These rate coefficients are used in the present work in order to build the rate coefficient matrix $\overline{K}$ (day^{-1}) as requested by the USEtox™ framework (Table 5).

Table 5 Matrix of first-order rate constant values K expressed in day^{-1} for environmental transport and removal processes (where atm= atmosphere, att= attachment, agg= aggregation) (J. a J. Meesters et al., 2014).

	Free in atm	Agg in atm	Att in atm	Free in rain	Agg in rain	Att in rain	Free in soil pore water	Agg in soil pore water	Att to solids soil	Free in water	Agg in water	Att in water	Free in sediment	Agg in sediment	Att in sediment
Free in atm	$-(\Sigma k_{rAfree})$	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Agg in atm	k_{aggA}	$-(\Sigma k_{rAagg})$	0	0	0	0	0	0	0	0	0	0	0	0	0
Att in atm	k_{attA}	0	$-(\Sigma k_{rAatt})$	0	0	0	0	0	0	0	0	0	0	0	0
Free in rain	$k_{\Lambda ARfree}$	0	0	$-(\Sigma k_{rRfree})$	0	0	0	0	0	0	0	0	0	0	0
Agg in rain	0	$k_{\Lambda ARagg}$	0	0	$-(\Sigma k_{rRagg})$	0	0	0	0	0	0	0	0	0	0
Att in rain	0	0	$k_{\Lambda ARatt}$	0	0	$-(\Sigma k_{rRatt})$	0	0	0	0	0	0	0	0	0
Free in soil pore water	$k_{depASfree}$	0	0	$k_{depRSfree}$	0	0	$-(\Sigma k_{rSfree})$	0	0	0	0	0	0	0	0
Agg in soil pore water	0	$k_{depASagg}$	0	0	$k_{depRSagg}$	0	k_{aggS}	$-(\Sigma k_{rSagg})$	0	0	0	0	0	0	0
Att to solids soil	0	0	$k_{depASatt}$	0	0	$k_{depRSatt}$	k_{attS}	0	$-(\Sigma k_{rSatt})$	0	0	0	0	0	0
Free in water	$k_{depAWfree}$	0	0	$k_{depRWfree}$	0	0	$k_{runSWfree}$	0	0	$-(\Sigma k_{rWfree})$	0	0	$k_{rsSEWfree}$	0	0
Agg in water	0	$k_{depAWagg}$	0	0	$k_{depRWagg}$	0	0	$k_{runSWagg}$	0	k_{aggW}	$-(\Sigma k_{rWagg})$	0	0	$k_{rsSEWagg}$	0
Att in water	0	0	$k_{depAWatt}$	0	0	$k_{depRWatt}$	0	0	$k_{erosionSWatt}$	k_{attW}	0	$-(\Sigma k_{rWatt})$	0	0	$k_{rsSEWatt}$
Free in sediment	0	0	0	0	0	0	0	0	0	$k_{depWSEfree}$	0	0	$-(\Sigma k_{rSEfree})$	0	0
Agg in sediment	0	0	0	0	0	0	0	0	0	0	$k_{depWSEagg}$	0	k_{aggSE}	$-(\Sigma k_{rSEagg})$	0
Att in sediment	0	0	0	0	0	0	0	0	0	0	0	$k_{depWSE}a_{tt}$	k_{attSE}	0	$-(\Sigma k_{rSEatt})$

Table 6 Fate factor Matrix (where atm= atmosphere, att= attachment, agg= aggregation) (Pini et al., 2015)

	Free in atm	Agg in atm	Att in atm	Free in rain	Agg in rain	Att in rain	Free in soil pore water	Agg in soil pore water	Att to solids soil	Free in water	Agg in water	Att in water	Free in sediment	Agg in sediment	Att in sediment
Free in atm	1.26	0	0	0	0	0	0	0	0	0	0	0	0	0	0
Agg in atm	9.44E-01	5.54	0	0	0	0	0	0	0	0	0	0	0	0	0
Att in atm	3.06E-03	0	2.14	0	0	0	0	0	0	0	0	0	0	0	0
Free in rain	3.07E-03	0	0	4.69E-03	0	0	0	0	0	0	0	0	0	0	0
Agg in rain	6.93E-04	4.07E-03	0	0	4.69E-03	0	0	0	0	0	0	0	0	0	0
Att in rain	5.51E-06	0	3.85E-03	0	0	4.69E-03	0	0	0	0	0	0	0	0	0
Free in soil pore water	2.55E-03	0	0	3.07E-03	0	0	3.17E-03	0	0	0	0	0	0	0	0
Agg in soil pore water	6.47E	3.79E+01	0	8.83E-03	3.83E+01	0	9.11E-03	3.95E+01	0	0	0	0	0	0	0
Att to solids soil	5.56E+05	0	6.68E+05	6.67E+05	0	6.68E+05	6.89E+05	0	6.89E+05	0	0	0	0	0	0
Free in water	3.14E-01	0	0	4.25E-01	0	0	1.10E-03	0	0	1.37E+01	0	0	2.86E-03	0	0
Agg in water	6.82E+01	3.53E+02	0	1.10E+01	3.53E+02	0	1.10E-01	3.53E+02	0	3.53E+02	3.53E+02	0	-8.00E-03	-3.53E+02	0
Att in water	1.98E-01	0	2.45E-01	2.38E-01	0	2.45E-01	2.45E-01	0	2.45E-01	1.09E-04	0	2.45E-01	-2.45E-01	0	-2.45E-01
Free in sediment	2.01E-08	0	0	2.73E-08	0	0	7.06E-11	0	0	8.80E-07	0	0	3.17E-03	0	0
Agg in sediment	-1.47	-7.61	0	-2.37E-01	-7.61	0	-2.37E-03	-7.61	0	-7.61	-7.61	0	-3.34E-03	-7.61	0
Att in sediment	-1.54	0	-1.90	-1.84	0	-1.90	-1.90	0	-1.90	-1.91E-03	0	-1.90	-1.90	0	-1.90

From this, the fate factor matrix $\overline{FF}$ as the the negative inverse matrix of the rate coefficient matrix ($-\overline{K}^{-1}$), (Rosenbaum, R. K., Margni, M., Jolliet, 2007) can then be calculated according to equation 13 (Table 6):

$$\overline{FF} = -\overline{K}^{-1} \quad \text{(eq. 13)}$$

Next, as shown in Figure 7.1, the intake fraction iF can be calculated by a multiplication of the fate factor matrix $\overline{FF}$ with the exposure factor $\overline{XF}$ according to equation 14 (Rosenbaum, R.K., Huijbregts, M.A.J., Henderson, A. D., Margni, M., McKone et al., 2011):

$$\overline{\imath F_o} = \overline{FF} * \overline{XF} \quad \text{(eq. 14)}$$

In this work here, we focus on direct human exposure by inhalation. Hence, the intake fraction calculation here needs to take into account only the part of the fate factor matrix related to air; namely free, aggregation, attachment in *atmosphere* and free, aggregation, attachment in *rain*.
The related $\overline{XF}$ vector is calculated according to equation 15, being therefore equal for each of the above mentioned air compartments, taken into account in this study here.

$$\overline{XF} = \frac{INH * POP_o}{V_o} \quad \text{(eq. 15)}$$

Equation 15 represents the outdoor exposure factor, where the index *o* represents outdoor environment, INH is the daily inhalation rate of a person (13 m^3/person/day) as in the indoor environment, POP_o is the number of people exposed and V_o is the volume of the exposure area (m^3). POP_o refers to population of Switzerland (8112200 inhabitants (J. a J. Meesters et al., 2014)) and V_o is calculated taking a 1000 m high compartment of the atmosphere (ECB, 2003), with the geographic area of Switzerland (4.13E10 m^2 (J. a J. Meesters et al., 2014)) as surface. For the remaining compartments (soil, water, sediment) the respective exposure values are set equal to zero due to this focus on direct exposure by inhalation.

7.4.2.2 ***Effects factor***

As mentioned above, the human-toxicological effect factor reflects the change in life time disease probability due to change in life time intake of a pollutant. The USEtox™ model accounts for both non-carcinogenic and carcinogenic effects. The human-toxicological effect factor (EF) is calculated (equation 16) under the assumption of linearity in the concentration-response up to the lifetime disease probability of 0.5 (USEtox™, 2014):

$$EF = \frac{0.5}{ED_{50h}^{lifetime}} \quad \text{(eq. 16)}$$

In general ED_x is defined as the effect dose generating an additional risk of x% over background. For carcinogenic effects, the $ED_{50h}^{lifetime}$ is the estimated life time dose generating 50% increase in cancer for human [kg/lifetime] and it is calculated as:

$$ED_{50h}^{lifetime} = \frac{ED_{50}^{a,t,j} * BW * LT * N}{AF_a * AF_t} \quad \text{(eq. 17)}$$

where $ED_{50}^{a,t,j}$ is the daily effect dose for animal *a*, time duration *t* and exposure route *j* that causes a disease probability of 50% [mg*kg^{-1}*day^{-1}]. AF_a is the extrapolation factor for interspecies differences and AF_t is the extrapolation factor for differences in time of exposure (2 for sub-chronic to chronic exposure and 5 for sub-acute to chronic exposure). BW is the body weight of humans, LT the average lifetime of humans and N the number of days per year (USEtox^{TM}, 2014).
For non-carcinogenic effects $ED_{50}^{a,t,j}$ can also be extrapolated from NOAEL or from LOAEL via the following equations:

$$ED_{50}^{a,t,j} = NOAEL^{a,t,j} * AF_N \quad \text{(eq. 18)}$$

$$ED_{50}^{a,t,j} = \frac{LOAEL^{a,t,j}}{AF_L} * AF_N \quad \text{(eq. 19)}$$

AF_N is there by the extrapolation factor from NOAEL to ED50, with a value of 9, and AF_L is the extrapolation factor from LOAEL to NOAEL with a value of 4 (Huijbregts et al., 2005).

7.4.3 Results: intake fraction, effect factors, characterization factors

Titanium dioxide nanoparticles have been considered here as an exemplary case study for demonstrating the applicability of the USEtox^{TM} framework on ENM releases. Nano-TiO_2 has been chosen since it is one of the most widely used ENMs, used in a large number of applications, e.g. to confer self-cleaning and anti-fogging properties to the materials. In addition its environmental fate is simpler than other ENM, e.g. nano-Ag, because it can be considered to be stable towards degradation (no dissolution), thus simplifying the fate assessment.

7.4.3.1 ***Intake Fraction***

The indoor intake factor, iF_i ,calculated according to equation 12 for human occupational indoor exposure, is 4.1E-04. As shown in equations 4 and 5, the iF_i is independent from the physical-chemical properties of the substance under investigation, i.e. all other ENMs would end up with the same value like nano-TiO_2. The resulting outdoor intake fraction (equation 15) iF_o value is 2.53E-05 and it has been determined by summing up all values of the resulting iF vectors. These iF vectors together with the corresponding XF vectors are reported in details in Table 7 and 8.

Table 7 Exposure factor vector (where atm= atmosphere, att= attachment, agg= aggregation) (Pini et al., 2015)

	Free in atm	Agg in atm	Att in atm	Free in rain	Agg in rain	Att in rain	Free in soil pore water	Agg in soil pore water	Att to solids soil	Free in water	Agg in water	Att in water	Free in sediment	Agg in sediment	Att in sediment
Switzerland air	2.554E-06	2.554E-06	2.554E-06	2.554E-06	2.554E-06	2.554E-06	0	0	0	0	0	0	0	0	0

Table 8 Intake factor vector (where atm= atmosphere, att= attachment, agg= aggregation) (Pini et al., 2015)

	Free in atm	Agg in atm	Att in atm	Free in rain	Agg in rain	Att in rain	Free in soil pore water	Agg in soil pore water	Att to solids soil	Free in water	Agg in water	Att in water	Free in sediment	Agg in sediment	Att in sediment
Switzerland air	5.636E-06	1.416E-05	5.474E-06	1.199E-08	1.199E-08	1.199E-08	0	0	0	0	0	0	0	0	0

7.4.3.2 ***Effect factor***

Carcinogenic effects

To date the actual knowledge of nano-TiO_2 toxicity largely depends on a limited number of experimental animal (*vivo*) or cell culture (*vitro*) studies, where extrapolation to human exposures and toxicity is required. Epidemiological studies so far have not been able to correlate any association between the occupational exposure to nano-TiO_2 and an increased risk for cancer. Pulmonary inflammatory responses and lung cancers to nano-TiO_2 exposures and are the most important adverse effect observed in animal experiments (Shi et al., 2013). The most relevant data for assessing the health risk to workers are results from a chronic animal inhalation study with ultrafine (< 100 nm) TiO_2 in which a statistically significant increase in adenocarcinomas has been observed (Heinrich et al., 1995). This is supported by a TiO_2 pattern that induced responses of persistent pulmonary inflammation in rats and mice (Everitt et al., 2000 and Bermudez et al., 2004) and cancer responses for particles related to their surface area. On the basis of all these studies, NIOSH has determined that an exposure to ultrafine TiO_2 (including engineered nanoscale) should be considered a potential occupational carcinogen. NIOSH has concluded that ultrafine TiO_2 is not a direct-acting carcinogen, but acts through a secondary genotoxicity mechanism that is not specific to TiO_2 but primarily related to particle size and surface area (NIOSH, 2011). Evidences suggest that the surface area matters more than the particle mass for a quantification of the lung inflammatory response to nanoparticles exposure and supports the concept that the surface area is the dose measurement that best predicts pulmonary toxicity (Donaldson et al., 2004 and Wittmaack, 2007). The benchmark dose response level used by NIOSH has been defined as the particle surface area per gram of lung tissue associated with a 4% inflammatory response of neutrophils, which has been considered to a low level inflammatory response (Tran et al., 1999).

For this work, the benchmark dose for particle surface area dose (m^2) per gram of lung, extrapolated by NIOSH from Bermudez et al. study (Bermudez et al., 2004), has been considered. In particular, this dose is associated with pulmonary inflammation response (PIR) in rats of 0.0144 m^2/g. Here, this value has been assumed as a daily exposure dose. Moreover, an equal sensitivity of rat lung surface area and rat body has been postulated. Then, the value from the study of Heinrich and co-workers (Heinrich et al., 1995) of 48 m^2/g has been used here as TiO_2 particle surface area (PSA). The benchmark dose is the model's best estimate of the effective dose (ED) (DPR MT-2., 2004).

Based on all this, an ED_4 value for human health *carcinogenic effects* can been calculated as follows:

$$ED_4^{rat,s-c,inhalation} = \frac{PIR}{\text{PSA}} = 0.30 \text{ mg/kg bw/day} \qquad \text{(eq. 21)}$$

With this ED_4 value (from equation 21) equations 9 and 10 are adapted, i.e. a 4% (instead of 50%) of effect increase in cancer response to the administered dose is considered in order to calculate the EF and $ED_{50h}^{lifetime}$ values:

$$EF = \frac{0.04}{ED_{4h}^{lifetime}} \qquad \text{(eq. 22)}$$

Where

$$ED_{4h}^{lifetime} = \frac{ED_4^{rat,s-c,inhalation} * BW * LT * N}{AF_a * AF_t} \quad \text{(eq. 23)}$$

Non-carcinogenic effects

For human health *non-carcinogens effects* a NOAEL value of 62.5 mg/kg-body weight/day and a LOAEL value of 5 mg/kg-body weight/day results from sub-chronic (s-c) oral study on mice (SCCS, 2013) have been considered to calculate $ED_{50}^{mice,s-c,inhalation}$ values following equations 11 and 12 and consequently $ED_{50h}^{lifetime}$ value (equation 17).

Indoor effect factor

Table 9 reports the EFs values for both carcinogenic and non-carcinogenic effects in an indoor environment. In order to calculate these values with the formula for EF shown in the previous chapter (i.e. equations 16 and 17), an N value representing the number of working days per year (potential exposure days) of 240 days/year (European labour law, 99/70/EC) and a lifetime of humans (LT) value of 45 years working lifetime (NIOSH, 2011) has been considered. Extrapolation factors for interspecies difference for rat and mice (4.1 and 7.3 respectively) and the transformation from sub-chronic to chronic exposure have been taken directly from the USEtox^{TM} model.

Table 9 Effect factors for Indoor environment, where s-c= sub-chronic and inh= inhalation

Human health effect	**Toxicity value**	**References**	**$ED_4^{a,t,j}$**	**$ED_{4h}^{lifetime}$**	**EF**	**Reference equations**
Carcinogenic	ED_4	NIOSH, 2011	$ED_4^{rat,s-c,inh}$	2.77E-2	1.45	22, 23
Human health effect	**Toxicity value**	**References**	**$ED_{50}^{a,t,j}$**	**$ED_{50h}^{lifetime}$**	**EF**	**Reference equations**
Non-carcinogenic	NOAEL	SCCS, 2013	$ED_{50}^{mice,s-c,inh}$	2.91E+1	1.72E-2	16, 18
Non-carcinogenic	LOAEL	SCCS, 2013	$ED_{50}^{mice,s-c,inh}$	5.87E-1	8.58E-1	16, 19

Outdoor effect factor

Similar as above, Table 10 reports the EFs for both carcinogenic and non-carcinogenic effects in the outdoor environment. In this case the number of days of exposure per year (N) and the average LT have been set to 365 days/year and 70 year/lifetime in accordance with the USEtox^{TM} model (USEtox^{TM}, 2014) and the extrapolation factors for interspecies difference and for differences in time of exposure values have been considered the same as for the indoor effect factor (see above).

Table 10 Effect factors for Outdoor environment, where s-c= sub-chronic and inh= inhalation

Human health effect	Toxicity value	References	$ED_4^{a,t,j}$	$ED_{4h}^{lifetime}$	EF	Reference equations
Carcinogenic	ED_4	NIOSH, 2011	$ED_4^{rat,s-c,inh}$	6.54E-2	6.11E-1	22, 23
Human health effect	**Toxicity value**	**References**	$ED_{50}^{a,t,j}$	$ED_{50h}^{lifetime}$	**EF**	**Reference equations**
Non-carcinogenic	NOAEL	SCCS, 2013	$ED_{50}^{mice,s-c,inh}$	6.89E+1	7.26E-3	16, 18
Non-carcinogenic	LOAEL	SCCS, 2013	$ED_{50}^{mice,s-b,inh}$	1.38	3.63E-1	16, 19

7.4.3.3 *Characterization factor*

By combining the exposure, fate and effects factors according to equation 8, midpoint characterization factors (CF_i and CF_o) for human toxicity impacts expressed in disease cases per kilogram emitted [cases/$kg_{emitted}$] can be calculated for both the indoor and the outdoor environment, as well as for carcinogenic and non-carcinogenic effects. The CF for carcinogenic effects is calculated by considering the ED_4 toxicity value (i.e. by using equation 22), the CF for non-carcinogenic effect is calculated by taking into account both NOAEL and LOAEL toxicity values.

If the severity factor (SF) is added, it is possible to obtain the endpoint characterization factors (CF_{Si} and CF_{So}), expressed in damage per kilogram emitted [DALY/$kg_{emitted}$]. Default damage severity factors for cancer and non-cancer effects proposed by Huijbregts et al. (Huijbregts et al., 2005), and based on world data in 1990 of 11.5 DALY per cancer case and of 2.7 DALY per non-cancer case have been used here. Table 11 show the identified human health CFs for indoor and outdoor environment combining even the severity step. Again, the CFs are split into carcinogenic and non-carcinogenic parts.

Table 11 Human health CFs for both indoor and outdoor environments and carcinogenic and non-carcinogenic effects, where S= severity, i= indoor and o= outdoor

	Indoor environment		Outdoor environment	
Human health effect	$\mathbf{CF_i}$ [cases/$kg_{emitted}$]	$\mathbf{CF_{S,i}}$ [DALY/$kg_{emitted}$]	$\mathbf{CF_o}$ [cases/$kg_{emitted}$]	$\mathbf{CF_{S,o}}$ [DALY/$kg_{emitted}$]
Carcinogenic (ED_4)	5.93E-04	6.82E-03	1.55E-05	1.78E-04
Non-carcinogenic (NOAEL)	7.04E-06	1.90E-05	1.84E-07	4.96E-07
Non-carcinogenic (LOAEL)	3.52E-04	9.51E-04	9.18E-06	2.48E-05

7.4.3.4 *Continental scale (Outdoor environment)*

The USEtox™ model distinguishes two geographical scales, the *continental scale* (distinguishing between urban air, rural air, freshwater, sea, coastal marine water, natural soil and agricultural soil) and the *global scale* (with air, freshwater, ocean, natural soil and agricultural soil only).

The scope of this further step was therefore to evaluate how the (above reported) outdoor CFs vary, when the system dimensions such as area, height and volume of atmosphere are modified – i.e. by changing the geographical area from Switzerland to a continental range (Europe). For this, the first-order rate constant values for environmental transport and removal processes of the scenario for Switzerland have been extended to the *continental* scale. The geographic area and the number of inhabitants are the only factors that change passing from *Switzerland* to such a *continental* scenario;

these factors for Europe are 11.4E14 m^2 and 9.98E8 persons, respectively. Table 12 shows the resulting midpoint and endpoint characterization factors for outdoor emissions calculated for this *continental* scale.

Table 12 Continental USEtox^{TM} scale: human health CFs for outdoor environments and both carcinogenic and non-carcinogenic effects, where S= severity, c= continental

	Outdoor environment	
Human health effect	**CF_c** [cases/$kg_{emitted}$]	**$CF_{S,c}$** [DALY/$kg_{emitted}$]
Carcinogenic (ED_4)	6.89E-07	7.93E-06
Non-carcinogenic (NOAEL)	8.18E-09	2.21E-08
Non-carcinogenic (LOAEL)	4.09E-07	1.10E-06

However, the whole fate factor matrix for such a *continental* scale might be improved by more adequate transport and removal rates; in particular, by considering input parameters such as nano-TiO_2 radius, nano-TiO_2 mass density, aggregation and attachment efficiency, distinctive of this geographic area. Therefor the authors recommend for the moment adopting in LCIA the CFs value reported in Table 11; the environmental transport and removal processes of nano-TiO_2 considered here represent the actual rates calculated for the applied geographic area, i.e. Switzerland.

7.5 Discussion and conclusion

The main aim of this thesis is to assess the sustainability of nano-TiO_2 functionalized building materials, extending the boundaries even to their application to the renovation of historical buildings. In order to take into account that release of ENMs into the environment can potentially occur throughout their entire life cycle (from the fabrication/application of ENMs, to the use and end of life phase), the potential risks and damage that these new materials provoke to human health and environment must necessarily to be analyzed. The two approaches above described (see chapters 7.2 and 7.3) represent a first attempt to establish a methodological framework to calculate human health characterization factors for nano-TiO_2 to be applied in LCIA steps and adopted within *IMPACT 2002+* and *USEtox^{TM}* modified methods. The first approach, which considers the Eco-indicator99 framework for carcinogenic substance, is a preliminary attempt to identify the potential human toxicity caused by nano-TiO_2 releases. This calculation may suffer from some assumptions such as considering the same fate factor of PM 2.5μm for nano-TiO_2 (outdoor environment); fixing, for nano-TiO_2 emissions inhaled by worker, the rate of emissions released into the production room during the production process, the rate of emissions that are captured by the vacuum system, the indoor production room volume or the number of workers in the production room (indoor environment). Moreover, aggregation, attachment and deposition rates in the indoor environment are not taken into consideration, for outdoor environment these rates coefficient are considered the same of PM 2.5μm under the assumption that the fate factor of PM 2.5μm is equal to the fate factor of nano-TiO_2. Even so, *IMPACT 2002+* method has the important quality to provide combined midpoint/damage approach, linking all types of life cycle inventory results to 14 midpoint categories (human toxicity, respiratory effects, ionizing radiation, ozone depletion, photochemical oxidant formation, aquatic ecotoxicity, terrestrial ecotoxicity, aquatic eutrophication, terrestrial

eutrophication and acidification, land occupation, global warming, non-renewable energy, mineral extraction) expressed in a midpoint unit (kg_{eq} C_2H_3Cl, kg_{eq} CO_2, kg_{eq} PM2.5, kg_{eq} CFC, kg_{eq} SO_2, etc.) and then, through the damage assessment step, to four damage categories: human health, ecosystem quality, climate change, and resources expressed in endpoint unit (DALY, PDF*m_2*yr, kg_{eq} CO_2, MJ surplus). Therefore, using this method a complete impact assessment is possible to perform. For this reason, a preliminary attempt to include nanotoxicity characterization factor within *IMPACT 2002+* method has been in this thesis proposed.

On the other hand, USEtox^{TM} model has developed a scientific consensus for human toxicity and ecotoxicity assessment of chemicals in life cycle impact assessment. Therefore, USEtox^{TM} has been further chosen to define the impacts related to human toxicity of nano-TiO_2 into air for both indoor and outdoor environments in LCA. In order to identify the human occupational exposure, an indoor iF_i has been calculated for a workplace characterized by the human inhalation rate, the air exchange rates and the volume per number of people exposed. Here, an average building volume per worker for the chemical industry in Switzerland has been used as basis. All these parameters for the indoor model (like e.g. room volumes, air exchange rates, etc.) may vary geographically because of climate conditions, cultural aspects, different ventilation practices, and so on. For instance, the number of people per cubic meter working in the chemical industry in countries with cheap labor costs is probably much higher than in industrial countries (Hellweg et al., 2009). Actually, a more sophisticated model with indoor spatial differentiation may be used as well, if specific information, for instance on the spatial distribution of sources and people in the room, can be made available (Hellweg et al., 2009). Moreover, aggregation, attachment and deposition rates in indoor environment could be taken in account beyond the air exchange rates - however, currently no data relating to these phenomena are available in the literature.

The outdoor intake fraction (iF_o) has been calculated here for the atmospheric compartment via the human inhalation rate and the fate factor. In order to take into account the specific characteristics of nanoparticles, the fate factor has been calculated with the SB4N multimedia model by Meesters and co-workers (J. a J. Meesters et al., 2014); a model that accounts for all environmental transport and removal processes of nanoparticles between the various compartments. In their publication of the SB4N model, Meesters and co-workers quantified as an example the fate of nano-TiO_2, taking into account nano-specific processes (e.g. aggregation, attachment, dry and wet deposition, gravitational settling, etc.), using Switzerland as geographical area and 1000 m as the atmospheric height.

This outdoor iF_o calculation step represents the only step where nano-specific behavior is taken into account and that is different from the evaluation of other chemicals. The availability of models such a SB4N allowed us to base the iF_o on an actual fate modeling of ENM.

Contrary to Hellweg et al. (Hellweg et al., 2009) the indoor intake fraction is in the present study only one order of magnitude higher than the outdoor compartment factor; using Switzerland as the geographical area. In order to widen the scope to a broader geographic scale, values for the rate constants of the environmental transport and removal processes for the Switzerland scenario have been extrapolated to the continental scale within the USEtox^{TM} framework (Rosenbaum et al., 2007). Geographic area and number of inhabitants are the only factors that change passing from the *Switzerland* to such a *continental* scenario. The resulting value for the continental scale is one order of magnitude lower than for the scenario *Switzerland*; nevertheless the authors recommend to use the scenario *Switzerland* since the environmental transport and removal processes of nano-TiO_2

used in this work represent the rate coefficient values obtained considering the geographic area of *Switzerland*.

When calculating the EF, the difference between indoor and outdoor is nested in the different values used for the potential human exposure, expressed in days per lifetime. As for the indoor environment an occupational workplace has been evaluated, the number of working days per year over a working lifetime of 45 years has been considered. For the outdoor environment, the average human life expectancy of 70 years, as recommended by USEtox^{TM}, has been considered. The main difficulty observed in the EF assessment is the calculation of the $ED_{50}^{a,t,j}$ values, as required by the USEtox^{TM} model. However, as mentioned above, no standardized toxicity data of ED_{50} for nano-TiO_2 performed *in vivo* on animal studies are available. Several EC_{50} (concentration of a compound where 50% of its maximal effect is observe) and LC_{50} (concentration at which the 50% of the tested population show a mortality effect) for nano-TiO_2 values carried out from cytotoxicity studies (*in vitro* assays) are available in literature (Sayes et al., 2006 and Soto et al., 2007). The extrapolation of *in vivo* data from *in vitro* assays might be considered using specific models such as physiologically based toxicokinetic (PBTK) models (Krishnan and Peyret, 2009), but often these models are considered to be quite complex, resource intensive, data hungry and requiring mathematical, programming expertise and sometime lack of inter-individual variability. Additionally, there may be a lack of understanding of how to interpret PBTK model outputs. These perceptions may explain the lack of rapid regulatory acceptance, of these modeling approaches (Bessems et al., 2014). Thus, in the present work this kind of extrapolation has not been considered.

Instead, based on the unique available data of an occupational exposure limit for nano-TiO_2 performed by NIOSH, an ED_4 has been extrapolated to evaluate the *carcinogenic effects*. NIOSH specified that it is possible that the 4% of pulmonary inflammation response used as benchmark response here is rather protective, and that a somewhat greater inflammatory response is required for a tumour initiation. It is also possible that the 25-fold uncertainty factor applied to the critical dose estimate for pulmonary inflammation may be overly conservative, since pulmonary inflammation is an early event in the sequence of events leading to lung tumours. Given that in this case the primary objective of preventing pulmonary inflammation is to prevent the development of lung tumours, and given that lung tumours can be adequately controlled by exposures many-fold higher than the inflammation-based exposure concentrations, NIOSH has concluded that it is appropriate to base RELs for nano-TiO_2 on lung tumors rather than pulmonary inflammation (NIOSH, 2011). Regarding *non-carcinogenic effects* NOAEL and LOAEL values obtained from the SCCS report (SCCS, 2013) have been taken into account and then converted in ED_{50} values, following the USEtox^{TM} model. But, in comparison to NOAEL and LOAEL definitions the values considered report that the LOAEL value is lower than the NOAEL value, this means that the data relating to *in vivo* toxicological assays suffer from variability. Hence, due to the lack of robustness of *in vivo* results, the EF calculation needs to be improved. Therefore, standardization of nano-TiO_2 toxicological data is urgent required.

Finally, the characterization factor for indoor releases, expressed in disease cases per kilogram of emitted nano-TiO_2 is two orders of magnitude higher than for the outdoor releases (for both carcinogens and non-carcinogens effects). If the severity (SF) assessment step is added the characterization factors unit becomes damage per $kilogram_{emitted}$ and the value of indoor is still two orders of magnitude higher than for outdoor for both carcinogens and non-carcinogens effects.

All in all, the second approach developed represents a first well-structured model for human toxicity characterization factors of nano-TiO_2. The described model can be readapted and/or improved by changing e.g. environmental transport and removal rate coefficients suitable for the Switzerland scenario with data relating to another geographical scale and by substituting ED_4, NOAEL, LOAEL values with respective standardized toxicological data as soon as these will be available. The drawback of USEtox^{TM} method is that it is based only on a midpoint approach. It includes only human toxicity (for both carcinogenic and non-carcinogenic substances) expresses in Comparative Toxic Units (CTUh) for human health impacts equivalent to incidence of cancer or non-cancer case (cases/$kg_{emitted}$) and ecotoxicity expresses in Ecotoxic Comparative Toxic Units (CTUe) equivalent to PAF*m^3*yr. Therefore, only a limit overview of the damage caused by the product under study is possible to obtain.

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8 Determination of some benefits derived from nano-TiO_2 application and their implementation in LCIA

As mentioned in chapter 6.3.1 nano-TiO_2 confers to the surface where is applied self-cleaning, antibacterial and antifogging features. In order to take into consideration in LCIA stage some of these benefits, both for indoor and outdoor nano-TiO_2 applications, new impact and damage categories have been needed introduce in LCIA method, in particular *IMPACT 2002+* method has been modified. The reduction of volatile organic compound (VOC) (e.g. Toluene), bacteria (e.g. Escherichia Coli) and inorganic compounds (e.g. NO_x, NO_2) has been considered.

8.1 Indoor benefits

Reduction of NO_2 indoor emissions

A reduction of 37% NO_2 indoor concentration generated by photocatalytic coating applied on walls of two buildings and proposed by ARPA Lombardia (ARPA Lombardia, 2003) has been here considered.

Whereas, the limit value of NO_2 concentration for the protection of human health is 40 $\mu g/m^3$ (annual average) (ARPA Emilia Romagna, 2012), it has been hypothesized that the effect due to the inhalation of 60 $\mu g/m^3$ of NO_2 caused to human a bronchitis lasting seven days. For this disease a disability class[3] equals to "1", a severity weight of 0.01(Goedkoop & Spriensma, 2001) and a probability of 10% that the NO_2 emission caused bronchitis has been postulated. Taking into account these values the damage assessment factor for NO_2 indoor emissions has been calculated as follow:

Damage assessment factor: 7days/365days/y*0.01*10%/60μg = 0.3196 DALY/kg/m^3

Modification of *IMPACT 2002+* method

IMPACT 2002+ has been modified adding a new substance *Nitrogen dioxide indoor* and a new impact category: **Respiratory inorganics indoor** with a characterization factor equals to the characterization factor of ***Nitrogen dioxide*** substance in **Respiratory inorganics** impact category, namely of 0.1273 kg/kg. Moreover, a new benefit category **Respiratory inorganics indoor** (DALY) with the calculated damage assessment factor of **0.3196 DALY/kg/m^3** has been added.

Normalization and weighting factors remain unchanged (normalization factor: 141; weighting factor: 1).

Reduction of Escherichia Coli bacteria

Caballero et al. studied the survival ratio of Escherichia Coli (E. Coli) when exposed to nano-TiO_2 (Caballero et al., 2009). They obtained that around 30% of CFU[4] (Colony Forming Unit) survival for a nano-TiO_2 loading of 15592 mg/m^2 and up to 15% survival for a nano-TiO_2 loading of 520 mg/m^2. A linear trend of survival ratio of E. Coli when exposed to different nano-TiO_2 loading has been assumed.

[3] The classification of disability classes has been drown considering the Global Burden of Disease Study of Murray et al. (Murray et al., 1996). Severity weights have been done for 22 indicator conditions by estimating the extent of loss of physical functioning associated with a certain indicator condition. Based on these weights seven disability classes have been performed. Subsequently, a group of independent experts established weights, ranging from 0 (perfect health) to 1 (death), for 100 indicator conditions.

[4] In microbiology, CFU is a rough estimate of the number of viable bacteria in a sample. In contrast in a microscopic evaluation, all cells, dead and living are counted.

It has been assumed that 1 CFU of Escherichia Coli caused on human health an urinary tract infection lasting seven days. For this disease, a disability class equals to "2", a severity weight of 0.01(Goedkoop & Spriensma, 2001), a probability of 10% that 1 CFU of E. Coli is ingested and once ingested a probability of 10% that this bacteria causes urinary tract infection has been considered.
Damage assessment factor: 7days/365days/y*0.1*10%*10%/1CFU/person = 1.918E-5 DALY/CFU/person.

Modification of *IMPACT 2002+* method
IMPACT 2002+ has been modified adding a new substance *Escherichia Coli in air* and a new impact category: **Non-carcinogens indoor** with a characterization factor equals to 1 CFU/person. Moreover, a new benefit category with the same name **Non-carcinogens indoor** with the calculated damage assessment factor of **1.918E-5 DALY/CFU/person** has been added.
Normalization and weighting factors remain unchanged (normalization factor: 141; weighting factor: 1).

8.2 Outdoor benefits

Titanium dioxide incorporation in building materials and its activation by the near-UV fraction of incident solar irradiation offers promising potential, namely the reduction of organic and inorganic pollutants. Therefore, the reduction of NO_x and Toluene (VOC) concentrations has been here considered for outdoor environment. In particular, the reduction of NO emissions in air equals to 4.01 mg/ h*m^2 proposed by Chen and Poon (Chen & Poon, 2009) and the reduction of Toluene (VOC) emissions in air equals to 100 mg/h*m^2 proposed by Demeestere (Demeestere, et al., 2008) due to the application of TiO_2 in building materials, to obtain photocatalytic features have been taken into consideration.
Since **Respiratory inorganics** and **Respiratory organics** *IMPACT 2002+*'s impact categories already take into consideration NO_x and Toluene substances, no modification to *IMPACT 2002+* method has been done. To evaluate the reduction in concentration of these substances in the LCA studies negative values of the NO_x and Toluene emissions, that are abated by TiO_2-photocatalytic building materials, have been considered as input data.

The following LCA case studies of nanofunctionalized building materials using *IMPACT 2002+* and *USEtox*^{TM} methods with the above calculated human health characterization factors of nano-TiO_2. The environmental benefits derived from nano-TiO_2 application have been evaluated only by *IMPACT 2002+* modified method.

9 LCA of functionalized building materials: case studies

As before mentioned TiO_2 is one of the most used and efficient photocatalytic material and, especially in the field of construction and building materials, it is the most widely used. In particular, nano-TiO_2 has been used to realize self-cleaning treatments in a large number of building elements, as cement mortars, exterior tiles, paving blocks, glasses, paints, finishing coatings, road-blocks, concrete pavements (Quagliarini et al., 2012). For this reason, the environmental performance of nano-TiO_2 functionalized building materials has been carried out through LCA methodology. To do this, the environmental assessment of a bottom-up hydrolytic synthesis of nano-TiO_2, which is used to functionalize the studied building materials, has been performed. This work is a part of a regional Italian project named ARACNE (ARACNE, 2009). The main aim of this project is to study and ecodesign eco-friendly building materials with higher technological properties for both indoor and outdoor environment. In particular, in ARACNE project the following four new building materials have been eco-designed and the environmental performance analyzed:

1. Self-cleaning and anti-bacterial nano-TiO_2 functionalized polyurea resin applied on an aluminum panel;
2. Self-cleaning and antismog nano-TiO_2 functionalized float glass;
3. Self-cleaning and antismog nano-TiO_2 functionalized enamel applied on an steel panel;
4. Self-cleaning and antismog nano-TiO_2 functionalized porcelainized stoneware.

For these four LCA case studies *IMPACT 2002+* and *USEtox*^{TM} methods have been used in LCIA phase. In particular, for the bottom-up hydrolytic synthesis of nano-TiO_2 case study *IMPACT 2002+* method has been solely adopted, since only nano-TiO_2 release in freshwater has been considered.

Impact assessment

For all the analyzed LCA case studies, ife cycle impact assessment (LCIA) results have been modeled using the *IMPACT 2002+* modified method as described below and the *USEtox*^{TM} modified method as reported in chapter 7.4. In the latter modified method, following calculated CFs have been implemented:

- carcinogens effects: 1.55E-05 (outdoor) and 5.93E-04 (indoor),
- non-carcinogens effects: 1.84E-07 (outdoor) 7.04E-06 (indoor).

Simapro 7 software (Goedkoop et al., 2010) has been used to perform the LCA case studies.

Bear in mind that, *USEtox*^{TM} method expresses the human toxicity (for both carcinogenic and non-carcinogenic substances) in Comparative Toxic Units (CTUh) for human health impacts equivalent to incidence of cancer or non-cancer case (cases/$kg_{emitted}$) and ecotoxicity in Ecotoxic Comparative Toxic Units (CTUe) equivalent to PAF*m^3*yr.

The Life Cycle Impact Assessment (LCIA), performed by *IMPACT 2002+* method, has been reported by both midpoint and endpoint assessment. Midpoint indicators link the cause-effects chain of an impact category. Common examples of midpoint characterization factors include ozone depletion potentials, global warming potentials, and photochemical ozone (smog) creation potentials. On the contrary the endpoint indicators are considered to be linked to the cause-effect chain for all categories of impact (e.g., human health impacts, in terms of disability adjusted life

years (DALY) for carcinogenicity, climate change, ozone depletion, photochemical ozone creation, or impacts in terms of changes in biodiversity, etc.) (Bare et al., 2000).

IMPACT 2002+ modified method covers more impact categories than other methods and includes more substances, but the following additions and modifications have been implemented in order to describe the system considered in a more representative manner:

- ✓ **Land use** has been estimated by considering basic indicators of both land occupation and transformation. In the present study *Transformation, to forest intensive, normal*, *Transformation, to forest intensive* and *Transformation, to arable* have been introduced.
- ✓ **Mineral extraction** has been characterized in consideration of some additional resources such as silver, gravel, sand, lithium, bromine and water in ground, derived from the category Minerals of Eco-indicator 99 with the same characterisation factors (Goedkoop & Spriensma, 2001)
- ✓ **Radioactive waste** category has been added; particularly both this kind of waste and its occupied volume have been evaluated considering the same characterization and normalization factors of EPID 2003 method (Potting and Hauschild, 2003). This category allows to take into account the possible damage of electric energy mix, which also includes the electricity generated by nuclear plants. This latter kind of energy produces radioactive waste, which have to be safely managed and disposed.
- ✓ Concerning the toxicity of nano-TiO_2 emissions, *IMPACT 2002+* method has been modified adding human health toxicity factors and ecotoxicity factor described in chapter 7.
- ✓ Finally, *IMPACT 2002+* method has been even modified in order to take into account the benefits derived from nano-TiO_2 application as reported in chapter 8.
- ✓ The impact categories considered in LCIA are global warming, non-renewable energy, mineral extraction, carcinogens, non-carcinogens, respiratory inorganics, respiratory organics, aquatic ecotoxicity, terrestrial ecotoxicity, ionising radiation, ozone layer depletion, terrestrial acidification, aquatic acidification, aquatic eutrophication, radioactive waste, land occupation, carcinogens inhaled, respiratory inorganics indoor, non-carcinogens indoor, nano-TiO_2 ecotoxicity in freshwater and nano-TiO_2 human toxicity.

9.1 Bottom-up hydrolytic synthesis of nano-TiO_2

Nowadays several evaluating parameters related to the environmental and human health impact of a particular chemical process are starting gaining increased interest and consideration side by side to the traditionally employed ones like yield, time and cost, as demanded by Green Chemistry, Green Engineering and Process Intensification developing philosophies. (Anastas and Waser, 1998; Anastas and Zimmerman, 2003; Stankiewicz and Moulijn, 2000; Jenck et al., 2004).
At this latter regard different metrics have been proposed during the last decades (Constable et al., 2002; Jiménez-González et al., 2012) among which the E-factor (Sheldon, 2007) and the mass index (MI) (Hudlicky et al., 1999; Jiménez-Gonzalez et al., 2011) expressed respectively by equations 24 and 25, constituted the most studied and applied ones, leading also to the design and development of the software EATOS (Environmental Assessment Tool for Organic Syntheses) by Eissen and Metzger (Eissen and Metzger, 2002).

$$E - factor = \frac{\sum waste(g)}{product(g)} \quad \text{(eq. 24)}$$

$$MI = \frac{\sum substrate(g) + solvent(g) + auxiliary\_materials(g) + catalyst(g) + \ldots}{product(g)} \quad \text{(eq. 25)}$$

Indeed, this free of charge software (Eissen and Metzger, 2014) allows utilization of easily available data for the calculation of the above mentioned mass metrics, and has been already applied to several studies, since it also permits to compare different synthetic strategies for the obtainment of a particular target compound (Eissen and Metzger, 2002; Eissen et al., 2003; Corradi et al., 2007; Protti et al., 2009; Villa et al., 2011; Piang-Siong et al., 2012).

However, the most significant limitation of every mass metrics, thus including also the software EATOS, is the lack of any energy analysis together with its intrinsic character of being usually devoted to the gate-to-gate boundaries of a particular research laboratory or manufacturing plant. This means that several fundamental steps into the life cycle of employed chemicals like extraction of raw materials, production, transportation, sales, distribution, use and their final fate are not considered by such mass metrics (Jiménez-González et al., 2012; Ribeiro & Machado, 2013).

All of these latter shortcomings can be, on the other hand, overcome by applying Life Cycle Assessment (LCA) methodology, which is based on a cradle-to-grave approach.(Tufvesson, et al, 2012). However, mainly due to LCA intrinsic highly comprehensive nature as well as to the difficulty in finding several necessary inventory data, its use has been mainly limited to large scale production processes, rather than to the early stages of research for innovative and greener synthetic routes, having in this latter cases the software EATOS already demonstrated its applicability (Protti et al., 2009). Nevertheless, numerous strategies have been proposed to simplify the LCA approach thus rendering it easily applicable also to a laboratory scale. Among these artifices for example it has been reported (Ravelli et al., 2010) (Ravelli et al., 2011) the possibility to substitute chemicals which are absent into the LCA software database, with some analogues. Particularly, in those works different synthetic strategies have been evaluated and compared through both EATOS and LCA approaches. Noteworthy is the fact that similar assessments resulted although the two significantly different approaches on which they are based. Although diffusion of the green chemistry developing philosophy usually involve the less environmentally-friendly considered organic reactions, it needs to be pointed out the impossibility to neglect the significant environmental impact that nanotechnology related research activities are increasingly engendering, particularly considering that the environmental as well as the human health effects of nano-sized materials are not yet fully established. In this last perspective, among the key issues related to minimisation of the impact of nanotechnology on the environmental and on the human health, which have been recently identified by Albrecht et al. (Albrecht et al., 2006), life cycle assessment and green chemistry metrics have been reported as mandatory. Thus, the possibility to decide at least for the more green approach for the synthesis of target engineered nanomaterials (being understood the desired particles size and shape) should be highly recommended in order to pursue a more and more sustainable development.

In this thesis, the photocatalyst engineered nanomaterial, nano-TiO_2, has been studied. In general, the preparation routes for this material produce anatase, rutile, or an amorphous solid, depending on the experimental synthetic conditions employed. Nanosized anatase is the most attractive crystalline

form of titanium dioxide for advanced and high-technological applications mainly because of its higher stability and photocatalytic activity with respect to rutile and brookite.
Consequently, the obtainment of anatase nanoparticles with high purity and precisely controlled structure and particle size is the main purpose of optimized synthetic methods, and many approaches have been proposed for that scope, such as inert gas condensation (Rubio et al., 1997), sol-gel method (Gupta and Tripathi, 2012; Corradi et al., 2005) and hydrothermal synthesis (Alphonse et al., 2010). Among these, the sol-gel technique is the most frequently applied for the synthesis of anatase nanoparticles with sizes ranging from 5 nm to several micrometers and a large variety of crystal shapes.
Aim of this environmental assessment is to apply two different green metrics evaluation tools, namely EATOS software and a detailed LCA study, to the hydrolytic sol-gel synthesis of nano-TiO_2, produced according to the method patented by one of the most important Italian company, supplier of chemicals for building and further industrial sectors (Colorobbia Italia S.p.A., 2014; Baldi et al., 2008), and following an ecodesign approach. Then it has been compared the obtained results to evaluate for the first time the applicability of these combined approaches to the field of inorganic synthesis of engineered nanomaterials.
Indeed, similarly to what recently started being accepted by a part of the organic chemistry community, an environmental impact evaluation should always accompany any new synthetic strategy proposed for the synthesis of inorganic engineered nanomaterials, and of course the same should be valid also for already established and recognized preparation procedures, with the present manuscript representing a pioneering work in that precise direction. Being the most of the recently developed synthetic approaches for the obtainment of engineered nanomaterials, based on meticulous reaction mechanism premises (thus no longer based on prolonged solid state diffusion-controlled high temperature treatments) it should not be surprising that the environmental assessment of their chemical synthesis could be, as the case of the present work, evaluated with the aid of EATOS software, i.e. a tool originally developed for organic syntheses.

9.1.1 Experimental

The environmental performance of the hydrolytic synthesis of anatase nano-TiO_2 has been evaluated by LCA methodology (according to the ISO 14040, 2006; ISO 14044, 2006) and by EATOS tool, according to the reaction mechanism considerations reported in the following paragraph.

9.1.1.1 *The hydrolytic sol-gel synthesis of nano-TiO_2*

The hydrolytic sol-gel synthesis of anatase nano-TiO_2 has been performed according to the procedure recently patented and actually employed by Colorobbia S.p.A., one of the most important Italian company supplier of chemicals for building and further industrial sectors for the preparation of aqueous TiO_2 suspensions (Colorobbia Italia S.p.A., 2014; Baldi et al., 2008). It is well known (Niederberger & Garnweitner, 2006) that in hydrolytic sol-gel syntheses of oxide nanomaterials, water acts both as a solvent and as a true reactant, with the reaction mechanism involving subsequent hydrolysis and condensation reactions. All of the possible hydrolytic reactions to which the organic metal precursors can undergo are reported in the following equations 26-29, in which titanium isopropoxide is considered as titanium precursor. Equation 30 can be alternatively used to summarise and group all the previous reactions.

$Ti(OiPr)_4 + H_2O \rightarrow Ti(OiPr)_3OH + iPrOH$ (eq. 26)

$Ti(OiPr)_3OH + H_2O \rightarrow Ti(OiPr)_2(OH)_2 + iPrOH$ (eq. 27)

$Ti(OiPr)_2(OH)_2 + H_2O \rightarrow TiOiPr(OH)_3 + iPrOH$ (eq. 28)

$TiOiPr(OH)_3 + H_2O \rightarrow Ti(OH)_4 + iPrOH$ (eq. 29)

$Ti(OiPr)_4 + nH_2O \rightarrow Ti(OiPr)_{4-n}(OH)_n + niPrOH$ (eq. 30)

The next condensation reactions can obviously occur between both two hydroxylated metal species, leading to a Ti-O-Ti bond under the release of a water molecule (equation 31), and between a hydroxide and an alkoxide leading to the formation of a Ti-O-Ti bond under the release of an isopropyl alcohol molecule (equation 32).

$\equiv Ti\text{-}OH + HO\text{-}Ti\equiv \rightarrow \equiv Ti\text{-}O\text{-}Ti\equiv + H_2O$ (eq.31)

$\equiv Ti\text{-}OiPr + HO\text{-}Ti\equiv \rightarrow \equiv Ti\text{-}O\text{-}Ti\equiv + iPrOH$ (eq. 32)

The chemical reactivity of the metal alkoxide towards hydrolysis and condensation mainly depends on the electrophilic nature of the metal atom, its ability to increase the coordination number, the steric hindrance of the alkoxy group, as well as the polarity, the dipole moment and the acidity of the solvent (Niederberger & Pinna, 2009). Therefore, the major problem of aqueous sol-gel methods based on the hydrolysis and condensation of molecular precursor is the control over the reactions rates. For most transition metal oxide precursors, these reactions are too fast, resulting in loss of morphological and structural control over the final oxide material. One of the possibilities to decrease and to adjust the reactivity of the precursor is the use of organic additives, which can act as chelating ligands thus modifying the reactivity of the precursors.
In the here reported specific case, for each Ti-O-Ti bridge formed a water or an alcohol molecule is generated and considering the product TiO_2 as the repetitive unit of the inorganic network and taking into account the octahedral coordination of Ti atoms and the trigonal-planar one of each oxygen atom, the stoichiometric reaction describing the overall hydrolytic sol-gel synthesis of nano-TiO_2 can be considered the one reported in the following equation 33.

$Ti(OiPr)_4 + 2H_2O \rightarrow TiO_2 + 4iPrOH$ (eq. 33)

The experimental synthetic procedure followed (Baldi et al., 2008) exploited the use of concentrated nitric acid and Triton X-100 in order to control the alkoxide reactivity as well as the hydrolysis and condensation reactions rates, the latter acting also as dispersant agent for the as synthesised nanocrystals. The previous reaction (equation 33), however, assumes that the complete hydrolysis of the metal precursor occurs first, leading to the formation of four molecules of isopropyl alcohol, with subsequent condensation reactions occurring only between tetra hydroxylated species, leading to the liberation of two water molecules for each TiO_2 repetitive unit formed.
In order to be more accurate as possible in pursuing an effective comparison between the two green metrics evaluation procedures (i.e. EATOS and LCA), reaction equation 33 has been considered.

This is slightly different from equation 32, in fact equation 34 consider the water also into the reaction products.

$Ti(OiPr)_4 + 4H_2O \rightarrow TiO_2 + 2H_2O + 4iPrOH$ (eq. 34)

9.1.1.2 ***Description of the life cycle of the bottom-up hydrolytic synthesis of nano-TiO_2***

Figure 9.1 shows the production process of the considered bottom-up hydrolytic synthesis of nano-TiO_2 suspension. In particular the process consists of two main steps: the sol preparation and the addition of auxiliary materials used to prevent the flocculation of titanium dioxide. Since titanium isopropoxide, required for the sol preparation, has been not present in LCA databases, the representation of its synthesis route from titanium tetrachloride has been included in the present LCA study. The same has been also applied to the synthesis of $TiCl_4$ precursor, thus a further step backward to its preparation from ilmenite has been necessarily accomplished (Piccolo et al., 1974).

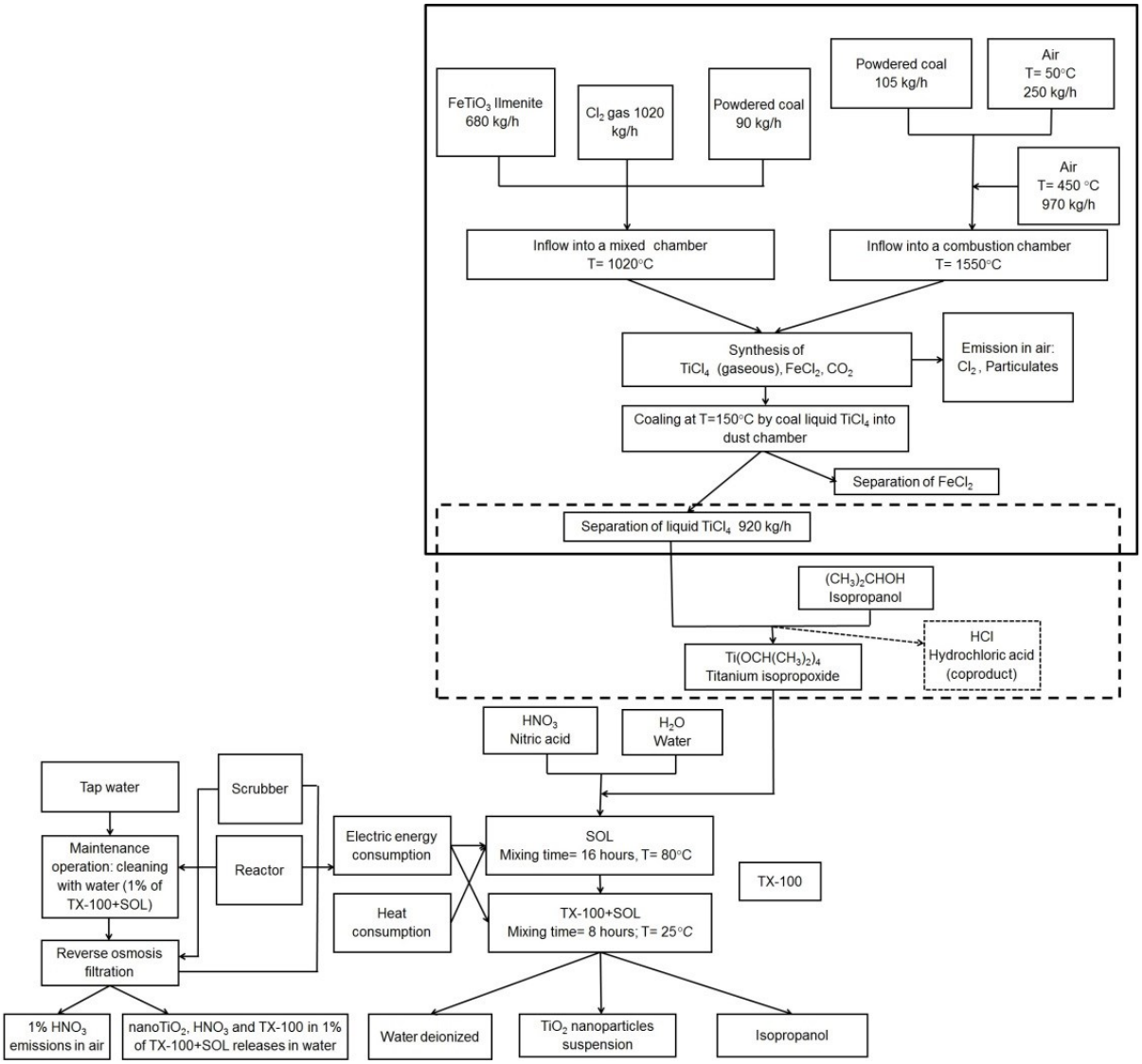

Figure 9-1 Bottom-up hydrolytic synthesis of nano-TiO_2 life cycle

✓ **Sol preparation**

The chemicals used to produce anatase nano-TiO_2 suspension are reported in Table 13. Titanium isopropoxide (TIP) and water are introduced in a closed 200 l volume glass reactor with nitric acid (HNO_3), as catalyst. This mixture is vigorously stirred for 16 hours at 80 °C, until it gradually transform into a translucent sol by peptization.

Table 13 Percent composition of chemicals used to produce nano-TiO_2 suspension (main product) and co-products

Chemicals	**wt%**
Titanium isopropoxide	23.22
Water	73.40
Nitric acid 63%	2.38
Triton X-100	1
Total	100
Recycled Isopropanol (*co-product*)	12
Remaining 88%	%
nano-TiO_2 suspension (*main product*)	85.71
H_2O (*co-product*)	14.29
Total	100

✓ **Addition of auxiliary material**

After the sol production, TX-100 is added to the colloidal suspension in order to avoid the flocculation of the obtained nanoparticles. After 8 hours of stirring at 25 °C the anatase nanoparticles are generated, together with isopropyl alcohol and water as co-products (according also to equation 34).

✓ **Maintenance operations**

The study evaluates the maintenance operations at the end of the process, particularly the cleaning of the reactor with water. It has been assumed that 1% of nano-TiO_2 suspension remains on the reactor walls, so that the water used to clean the reactor results contaminated by nanoparticles. A reverse osmosis filtration process has been considered in order to purify the as-contaminated water.

✓ **Energy consumption**

In the sol preparation step the heat consumptions to warm up the solution at 80°C and to keep the temperature constant for 16 hours have been evaluated. Similarly, the electric energy consumptions to mix the sol for 16 hours and to mix the TX-100 and the sol for 8 hours have been assessed. Moreover, the electricity used for the vacuum system and the reverse osmosis filtration has been considered. The electrical energy supply is assumed to be the Italian mix electrical energy generated by Ecoinvent database (Ecoinvent Database, 2009).

✓ **Emissions and vacuum systems: assumptions and general considerations**

The studied production system consists in a closed reactor, which allows avoiding nanoparticles air emissions, thus the only emissions to be assessed are those occurring in cleaning water (during maintenance operations).

The following assumptions have been considered:

- ✓ during the production and the purification steps a release into air of HNO_3 occurs and particularly the 1% of the total amount of material has been assumed to be emitted.

- ✓ during the maintenance operations, in particular in the purification process, the 1% of the nano-TiO_2 suspension produced and composed of TiO_2, HNO_3, TX-100 and H_2O has been assumed to be released into the cleaning water.

Due to the above-mentioned emissions, a reverse osmosis filter equipped with a scrubber system, and a scrubber system solely, have been considered in the maintenance operations and production process respectively. The scope has been the reduction of the emissions to water and to air. In particular the scrubber system is able to capture the HNO_3 emissions while, the titanium dioxide nanoparticles, present in the obtained aqueous suspension, are entrapped by the reverse osmosis filter. The efficiency of the filter considered in the production process is 99.97%. The installation of reverse osmosis filter with high efficiency allows reducing the environmental impacts according to the ecodesign approach.
Regarding the end of life treatments, the part of filter that capture the emissions, together with the entrapped chemical substances, have been conferred recovered in a residual material landfill.

✓ **Mass balance**

Table 13 shows the mass balance of the chemical synthesis; in particular 12% of the total is recovered as isopropanol (i.e. a reaction co-product) after the synthetic procedure. The remaining 88% is composed by 85.71% of nano-TiO_2 suspension in water (main product) and a 14.29% of recoverable water considered as co-product.
The physical-chemical properties of the nano-TiO_2 suspension are reported in Table 14. Particularly, the amount of nano-TiO_2 in the aqueous suspension results of 6 wt%, and this value has been used to calculate a chemical reaction effective yield of 69.34%, which will be considered in the following EATOS calculations (see chapter 9.1.4).

Table 14 Physical and Chemical properties of nano-TiO_2 suspension

Physical and Chemical properties	Amount
TiO_2 concentration (%w/w)	6
Density (g/ml)	1.15
Viscosity 20°C (mPa/s)	2
Nanoparticle size (nm)	30
Polydispersity index (pdI)	0.25
pH	5.5

9.1.2 Life Cycle Assessment

9.1.2.1 *Goal and scope definition*

The aim of this LCA study is to assess the environmental impacts of a hydrolytic sol-gel synthesis of titanium dioxide nanoparticles suspension produced according to the procedure recently patented and actually employed by Colorobbia S.p.A. for the preparation of aqueous nano-TiO_2 suspensions, (Colorobbia Italia S.p.A., 2014; Baldi et al., 2008) in order to identify its environmental loads.

9.1.2.2 *System, functional unit and function of the system*

The represented system is a multi-output process, which is based on the mass allocation criteria. The functional unit is represented both by the main product that is 0.75425 kg of the nano-TiO_2

suspension and two co-products namely 0.12 kg of recovered isopropanol and 0.12575 kg of recovered water.

9.1.2.3 *System boundaries*

Figure 9.1 highlights the system boundaries for the analysis, which include the upstream phases, from raw material extraction and chemicals production, till to the finished product packaging, thus obtaining "a cradle to the gate" overview. The production, maintenance and disposal of facilities, as well as the environmental burdens related to the production and disposal of packaging materials and other auxiliary materials have been also included in the present study. Emissions into the air and water, as well as the disposal of the part of filter that captures the nanoparticles or the volatile chemical compounds such as nitric acid have been taken into account. The transportation of chemical materials, facilities and packaging materials to the company that used them and the transportation of waste materials to a treatment facility have been also considered. In addition, energy consumptions required in all life cycle steps of nano-TiO_2 suspension production have been evaluated as well.

9.1.3 Data quality

The data for the study have been collected both directly from the authors of the patented procedure (primary data) (Baldi et al., 2008) and from scientific literature (secondary data). In particular, primary data, referring to the optimized method for the preparation of aqueous dispersion of nano-TiO_2 (Colorobbia Italia S.p.A., 2014; Baldi et al., 2008) consist of the composition and the physical/chemical properties of nano-TiO_2 suspension and energy consumptions. Where the data were somehow missing the study has been completed on the basis of secondary data obtained from the Ecoinvent database that exploited them to model the background processes (land use, materials production, fuel and electricity production and transports).

9.1.3.1 *Life cycle inventory*

In a LCA study, the quality and credibility of the results largely depend on the quality of the data included in the Life Cycle Inventory (LCI) stage. In accordance with ILCD Handbook (JRC-IES, 2010a) the inventory must state, in a specific and reliable way, all the inputs in the form of material and energy resources and all the outputs in the form of air emissions, emissions into water and soil, as well as the solid waste that is generated, for each of the stages of the life cycle of the system being studied (according to ISO 14040, 2006). The inventory data has been modelled in SimaPro 7 (Goedkoop et al., 2010), taking the Ecoinvent database as reference to configure the inventory of some chemicals (i.e. nitric acid and TX-100), natural gas, electricity, heat, transport, infrastructure, machinery and waste treatments. In those cases where the chemicals were missing, such as the case of titanium isopropoxide (reagent) and titanium tetrachloride (titanium isopropoxide precursor), they have been created using literature data (Piccolo et al., 1974). The same approach has been followed for the vacuum system and the purification processes.

9.1.4 EATOS calculations

The list of the starting substances considered in the assessment made by means of the software EATOS and the categories to which they have been considered to belong are reported in Table 15.

Table 15 List of product and coupled products considered in the EATOS environmental assessment of the hydrolytic sol-gel synthesis of nano-TiO_2, considering the stoichiometric reaction reported in equation 32

Substance	Category	Molecular weight (g/mol)	Useful quantity (% or g)	Yield (%), referred to the key substrate
TiO_2	product	79.8788	-	69.34
H_2O	coupled product	18.0152	69.34%	-
C_3H_8O	coupled product	60.0956	120 g	-

Table 15 summarizes the yield of the synthetic procedure as well as the useful amounts of obtained coupled products, the latter accounting for their possibility to be recovered and eventually recycled. All of the amounts reported in the two above-mentioned tables are in accordance with the functional unit considered into the LCA analysis (i.e. the amount of TiO_2 obtained from 1 kg of starting materials).

Table 16 List of starting substances used for the EATOS environmental assessment of the hydrolytic sol-gel synthesis of nano-TiO_2, considering the stoichiometric reaction reported in equation 34

Substance	Category	Molecular weight (g/mol)	Quantity (g)
$Ti(OiPr)_4$	key substrate	284.2308	232.2
H_2O	substrate	18.0152	58.87
H_2O	solvent	18.0152	675.13 (recyclable quantity =100%)
HNO_3, 63%	catalyst	63.0128	23.8
Triton X-100	auxiliary material	646.8572	10

The amount of solvent has been considered completely recyclable (see Table 16), while the useful quantities of isopropyl alcohol and the remaining water (i.e. the second coupled product) have been settled in accordance to what indicated by the patented procedure (Baldi et al., 2008) and of course to the amounts used into the LCA assessment, as reported in Table 13. In detail 120 g constituted the effectively recovered amount of isopropyl alcohol, while the maximum useful amount of the coupled product water has been established according to the yield of the reaction, assuming thus a maximum value of 69.34% of that theoretically obtainable. This yield value corresponds to a water amount which is significantly lower with respect to what indicated (Table 13) and considered in the LCA framework. The reason needs to be found in the fact that what considered by LCA as the water co-product, indeed refers to the amount of water effectively recovered after the synthetic procedure, the latter comprising both the effective water co-product and part of the water originally intended as the solvent.

The software EATOS allows calculating four important environmental parameters: the mass index MI (equation 25), the environmental factor E (equation 24) together with EI_in and EI_out corresponding to the former ones in which each substance quantity is multiplied by its specific total weighting factor, *Qtot,* which represents a mean value calculated among the different weighting factors Q_i values. In detail the weighting factors allow evaluating and examining the specific chemical reaction with particular regard to the potential environmental and human health relevance of each substance employed (Eissen and Metzger, 2014). The index *i* in the Q*i* notation, accounts for the i^{th} weighting category among claiming of resources, risk, human toxicity, chronic toxicity, ecotoxicology, ozone creation, air pollution, accumulation, degradability, greenhouse effect, ozone

depletion, nutrification and acidification. Each Q*i* can assume values ranging from 1 to 10 according to specific classifications internally made by the software algorithms. The software EATOS allows also selecting the opportune significance to associate to each weighting category.
The relevant information which determine the Q*i* value for that particular substance can be easily found into the Material Safety Data Sheet (MSDS) available from the supplier. Particularly in this work the MSDS considered have been those available on the Sigma Aldrich website (Materials Safety Data Sheet (MSDS), 2014), and as concern the price, the biggest amount available has been selected.

9.1.5 Results and discussion

The Life Cycle Impact Assessment (LCIA) has been reported by both midpoint and endpoint assessment. Midpoint indicators are considered to be linked to the cause-effect chain (environmental mechanism) of an impact category. Common examples of midpoint characterization factors include ozone depletion potentials, global warming potentials, and photochemical ozone (smog) creation potentials. Endpoint indicators are instead considered to be linked to the cause-effect chain for all categories of impact (e.g., human health impacts, in terms of disability adjusted life years for carcinogenicity, climate change, ozone depletion, photochemical ozone creation, or impacts in terms of changes in biodiversity, etc.) (Bare et al., 2000).

9.1.5.1 *LCA results: IMPACT 2002+* **modified method**

Single score damage is 988.87μPt for 1 kg of nano-TiO_2 suspension produced. As Figure 9.2 shows, the electric energy consumption to mix the colloidal solution (sol) for 16 hours (indicated as E1) and the one necessary to mix the sol and TX-100 for 8 hours (indicated as E2) are the two contributions which are mainly responsible for the total damage (38.76% and 19.38% respectively), followed by the titanium isopropoxide (TIP) production (13.65%) and by the heat consumption (indicated as H2) to maintain the solution at 80°C (10.33%). A midpoint category interpretation is conducted, being the latter more appropriate to evaluate the environmental impacts of the various substances counted in the life cycle inventory. The impact categories considered are global warming, non-renewable energy, mineral extraction, carcinogens, non-carcinogens, respiratory inorganics, respiratory organics, aquatic ecotoxicity, terrestrial ecotoxicity, ionizing radiation, ozone layer depletion, terrestrial acidification, aquatic acidification, aquatic eutrophication, radioactive waste, land occupation, nano-TiO_2 ecotoxicity in freshwater and nano-TiO_2 human toxicity.

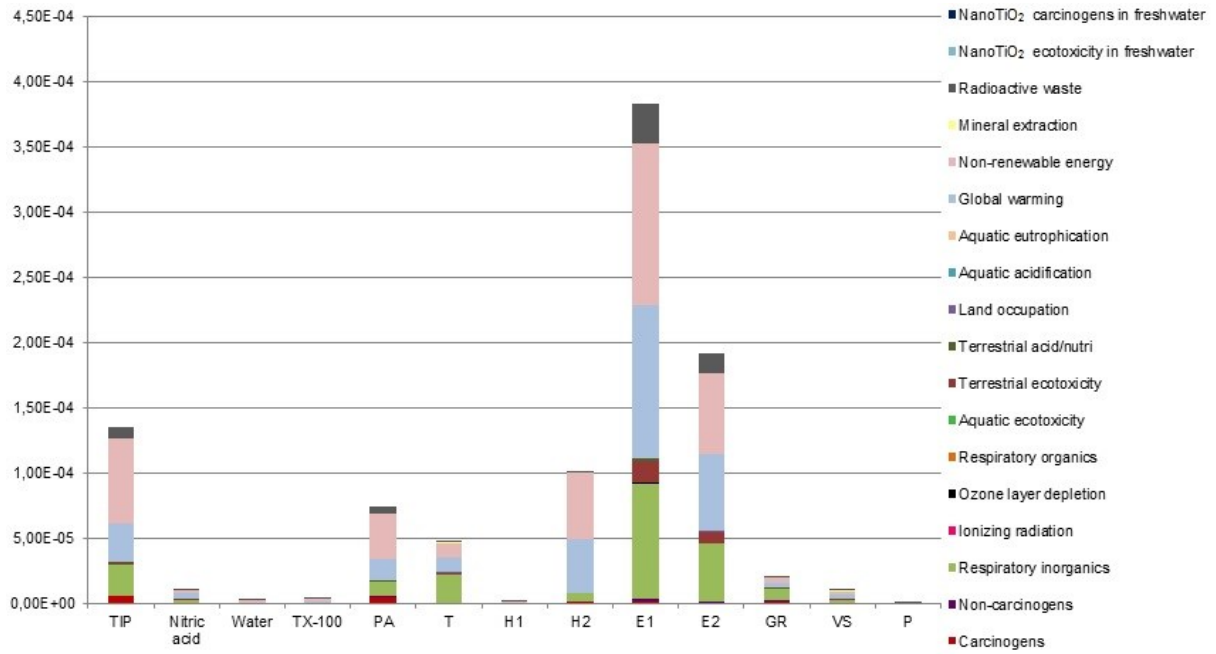

Figure 9-2 Evaluation by single score of 1 kg of a bottom-up hydrolytic synthesis of nano-TiO_2, where TIP= Titanium isopropoxide; TX-100= Triton X-100; PA= Packaging of raw materials; T= Transport of raw materials; H1= Heat to warm up the solution at 80°C; H2= Heat to maintain the solution at 80°C; E1= Electric energy to mix the sol for 16 hours; E2= Electric energy to mix the sol and TX-100 for 8 hours; GR= Glass Reactor; VS= Vacuum system; WP= Water Purification.

Table 17 sums up the outcomes of the midpoint and endpoint analysis that are explained in detail hereafter. In particular, for the midpoint analysis the contributions of the main impact categories on the total damage are reported.

Table 17 Characterized LCIA results

Midpoint results			**Endpoint results**		
Impact category	**Unit**	**Total**	**Damage category**	**Unit**	**Total**
Carcinogens	kg C_2H_3Cl eq	4,43E-2	Human Health	DALY	1,68E-06
Non-carcinogens	kg C_2H_3Cl eq	1,63E-2			
Respiratory inorganics	kg PM2.5 eq	2,13E-3			
Ionizing radiation	Bq C-14 eq	48			
Ozone layer depletion	kg CFC-11 eq	3,95E-7			
Respiratory organics	kg C_2H_4 eq	1,06E-3			
Aquatic ecotoxicity	kg TEG water	1,70E2	Ecosystem Quality	PDF*m^2*yr	0,503
Terrestrial ecotoxicity	kg TEG soil	52,8			
Terrestrial acid/nutri	kg SO_2 eq	4,39E-2			
Land occupation	m^2org.arable	2,91E-2			
Aquatic acidification	kg SO_2 eq	1,27E-2			
Aquatic eutrophication	kg PO4 P-lim	8,17E-4			
Global warming	kg CO_2 eq	2,86	Climate Change	kg CO_2	2,863
Non-renewable energy	MJ primary	55	Resources	MJ primary	55,15
Mineral extraction	MJ surplus	1,53E-1			
Radioactive waste	Kg	6,37E-5	Radioactive waste	kg	6,37E-05
Nano-TiO_2 ecotoxicity in freshwater	Kg	6,63E-9	Nano-TiO_2 ecotoxicity in freshwater	PAF*m^3*day	1,86E-09
Nano-TiO_2 carcinogens in freshwater	Kg	6,63E-9	Nano-TiO_2 carcinogens in freshwater	DALY	4,73E-14

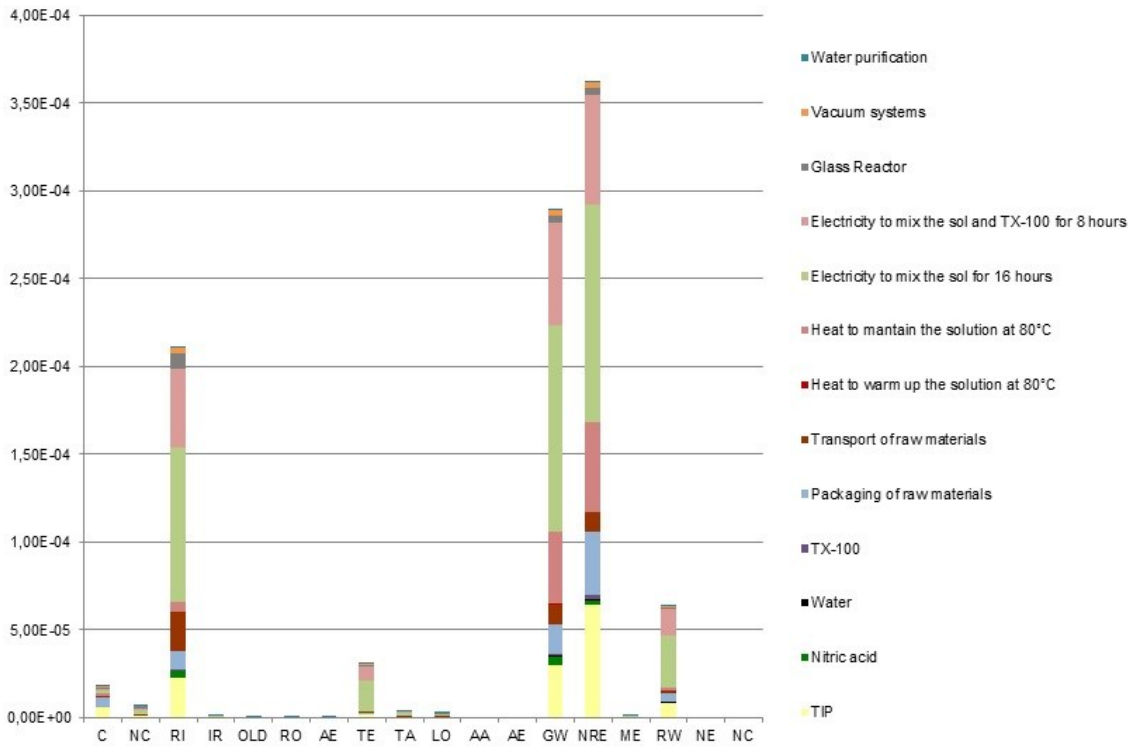

Figure 9-3 Evaluation by impact categories of 1 kg of a bottom-up hydrolytic synthesis of nano-TiO_2, where C= Carcinogens; NC= Non-Carcinogens; RI= Respiratory Inorganics; IR= Ionizing Radiation; OLD= Ozone Layer Depletion; RO= Respiratory Organics; AE= Aquatic Ecotoxicity; TE= Terrestrial Ecotoxicity; TA= Terrestrial acid/nutri; LO= Land Occupation; AA= Aquatic Acidification; AE= Aquatic Eutrophication; GW= Global Warming; NRE= Non-renewable Energy; ME= Mineral Extraction; RW= Radioactive Waste; NE= Nano-TiO_2 ecotoxicity in freshwater; NC= Nano-TiO_2 carcinogens in freshwater.

Figure 9.3 highlights that the most significant contribution to the total damage is due to Non-renewable Energy impact category which is primarily affected by natural gas (52.31%), crude oil (25.58%) and hard coal (11.23%) emissions. For all types of emissions the electric energy consumption to mix the sol for 16 hours is the process that produces the major environmental load (33.09%, 25.5% and 49.18% respectively). In particular in this process the emissions are mainly caused by the natural gas and crude oil production and the hard coal mining respectively. Successively, the second major contribute to the total damage is generated by the Global warming impact category, mainly due to GHG (greenhouse gas) emissions (96.17%), which are for the 41.24% belonging to the electric energy consumption to mix the sol for 16 hours and in particular generated by the natural gas used to produce the electricity. In Respiratory Inorganics the major contributions are due to the following emission to air: 37.3% of NO_x, 28.91% of SO_2 and 18.61% of particulates < 2.5 μm. All of these are mainly due to the electric energy consumption to mix the sol for 16 hours (38.77%, 49.65% and 45.54% respectively) and, in particular, generated for the first two (NO_x and SO_2) during the heavy fuel oil combustion while for the latter one during the hard coal combustion. In Radioactive Waste impact category, the volume occupied by low-active radioactive waste contributes for 65.31% on the total damage due to the electric energy production by nuclear power plants. About the Nano-TiO_2 ecotoxicity in freshwater and Nano-TiO_2 carcinogens in freshwater impact categories the damage is totally due to the release of 6.63 μg of

Particulates,<100 nm, in freshwater and 6.63 μg *nano-TiO_2 human toxicity in freshwater* during the purification of contaminated water, which are obtained by the maintenance operation.

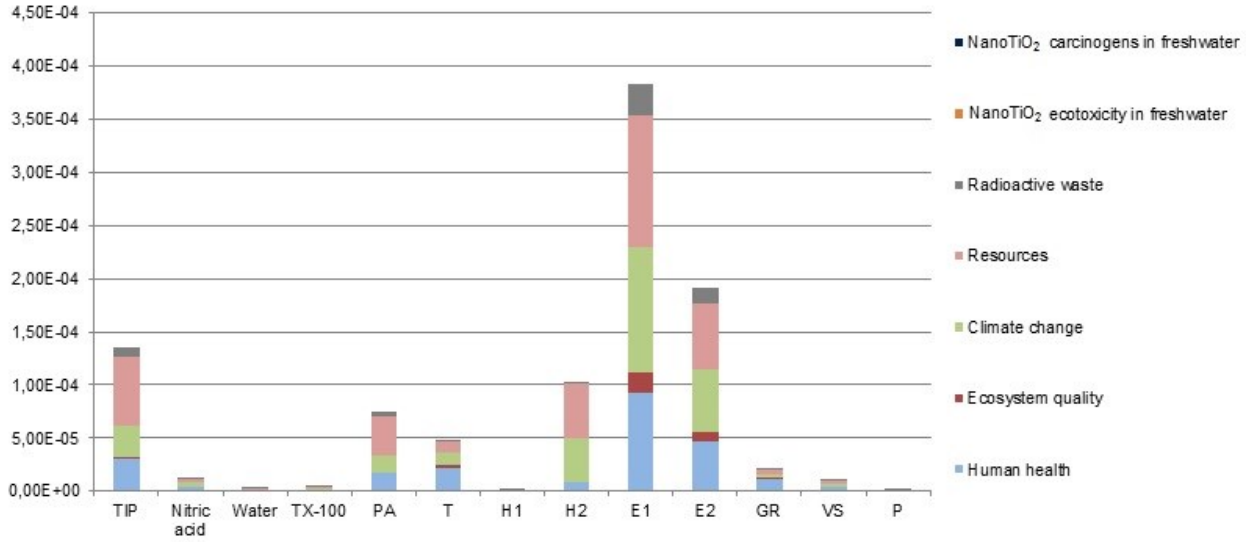

Figure 9-4 Evaluation by damage categories of 1 kg of a bottom-up hydrolytic synthesis of nano-TiO_2, where TIP= Titanium isopropoxide; TX-100= Triton X-100; PA= Packaging of raw materials; T= Transport of raw materials; H1= Heat to warm up the solution at 80°C; H2= Heat to maintain the solution at 80°C; E1= Electric energy to mix the sol for 16 hours; E2= Electric energy to mix the sol and TX-100 for 8 hours; GR= Glass Reactor; VS= Vacuum system; WP= Water Purification

The endpoint analysis highlights (Figure 9.4) that the total damage is affected for 23.9% the Human Health (2.36E-4 Pt), for 36.7% the Resources (3.63E-4 Pt), for 29.24% the Climate Change (2.89E-4 Pt), for 3.71% the Ecosystem Quality (3.67E-5 Pt), for 6.44% the Radioactive waste (6.37E-5 Pt), for 3.36E-6% the Nano-TiO_2 ecotoxicity in freshwater (3.32E-11 Pt) and for 6.75E-7% the Nano-TiO_2 carcinogens in freshwater (6.67E-12 Pt). In these latter two cases the damage is restrained since, as mentioned before, the LCA study has been set in an ecodesign approach, thus installing a specific filter for nanoparticles with a high efficiency (99.97%), in order to limit the nanoparticle releases.

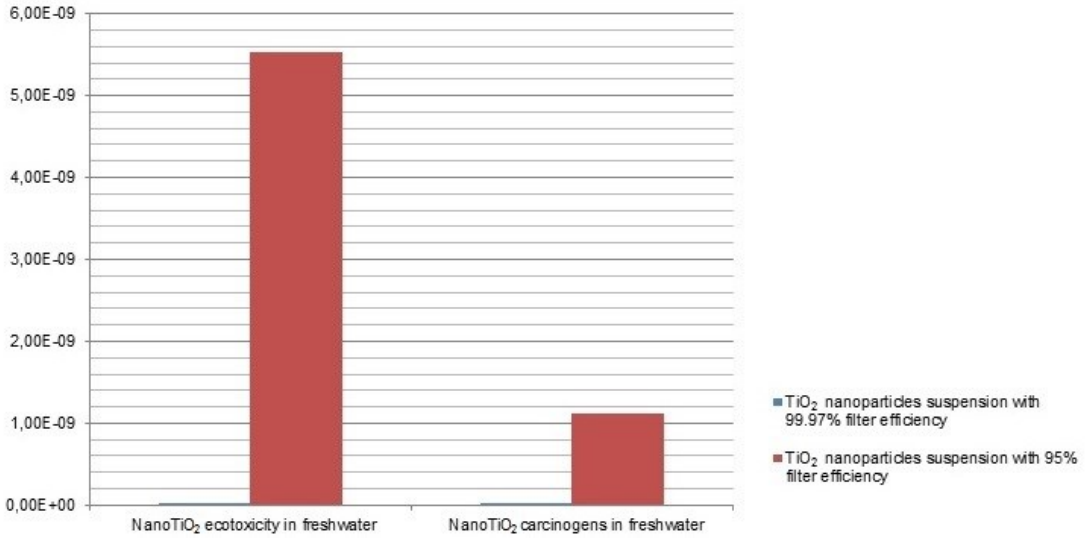

Figure 9-5 Comparison of environmental impact values (Pt) for 99.97% and 95% filter efficiency

Indeed, Figure 9.5 shows that the variation of the sole filter efficiency from 99.97% to 95% leads to an increase of the damage in Nano-TiO_2 ecotoxicity in freshwater and Nano-TiO_2 carcinogens in freshwater impact categories equal to 165.67%. Furthermore, a life cycle cost analysis has been carried out. Internal and external costs have been assessed. The first takes into account all input materials cost and the latter considers environmental costs caused by the hydrolytic synthesis of nnao-TiO_2. The results for 1 kg of nano-TiO_2 suspension show that internal and environmental costs values are 29.125 euro and 1.289 euro respectively, being them mainly caused by electric energy consumptions.

9.1.5.2 *EATOS results*

Results returned by the software EATOS in terms of the evaluation of histograms for the metrics MI, E-factor, EI_in and EI_out are reported in Figure 9.6.

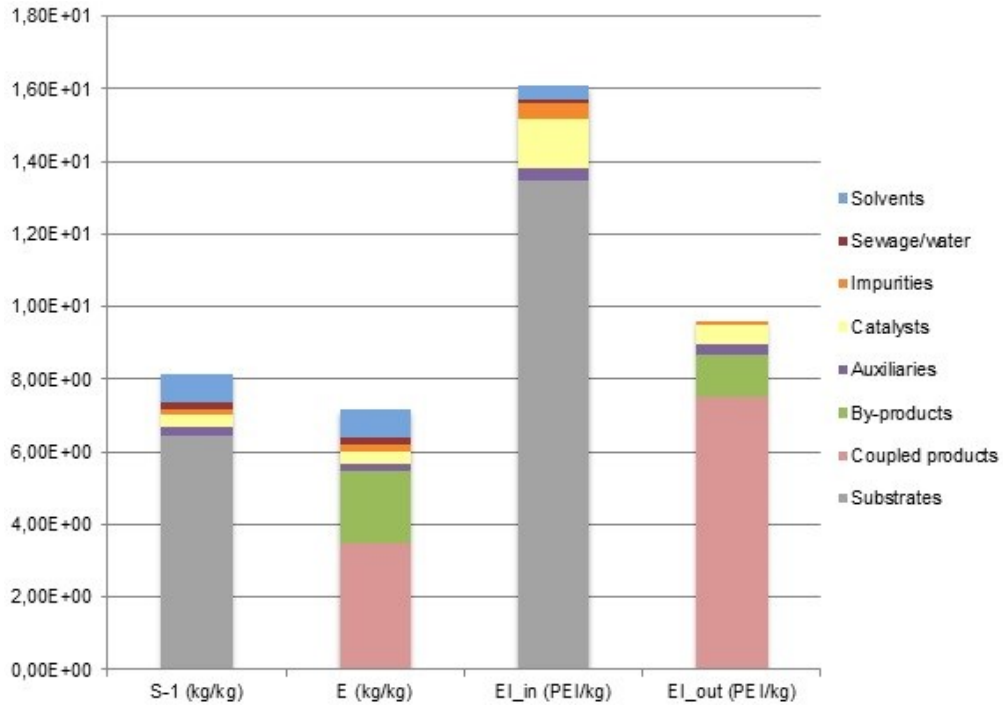

Figure 9-6 EATOS results

The green metric EI_out parameter, expressed in Potential Environmental Impact (PEI; the bigger its value is, the worse the process will impact on the environment) per kg of product, accounts for the environmental damage potentially induced by the reaction waste. Particularly, as detailed in Table 18 its total value of 9.6195 is mainly attributed to coupled products, since only a limited amount of isopropyl alcohol is recovered.

Table 18 Contributions of all the substances to the metrics S-1, E, EI_in and EI_out

Category	Substance	S^{-1} (kg of starting material/kg of product)	E (kg of waste/kg of product)	EI_in (PEI/kg)	EI_out (PEI/kg)
Substrates	Titanium isopropoxide and water	6.4728	0.0402	13.4997	/
Coupled products	Isopropanol and water	/	3.4604	/	7.5233
By-products	Unspecified	/	1.9723	/	1.18
Auxiliaries	Triton X-100	0.2278	0.2278	0.3418	0.2848
Catalysts	Nitric acid	0.3416	0.3416	1.3665	0.5124
Impurities	Unspecified	0.1587	0.1587	0.3968	0.119
Sewage/water	Water+unspecified	0.2006	0.2006	0.1003	/
Solvents	Water	0.7691	0.7691	0.3845	/
Total		**8.1706**	**7.1707**	**16.0896**	**9.6195**

The category by-products accounts for the fact that being the yield of the synthetic process equal to 69.34 some unspecified by-products need to be considered. More interestingly, in the particular framework of a direct comparison with the LCA results, the potential environmental and human health relevance of each substance employed in the total inward materials flux related to the hydrolytic synthesis of anatase nano-TiO_2 suspension should be considered. At this latter regard, the

green metrics parameter EI_in reaches a total value of 16.0896 PEI/kg, and it is for its 83.9% due to the titanium isopropoxide precursor, for its 8.5% to catalyst, for its 2.1% to auxiliary materials and for its 2.4% to the solvent (i.e. water). Noteworthy is that this latter finding is in perfect agreement with previously discussed LCA results. Indeed, by simply neglecting the energy contributions, the LCA outcomes show that the total damage is mainly caused by titanium isopropoxide for the 87.98% and by nitric acid for the 7.22%.

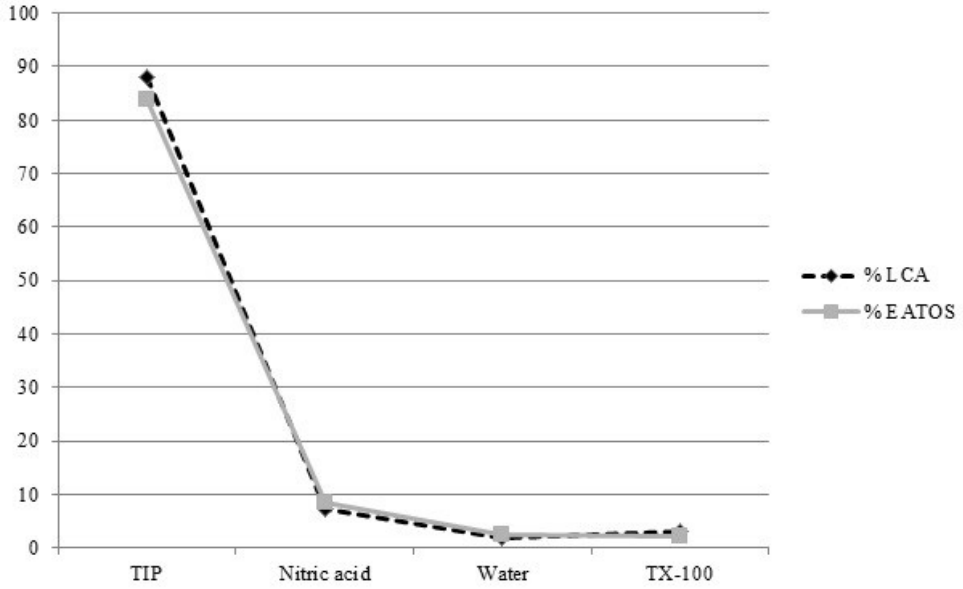

Figure 9-7 EATOS and LCA (excluding energy consumptions) results comparison

According to this latter approximation, Figure 9.7 reports the comparison between LCA and EATOS outcomes in terms of the main factors affecting the single score damage and EI_in respectively, revealing a tremendously similar trend. It needs to be specified that for the present EATOS analysis the weighting categories considered have been those in which the corresponding values for at least one substance have been found and consequently inserted, i.e. human toxicity, chronic toxicity, ecotoxicology and accumulation (to which an influence of 25 % has been assigned). The possibility of Q=0 assignment has been considered as well. A further possibility offered by the EATOS software, is to calculate and present the different entry items, such as substrates, solvents, and so on by the so-called economic index, i.e. COST INDEX (CI). The different contributions to the CI (expressed in eur/kg) deriving from the different input materials used for the synthesis under consideration are detailed in Table 19.

Table 19 Detailed quantification of the different contributions to the CI, for the hydrolytic sol-gel synthesis of anatase nano-TiO_2 investigated with EATOS tool.

Substance category	CI (EUR/kg)
Substrates	454.948
Auxiliaries	8.9115
Catalysts	17.6381
Impurities	13.6392
Solvent	**7.9986**
Sewage/water	**2.0866**
Total	**505.222**

9.1.6 Conclusions

The environmental assessment of the bottom-up hydrolytic sol-gel synthesis of anatase nano-TiO_2 has been concurrently performed by the software EATOS and by LCA methodology and, although the different philosophies on which they are based, similar conclusions can in some conditions be drawn. EATOS software has been originally developed for organic chemists and mainly applies to fine chemical processes, relying on data which are easily available from the material safety data sheets. On the contrary, Life Cycle Assessment is a much more detailed and versatile method, suitable to assess industrial scale procedures, but it is hardly adaptable to small scale ones (Ravelli et al., 2011), due to its intrinsic time-consuming nature and to the difficulty to source necessary inventory data. Particularly for chemical processes, the databases to which the LCA methodology refers to, are still significantly inadequate, so that when the required chemical is not included in databases it is necessary either to consider chemicals with similar properties, among those comprised in the databases, or to recreate the synthesis of that particular substance ex novo. Despite its immediacy, EATOS suffers from the major strong approximation of neglecting any energetic contribution. Precisely the typical limitations and drawbacks of both EATOS and LCA contributed to highlight their complementary character, which has been extensively exploited in the environmental and human health assessments of several organic reactions. The present work represents, to the best of authors' knowledge, the first example in which, the synergy between life cycle assessment and EATOS software, has been applied to the green metrics evaluation of the inorganic synthesis of engineered nanomaterials. In details the studied hydrolytic sol-gel synthesis route generates a suspension of nano-TiO_2, characterized by high purity and crystallinity, according to the patented procedure. The ecodesign approach followed (based on the installation of 99.97% efficiency filter and the use of closed reactor) together with the aqueous solvent employed and the low processing temperature contribute to well fit the here presented synthetic protocol into a green chemistry perspective, with respect to other nano-TiO_2 manufacturing procedures. The LCA results evidenced that the most environmental loads are generated by the electric energy consumption (58.14%), followed by titanium isopropoxide (13.65%) and heat consumption to maintain the solution at 80°C (10.33%). Reasonably, a better environmental performance can be achieved by renewable energy sources (e.g. solar power, geothermal, biomass, etc.). A more immediately feasible strategy could be represented by the use of microwave dielectric heating of reaction mixture, which has recently been significantly employed not only in organic chemistry but also in inorganic synthesis of a wide variety of engineered nanomaterials (Baghbanzadeh et al., 2011) due to its intrinsic advantages over conventional heating techniques based on heat transfer mechanisms (rather than on energy transfer ones). This latter alternative will surely constitute the next necessary subject of a dedicated life cycle assessment study, since the microwaves' greenness and energy efficiency have been recommended to be considered on a case-to-case basis (Moseley and Kappe, 2011). The substitution of the titanium tetraisopropoxide with a different metal oxide precursor, more environmentally friendly and less costly, is a further possibility to greatly reduce the environmental and human health impact of the hydrolytic sol-gel synthesis of nano-TiO_2. At this latter regard, the use of the software EATOS alone, can furnish a first reliable approximation for the environmental evaluation of synthetic strategies employing different metal oxide precursors. Indeed, the comparison obtained in the present work for the hydrolytic sol-gel synthesis of anatase nano-TiO_2 as detailed in (Baldi et al, 2008), if performed by neglecting any energy contributions, highlighted the reaching of similar conclusions from both the utilized approaches. Particularly, they

returned very similar environmental impacts with the more affecting factor resulting in the titanium alkoxide, followed nitric acid and with aqueous solvent and auxiliary triton X-100 showing pretty close contributions. In conclusion EATOS provides fast and functional results, which are comparable to LCA results when energy consumptions are neglected. Furthermore, EATOS is a free of charge and user-friendly software, so it is particularly suitable when a choice among different synthetic strategies needs to be considered for the preparation of the desired engineered nanomaterial. This work represents the first example of the application of this software (originally developed for the synthesis of fine chemicals) to inorganic synthesis of transition metal oxide nanostructures, and the natural progression of the research activities in this direction, actually in progress, will involve the comparison among the most widely employed synthetic strategies for the obtainment of the desired inorganic nanocrystals, among which hydrolytic and non-hydrolytic sol-gel, hydrothermal and solvothermal syntheses, inverse micelles method, synthesis in ionic liquids solution combustion synthesis and carbon combustion synthesis, simply represent some examples. However, a later deeper investigation by a complete life cycle assessment should be carried out since LCA methodology provides more detailed and accurate results. Indeed midpoint and endpoint analysis give a complete knowledge on the damage categories that mainly affect the total environmental and human health impact of the studied process, the substances that cause these impacts and the compartments (air, soil, water, raw) that result more paining. The main conclusion of the present work, which would like to be a recommendation to inorganic chemists and materials scientists worldwide, is to always combine an environmental impact evaluation to any new proposed strategy for the synthesis of engineered nanomaterials, so that the strict requirement of using the most environmentally friendly procedure very soon could accompany traditional requests of a desired size and shape. The assessment by means of easily available and accessible EATOS tool, although able to furnish trustworthy indications, should be later on integrated by a complete life cycle assessment, thus allowing considering also the impacts of the energy consumption, which usually represents the most impacting parameter of the whole process.

This work has been published to the “Green Chemistry” (Pini et al., 2015) and won the SETAC Europe Award 2015 for the best publication in “chemical analysis and environmental monitoring”.

Acknowledgement

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9.2 Nano-TiO_2 functionalized polyurea resin applied on an aluminum panel

The polyurea elastomer coating technology has shown some very significant inroads since the introduction of the technology back in the late 1980’s. Initially, the polyurea technology had set itself in a different class of coating systems as compared to conventional urethane ones. This has been primarily due to the unique characteristics of the technology, both in processing and performance (Dudley, 2004). Polyurea resin derived from the reaction between an isocyanate

prepolymer and a polyamine resin, a simple illustration of the polyurea reaction is given below (Figure 9.8):

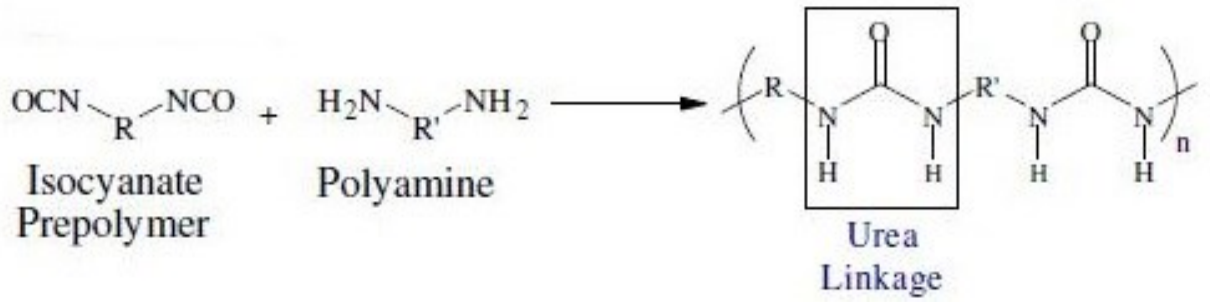

Figure 9-8 R, R'= radicals of isocyanate and polyamine (Source: Dudley, 2004)

Two-component polyurea elastomeric coating systems are one of the newest technology to the protective coating industry. The key feature of the elastomeric polyurea coatings technology is that the amine/diisocyanate reaction is almost instantaneous (typical gel time 3 to 10 seconds) (Shiwei & Guan, 2003). While the fast reaction / rapid dry time is virtually unaffected by ambient moisture, the presence of moisture on a substrate must be considered when achieving adhesion to that substrate. This is all made possible by a unique chemistry of raw materials used to develop the two-component polyurea systems (Dudley, 2004). Polyurea technology can be used in a wide variety of coating applications, e.g. over concrete, geotextile membranes, various metals (i.e. aluminum) for:

- *Waterproofing applications*:
  - ✓ Parking, traffic area, roofing, flooring and recovery actions.
- *Corrosion protection and decorative / architectural applications*:
  - ✓ Industry applications: piping, petrochemical, food, energy and mining.
  - ✓ Building applications: residential buildings, showrooms and offices.

  The polyurea can be applied directly on the floor or on the metal panels which are installed to create the walls.
- *Mechanical resistance*:
  Industrial plants often use resin coatings to provide mechanical properties and to extend the durability when they are subjected to extreme environmental conditions.

The addiction of photocatalyst, such as nano-TiO_2, could improve the quality and the performance of polyurea resin. Indeed, thanks to the well-known photocatalytic activity of nano-TiO_2 it is possible confer to the surface, on which polyurea is applied, superhydrophilic, antibacterial, antismog and self-cleaning properties. Moreover, the presence of photocatalytic reduce the possibility of polymer degradation when coatings is exposed to UV light.

9.2.1 Ecodesign approach

The present study concerns the ecodesign of the application of nano-TiO_2 functionalized polyurea resin functionalized on an aluminum panel with spraying system through LCA methodology, in order to define the most critical aspects of the process and try to minimize the environmental burdens during the implementation of the production process.

Because of the limited knowledge currently available regarding the nano-TiO_2 effects may have on environment or human health (Iavicoli et al., 2012), a safe behavior has been adopted in all life

cycle steps where can be a risk to have a release of nanoparticle emissions by nanocoating surface and workers can come into contact with or inhale nanoparticles released. Installation of *high efficiency particulate air filter* (HEPA), closed manufacturing system, use of specific packaging to limit the release of nanoparticle emissions during the transports, *personal protective equipment (*PPE) (gloves, coverall, eyewear, face mask with 95% of efficiency) and aspecific waste treatment have been taken into consideration. nano-TiO_2 emissions released during production, application, use and end of life phases have been assumed. Since, an indoor application has been in this study considered, the benefit derived from the application of nano-TiO_2 into polyurea resin has been also assessed, i.e. the reduction of NO_2 concentrations and Escherichia Coli bacteria (see chapter 8).

9.2.2 Life cycle of nano-TiO_2 functionalized polyurea resin applied on an aluminum panel

The entire life cycle of nano-TiO_2 functionalized polyurea resin applied on an aluminum panel is reported in Figure 9.9; it comprises all life cycle stages following a cradle to grave perspective, from the raw materials extraction, production and supplying, application, packaging, application, use and end of life of the coated aluminum panel.

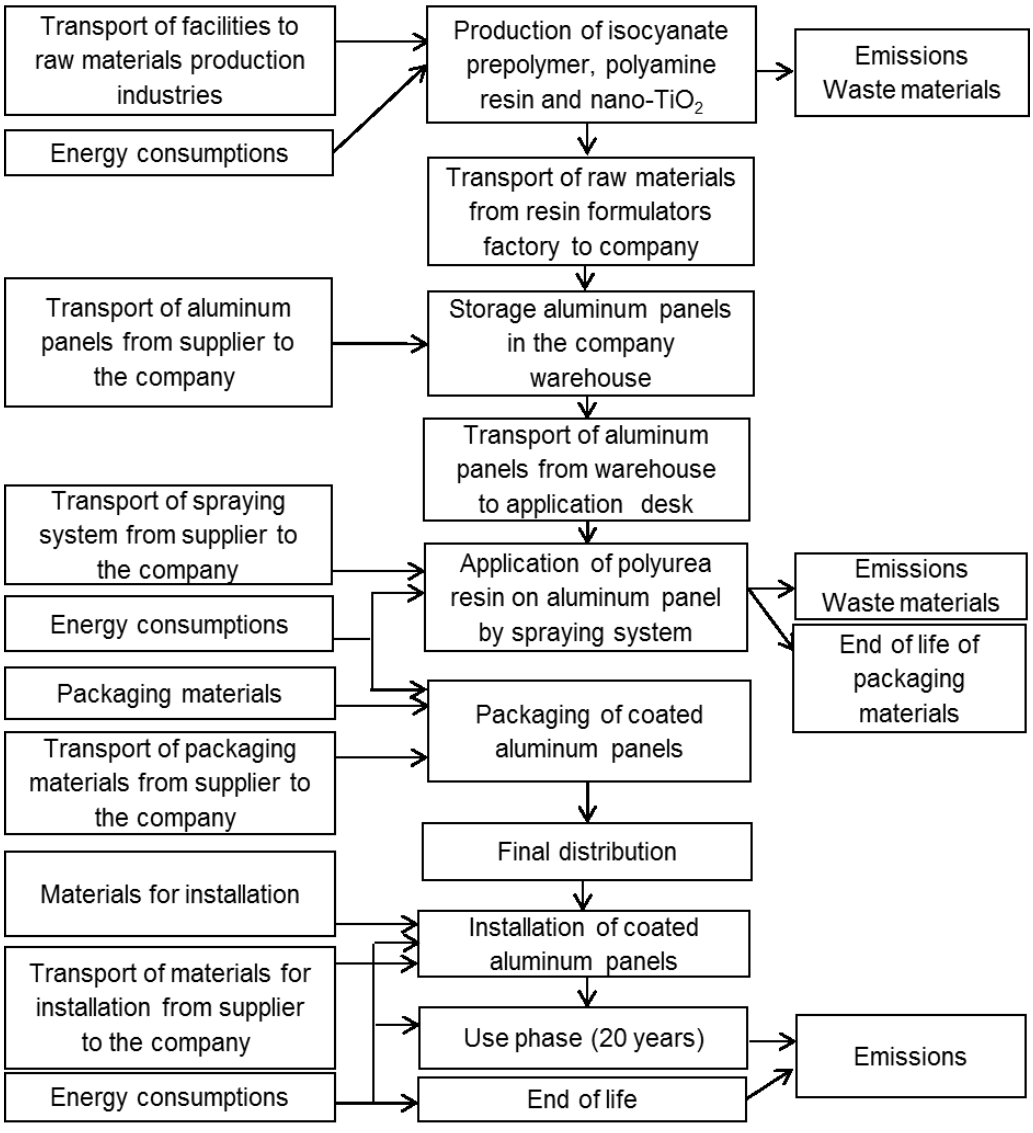

Figure 9-9 Flow chart of nano-TiO_2 functionalized polyurea resin applied on an aluminum panel

9.2.2.1 ***Production of polyurea resin***

As mentioned before, polyurea resin is formulated starting from isocyanate prepolymer and polyamine resin. In particular, for the production of 1 kg of polyurea resin the composition reported in Table 20 has been considered.

Table 20 Chemicals composition (wt%) for 1 kg of polyurea resin production

Chemicals	wt%
Isocyanate prepolymer	52,38
Polyamine resin	47,62

Delving into the chemical composition of the two main substances used to produce polyurea resin, Table 21 describes the amount of chemicals used to generate 1 kg of isocyanate prepolymer and 1 kg of polyamine resin.

Table 21 Chemicals composition (wt%) for 1 kg of isocyanate prepolymer and 1 kg of polyamine resin production

Chemicals	wt%
Isocyanate prepolymer	
Methylene diphenyl diisocyanate (MDI-50)	48,53%
Polyol polyether	41,47%
Propylene carbonate	10%
Polyamine resin	
Polyoxypropylenediamine ($C_9H_{18}N_2O_2$)	74,7%
2-3,5 diethyltoluene-2,4-diamine ($C_{11}H_{18}N_2$)	25,3%

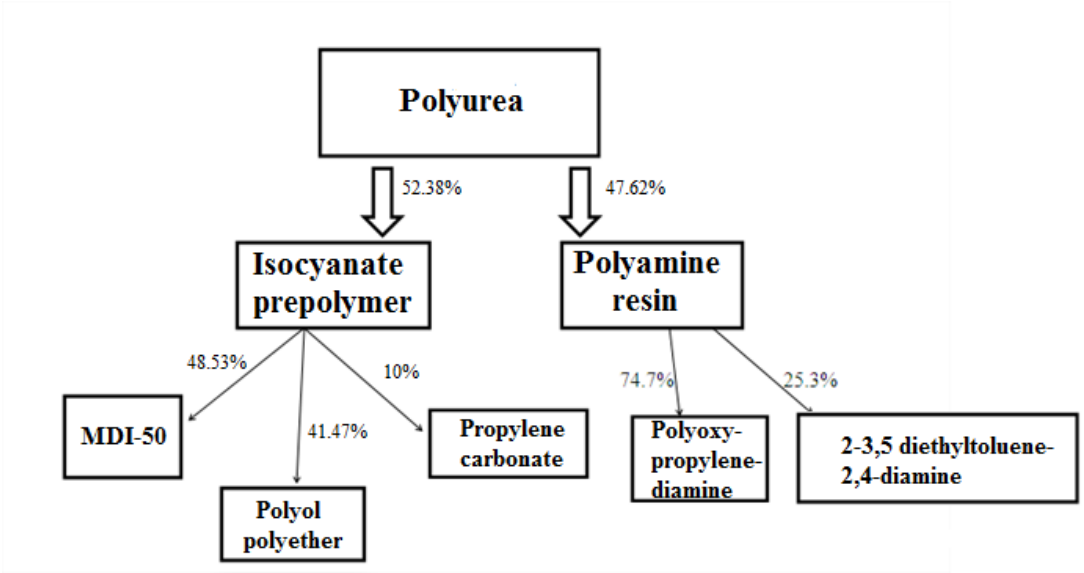

Figure 9-10 Flow chart of polyurea composition

Figure 9.10 summarizes the polyurea resin composition, which has been used in the LCI stage. Once the polyurea resin is produced, during its application on a surface, it is necessary to add a 20 wt% of hardener (N,N'-(dicyclohexylmethane-4,4'-diyl)-bis-aspartic acid tetraethyl ester,

$C_{29}H_{50}N_2O_8$) to 1 kg of polyurea resin. Finally, a 2 wt% of nano-TiO_2 suspension has been added to the mixture of hardener and polyurea resin. The total amount of polyurea resin, hardener and nano-TiO_2 suspension (nano-TiO_2 polyurea resin) is equal to (1+0.2)*1.02kg = 1.224kg

9.2.2.2 *Application of nano-TiO_2 polyurea resin on aluminum panel*

Nano-TiO_2 polyurea resin is applied on an aluminum panel of 1000mm x 3000mm x 2mm. This application is made in a factory through a spraying system. A company's supplier supply isocyanate prepolymer and polyamine resin in a steel drum of 5 liter capacity, hardener and nano-TiO_2 suspension in a jerry can of 20 and 2.5 liters capacity respectively. Isocyanate prepolymer and polyamine resin are placed on a pallet, which is used five times. Aluminum panel is supplied on pallet (30 panels per pallet) and is wrapped with low-density polyethylene. Isocyanate prepolymer and polyamine resin are poured into a mixing tank, in which a mechanical agitator is placed to maintain uniform the mixture of two materials. Mixture of isocyanate prepolymer and polyamine resin, hardener and nano-TiO_2 suspension are extracted from each container, pumped, mixed by an electronic proportioning and through a flexible tube are conducted into a spray gun, these latter equipment allowing to obtain a proper nebulization of nano-TiO_2 polyurea resin. Finally, a direct application on an aluminum panel by using spray gun has been evaluated. The spraying system is reported in Figure 9.11.

Figure 9-11 Spraying system for nano-TiO_2 functionalized polyurea resin application on an aluminum panel

Basing on literature data, during the nano-TiO_2 polyurea resin application, 8 wt% of material is wasted. Moreover, it has been assumed that, of the total amount of isocyanate prepolymer and polyamine resin, 0.2 wt% remains attached on the drum walls and 0.1 wt% on the mixing tank walls. The total waste material lost during the application process is 8.3 wt%. Regarding NMVOC and particulates < 2.5 μm emissions to air, it has been assumed to respect the European limit of 50

mg/Nm^3 and 14.5 μg/m^3 respectively. Finally, for nano-TiO_2 emissions the amount present in the 8.3% of waste materials has been calculated. Then, it has been postulated that 99% of this quantity is entrapped by HEPA filter and the remaining part is released to production room and consequently inhaled by worker. The considerations reported in chapter 7 have been taken into account.

9.2.2.3 *Installation and Use phase*

The aluminum panel coated with nano-TiO_2 polyurea resin lifetime has been assumed of 20 years. The functionalized panel has been installed in indoor environment, in particular in a sterilized environment, which requires a low level of bacteria per unit volume. A manual installation using silicone and plastic supports have been considered and the electric energy consumption as well. Moreover, the reduction of Escherichia Coli (bacteria) and NO_2 emissions concentrations have been evaluated. Moreover, 0.01% of nano-TiO_2 emissions released to indoor environment in 20 years, due to indoor thermal actions and maintenance operations, has been assumed.

9.2.2.4 *End of Life*

Following an ecodesign approach and due to the lack of knowledge of end of life treatment of nanoproduct a precautionary approach has been adopted. The end of life treatment of the aluminum panel coated with nano-TiO_2 polyurea resin is made in order to separate polyurea resin from aluminum panel and consequentially recycling the aluminum panel. Therefore, a heat treatment with a temperature of 660°C (aluminum melting point: 660°C) allows to evaporate the residual nano-TiO_2 polyurea resin (resin melting point: 350°C) and so to separate it from the aluminum panel. As well in this stage nano-TiO_2 emissions released during the heat treatment has been determined. The amount of nano-TiO_2 emissions has been calculated as the total of nano-TiO_2 added into polyurea resin less the quantity of nano-TiO_2 emissions released during application and use phases.

9.2.3 Life Cycle Assessment

9.2.3.1 *Goal and scope definition*

The aim of this study is to assess the environmental performance of nano-TiO_2 functionalized polyurea resin applied on an aluminium panel in order to define the most critical aspects of the process and minimize the environmental burdens.

9.2.3.2 *Functional unit, function of the system and system boundaries*

The surface of one aluminum panel, namely of 3 m^2 (size 1000 mm x 3000 mm x 2 mm) is used as functional unit. The function of the system function is that of architectural element, designed for covering walls and vertical surfaces. The application of nanofunctionalized aluminum panel in indoor environment, thanks to the TiO_2 photocatalytic and superhydrophilicity properties, generate an antibacterial and self-sterilized environment. System boundaries cover the entire life-cycle including raw materials extraction, production, distribution, installation, use and end of life phases, thus obtaining “a cradle to the grave” overview according with the LCA approach. Plants, devices, equipment, transport and energy consumptions (electricity and heat) have been also considered in the study as well as all emissions that occur into the entire life cycle.

9.2.3.3 ***Data quality***

Primary data related to raw materials and to the production and storage of a traditional aluminum panel coated with polyurea resin (without nano-TiO_2) have been collected directly from two Italian companies: one specialized in the production of isocyanate prepolymer and polyamine resin and the other one specialized in polyurea application. Whenever lacking, data (i.e. raw materials production, filters, plant emissions) have been completed on the basis of information from literature and from the Ecoinvent database (Ecoinvent Database, 2009).

The following assumptions have been made:

- ✓ Installation, in application process and end of life stage, of HEPA (*High Efficiency Particulate Air filter* → 99.97%) air filter to minimize nanoparticles emissions to air,
- ✓ in the application process, nano-TiO_2 emissions to air have been assumed to be 0.1%, partly retained by an HEPA filter then disposed in a landfill for residual materials and partly released into the production site and inhaled by workers. Moreover, during this phase a closed manufacturing system has been designed,
- ✓ in the use phase, nano-TiO_2 emissions to indoor environment have been assumed to be 0.01%,
- ✓ during the end of life treatment it has been assumed that the reaming part of nano-TiO_2 emissions which are in polyurea resin is totally released and partly retained by an HEPA filter,
- ✓ PPE (*Personal Protective Equipment*): face mask with 95% of efficiency to protect workers from dust and nanoparticles inhalations,
- ✓ use of specific packaging to limit the release of nanoparticles emissions during the transports,
- ✓ transports from application site to the waste treatment sites have been calculated using a distance of 100km, as required by the Environmental Product Declaration Product Certification (EPD) (EPD, 2008),
- ✓ the electricity energy supply has been assumed to be the Italian mix electric energy generated by Ecoinvent.

9.2.4 Life Cycle Inventory

The compilation of inventory data has been carried out using databases included in SimaPro 7 software (Goedkoop et al., 2010). Ecoinvent database has been taken into consideration for the inventory of some materials (i.e. aluminum production), chemicals (i.e. MDI-50), natural gas, electric energy, transport, etc. Auxiliary processes, such as the spraying system, some chemicals (i.e. the hardener $C_{29}H_{50}N_2O_8$) percentage of emission or waste materials, have been created using primary data. For the upstream processes, the I/O data refer to the annual production of aluminum panels. Table 22 shows some of the most relevant inventory data.

Table 22 Data inventory for 3 m^2 of nano-TiO_2 functionalized polyurea resin application on an aluminum panel

Category	Components	Quantity	Unit	Source
Energy input	Electricity consumption	1355.23	kWh	Straight from the company.
Materials I/O	Polyamine resin	2.5456	kg	
	Isocyanate prepolimer	2.8001	kg	
	nano-TiO_2 suspension	0.1283	kg	
	Hardener	1.0691	kg	

	Aluminum panel	16.2	kg	
	Cardboard	3.6	kg	
	EUR-pallet	0.0417	kg	
	Plastic protective films	0.2052	kg	
Emissions to air	Particulates < 2.5 μm	0.16753	kg	Emissions were derived from literature.
	NO_2	1.79E-5	kg	
	CO_2	0.0022111	kg	
	Water	0.065804	kg	
	NMVOC	0.32167	kg	
	Ammonia	0.024866	kg	
	Ethyne	3.31E-5	kg	
	Aluminum	0.046231	kg	
Transports	Road	4115.15	kgkm	Straight from the company. Transport processes I/O data derived from Ecoinvent database.
	Freight	8481.69	kgkm	
Waste of materials	Waste of polyurea resin with nano-TiO_2 retained by air filter	0.51098	kg	Disposal scenario was given from the company. Waste treatment were derived from Ecoinvent process.
	Waste of polyamine resin remained into drums	6E-4	kg	

9.2.5 Impact assessment and conclusions

9.2.5.1 *IMPACT 2002+* modified method

First, the impact assessment has been discussed at a mid-point level than a damage-oriented approach has been performed, in order to translate environmental impacts from impact categories into damage categories.

Single score damage for 1 m^2 of nano-TiO_2 functionalized polyurea resin application on an aluminum panel is equal to 11.9 mPt. The results of the analysis at mid-point level reported in Table 23 and Figure 9.12 show that the production stage has the highest environmental damage (93.25%) producing a significant impact in most of the considered environmental impact categories. Installation and use phase and end of life influence the total damage only for 6.43% and 0.326% respectively.

Table 23 Characterized LCIA results of 1 m^2 of nano-TiO_2 functionalized polyurea resin application on an aluminum panel

Impact category	Unit	Total	Production	Installation and Use phase	End of Life
Carcinogens	kg $C_2H_3Cl_{eq}$	6,40E-01	5,66E-01	7,35E-02	9,30E-04
Non-carcinogens	kg $C_2H_3Cl_{eq}$	6,54E-01	6,37E-01	1,17E-02	5,01E-03
Respiratory inorganics	kg $PM2.5_{eq}$	2,99E-02	2,79E-02	1,91E-03	7,68E-05
Ionizing radiation	Bq $C\text{-}14_{eq}$	6,13E+02	5,47E+02	6,22E+01	4,39E+00
Ozone layer depletion	kg $CFC\text{-}11_{eq}$	3,30E-06	2,90E-06	3,90E-07	6,69E-09
Respiratory organics	kg $C_2H_{4\,eq}$	1,27E-02	1,15E-02	1,10E-03	2,01E-05
Aquatic ecotoxicity	kg TEG water	2,94E+03	2,79E+03	8,50E+01	6,54E+01
Terrestrial ecotoxicity	kg TEG soil	1,48E+03	1,45E+03	2,21E+01	1,99E+00
Terrestrial acid/nutri	kg $SO_{2\,eq}$	4,39E-01	3,99E-01	3,83E-02	1,38E-03

Land occupation	m2org.arable	1,06E+00	1,01E+00	4,69E-02	2,72E-03
Aquatic acidification	kg $SO_{2\ eq}$	1,19E-01	1,09E-01	9,53E-03	3,48E-04
Aquatic eutrophication	kg PO_4 P-lim	9,03E-03	8,66E-03	3,44E-04	3,07E-05
Global warming	kg $CO_{2\ eq}$	2,70E+01	2,39E+01	2,97E+00	9,95E-02
Non-renewable energy	MJ primary	5,55E+02	4,89E+02	6,38E+01	1,42E+00
Mineral extraction	MJ surplus	4,90E+00	4,21E+00	6,87E-01	2,84E-03
Radioactive waste	kg	8,40E-04	7,49E-04	8,54E-05	5,88E-06
Carcinogens inhaled	kg	2,36E-07	2,55E-10	2,35E-07	7,51E-12
Respiratory inorganics indoor	kg	1,03E-05	-	1,03E-05	-
Non-carcinogens indoor	CFU/pers	-1,54E-02	0,00E+00	-1,54E-02	0,00E+00
Nano-TiO_2 ecotoxicity in freshwater	kg	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	kg	-	-	-	-
Total	mPt	11,39	10,62	0,7322	0,0371

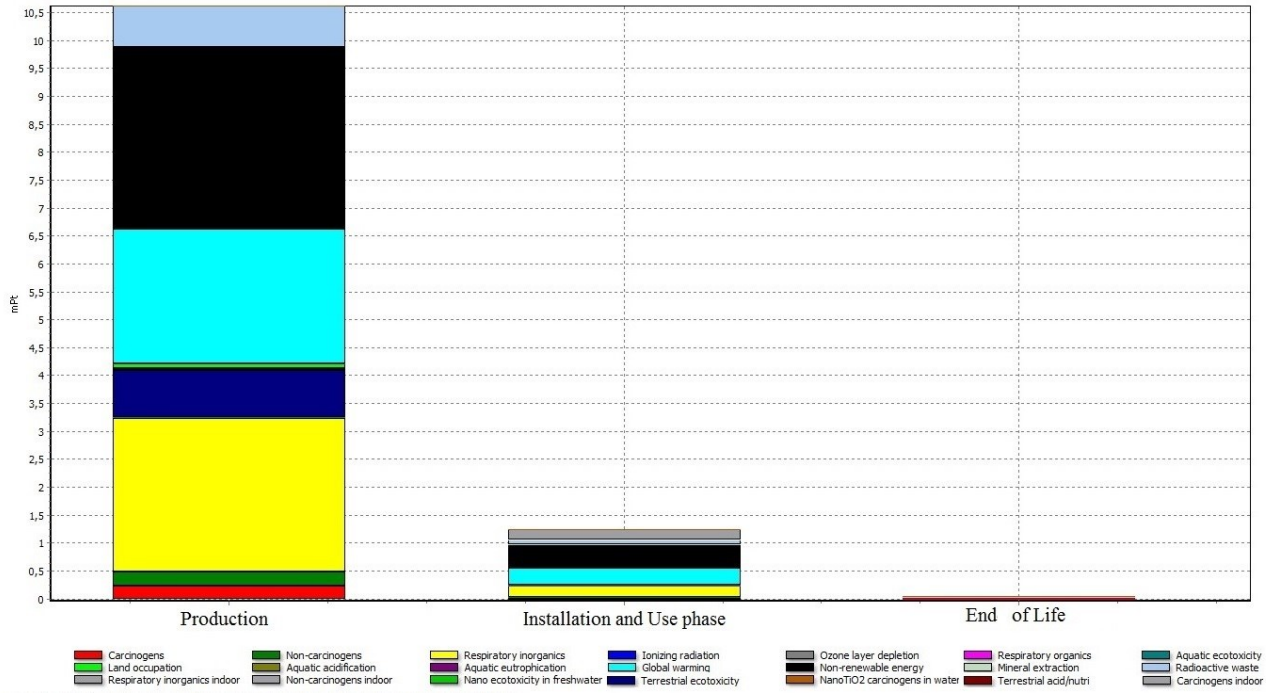

Figure 9-12 Evaluation by impact categories of 1 m^2 of nano-TiO_2 functionalized polyurea resin application on an aluminum panel

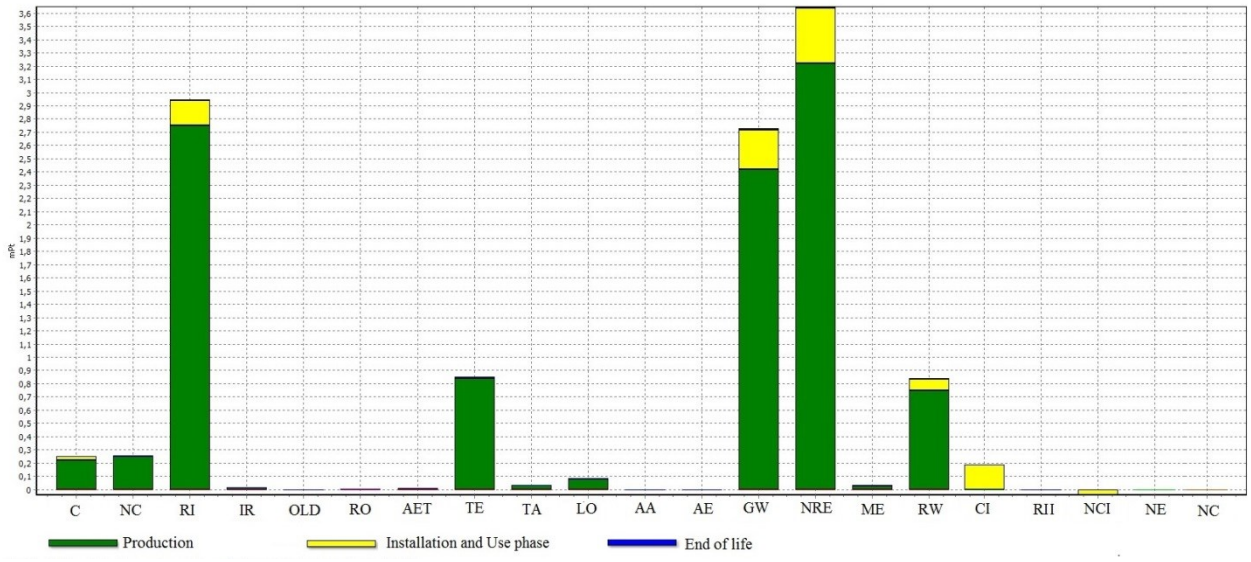

Figure 9-13 Evaluation by impact categories of 1 m^2 of nano-TiO_2 functionalized polyurea resin application on an aluminum panel, where C= Carcinogens; NC= Non-Carcinogens; RI= Respiratory Inorganics; IR= Ionizing Radiation; OLD= Ozone Layer Depletion; RO= Respiratory Organics; AET= Aquatic Ecotoxicity; TE= Terrestrial Ecotoxicity; TA= Terrestrial acid/nutria; LO= Land Occupation; AA= Aquatic Acidification; AE= Aquatic Eutrophication; GW= Global Warming; NRE= Non-renewable Energy; ME= Mineral Extraction; RW= Radioactive Waste; CI= Carcinogens Inhaled; RII= Respiratory Inorganics; NC= Non-Carcinogens indoor; NE= NanoTiO_2 ecotoxicity in freshwater; NC= NanoTiO_2 carcinogens in freshwater;

Figure 9.13 highlights that the most significant contribution to the total damage is due to Non-renewable energy impact category (32.04%), mainly due to *gas, natural, in ground* (44.92%), which is caused by the production stage (84.7%), in particular for aluminum panel production. Successively, the second major contribute to the total damage is generated by Respiratory inorganics impact category (25.88%) which is primarily affected by *particulates, < 2.5 μm* (34.93%), *nitrogen oxides* (26.8%) and *sulfur dioxide* (18.18%) emissions. For all these emissions the production phase is the process that causes the major environmental load (95.5%, 90.1% and 92.4% respectively), in particular, for the first two emissions, for isocyanate prepolymer production and for the last one, for aluminum panel manufacture. Global warming impact category (23.94%) is mainly influenced by 96.1% of *carbon dioxide, fossil* and the production process determines the main environmental burden (88.7%), in particular for electric energy consumption. In Terrestrial ecotoxicity impact category (7.48%), releases of *zinc* in air contribute for 55.66% mainly due to the production stage, in particular for aluminum panel production. In Radioactive Waste impact category (7.38%), the *volume occupied by low-active radioactive waste* contributes for 99.9% mainly due to the electricity energy consumption in the production phase, where part of the electric energy mix is made by nuclear power plants.

Regarding Carcinogens inhaled impact category (1.62%) the damage is totally due to the releases of 2.36E-7 kg of *particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles) by humans especially during end of life treatment. Carcinogens impact category (2.22%) is affected by 2.6E-6 kg of *particulates, < 100 nm in air*. In Non-carcinogens indoor (-0.366%) the reduction of -0.0154 CFU/pers *Escherichia Coli* derived from the benefit of nano-TiO_2 application. Finally, another

nano-TiO_2 benefit emerges in Respiratory inorganics indoor (-4.08%) thanks to the reduction of -8.1E-5 kg *Nitrogen dioxide indoor* concentration in the room.

Table 24 LCIA results at end-point level of 1 m^2 of nano-TiO_2 functionalized polyurea resin application on an aluminum panel

Damage category	Unit	Total	Production	Installation and Use phase	End of Life
Human health	DALY	2,47E-05	2,30E-05	1,59E-06	7,14E-08
Ecosystem quality	PDF*m2*yr	1,34E+01	1,31E+01	2,70E-01	2,34E-02
Climate change	kg CO2 eq	2,70E+01	2,39E+01	2,97E+00	9,95E-02
Resources	MJ primary	5,60E+02	4,94E+02	6,45E+01	1,42E+00
Radioactive waste	kg	8,40E-04	7,49E-04	8,54E-05	5,88E-06
Carcinogens inhaled	DALY	1,31E-06	1,41E-09	1,31E-06	4,17E-11
Respiratory inorganics indoor	DALY	-3,30E-06	-	-3,30E-06	-
Non-carcinogens indoor	DALY	-2,95E-07	-	-2,95E-07	-
Nano-TiO_2 ecotoxicity in freshwater	PAF*m3*day	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	DALY	-	-	-	-

The endpoint analysis highlights (Table 24) that the total damage is affected by 30.6% to Human Health (3.48E-3 Pt), 32.3% to Resources (3.68E-3 Pt), 23.9% to Climate Change (2.73E-3 Pt), 8.61% to Ecosystem Quality (9.81E-4 Pt), 7.38% to Radioactive waste (8.4E-4 Pt), 1.62% to Carcinogens inhaled (1.85E-4 Pt) and is balanced by -0.366% to Non-carcinogens indoor (4.17E-5 Pt) and -4.08% to Respiratory inorganics indoor (4.65E-4 Pt). In these latter two cases the damage is contained, since the LCA study has been set in an ecodesign approach in order to limit the nano-TiO_2 emission releases.

9.2.5.2 *USEtox™ modified method*

The results of the analysis at mid-point level reported in Figure 9.14 and Table 25 show that the phases of the life cycle with the highest environmental loads are the production due to Human toxicity, cancer (95.3%), Human toxicity, non-cancer (93.9%) and Ecotoxicity (95.5%) impact categories and the installation end use phase caused by Human toxicity, cancer, indoor (99.9%) and Human toxicity, non-cancer, indoor (99.9%).

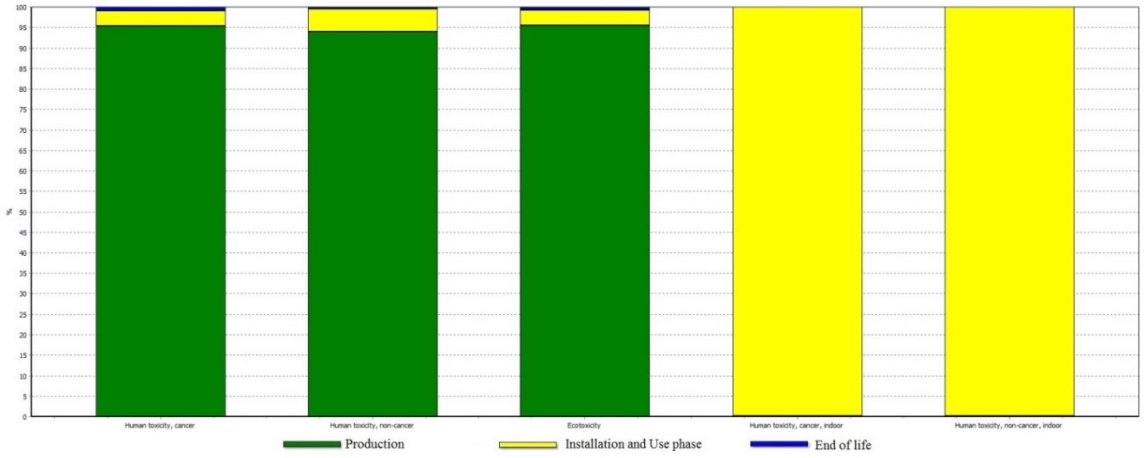

Figure 9-14 Evaluation by impact categories of 1 m^2 of nano-TiO_2 functionalized polyurea resin application on an aluminum panel

Table 25 Characterized LCIA results of 1 m^2 of nano-TiO_2 functionalized polyurea resin application on an aluminum panel

Impact category	Unit	Total	Production	Installation and Use phase	End of Life
Human toxicity, cancer	CTUh[#]	2,52E-06	2,40E-06	9,50E-08	2,34E-08
Human toxicity, non-cancer	CTUh	1,24E-07	1,17E-07	7,07E-09	5,18E-10
Ecotoxicity	CTUe[§]	2,80E+01	2,68E+01	1,02E+00	2,37E-01
Human toxicity, cancer, indoor	CTUh	1,40E-10	1,51E-13	1,40E-10	4,46E-15
Human toxicity, non-cancer, indoor	CTUh	1,66E-12	1,79E-15	1,66E-12	5,29E-17
# CTUh = cases/$kg_{emitted;}$ § CTUe = PAF*m^3*yr					

The total damage of Human toxicity, cancer impact category is mainly due to *Chromium VI* in air (96.8%), which is caused by the production stage (97.6%) to produce the steel of machineries used in this stage. Successively, in Human toxicity, non-cancer, *Mercury* in water generates major environmental load (32.1%), in particular affected by the production phase (92.4%) in particular during the electric energy production. Ecotoxicity impact category is mainly influenced by 86.2% of *Chromium VI* in water and again the production process determines the main environmental burden (95.3%), in particular in the steel drums manufacture. In Human toxicity, cancer, indoor and Human toxicity, non-cancer, indoor impact categories, the damage is totally due to the releases of 2.36E-07 kg of *particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles inhaled by people that are in the room) in indoor environment and is mainly due to installation and use phase stages (99.89% for both impact categories). Releases of 2.6E-6 kg of *particulates, < 100 nm in air* affect Human toxicity, cancer for 1.6E-3% and Human toxicity, non-cancer for 3.8E-4% and is mainly due to the production stage (80.58% for both impact categories).

Acknowledgement

I would like to acknowledge the Department of Sciences and Methods for Engineering - University of Modena and Reggio Emilia, in particular Prof. Rimini Bianca and Prof. Rita Gamberini, for the scientific support and SRS S.p.A. company for data collection.

9.3 Nano-TiO_2 self-cleaning coated float glass

There are several coating methods to create a thin film on glass surface, the mainly are: vaccum arc deposition (Tölke et al., 2010), reactive dc-sputtering (Vershinin et al., 2000), alkaline hydrothermal method (Wu et al., 2011), hydrothermal method (Myint et al., 2011), chemical solution method (Eskandari et al., 2011), reactive dc-sputtering (Tölke et al., 2010), successive-ionic-layer-adsorption and-reaction (SILAR) method (Park et al., 2010), etc. In this work, a modified coating method consisting in first a decrease of the initial substrate roughness with acetic acid and then dip-coating of the softened glass into a TiO_2 nanosuspension has been used with the aim to produce films with enhanced adhesion to the substrate.

Saint Gobain soda-lime float glass has been used as substrate. With the aim of increasing the adhesion of the coating and based on previous investigations made by ARACNE group, a decrease of the surface roughness of the substrate has been carried out before the TiO_2 deposition. This has been made by soaking the glass in 96% CH3COOH for 4h. The chemical etched glass has been

coated by dip coating with 5 layers of a commercial anatase nano-TiO_2 suspension provided by Colorobbia S.p.A. (Baldi et al., 2008), using a dipping rate of 85 mm/min. Finally, the film has been dried at 100 °C for 1 h (Cedillo-González et al., 2014).

9.3.1 Ecodesign of an industrial scale process

As above mentioned, the present LCA study is an accompanying study within regional Italian project named "ARACNE". The research project has optimized the method of coating of float glass thanks to experimental texts that have been carried out in a laboratory. The research continued with the intent to design the industrial scale up of the developed coating method. The LCA analysis of the process on a laboratory scale has not been considered since, in according with Shibasaki et al. (Shibasaki et al., 2006), the LCA results of laboratory scale do not necessarily represent the environmental burdens which would be caused after scaling up to a typical mass production. The reasons are:

- ✓ there might be changes due to scale up in process yield as well as in energy efficiency of the process. These can influence the environmental burdens, as these affects the material and energy use as well as the amount of emissions and waste.
- ✓ there might be changes in technology and for the material or energy provision affects the LCA results as well.
- ✓ in LCA analysis of pilot/laboratory plants, processes are often seen as isolated or independent of each other. The effects due to changes in plant utilization are not considered sufficiently.

9.3.2 Life cycle of a a nano-TiO_2 self-cleaning float glass

The entire life cycle of a nano-TiO_2 self-cleaning coated float glass shown in Figure 9.15, consists of four main steps: 1) production, 2) installation, 3) use and 4) end of life. The production step, in turn, is divided in: a) cutting, b) lapping, c) ultrasonic cleaning, d) soaking in acetic acid, e) dip-coating.

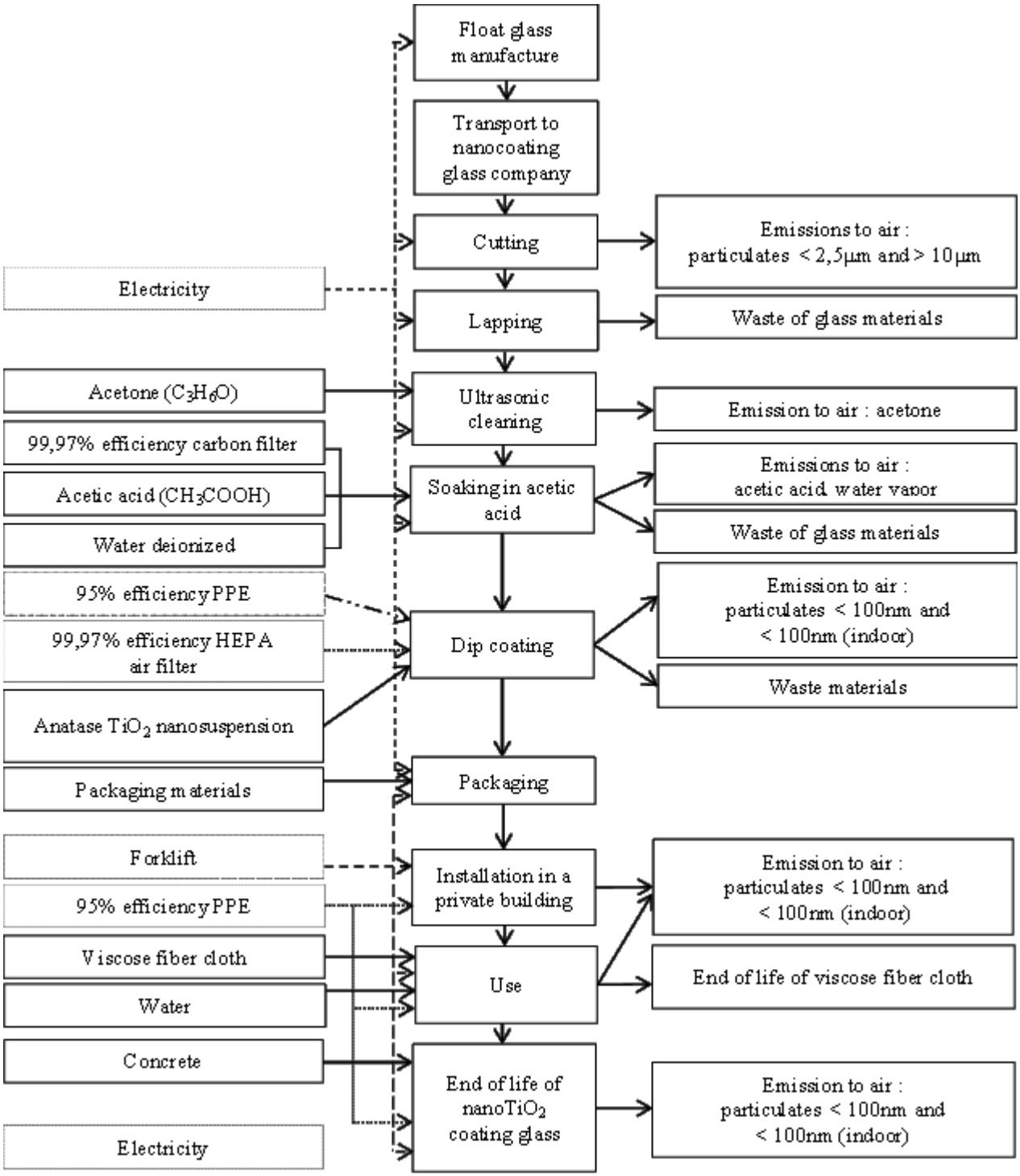

Figure 9-15 Flow chart of nano-TiO_2 self-cleaning coated float glass

The present study considers the outdoor application of a self-cleaning float glass in private building. A safe behavior in all life cycle steps where workers can come into contact with or inhale nanoparticles has been considered. In particular, in nano-TiO_2 film application, glazing installation, use and end of life steps is likely to have release of nanoparticles emissions by nanocoating surface. For these reasons air filters and personal protective equipment have been included in this study. The main steps of the life cycle of nano-TiO_2 self-cleaning coated float glass are described below.

9.3.2.1 ***Production***

a) First of all the Saint Gobain soda-lime float glass is cut in customer required size,
b) the obtained glass are then polished to bevel the edges and corners,
c) ultrasonic cleaning is a process that is able to clean the glass surface through the use of ultrasound and acetone as solvent media,
d) the clean glass is soaked in 96% CH3COOH for 4h, in order to decrease the surface roughness of the substrate,
e) finally, the etched glass is coated with 5 layers of a nano-TiO_2 suspension.

9.3.2.2 ***Installation and Use phase***

The nano-TiO_2 self-cleaning coated float glass has been applied in private building as windows glass. In the installation step it has been evaluated the transport by lorry from the company, where the nano-TiO_2 self-cleaning coated float glass has been produced, to the installation site and the handling of glasses from lorry to private building. It has been considered the installation of a single glass with nano-TiO_2 coating side oriented externally (outdoor environment).

In the use phase nano-TiO_2 self-cleaning coated float glass has been considered for applications as windows, external windows, conservatories, etc. In according with Fujishima et al. (Fujishima et al., 2000) the duration of ten years of nano-TiO_2 coating effects has been assumed. In the study, the heat reflected outside (thanks to the nanocoating) and the heat that transferred through the glass have been assessed. Therefore, in summertime the nano-TiO_2 coating allows to keep the indoor room cooler thus obtaining a benefit. In the contrary, in winter this phenomenon determines that part of solar heat does not pass through the glass windows, decreasing the radiation heat inside the room. Furthermore, the benefits of nanocoating such as the reduction of NOx and VOCs concentrations have been evaluated. Finally, annual maintenance of glazing with only water and viscose fiber cloth have been included.

9.3.2.3 ***End of life***

In order to protect the human health and considering the uncertainty on the potential damage caused by nanoparticles after ten years (duration of nano-TiO_2 coating effects), it has been assumed to make inert the glass through specific waste treatment: cover waste glasses with concrete and then bury the obtained concrete matrix. Different waste treatment scenario has been evaluated such as the re-functionalization of glass after ten years. Therefore, considering a glass lifetime of 30 years two functionalizations are needed, followed by the inertization treatments has been considered.

9.3.3 Life Cycle Assessment

9.3.3.1 ***Goal and scope definition***

The goal of the study is to assess the environmental impacts of a nano-TiO_2 self-cleaning coated float glass over its entire life cycle in order to identify the hot spots of the system during the entire life cycle.

9.3.3.2 ***Functional unit, function of the system and system boundaries***

The system studied is a self-cleaning glass coated with nano-TiO_2 film to create a surface that remains cleaner for longer than conventional glass. A transparent coating on the external surface of the glass harnesses the power of UV rays and rain or water to break down airborne pollutions and grime. The function of self-cleaning is the applications for private buildings, such as traditional

windows and curtain walls as well as glazing. A single nano-TiO_2 self-cleaning coated float glass of 0.75 m^2 (size 1500 mm x 500 mm x 4 mm) is analyzed. The system boundaries cover the entire life cycle of the system analyzed, following the LCA approach. As can be seen in Figure 9.15, the analysis includes the supply of all raw materials involved in the coating process, packing, installation and end of life. The production, maintenance and disposal of facilities as well as the environmental burdens related to the production of chemicals, packaging and other auxiliary materials are also included in the present study. Emissions into the air and water, as well as the solid waste produced in each step are taken into account. The transportation to treatment facility of the solid wastes is also considered.

9.3.3.3 *Data quality*

Starting from laboratory data, the best environmental performance of the industrial scale up process of nano-TiO_2 self-cleaning coated float glass has been evaluated. In order to ecodesign the industrial scale process it has been necessary to consider literature data and databases included in SimaPro 7 software (e.g. Ecoinvent database has been used to model the float glass process), since the laboratory scale does not give meaningful information about plants, equipment, internal transports, ordinary maintenance operations of equipment and machineries. In addition, because the data related to the installation operations, use phase and end of life of nano-TiO_2 self-cleaning coated float glass has not been considered in the laboratory scale process it has been necessary to study and ecodesign these aspects. A life cycle assessment of nano-TiO_2 self-cleaning coated glass has been carried out in order to assess the most critical environmental burdens.
For the studied system the following assumptions have been hypnotized:

- ✓ Installation of HEPA air filter (with 99.97% of efficiency) during cutting, soaking in acetic acid and coating steps,
- ✓ use of PPE, face mask with 95% of efficiency to protect workers from dust and nanoparticles inhalations, during coating, installation, use and end of life steps,
- ✓ a closed manufacturing system has been designed,
- ✓ use of specific packaging to limit the release of nanoparticles emissions during the transports,
- ✓ the transport of facilities, raw material, chemicals, materials for packaging is supposed with a scenario of 100 km from the producer to the customers, as is required by the environmental product declaration product certification (EPD) (EPD, 2008),
- ✓ the electricity energy production is assumed to be the Italian mix electric energy created by Ecoinvent.

9.3.4 Life Cycle Inventory

The compilation of inventory data was carried out using databases included in SimaPro 7 software (Goedkoop et al., 2010). The ecodesign of industrial scale up production of self-cleaning glass coated with nano-TiO_2 film has been performed on lab data carried out by the experiments to determinate the optimized coating method. The remaining data have been obtained from specialized databases and literature such as devices, machineries, plants, internal transports, ordinary maintenance operations and all data regarding installation, use and end of life steps. A selection of important data used in LCI (Life Cycle Inventory) of nano-TiO_2 self-cleaning coated float glass (size 1500 mm x 500 mm x 4 mm) is reported in Table 26.

Table 26 Inventory data of 1 m^2 of nano-TiO_2 self-cleaning coated

Category	Components	Quantity	Unit
Energy input	Electricity consumption	183,34	kWh
Materials I/O	Float glass uncoated	7431,21	g
	Protection film (LDPE)	14,40	g
	Tap water	39,58	l
	Acetone	197500	g
	Acetic acid	3,28	kg
	Water deionised	1,79	kg
	Compressed air	317,5	l
	nano-TiO_2 suspension	4,38	g
	Viscose fiber cloth	100	g
	Concrete	0,18	m^3
	Heat gain in summer season due to nanocoating	618,93	kW
	Heat lost in winter season due to nanocoating	565,63	kW
Emissions to air	Particulates < 2.5 μm	10,7	g
	Particulates > 10 μm	19,59	g
	Particulates > 2.5 μm and < 10 μm	4,865	g
	Acetic acid	54.05	g
	Water	9.68	g
	Acetone	2,48E-3	g
	Particulates, < 100 nm in air	5,07	g
	Particulates, < 100 nm inhaled	558,87	μg
	NOx	- 87,82	g
	Nitric acid	184,42	g
	Toluene	- 2,19	kg
	CO_2	29,42	kg
Transports	Road	64117,22	kgkm
Waste to treatment	Disposal to residual landfill of nano-TiO_2 particulates captured by filter	3,012E-1	g
	Acetone wastes capture by filter	378,6	cm^3
	Acetic acid wastes capture by filter	3,25	kg
	Wastewater treatment (water used during the maintenance operations of equipment)	39,58	l
	Disposal wastes glass	6029,84	g
	Disposal of particulates < 2,5 um and > 10 um dust captured by filter to residual landfill	936,16	g

9.3.5 Impact assessment and conclusions

9.3.5.1 *IMPACT 2002+ modified method*

In Figure 9.16 the environmental loads at the impact categories level of each single steps of 1 m^2 of nano-TiO_2 self-cleaning coated float glass is reported. Single score damage is equal to 25.15 mPt. The results of the analysis at mid-point level reported in Table 27 and Figure 9.16 show that the phases of the life cycle with the highest environmental burdens are the production (65.06%) and the use phase (28.04%) stages, following by end of life (6.22%) and installation (0.67%).

Table 27 Characterized LCIA results of 1 m^2 of nano-TiO_2 self-cleaning coated

Impact category	Unit	Total	Production	Installation	Use phase	End of Life
Carcinogens	kg C_2H_3Cl $_{eq}$	9,95E-01	6,35E-01	2,33E-03	3,37E-01	1,99E-02
Non-carcinogens	kg C_2H_3Cl $_{eq}$	7,11E-01	6,14E-01	3,02E-03	5,15E-02	4,30E-02
Respiratory inorganics	kg PM2.5 $_{eq}$	3,32E-02	4,60E-02	3,58E-04	-1,63E-02	3,11E-03
Ionizing radiation	Bq C-14 $_{eq}$	1,08E+03	8,20E+02	4,17E+00	1,88E+02	6,35E+01
Ozone layer depletion	kg CFC-11 $_{eq}$	1,43E-05	7,75E-06	1,01E-07	6,14E-06	3,51E-07
Respiratory organics	kg C_2H_4 $_{eq}$	-1,83E+00	2,13E-02	2,78E-04	-1,86	2,69E-03
Aquatic ecotoxicity	kg TEG water	6,64E+03	5,46E+03	3,58E+01	9,13E+02	2,31E+02
Terrestrial ecotoxicity	kg TEG soil	7,75E+02	5,88E+02	8,05E+00	1,10E+02	6,83E+01
Terrestrial acid/nutri	kg SO_2 $_{eq}$	2,76E-02	7,76E-01	9,62E-03	-8,25E-01	6,78E-02
Land occupation	m2org.arable	3,27E+00	5,30E-01	5,79E-03	4,91E-01	2,24
Aquatic acidification	kg SO_2 $_{eq}$	2,84E-01	2,29E-01	1,62E-03	4,07E-02	1,24E-02
Aquatic eutrophication	kg PO_4 P-lim	9,11E-03	7,15E-03	2,69E-05	1,58E-03	3,43E-04
Global warming	kg CO_2 $_{eq}$	8,52E+01	4,21E+01	2,41E-01	3,99E+01	2,96
Non-renewable energy	MJ primary	1,45E+03	8,31E+02	4,44E+00	5,83E+02	3,39E+01
Mineral extraction	MJ surplus	3,12	2,85	5,58E-03	1,85E-01	8,19E-02
Radioactive waste	kg	1,41E-03	1,10E-03	3,82E-06	2,23E-04	8,17E-05
Carcinogens inhaled	kg	7,45E-07	4,44E-12	8,78E-08	1,45E-07	5,12E-07
Respiratory inorganics indoor	kg	-	-	-	-	-
Non-carcinogens indoor	CFU/pers	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	kg	-	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	kg	-	-	-	-	-
Total	mPt	25,15	16,37	0,17	7,05	1,56

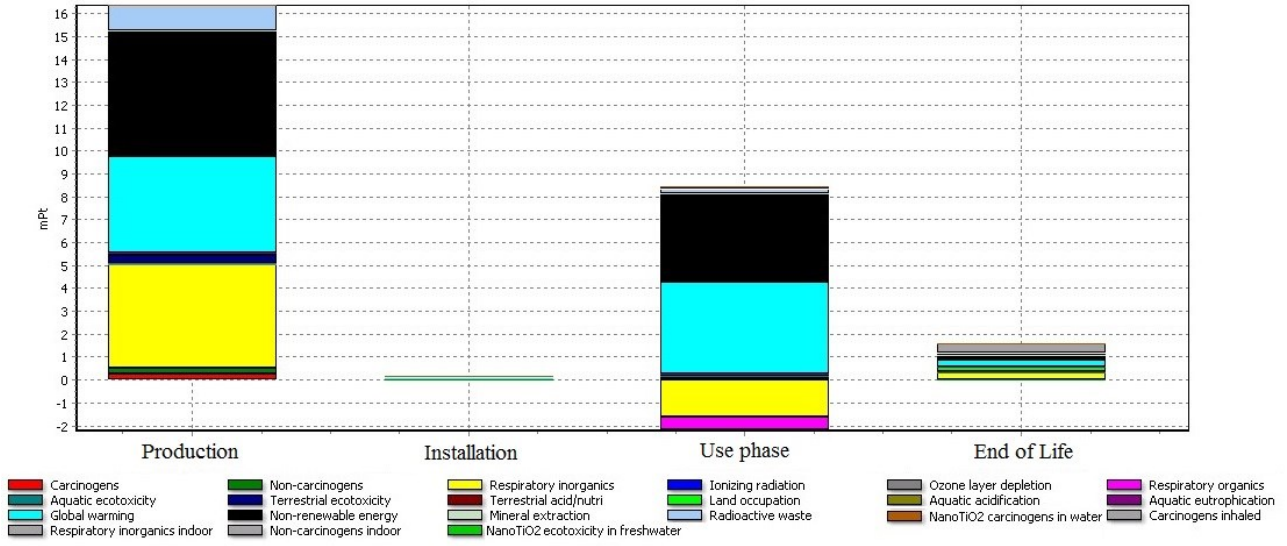

Figure 9-16 Evaluation by impact categories of 1 m^2 of nano-TiO_2 self-cleaning coated float glass

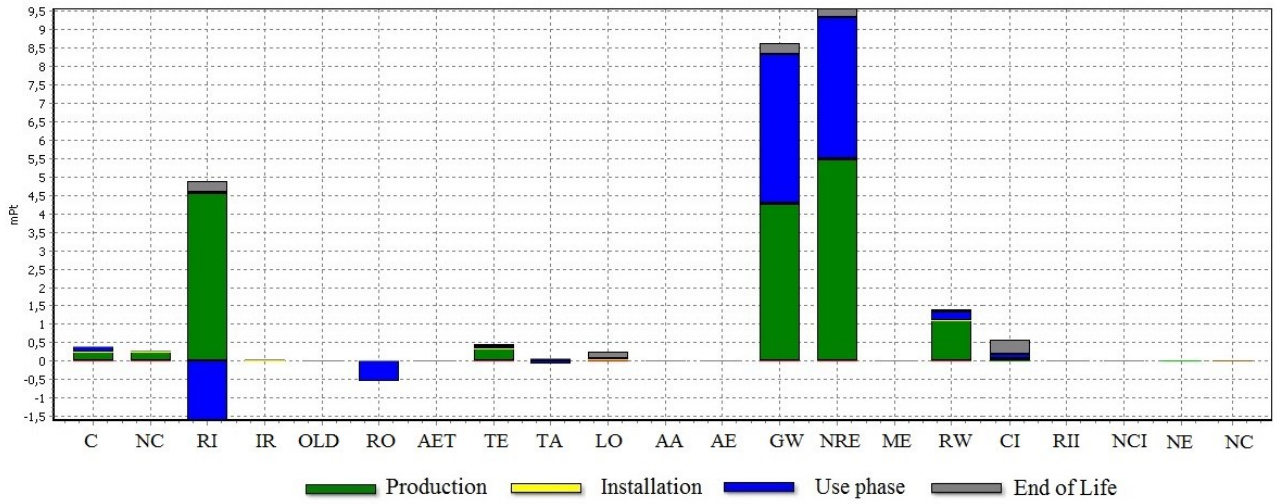

Figure 9-17 Evaluation by impact categories of 1 m^2 of nano-TiO_2 self-cleaning coated float glass, where C= Carcinogens; NC= Non-Carcinogens; RI= Respiratory Inorganics; IR= Ionizing Radiation; OLD= Ozone Layer Depletion; RO= Respiratory Organics; AET= Aquatic Ecotoxicity; TE= Terrestrial Ecotoxicity; TA= Terrestrial acid/nutria; LO= Land Occupation; AA= Aquatic Acidification; AE= Aquatic Eutrophication; GW= Global Warming; NRE= Non-renewable Energy; ME= Mineral Extraction; RW= Radioactive Waste; CI= Carcinogens Inhaled; RII= Respiratory Inorganics; NC= Non-Carcinogens indoor; NE= NanoTiO_2 ecotoxicity in freshwater; NC= NanoTiO_2 carcinogens in freshwater;

Figure 9.17 highlights that the most significant contribution to the total damage is due to Non-renewable energy impact category (37.98%) which is primarily affected by *gas, natural, in ground* (63.35%) due to production phase (41.7%), in particular for electric energy consumption. Successively, the second major contribute to the total damage is generated by Global warming impact category (34.02%), mainly due to *carbon dioxide, fossil* (96.73%), which is caused by production process (49.6%) and use phase (46.68%), in particular for glass manufacture and air-conditioning respectively. Respiratory inorganics impact category (16.16%) is mainly influenced by 37.33% of *particulates, < 2.5 μm,* and 32.02% of *sulfur dioxide* and the production process determines the main environmental burden (86.56% and 86.13% respectively), in particular for lapping process and glass manufacture. This category is also affected by *nitrogen oxides* in air (8.69%) the production process determines the main environmental burden (385.35%) balance by use phase benefit (-331%). In Radioactive Waste impact category (5.6%), the *volume occupied by low-active radioactive waste* contributes for 65.09% mainly due to the electricity energy consumption (part of the electric energy mix is made by nuclear power plants) in the production phase (78.15%). In Carcinogens inhaled impact category (2.32%) the damage is totally due to the releases of 7.45E-07 kg of *particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles) by human especially during end of life (68.76%) and use phase (19.45%) stages. In Terrestrial ecotoxicity impact category (1.78%), releases of *aluminium* in soil (30.31%), *aluminium* in air (24.1%), both due to the production process (68.28% and 86.73% respectively), in particular both for glass production. Carcinogens impact category (1.56%) is affected by of 7.25E-4 kg of *particulates, < 100 nm in air* during the use phase. In Respiratory organics impact category (-2.186%) the reduction of -2.92 kg of *Toluene* (VOC) emission to air (-100%) derived from the benefit of nano-TiO_2 application in the use phase.

Table 28 LCIA results at end-point level of 1 m^2 of nano-TiO_2 self-cleaning coated float glass

Damage category	Unit	Total	Production	Installation	Use phase	End of Life
Human health	DALY	2,43E-05	3,59E-05	2,67E-07	-1,42E-05	2,37E-06
Ecosystem quality	PDF*m2*yr	1,01E+01	6,31E+00	8,18E-02	5,94E-01	3,07E+00
Climate change	kg CO2 eq	8,52E+01	4,21E+01	2,41E-01	3,99E+01	2,96E+00
Resources	MJ primary	1,46E+03	8,34E+02	4,44E+00	5,83E+02	3,40E+01
Radioactive waste	kg	1,41E-03	1,10E-03	3,82E-06	2,23E-04	8,17E-05
Carcinogens inhaled	DALY	4,14E-06	2,46E-11	4,88E-07	8,05E-07	2,85E-06
Respiratory inorganics indoor	DALY	-	-		-	-
Non-carcinogens indoor	DALY	-	-		-	-
Nano-TiO_2 ecotoxicity in freshwater	PAF*m3*day	-	-		-	-
Nano-TiO_2 carcinogens in freshwater	DALY	-	-		-	-

The endpoint analysis highlights (Table 28) that the total damage is affected by 14.1% to Human Health (2.35E-3 Pt), 39.34% to Resources (9.57E-3 Pt), 35.35% to Climate Change (8.6E-3 Pt), 3.01% to Ecosystem Quality (7.34E-4 Pt), 5.79% to Radioactive waste (1.41E-3 Pt) and 2.4% to Carcinogens inhaled (5.84E-4 Pt).

9.3.5.2 *USEtox™ modified method*

The results of the analysis at mid-point level reported in Figure 9.18 and Table 29 show that the phases of the life cycle with the highest environmental loads are the production stage due to Human toxicity, cancer (85.5%), Human toxicity, non-cancer (80.6%) and Ecotoxicity (83.6%) impact categories and the end of life stage due to Human toxicity, cancer, indoor (68.8%) and Human toxicity, non-cancer, indoor (68.8%).

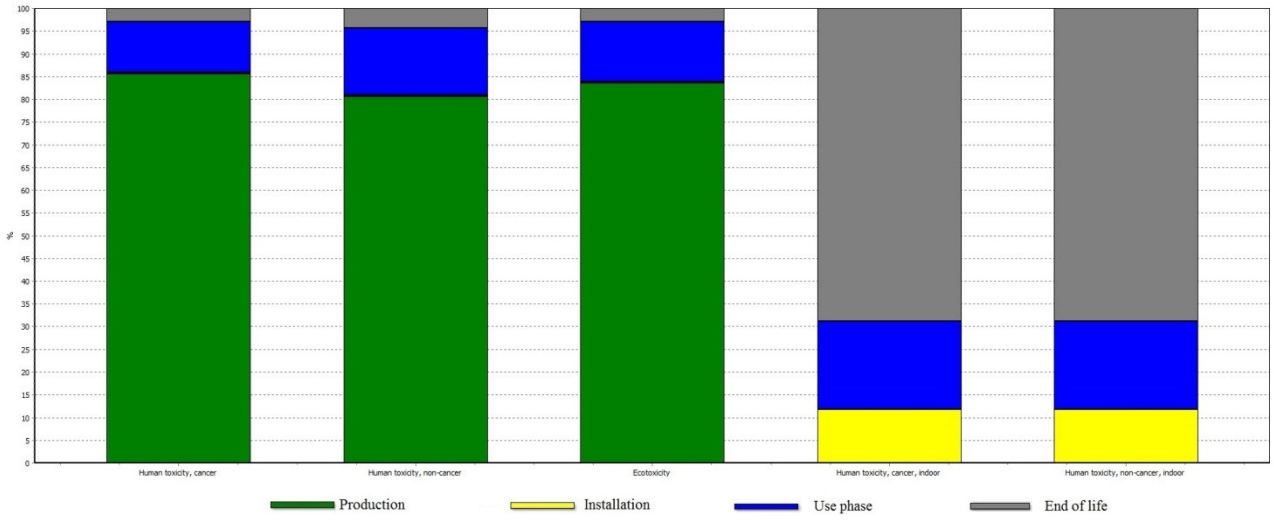

Figure 9-18 Evaluation by impact categories of 1 m^2 of nano-TiO_2 self-cleaning coated float glass

Table 29 Characterized LCIA results of 1 m^2 of nano-TiO_2 self-cleaning coated float glass

Impact category	Unit	Total	Production	Installation	Use phase	End of life
Human toxicity, cancer	CTUh	4,315E-06	3,692E-06	1,425E-08	4,802E-07	1,292E-07
Human toxicity, non-cancer	CTUh	1,565E-07	1,261E-07	6,657E-10	2,297E-08	6,797E-09
Ecotoxicity	CTUe	46,236702	38,666071	0,1488913	6,0468404	1,3748995
Human toxicity, cancer, indoor	CTUh	4,419E-10	2,631E-15	5,209E-11	8,594E-11	3,038E-10
Human toxicity, non-cancer, indoor	CTUh	5,246E-12	3,123E-17	6,184E-13	1,02E-12	3,607E-12
# CTUh = cases/$kg_{emitted;}$ § CTUe = PAF*m^3*yr						

The total damage of Human toxicity, cancer and Ecotoxicity impact categories is mainly due to *Chromium VI* in water (97.2% and 89.8% respectively), which is caused by the production stage (86%), in particular for steel manufacture used to produce air filter. Successively, in Human toxicity, non-cancer, *Barium* in water generates major environmental load (42.1%), in particular affected by the production stage (77.6%) in particular to produce heavy fuel oil necessary to flat glass production. In Human toxicity, cancer, indoor and Human toxicity, non-cancer, indoor impact categories, the damage is totally due to the releases of 7.45E-07 kg of *particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles inhaled by people that are in the room) in indoor environment and is mainly due to end of life phase (68.76% for both impact categories). Releases of 2.6E-6 kg of *particulates, < 100 nm in air* affect Human toxicity, cancer for 2.608E-1% and Human toxicity, non-cancer for 8.53E-2% and is mainly due to the installation and use phase (98.62% for both impact categories).

Acknowledgement
I would like to thanks the Department of Engineering "Enzo Ferrari", Modena - University of Modena and Reggio Emilia, in particular Prof. Cristina Siligardi and Dr. Erika Iveth Cedillo-González.

9.4 Nano-TiO_2 functionalized enamel applied on an steel panel

Today, in the architectural and decorative field, enameled steel is considered among the best available material for coating surfaces. This is due to some salient characteristics that distinguish it clearly from its competitors, such as stone, marble, asphalt, ceramics and aluminum. It is a perfect symbiosis between steel, that ensures mechanical strength, and enamel, which provides durability and a glossy appearance with a pleasant visual impact (Pezzotti, 2007). Hygienic qualities (Palmisano, 2011) and resistance to fire, heat, cold and to aggression from multiple sources, make enameled steel a very good coating for domestic applications such as water boilers, oven and stove components (Zhou et al., 2003; Tang et al., 2000; Rodtsevich et al., 2003). Moreover, in recent years, there has been an improvement also in the aesthetic and functional properties of enamel coatings on steel. The adhesion between enamel and steel substrate has been widely investigated, with and without the NiO precoat (Bodaghi & Davarpanah, 2011) or with the addition of nano-Al_2O_3 additive to enamels (Ling & He, 2004), by studying the effects of the chemical pre-treatment (Barcova et al., 2006) or by developing new application technologies and coating techniques, such as spray coating and electrostatic powder coatings (Scrinzi & Rossi, 2010). The quality of enamel coatings has then been improved and some defects like bubbles or drop formations disappeared (Yang et al., 2004). This fact has given to enameled steel also esthetic qualities and nowadays it is highly used in many different fields, particularly in architectural and decorative applications.

Enameled steel can be used in the interiors of public places, such as stations, airports, metro stations as a wall-covering and for false ceilings, partitions and lift or as a non-flammable and easy-to-clean material. It can be also used as a cladding for buildings because of its weather and UV resistance, lightweight and decorative function (Arcelor Mittal Flat Carbon Europe, 2014). In addition the chemical composition of the frit used for enameling has been developed, including the addition of nano-TiO_2. The presence of the well-known nano-TiO_2 photocatalyst it is possible confer to the surface, on which glaze is applied, superhydrophilic, antismog and self-cleaning properties.

9.4.1 Ecodesign approach

The present study concerns the ecodesign of industrial scale up of a nano-TiO_2 enamel steel panel production performed by LCA methodology. In agreement with the ecodesign approach, the production choices adopted in the present study have been finalized to minimize the environmental burdens. Because of the limited knowledge currently available regarding the nano-TiO_2 effects may have on environment or human health (Iavicoli et al., 2012), a safe behavior has been adopted in all life cycle steps where workers can come into contact with or inhale nanoparticles released by nanocoating surface. Air filters and personal protective equipment have been included in this study. The study takes into account the use of a self-cleaning steel panel for building external coating with a 20 years life time of the nano-TiO_2 glazing effects. Since there is a reduction in the effectiveness of nano-TiO_2 due to deposition of organic material on the support it has been considered necessary to clean yearly the panel. Finally, in the end of life step, it has been assumed to make inert the panel through specific waste treatment, covering the waste panel with concrete and then burying the obtained concrete matrix, in order to prevent any potential damage caused by nanoparticles on human health (NIOSH, 2011). For the same reason, emissions to air of particulates and nano-TiO_2 inhaled by workers handling the nanoenameled panel have been estimated during production, application, use and end of life phases. The benefit of functionalized enamel on external surfaces has been also evaluated, such as the reduction of NO_x (Maggos et al., 2007) and VOCs concentrations, as described in chapter 8.

9.4.2 Life cycle of nano-TiO_2 functionalized enamel applied on an steel panel

The entire life cycle is shown in Figure 9.19. It comprises various stages: supply of raw materials, cutting and cleaning of the panel, enameling process, packaging, application, use and end of life of the steel panel.

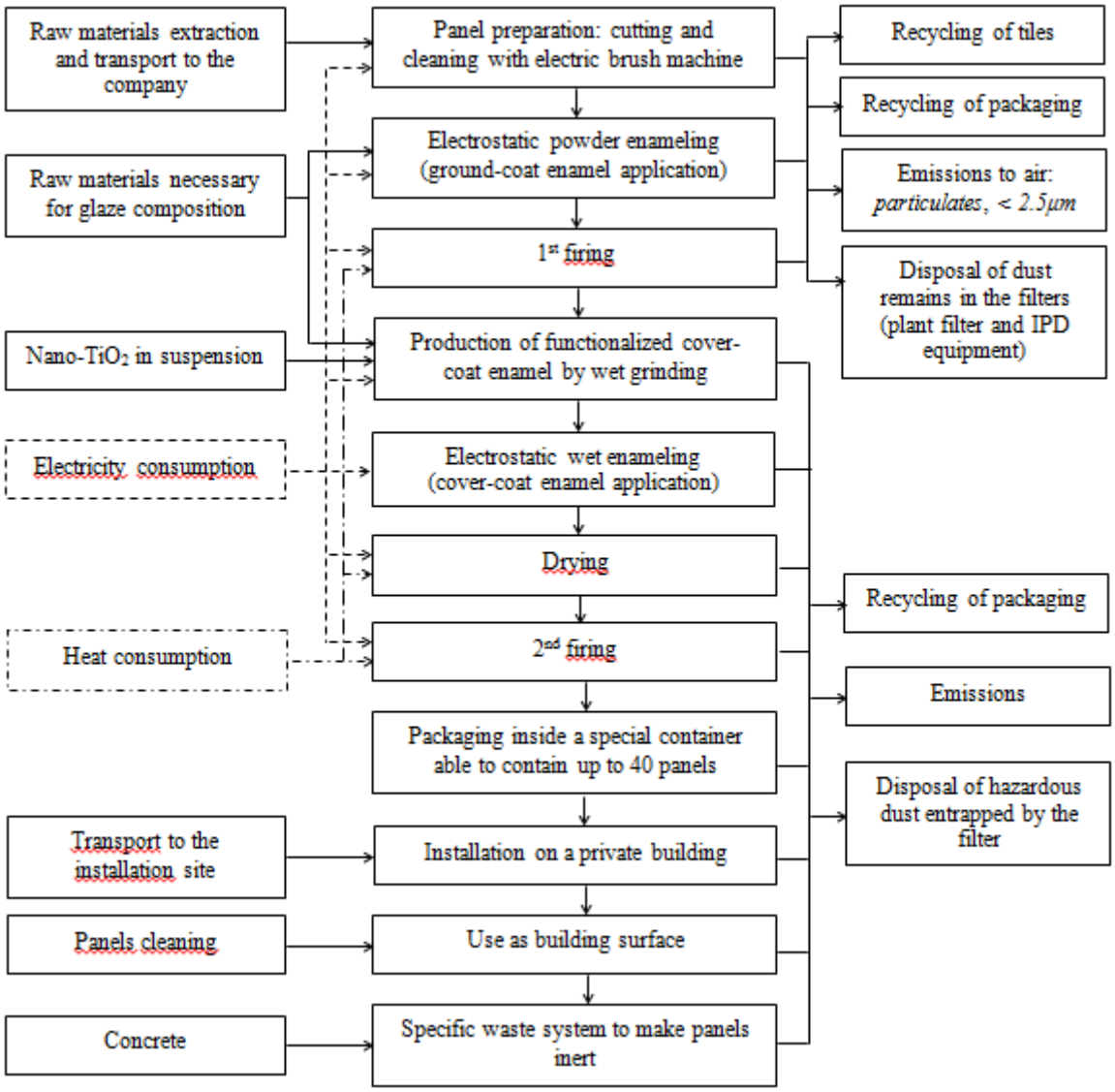

Figure 9-19 Flow chart for 1m^2 of nano-TiO_2 functionalized enamel applied on an steel panel

9.4.2.1 *The enameling process*

The enameling process comprises several main steps:

- preparation of the steel surface
- preparation of the enamel
- application of the enamel to the steel surface
- drying
- firing at high temperature.

The steel used as substrate is characterized by a low carbon content, which falls under the category of "medium molding" DC03ED, as defined by the UNI EN 10209 (EN10209, 2013). The surface is cut in the required dimension and later cleaned with a brushing machine to eliminate any residues of dust.

The enameling process involves applying and firing two layers of enamel on one side of the steel substrate. The first layer is composed by a ground-coat enamel characterized by a mixture of special frits containing a higher proportion of metal oxides (Ni, Co, Cu oxides), that guarantees a fast formation of the adhesion layer and protects against corrosion. The second layer is a cover-coat enamel, that gives aesthetic qualities and helps to increase the chemical resistance of the substrate.

In this study the cover-coat enamel is characterized by the addition of a 3% of nano-TiO_2 suspension, obtained by a liquid-phase process as describe in chapter 9 (Pini et al., 2015) to the enamel composition. Steel is supplied by Arcelor Mittal while frits, in 25 kg fiber drums, and nano-TiO_2 suspension, in 25 l plastic drums, are purchased from a company leader in the production of building materials. Table 30 shows the composition of the two different mixture of frits.

Table 30 Enamels composition

Oxide component	Ground-coat enamel [wt %]	Cover-coat enamel [wt %]
Silicon oxide	51.80	43.75
Boron oxide	14.80	14.75
Aluminuim oxide	1.80	1.25
Potassium oxide	2.80	2.75
Sodium oxide	10.80	10.75
Lithium oxide	2.30	0.75
Fluorine	0.80	1.75
Calcium oxide	1.30	-
Cobalt tetraoxide	0.80	-
Copper oxide	1.30	-
Iron oxide	3.80	-
Chromium oxide	0.80	-
Manganese oxide	2.80	-
Titanium oxide	2.80	18.75
Zirconium oxide	1.30	-
Phosphorus pentoxide	-	1.75
Magnesium oxide	-	0.75
nano-TiO_2 suspension	-	3.00

The ground-coat enamel is applied in powder form thanks to an electrostatic powder spraying. The process is based on both electrostatic charge of powder and recycle of dust that does not adhere to the piece. The powder is drawn from a container and sent to a dispenser that provides to charge it electrostatically. Thanks to this effect the powder adheres to the panel electrically grounded through the hook-holder and the carrier plane. The enameling process takes place inside a cabin equipped with 30 dispensing guns and a suction system that retrieves the enamel which does not adhere to the panel. The powder contains fine particles and larger particles. The intake system of filters inside the cabin allows to recover the fine particles, while the larger ones tend to fall to the bottom of the cabin. These are retrieved, mixed with the primary powder and reused again. In this study the 1% is supposed to be retrieved to any glazing operation. The amount of enamel necessary to cover one side of the substrate is 0.25 kg/m^2. 150 panels are enameled per hour and then transferred to the tunnel-furnace for a thermal treatment at 850 °C for about 5 minutes.
The panel is than removed from the hook-holder, placed in a cage and moved with the forklift in another area of the plant ready for the application of the cover-coat nano-TiO_2 functionalized enamel. The frit is mixed with water to form slurry that is successively applied by electrostatic wet spraying following the same operations considered in the previous stage. The amount of functionalized enamel necessary to enamel one face of the panel is 0.51 kg/m^2. The fraction of the enamel which does not adhere to the panel is assumed to be not recovered to limit any further emissions of nanomaterial. It is also assumed to wash the cabin at the end of a working day (8

hours). The wet coating cannot be directly fired because the aqueous phase contained in turbid, decomposes because of the high temperature inside the furnace. For this reason and for difficulties to transport pieces still wet, comes the need to provide, after the step of applying wet enamel, a drying system. The dryer is gas powered and equipped with a fan for circulating hot air to accelerate the process (forced ventilation). The residence time of the panel in the drier is about 1.4 minutes. Than the panel is fired into the tunnel furnace equipped with 27 radiant tubes in nickel-chromium and consuming 5.5 Nm^3/h of methane.

9.4.2.2 *Installation and Use phase*

The nano-TiO_2 enamelled steel panels are packed into a box that is transported by lorry from the company where the tiles have been produced or where the box has been finally distributed to the installation site where a LGV unloads the box from lorry and carries it to private building. The present study considers the use of the functionalized steel panels for building external coating, namely outdoor application. Aging tests (CISP, 2009) demonstrated that nano-TiO_2 coating is active even after 7000 cleaning cycles with water and solvent and that there is a reduction of nano-TiO_2 properties due to deposition of organic material on the support. Consequently, it has been considered a life-time of enameled panels of 20 years and an annual cleaning with water and viscose fiber clothes.

9.4.2.3 *End of life*

In order to protect the human health from the potential damage caused by nanoparticles, in the end of life step it has been assumed to make inert the panels through a specific waste treatment, covering the waste panels with concrete and then burying the obtained concrete matrix.

9.4.3 Life Cycle Assessment

9.4.3.1 *Goal and scope definition*

The present study concerns the ecodesign of an industrial scale-up of nano-TiO_2 emalled steel panel production performed by LCA methodology. The aim of this study is to assess the environmental balance between benefits and potential risks due to the use of engineered nanomaterials in all life cycle phases.

9.4.3.2 *Functional unit, function of the system and system boundaries*

The surface treatment of 1 m^2 of steel panel (size 1000 mm x 1000 mm x 1 mm) is used as functional unit. The system function is that of architectural element, designed for covering walls and vertical surfaces: the application of enamels on steel substrates can exert both decorative and protective functions, giving a pleasant visual impact and saving steel from the corrosive action of atmospheric agents. Moreover, thanks to the TiO_2 photocatalytic and superhydrophilicity properties, it has been assumed to use them in building envelopes (outdoor application), for example as the outermost layer of a ventilated wall. Considering the use of such panels supposed, it has been assumed to enamel only the external side of the surface. System boundaries cover the entire life-cycle including raw materials extraction, production, distribution, installation, use and end of life phases, thus obtaining "a cradle to the grave" overview according with the LCA approach (EPA, 1993). Plants, devices, equipment, transport and energy consumptions (electricity and heat) have been also considered in the study. Emissions into air, water and soil, as well as the solid waste, have been taken into account.

9.4.3.3 ***Data quality***

Primary data related to raw materials and to the production and storage of a traditional enameled steel panel (without nano-TiO_2) have been collected directly from two Italian companies: one leader in the production of materials for producing ceramic and the other manufacturer of enamel coatings. Whenever lacking, data (i.e. raw materials production, filters, plant emissions) have been completed on the basis of information from literature and from the Ecoinvent database (Ecoinvent Database, 2009). The following assumptions have been made:

- ✓ in the production stage, emissions to air have been assumed to be 0.1%, partly retained by an HEPA filter then disposed in a landfill for residual materials and partly released into the production site and inhaled by workers;
- ✓ in the use phase, emissions to air have been assumed to be 20% (during whole life-span);
- ✓ in the end of life phase, emissions to air have been assumed to be 0.1%;
- ✓ all the designed filters have been supposed to have an efficiency of 99.97%;
- ✓ workers handling panels have been supposed to have PPE. The type considered is FFP" (Filtering Face Piece) with an efficiency of 95% as indicated in the European Standard EN149 (EN149:2001+A1, 2009);
- ✓ transports from application site to the waste treatment sites have been calculated using a distance of 100km, as required by the Environmental Product Declaration Product Certification (EPD) (EPD, 2008),
- ✓ the electricity energy supply has been assumed to be the Italian mix electric energy generated by Ecoinvent.

9.4.4 Life Cycle Inventory

The inventory data has been modelled in SimaPro 7 (Goedkoop et al., 2010), taking the Ecoinvent database as reference to configure the inventory of some materials (i.e. steel), chemicals (i.e. deflocculant), natural gas, electricity, transport, infrastructure and machinery. Auxiliary processes, such as components of frits, alumina balls, grinding-mill, have been created using primary data. For the upstream processes, the I/O data refer to the annual production of steel panels. Table 31 shows some of the most relevant I/O data.

Table 31 Data inventory for 1m^2 of nano-TiO_2 functionalized enamel applied on an steel panel

Life cycle stage	Unit	Production	Use*	End of life	Data source
Energy input - electricity consumption - heat consumption - methane consumption	 Wh kJ dm^3	 411.03 49.53 166.67	 - - -	 - - -	Straight from the company
Materials I/O - input of raw materials (ground-coat enamel) - input of raw materials (cover-coat enamel) - input of water (adds to raw materials for the cover-coat enamel)	 kg kg kg	 0.37# 79.01° 40.76	 - - -	 - - -	Straight from the company
Transports - road	tkm	8.62	31.48	8.15	Straight from the company
Waste to treatment - disposal of dust retained by filter	g	5.74	-	-	Estimated from literature

Emissions to air					
- particulates, < 2,5 μm	g	5.01	3.08	1.23	I/O data
- particulates, > 2,5 μm and < 10 μm	g	7.47	2.68	0.89	derived from
- particulates, < 100 nm in air	g	0.01	0.40	0.02	Ecoinvent
- NO_x	g	37.34	-	25.32	database and
- NMVOC	g	8.68	9.69	4.06	estimated from
- SO_x	g	30.22	16.79	6.58	literature
- Heat, waste	MJ	187.34	125.81	66.05	
* referred to the use of $1m^2$ of nano-TiO_2 enameled steel panel for 20 years # frit necessary to enamel $150m^2$ with the ground-coat enamel ° total of frit, clay, alumina grinding balls, deflocculants and nano-TiO_2 solution necessary to enamel $150m^2$					

9.4.5 Impact assessment and conclusions

9.4.5.1 *IMPACT 2002+* modified method

First, the impact assessment has been discussed at a mid-point level than a damage-oriented approach has been conducted, in order to translate environmental impacts from impact categories into damage categories. Single score damage is equal to 25.15 mPt.

The results of the analysis at mid-point level reported in Table 32 and Figure 9.20 show that the phases of the life cycle with the highest environmental burdens are the production (78.5%) and the end of life (19%) stages, following by end of life (7.39%). The use phase thanks to nano-TiO_2 application produces a positive environmental load (-4.84%).

Table 32 Characterized LCIA results of $1m^2$ of nano-TiO_2 functionalized enamel applied on an steel panel

Impact category	Unit	Total	Production	Installation	Use phase	End of life
Carcinogens	kg $C_2H_3Cl_{eq}$	3.245	3.065	0.086	0.035	0.058
Non-carcinogens	kg $C_2H_3Cl_{eq}$	2.365	1.920	0.073	0.029	0.343
Respiratory inorganics	kg $PM2.5_{eq}$	0.008	27.09E-3	2.89E-3	-27.6E-3	5.84E-3
Ionizing radiation	Bq $C\text{-}14_{eq}$	683.3	485.57	28.91	71.62	97.21
Ozone layer depletion	kg $CFC\text{-}11_{eq}$	4.38E-6	1.41E-6	2.33E-7	2.12 E-6	6.25 E-7
Respiratory organics	kg $C_2H_{4\ eq}$	-3.715[#]	6.56E-3	1.07E-3	-3.725	2.77 E-3
Aquatic ecotoxicity	kg TEG_{water}	8867.78	3097.39	228.15	725.26	4816.97
Terrestrial ecotoxicity	kg TEG_{soil}	1295.76	971.92	193.85	30.06	99.88
Terrestrial acid/nutri	kg $SO_{2\ eq}$	-0.713[#]	0.344	0.039	-1.246	0.149
Land occupation	m^2org.arable	1.597	0.928	0.078	0.244	0.347
Aquatic acidification	kg $SO_{2\ eq}$	0.225	0.093	0.008	0.099	0.025
Aquatic eutrophication	kg PO_4 P-lim	16.96E-3	15.76E-3	2.69E-4	3.94 E-4	5.02E-4
Global warming	kg $CO_{2\ eq}$	46.079	14.97	1.62	21.44	8.05
Non-renewable energy	MJ primary	399.25	261.96	30.14	39.73	67.42
Mineral extraction	MJ surplus	2.143	1.628	0.118	0.230	0.165
Radioactive waste	Kg	0.87E-3	6.6E-4	3.69E-5	4.37 E-5	0.00012
Carcinogens inhaled	Kg	1.06E-6	1.38E-10	1.06E-10	1.06E-6	1.06E-9
Respiratory inorganics indoor	Kg	-	-	-	-	-
Non-carcinogens indoor	CFU/pers	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	Kg	-	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	Kg	-	-	-	-	-
Total	mPt	11.8	9.24	0.871	-0.57	2.23
*Environmental damage recovered by the advantage (negative score) given by the use phase						
# Almost total environmental advantage (negative score) given by the use phase						

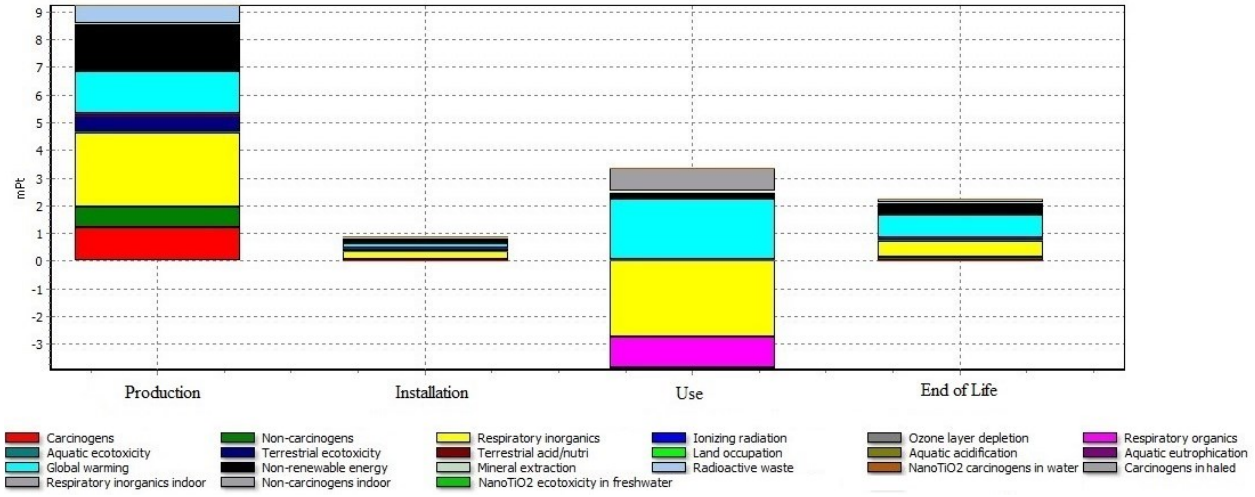

Figure 9-20 Evaluation by impact categories of 1m^2 of nano-TiO_2 functionalized enamel applied on an steel panel

A detailed analysis of the production stage, with a focus on the entire production process, is reported in Table 33. The cover-coat wet enameling stage affects Carcinogens (91.74%) and Non-carcinogens (96.25%) impact categories because of arsenic ion emissions to water (70.96%) and *hydrocarbons aromatic* emissions to air (21.27%) attributable to emissions released during the enamel spraying and to the disposal of water used for cleaning the cabin. Ionizing radiation is affected by *radon-222* (63.64%) and *carbon-14* (31.17%) emissions to air released in wet and dry enameling stages, that account for 64.75% and 31.05% respectively. The damage in Terrestrial ecotoxicity is due to *aluminum* emission to air (39.06%) and to soil (13.30%) coming from frit oxides components production of both the ground-coat (47.22%) and the cover-coat (47.86%). *Phosphate* emissions to water (97.03%) coming from the cover-coat wet enamel production control overall the Aquatic eutrophication impact category (90.18%). The environmental burdens of Non-renewable energy are attributable to natural gas (49.09%) and heavy fuel oil (21.10%) consumption during the drying process (75.50%). The two enameling phases contribute most to the damage to Mineral extraction because of releases of *water, cooling, unspecified natural origin* (48.22%), the wet enameling for 66.25% and the powder enameling for 29.99%.

Table 33 Characterized LCIA results of the production process

Impact category	Unit	Total	Cutting and cleaning	Ground-coat powder enameling	1st firing	Wet grinding	Cover-coat wet enameling and drying	2nd firing
Carcinogens	kg $C_2H_3Cl_{eq}$	55.12E-3	0.69E-3 [1.25%]	3.89E-3 [7.07%]	1.12E-5 [0.02%]	4.53E-5 [0.08%]	50.46E-3 [91.74%]	2.32E-5 [0.04%]
Non-carcinogens	kg $C_2H_3Cl_{eq}$	422.8E-3	0.71E-3 [0.17%]	14.85E-3 [3.51%]	2.22 E-6 [3.E-4%]	0.28E-3 [0.069%]	0.41 [96.25%]	2.67E-6 [0.0007%]
Respiratory inorganics	kg $PM2.5_{eq}$	2.98E-3	9.63E-5 [3.23%]	0.85E-3 [28.5%]	2.53E-7 [0.01%]	7.92E-6 [0.27%]	2.024E-3 [67.97%]	4.87E-7 [0.02%]
Ionizing radiation	Bq $C\text{-}14_{eq}$	57.91	2.35 [4.05%]	17.98 [31.05%]	3.145E-3 [0.01%]	74.23 E-3 [0.13%]	37.50 [64.75%]	6.39E-3 [0.01%]
Ozone layer depletion	kg $CFC\text{-}11_{eq}$	2.77E-7	1.07E-8 [3.85%]	4.3E-8 [15.51%]	1.74E-10 [0.06%]	3.66E-10 [0.13%]	2.23E-7 [80.31%]	3.62E-10 [0.13%]
Respiratory organics	kg $C_2H_{4\ eq}$	0.60E-3	2.44 E-5 [4.1%]	0.12E-3 [20.04%]	2.25E-7 [0.04%]	1.18 E-6 [0.20%]	0.457E-3 [75.61%]	4.65E-7 [0.08%]
Aquatic ecotoxicity	kg TEG_{water}	530.02	6.46 [1.22%]	72.89 [13.75%]	30.64E-3 [0.01%]	0.36 [0.07%]	450.24 [84.95%]	31.57E-3 [0.01%]
Terrestrial ecotoxicity	kg TEG_{soil}	42.34	1.98 [4.68%]	19.99 [47.22%]	3.71E-3 [0.01%]	0.08 [0.21%]	20.26 [47.86%]	7.65E-3 [0.02%]
Terrestrial acid/nutri	kg $SO_{2\ eq}$	0.04	1.79E-3 [4.3%]	10.96E-3[26.32%]	5.83E-6 [0.01%]	9.78E-5 [0.23%]	28.78E-3 [69.11%]	1.2E-5 [0.03%]
Land occupation	m^2org.arable	0.089	8.8E-4 [0.983%]	0.02 [26.21%]	6.95E-6 [0.007%]	7.25E-5 [0.080%]	0.06 [72.70%]	1.39E-5 [0.015%]
Aquatic acidification	kg $SO_{2\ eq}$	13.7 E-3	0.57E-3 [4.19%]	3.72E-3 [27.06%]	1.41E-6 [0.01%]	3.72E-5 [0.27%]	9.405E-3 [68.44%]	2.91E-6 [0.02%]
Aquatic eutrophication	kg PO_4 P-lim	2.96E-3	1.78E-5 [0.6%]	0.26E-3 [8.8562%]	2.06 E-8 [7E-4%]	1.1E-5 [35.6E-2%]	2.67E-3 [90.1844%]	4.2E-8 [0.0014%]
Global warming	kg $CO_{2\ eq}$	2.05	0.12 [5.84%]	0.43 [20.87%]	1.202E-3[0.06%]	4.09E-3 [0.20%]	1.49 [72.91%]	2.49E-3 [0.12%]
Non-renewable energy	MJ primary	39.58	1.94 [4.89%]	7.64 [19.28%]	0.02 [0.06%]	0.05 [0.14%]	29.89 [75.50%]	0.05 [0.12%]
Mineral extraction	MJ surplus	0.16	5.11E-3 [3.1%]	0.05 [30%]	5.42E-6 [0.003%]	1.09E-3 [0.658%]	0.11 [66.250%]	1.12E-5 [0.007%]
Radioactive waste	Kg	7.89E-5	3.08 E-6 [3.9%]	2.46E-5 [31.152%]	4.21E-9 [0.005%]	9.2E-8 [0.116%]	5.11E-5 [64.808%]	8.57E-9 [0.010%]
Carcinogens inhaled	Kg	1.38	-	-	-	5.55E-13 [0.402%]	1.37E-10 [99.596%]	2.96E-15 [0.002%]
Respiratory inorganics indoor	Kg	-	-	-	-	-	-	-
Non-carcinogens indoor	CFU/pers	-	-	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	Kg	-	-	-	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	Kg	-	-	-	-	-	-	-

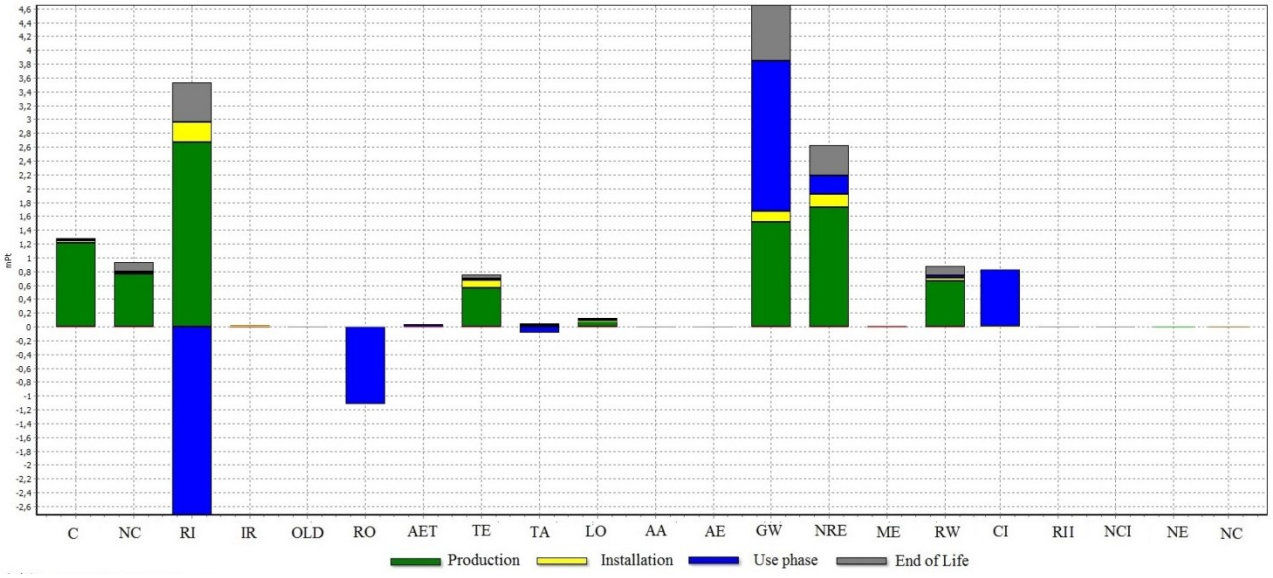

Figure 9-21 Evaluation by impact categories of 1 m^2 of nano-TiO_2 functionalized enamel applied on an steel panel, where C= Carcinogens; NC= Non-Carcinogens; RI= Respiratory Inorganics; IR= Ionizing Radiation; OLD= Ozone Layer Depletion; RO= Respiratory Organics; AET= Aquatic Ecotoxicity; TE= Terrestrial Ecotoxicity; TA= Terrestrial acid/nutria; LO= Land Occupation; AA= Aquatic Acidification; AE= Aquatic Eutrophication; GW= Global Warming; NRE= Non-renewable Energy; ME= Mineral Extraction; RW= Radioactive Waste; CI= Carcinogens Inhaled; RII= Respiratory Inorganics; NC= Non-Carcinogens indoor; NE= NanoTiO$_2$ ecotoxicity in freshwater; NC= NanoTiO$_2$ carcinogens in freshwater;

Figure 9.21 highlights that the most significant contribution to the total damage is due to Global warming impact category (39.5%), mainly due to *carbon dioxide, fossil* (96.6%), which is caused by use phase (46.8%). Non-renewable energy impact category (22.3%) is primarily affected by *oil, crude, in ground* (31.4%) and *gas, natural, in ground* due to production phase (55.8% and 78.9% respectively), in particular for steel panel manufacture. Successively, the following major contribute to the total damage is generated by Carcinogens impact category (10.9%), mainly due to *hydrocarbons, aromatic* (88.4%), which is caused by production process (95.9%). Moreover, it is also affected by of 4.12E-4 kg of *particulates, < 100 nm in air* released during the use phase. Non-carcinogens impact category (7.93%) is primarily affected by *arsenic, ion* (51.2%) due to production phase (75.1%), in particular for steel panel manufacture. In Radioactive Waste impact category (7.38%), the *volume occupied by low-active radioactive waste* contributes for 65.2% mainly due to the electricity energy consumption (part of the electric energy mix is made by nuclear power plants) in the production phase (76.1%). In Carcinogens inhaled impact category (7.04%) the damage is totally due to the releases of 1.06E-06 kg of *particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles) by human especially during use phase (99.9%). Respiratory inorganics impact category (6.88%) is mainly influenced by 127% of *particulates, < 2.5 μm,* and 88.9% of *particulates, >2.5 μm and < 10 μm* and the production process determines the main environmental burden (77.4% and 80.7% respectively), in particular for steel panel manufacture. This category is also positively affected by *nitrogen oxides* in air (-230%) thanks to benefit derived from nano-TiO_2 application during the use phase stage (-155%). In Respiratory organics impact category (-9.47%), the environmental benefit (derived from nano-TiO_2 application) is mainly influenced by the reduction of -5.84 kg of *Toluene* (VOC) (-100%) during the use phase stage.

Table 34 LCIA results at end-point level of 1m^2 of nano-TiO_2 functionalized enamel applied on an steel panel

Damage category	Unit	Total	Production	Installation	Use phase	End of life
Human health	DALY	1.37E-5	3.3E-5	2.48E-6	-2.70E-5	5.24E-6
Ecosystem quality	PDF*m^2*yr	11.69	9.21	1.67	-0.76	1.56
Climate change	kg $CO_{2\ eq}$	46.08	14.97	1.62	21.44	8.05
Resources	MJ primary	401.39	263.58	30.26	39.96	67.58
Radioactive waste	Kg	0.00087	0.00066	3.69E-5	4.37E-5	0.00012
Carcinogens inhaled	DALY	5.88E-6	7.67E-10	5.88 E-10	5.87E-6	5.87E-9
Respiratory inorganics indoor	DALY	-	-		-	-
Non-carcinogens indoor	DALY	-	-		-	-
Nano-TiO_2 ecotoxicity in freshwater	PAF*m3*day	-	-		-	-
Nano-TiO_2 carcinogens in freshwater	DALY	-	-		-	-

The endpoint analysis highlights (Table 34) that the total damage is affected by 16.4% to Human Health (1.93E-3 Pt), 22.4% to Resources (2.64E-3 Pt), 39.5% to Climate Change (4.65E-3 Pt), 7.25% to Ecosystem Quality (8.54E-4 Pt), 7.38% to Radioactive waste (0.87E-3 Pt) and 7.04% to Carcinogens inhaled (8.29E-4 Pt).

The life cycle assessment approach was used to determine the environmental balance between benefits and potential risks due to a nano-TiO_2 enameled steel panel in the entire life cycle, from production to final disposal. The impact assessment results reveal that the highest environmental burden is due to the cover-coat layer application by electrostatic wet enameling because of arsenic ion emissions to water (70.96%) and hydrocarbons aromatic emissions to air (21.27%) attributable to emissions released during the enamel spraying and to the disposal of water used for cleaning the cabin. Environmental advantages are given in by nano-TiO_2 properties to reduce airborne pollutants (toluene and of NO_x and SO_2 emissions) from air during the use phase. The present work is an attempt to quantify the sustainability of an engineered nanomaterial using LCA method. According to the life cycle thinking, all manufacturing processes are conceived with the idea to minimize all environmental loads, by adopting the presence of a suction systems and personal protective equipment to prevent the exposure of workers to dust and nanoparticles emissions in the whole life cycle, including the use and the end of life stages. There are still several elements missing for a truly result, becoming from the lacking in knowledge of nanoparticles: e.g. their aggregation in the environment, their potential release to environmental compartments and technosphere during the life cycle and their effects on biota and humans. Those are crucial elements necessary to a correct inventory analysis. Awaiting more reliable data regarding release of nanoparticles and health effects associated with exposure to nano-TiO_2 in general and occupationally-exposed population, this study is based on assumptions regarding the possible release of substances.

9.4.5.2 *USEtox^{TM} modified method*

The results of the analysis at mid-point level reported in Figure 9.22 and Table 35 show that the phases of the life cycle with the highest environmental loads are the production due to Human toxicity, cancer (92.9%), Human toxicity, non-cancer (89%) and Ecotoxicity (92.6%) impact categories and the use phase caused by Human toxicity, cancer, indoor (99.9%) and Human toxicity, non-cancer, indoor (99.9%).

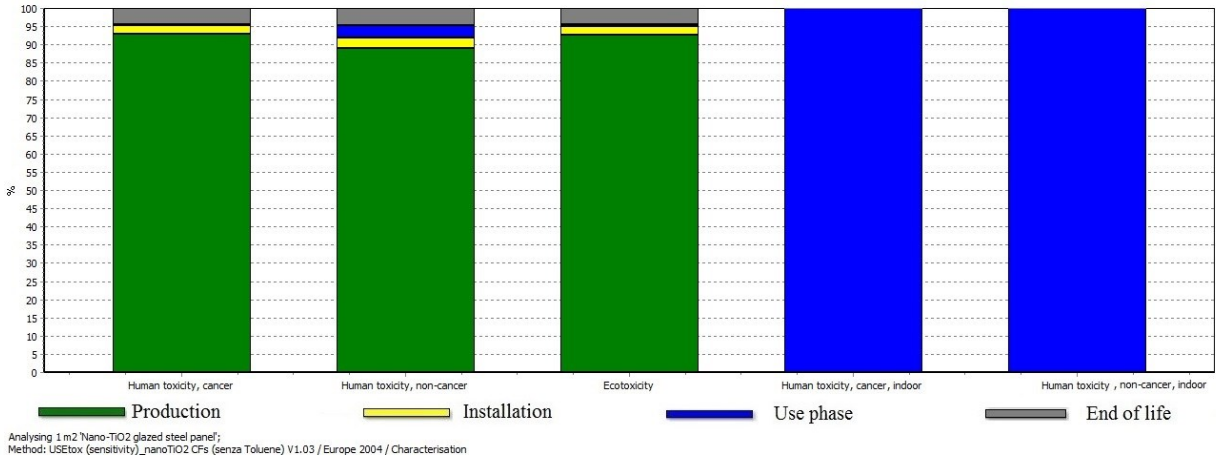

Figure 9-22 Evaluation by impact categories of 1 m^2 of nano-TiO_2 functionalized enamel applied on an steel panel

Table 35 Characterized LCIA results of 1 m^2 of nano-TiO_2 functionalized enamel applied on an steel panel

Impact category	Unit	Total	Production	Installation	Use phase	End of Life
Human toxicity, cancer	CTUh[#]	3,47E-05	3,22E-05	8,09E-07	1,28E-07	1,53E-06
Human toxicity, non-cancer	CTUh	3,02E-07	2,69E-07	8,49E-09	1,03E-08	1,44E-08
Ecotoxicity	CTUe[§]	346,8716	321,2753	8,079037	2,282719	15,23454
Human toxicity, cancer, indoor	CTUh	6,28E-10	8,18E-14	6,27E-14	6,27E-10	6,27E-13
Human toxicity, non-cancer, indoor	CTUh	7,45E-12	9,72E-16	7,45E-16	7,44E-12	7,44E-15
# CTUh = cases/$kg_{emitted;}$ § CTUe = PAF*m^3*yr						

The total damage of Human toxicity, cancer and Ecotoxicity impact categories is mainly due to *Chromium VI* in water (99.9% and 98.9% respectively), which is caused by the production stage (92.9%), in particular for steel panel manufacture. Successively, in Human toxicity, non-cancer, *Barium* in water generates major environmental load (28.7%), in particular affected by the production stage (83.2%) in particular for the waste treatment of washing water. In Human toxicity, cancer, indoor and Human toxicity, non-cancer, indoor impact categories, the damage is totally due to the releases of 1.06E-06 kg of *particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles inhaled by worker) and is mainly due to the use phase (99.88%). Releases of 4.21E-4 kg of *particulates, < 100 nm in air* affect Human toxicity, cancer for 1.88E-2% and Human toxicity, non-cancer for 2.56E-2% and is mainly due to the installation and use phase (94.93% for both impact categories).

Acknowledgement

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9.5 Nano-TiO_2 functionalized porcelainized stoneware tiles

This LCA case study analyses the application of a nano-TiO_2 functionalized enamel on a porcelain stoneware tile in order to exploit TiO_2 properties when exposed to UVA radiation. Excited TiO_2 nanoparticles improve the cleanability and the antibacterial activity of surfaces and reduce the concentrations of air pollutants such as nitrogen oxides (NO_x) and volatile organic compounds (VOC_s) deposited on the material surface. In this study, the coating method consists in first a heating (125°C) of the ceramic tile to facilitate evaporation of the water contained in TiO_2 nanosuspension and then five consecutive sprayings of the nanosuspension to deposit a homogeneous and uniform nanofilm on the tile surface.

9.5.1 Ecodesign approach

As all others LCA case studies, this work follows the Ecodesign approach giving a guidance on how it should be the production, the handling, the transport and the end of life of nanoparticles/nanomaterials.

9.5.2 Life cycle of nano-TiO_2 functionalized porcelain stoneware tile

As shown in Figure 9.23, the life cycle of a nano-TiO_2 functionalized porcelain stoneware tile consists of various phases: 1) supply of raw materials, 2) slip and enamel production, 3) partial cycle, 4) cutting and grinding, 5) storage and final distribution, 6) installation, 7) use and 8) end of life. In turn, the partial cycle is divided in: a) pressing, b) drying, c) glazing, d) 1st firing, e) nano-TiO_2 application and 2nd firing, f) sorting.

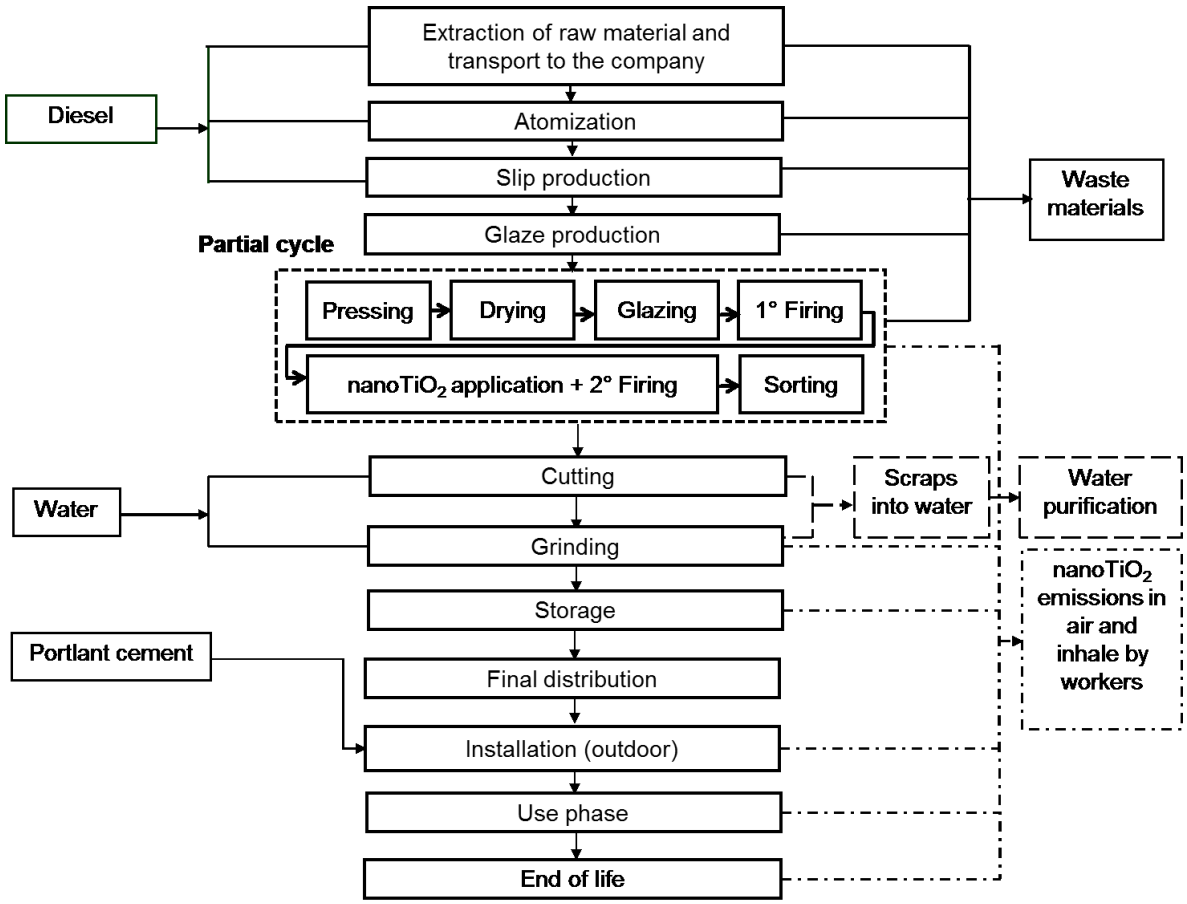

Figure 9-23 Flow chart of nano-TiO_2 functionalized porcelain stoneware tile

According to studies and researches on the potential toxicity of nanoparticles, air filters and personal protective equipment have been included in this study because a release of nanoparticles emissions from functionalized surface has been supposed in many steps. The main steps of the life cycle are described below.

9.5.2.1 *Production*

The core of the tile production cycle has been called partial cycle: at the end of this, it will get a functionalized tile with shape and well-defined characteristics.

After the atomisation phase where the ceramic slip with about 30% moisture is spray dried in order to obtain a powder with suitable grain size and humidity (about 5-6%):

a) the atomised material is compacted into a rectangular structure by a press system;

b) the raw tile is sent to the drier where the inside temperatures are about 150-170 °C that are necessary to reduce the moisture content from 6% to 0.5%,

c) the enamel is then applied to the raw tile to improve its surface quality (applied quantity varies from 0.40 kg/m^2 to a maximum of 2.02 kg/m^2 depending on the finished product type that it wants to get),

d) the enamelled tile is fired at 1100-1200 °C for about 30 minutes: tile dimensions are 610 mm x 602 mm x 10,5 mm and its weight decreases from 26.34 kg/m^2 to 24.88 kg/m^2 (Manicardi M., 2012),

e) the ceramic tile undergoes the nanocoating method (ARACNE, 2009):

- pre-heating to 125 °C to facilitate evaporation of the water contained in nano-TiO_2 suspension,
- spraying of 40 g/m^2 of solution with a concentration of nanoparticles of 13.52% on tile surface in 5 layers,
- firing at 850 °C for 20 minutes to improve the adhesion of the coating and the tile surface,

f) finally, the functionalized tile is checked according to geometric features and dimensional tolerances.

On all of these plants are installed air filters to reduce emissions into the atmosphere.

9.5.2.2 *Installation and Use phase*

Forty functionalized tiles are packed into a box who is transported by lorry from the company where the tiles have been produced or where the box has been finally distributed to the installation site where a LGV unloads the box from lorry and carries it to private building. It has been considered the installation of nanocoated tiles as exterior walls for private buildings. It has been supposed a fixing system that does not require breaking the tile at the time of separation from the wall in the end of life phase. Indeed, grinding the tile would cause the release of much of the content of nanoparticles into the atmosphere, resulting in damage on the ecosystem. On each tile, five plastic plugs (four at the corners and one in the middle) are glued with silicone and as many pieces of steel are fixed by a steel screw to the wall. Two plugs are connected together by a steel pin that is screwed in the hole of the plug of the wall and is fitted for pressure in the hole of the plug of the tile.

Ten years it has been assumed the duration of nano-TiO_2 coating effects (Fujishima et al., 2000) and it has been included annual maintenance with only water and viscose fiber cloth. It has been assessed the environmental and health consequences caused by the release in atmosphere of 50% of

nanocoating during 10 years of use. During this phase, it has also been evaluated the benefits of nano-TiO_2 during the day, namely the reduction of NO_x and VOC_s concentrations as the average during the period of natural light of eight hours a day from 9:00 to 17:00, 365 days a year.

9.5.2.3 *End of life*

Release of nanoparticles into the environment can also occur at the end of life of nanoproducts. According to the largely unknown risks to human health and ecosystems presented by nanomaterials, it has been supposed to consider the functionalized tiles as a hazardous waste, making them inert by covering waste tiles with concrete and then burying the obtained concrete matrix. The disposal of nanoproducts as well as their recyclability are still open questions and they will need clarity over regulation (Som et al., 2010).

9.5.3 Life Cycle Assessment

9.5.3.1 *Goal and scope definition*

The goal of the study is to assess the environmental impacts of nano-TiO_2 coated self-cleaning porcelain stoneware tile in order to define the most critical aspects of the process and minimize the environmental burdens.

9.5.3.2 *Functional unit, function of the system and system boundaries*

The system studied is a porcelain stoneware tile coated with a thin layer of nano-TiO_2 that creates a self-cleaning, antismog and antibacterial surface. This tile could be used to cover floors and walls for many indoor and outdoor applications, but according to numerous studies on the potential toxicity on human health of titanium dioxide nanoparticles, it is not recommended for use as flooring because, being subjected to wear and tear, the probability of detachment of the nanoparticles from the tile increases.

Therefore, the function of the system is the exterior wall applications for private buildings. For the purpose of this study, $1m^2$ of a nano-TiO_2 functionalized porcelain stoneware tile is analysed and it has been assumed a lifetime of 10 years. The system boundaries cover the entire life cycle of the system analysed, in accordance with the LCA approach. As can be seen in Figure 9.23, the analysis includes raw materials extraction and utilisation in ceramic tile production, cutting of the slab into 600 mm x 300 mm sized items, packing, final distribution, installation, use and end of life. The production, maintenance and disposal of facilities, as well as the environmental burdens related to the production of chemicals, packaging and other auxiliary materials are also included in the present study. Emissions into the air and water, as well as the solid wastes produced in each step are all taken into account. The transportation of the solid wastes to treatment facility is also considered. The transport is supposed with a scenario of 100 km from the producer to the customers, as is required by the environmental product declarations (EPD) (EPD, 2008). The electrical energy supply is assumed to be the Italian electricity mix generated by Ecoinvent.

9.5.3.3 *Data quality*

Primary data have been provided by a previous LCA case study on porcelain stoneware tile based on data collected from tile production by Emilceramica S.p.A in 2012 (Manicardi M., 2012). Colorobbia Italia S.p.A. has provided the composition of nano-TiO_2 suspension. Secondary data have been obtained from the Ecoinvent database (Ecoinvent Database, 2009) as reference to configure the inventory of some materials, chemicals, natural gas, electricity, transport,

infrastructure and machineries. The remaining data derive from previous studies on other nano-TiO_2 functionalized materials and from specialized literature and they have been used to model some phases such as installation, use and end of life steps.
The following assumptions have been supposed:

- ✓ Installation of HEPA air filter (with 99.97% of efficiency) to minimize nanoparticles emissions to air,
- ✓ the use of PPE, face mask with 95% of efficiency to protect workers from dust and nanoparticles inhalations,
- ✓ a closed manufacturing system has been designed,
- ✓ special waste treatment
- ✓ use of specific packaging to limit the release of nanoparticles emissions during the transports,
- ✓ transports from application site to the waste treatment sites have been calculated using a distance of 100km, as required by the Environmental Product Declaration Product Certification (EPD) (EPD, 2008),
- ✓ the electricity energy supply has been assumed to be the Italian mix electric energy generated by Ecoinvent.

9.5.4 Life Cycle Inventory

A selection of important data used in LCI (Life Cycle Inventory) of nano-TiO_2 functionalized porcelain stoneware tile (600 mm x 300 mm x 10.5 mm) is reported in Table 36.

Table 36 Inventory data of nano-TiO_2 functionalized porcelain stoneware tile

Category	Components	Quantity	Unit
Energy	Electricity	26,32	kWh
Materials I/O (slip production)	Water	13,27	kg
	Clay	4,42	kg
	Feldspar	5,53	kg
	Sand	3,82	kg
	Fluidizer (sodium silicate)	0,054	kg
Materials I/O (glaze production)	Water	0,081	kg
	Clay	0,34	kg
	Feldspar	0,43	kg
	Sand	0,29	kg
	Kaolin	1,28	g
	Engobe	11,42	g
	Zirconium silicate	0,35	g
	Petalite	0,087	kg
Materials I/O (functionalized porcelanaized stoneware tile)	Porcelanaized stoneware tile	24,15	kg
	nano-TiO_2 suspension	40	g
Emissions to air	Particulates < 2.5 μm	13,86	g
	Particulates > 10 μm	26,72	g
	Particulates > 2.5 μm and < 10 μm	14,36	g
	Water	73,38	g
	Particulates, < 100 nm in air	0,28	g
	Particulates, < 100 nm inhaled	0,18	mg

	NOx	- 105,36	g
	Nitric acid	245,84	g
	Toluene	- 2922,52	g
	CO_2	54,18	kg
Emissions into water	Particulates, < 100 nm in water	1,89	mg
Trasports	Raw materials for slip production	25,59	tkm
	Raw materials for glaze production	2,51	tkm
Waste treatment	Particulates entrapped by air filter	5,44	kg
	nano-TiO_2 entrapped by HEPA filter	0,94	kg
	nano-TiO_2 entrapped by reverse osmosis filter	6,31	g
	nano-TiO_2 entrapped by face mask of workers	3,58	mg

9.5.5 Impact assessment and conclusions

9.5.5.1 *IMPACT 2002+* modified method

Single score damage is 12.08 mPt for 1 m^2 of nano-TiO_2 functionalized porcelainized stoneware tiles produced. As Figure 9.24 shows, production and use phase are the contributions which are mainly responsible for the total damage (61.4% and 28.4% respectively), followed by the installation phase (9.67%) and end of life (0.556%).

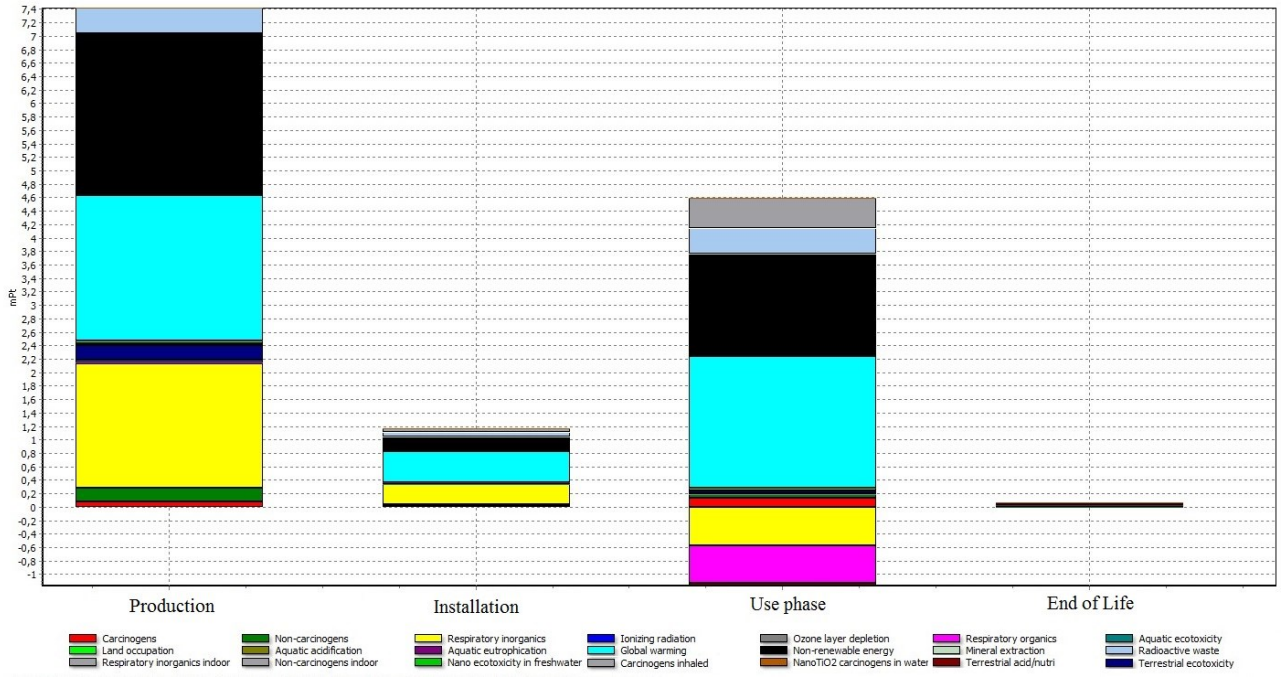

Figure 9-24 Evaluation by single score of 1 m^2 of nano-TiO_2 functionalized porcelainized stoneware tiles

Table 37 Characterized LCIA results of 1m^2 of nano-TiO_2 functionalized porcelainized stoneware tiles

Impact category	Unit	Total	Production	Installation	Use phase	End of Life
Carcinogens	kg $C_2H_3Cl_{eq}$	5,66E-01	2,15E-01	2,41E-02	3,26E-01	7,46E-04
Non-carcinogens	kg $C_2H_3Cl_{eq}$	7,19E-01	5,09E-01	7,62E-02	1,33E-01	1,10E-03
Respiratory inorganics	kg $PM2.5_{eq}$	1,60E-02	1,87E-02	2,96E-03	-5,83E-03	1,77E-04

Ionizing radiation	Bq C-14 $_{eq}$	6,18E+02	2,90E+02	5,22E+01	2,72E+02	3,50E+00
Ozone layer depletion	kg CFC-11 $_{eq}$	4,97E-06	2,46E-06	5,69E-07	1,92E-06	2,02E-08
Respiratory organics	kg C_2H_4 $_{eq}$	-1,85E+00	6,44E-03	1,44E-03	-1,86E+00	6,05E-05
Aquatic ecotoxicity	kg TEG $_{water}$	1,16E+04	9,44E+03	2,26E+02	1,92E+03	1,33E+01
Terrestrial ecotoxicity	kg TEG $_{soil}$	5,21E+02	3,91E+02	4,40E+01	8,07E+01	5,24E+00
Terrestrial acid/nutri	kg SO_2 $_{eq}$	-1,00E-01	3,35E-01	6,43E-02	-5,03E-01	3,92E-03
Land occupation	m^2org.arable	1,02E+00	5,31E-01	3,25E-02	4,55E-01	2,40E-03
Aquatic acidification	kg SO_2 $_{eq}$	1,79E-01	8,26E-02	1,22E-02	8,34E-02	1,02E-03
Aquatic eutrophication	kg PO_4 P-lim	7,19E-03	4,81E-03	2,16E-04	2,13E-03	3,15E-05
Global warming	kg CO_2 $_{eq}$	4,55E+01	2,13E+01	4,49E+00	1,95E+01	1,94E-01
Non-renewable energy	MJ primary	6,31E+02	3,63E+02	3,43E+01	2,30E+02	3,21E+00
Mineral extraction	MJ surplus	3,22E+00	2,61E+00	5,31E-02	5,52E-01	6,77E-03
Radioactive waste	Kg	8,30E-04	3,86E-04	6,51E-05	3,74E-04	4,59E-06
Carcinogens inhaled	Kg	6,58E-07	1,38E-11	7,11E-08	5,87E-07	0,00E+00
Respiratory inorganics indoor	Kg	-	-	-	-	-
Non-carcinogens indoor	CFU/pers	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	Kg	1,90E-06	1,90E-06	-	-	-
Nano-TiO_2 carcinogens in freshwater	Kg	1,90E-06	1,90E-06	-	-	-
Total	mPt	12,08	7,42	1,17	3,42	0,07

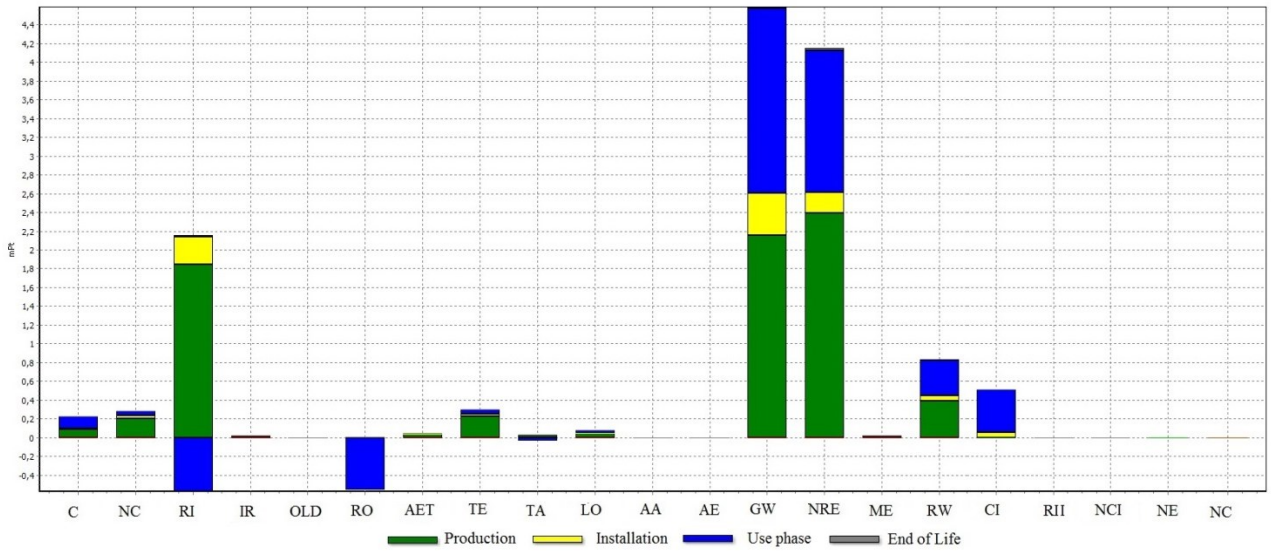

Figure 9-25 Evaluation by impact categories of 1 m^2 of nano-TiO_2 functionalized porcelainized stoneware tiles, where GW= Global Warming; NRE= Non-renewable Energy; RI= Respiratory Inorganics; RW= Radioactive Waste; CI= Carcinogens Inhaled; TE= Terrestrial Ecotoxicity; NC= Non-Carcinogens; C= Carcinogens; LO= Land Occupation; AE= Aquatic Ecotoxicity; TA= Terrestrial acid/nutria; ME= Mineral Extraction; IR= Ionizing Radiation; OLD= Ozone Layer Depletion; NE= Nano-TiO_2 ecotoxicity in freshwater; NC= Nano-TiO_2 carcinogens in freshwater; RO= Respiratory Organics; AEU= Aquatic Eutrophication; AE= Aquatic Acidification

Table 37 and Figure 9.25 report the contributions of the main impact categories on the total damage. Therefore, highlight that the most significant contribution to the total damage is due to Global warming impact category (38%), mainly due to *carbon dioxide, fossil*s (97.5%), which are caused by production process (46.8%), in particular due to firing process and use phase (43%) (direct emissions). Successively, the second major contribute to the total damage is generated by Non-renewable energy impact category (34.36%) which is primarily affected by *gas, natural, in ground* (48.2%), *oil, crude, in ground* (28.5%) and *uranium, in ground* (10.3%) emissions. For the first

emission the production phase, in particular due to the production of electric energy used in nano-TiO_2 suspension application, is the process that produces the major environmental load (75.1%), the latter two emissions are mainly due to the use phase stage (54.3% and 49.2% respectively).
In Respiratory Inorganics (13.1%) the major contributions are determined by the following emissions to air: 55.2% of *particulates, < 2.5 μm*, 35.9% of *sulfur dioxide* and 21.9% of *particulates, > 2.5 μm, and <10 μm*. For the first and latter emissions the production process causes the mainly environmental burden (62.4% and 54.5%), in particular for alumina manufacture and for the second emission (60.2%) again the production stage determines the major contribute but in this case due to the production of electric energy used in nano-TiO_2 suspension application. In this impact category the total damage is balanced by the NO_x reduction (-28.3%) in particular due to use phase stage (-274%), where the benefits derived from nano-TiO_2 application.
In Radioactive Waste impact category (6.87%), the *volume occupied by low-active radioactive waste* contributes for 64.9% due to the electric energy consumption in the production process (46.8%), where part of the electric energy mix is made by nuclear power plants. About the Carcinogens inhaled impact category the damage is totally due to the releases in air of 6.58E-07kg of *particulates, < 100 nm inhaled* by human especially during the use phase stage. Nano-TiO_2 ecotoxicity in freshwater and Nano-TiO_2 carcinogens in freshwater impact categories the damage is totally due to the releases in water of 1.9E-06 kg of *particulates, < 100 nm in water* (anatase TiO_2 nanoparticles) and 1.9E-06 kg of *nanoTiO_2 human toxicity* in freshwater during the grinding process in the partial cycle stage. In Respiratory organics (-4.6%) the reduction of *Toluene* (VOC) emissions (-101%) derived from the benefit of nano-TiO_2 application, which contributed not only reducing the impact but even giving a positive value (environmental advantage) in this category.

Table 38 LCIA results at end-point level of 1m^2 of nano-TiO_2 functionalized porcelainized stoneware tiles

Damage category	Unit	Total	Production	Installtion	Use phase	End of Life
Human health	DALY	1,10E-05	1,52E-05	2,37E-06	-6,69E-06	1,30E-07
Ecosystem quality	PDF*m2*yr	5,71	4,49E+00	4,62E-01	7,06E-01	4,88E-02
Climate change	kg CO2 eq	4,55E+01	2,13E+01	4,49	1,95E+01	1,94E-01
Resources	MJ primary	6,34E+02	3,66E+02	3,43E+01	2,31E+02	3,21
Radioactive waste	Kg	8,30E-04	3,86E-04	6,51E-05	3,74E-04	4,59E-06
Carcinogens inhaled	DALY	3,66E-06	7,69E-11	3,95E-07	3,26E-06	-
Respiratory inorganics indoor	DALY	-	-	-	-	-
Non-carcinogens indoor	DALY	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	PAF*m3*day	5,31E-07	5,31E-07	-	-	-
Nano-TiO_2 carcinogens in freshwater	DALY	1,35E-11	1,35E-11	-	-	-

The endpoint analysis highlights (Table 38) that the total damage is affected by 12.9% to Human Health (1.55E-3 Pt), 34.5% to Resources (4.17E-3 Pt), 38% to Climate Change (4.59E-3 Pt), 3.45% to Ecosystem Quality (4.17E-4 Pt), 6.87% to Radioactive waste (8.3E-4 Pt), 4.27% to Carcinogens inhaled (5.15E-4 Pt), 7.86E-5% to Nano-TiO_2 ecotoxicity in freshwater (9.5E-9 Pt) and 1.58E-5% to Nano-TiO_2 carcinogens in freshwater (1.91E-9 Pt). In these latter two cases the damage is restrained since the LCA study has been set in an ecodesign approach, thus installing a specific filter for nanoparticles with a high efficiency (99.97%), in order to limit the nanoparticle releases.

9.5.5.2 *USEtox™ modified method*

The results of the analysis at mid-point level reported in Figure 9.26 and Table 39 show that the phases of the life cycle with the highest environmental loads are the production due to Human toxicity, cancer (79.5%), Human toxicity, non-cancer (66.4%) and Ecotoxicity (78%) impact categories and the use phase caused by Human toxicity, cancer, indoor (89.2%) and Human toxicity, non-cancer, indoor (89.2%).

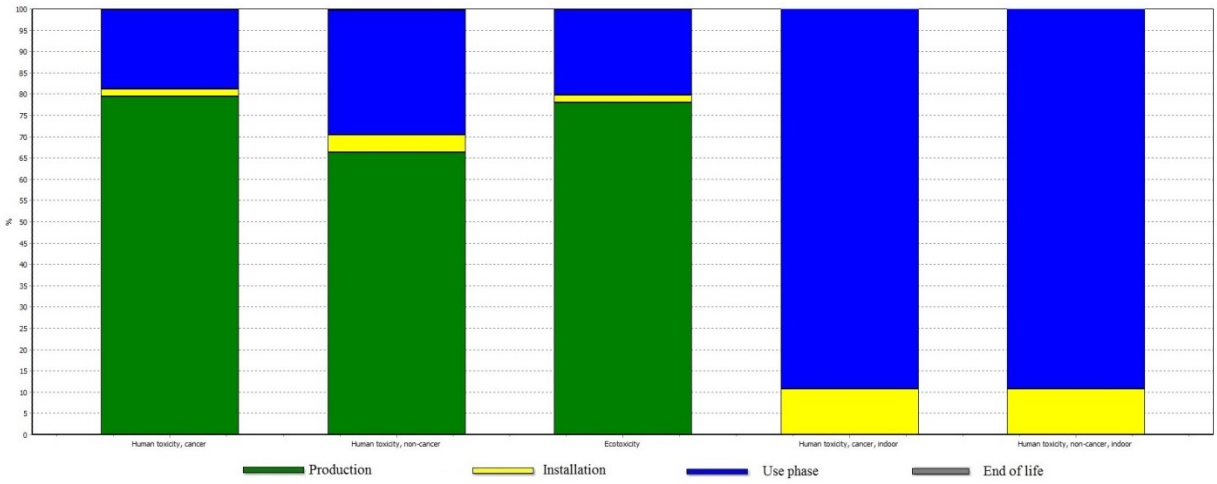

Figure 9-26 Evaluation by impact categories of 1 m^2 of nano-TiO_2 functionalized porcelainized stoneware tiles

Table 39 Characterized LCIA results of 1 m^2 of of nano-TiO_2 functionalized porcelainized stoneware tiles

Impact category	Unit	Total	Production	Installation	Use phase	End of life
Human toxicity, cancer	CTUh[#]	4,62E-06	3,68E-06	7,55E-08	8,64E-07	8,4E-09
Human toxicity, non-cancer	CTUh	1,31E-07	8,71E-08	5,22E-09	3,85E-08	4,69E-10
Ecotoxicity	CTUe[§]	47,73021	37,24342	0,812091	9,586083	0,08861
Human toxicity, cancer, indoor	CTUh	3,9E-10	8,21E-15	4,22E-11	3,48E-10	0
Human toxicity, non-cancer, indoor	CTUh	4,63E-12	9,75E-17	5,01E-13	4,13E-12	0
# CTUh = cases/$kg_{emitted;}$ § CTUe = PAF*m^3*yr						

The total damage of Human toxicity, cancer and Ecotoxicity impact categories is mainly due to *Chromium VI* in water (79.5% and 93.7% respectively), which is caused by the production stage (79.5%), in particular for treatment spent lime (waste material of firing process). Successively, in Human toxicity, non-cancer, *Mercury* in water generates major environmental load (38.8%), in particular affected by the production stage (70.7%) to treat the spent lime. In Human toxicity, cancer, indoor and Human toxicity, non-cancer, indoor impact categories, the damage is totally due to the releases of 6.58E-07 kg of *particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles inhaled by worker) and is mainly due to the use phase (89.2%). Releases of 5.89E-4 kg of *particulates, < 100 nm in air* affect Human toxicity, cancer for 0.197% and Human toxicity, non-cancer for 8.25E-2% and is mainly due to the installation and use phase (98.97% for both impact categories).

Acknowledgement

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9.6 Comparative LCA of nano-TiO_2 functionalized building materials and the conventional ones

In order to understand which differences, in terms of environmental performance, could be occurred between nano-TiO_2 functionalized building materials and the conventional ones, the nano-TiO_2 functionalized float glass case study has been taken into account as an example. A single float uncoated glass (conventional building material) has been compared with the nano-TiO_2 functionalized float glass (innovative building material). For the latter building material two different lifetime scenario have been considered. The first one considers that the float glass and the nano-TiO_2 coating have the same lifetime (10 years) (it has been assumed that after 10 years the nanocoating does not produce benefits anymore). The second one considers: float glass lifetime equal to 30 years and the nano -TiO_2 coating lifetime equal to 10 years. Therefore, others two re-functionalization process, after every 10 years, have been needed in 30 years. As before mentioned, for both two scenario the inertization process with concrete has been take into account as end of life treatment.

Fig 9.27 shows the flow chart of an uncoated float glass, the following considerations have been considered:

- "*Flat glass, uncoated, at plant/RER*" Ecoinvent process has been use to represent the glass manufacturing process;
- cutting and lapping have been taken into consideration,
- installation of uncoated glass as windows to a private building, but contrary to nano-TiO_2 functionalized float glass no precautionary behaviors, such as special packaging and PPE, have been needed to consider;
- transport by lorry from the company, where the uncoated glass has been manufactured, to the installation site and the handling of glasses from lorry to private building have been assessed;
- the phenomenon of radiation heat is the same before described for nanocoated glass, but in this case the sunlight radiation that passes through the uncoated glass is greater than nanocoated glass one, since the solar factor[5] of uncoated glass is greater than nanocoated glass one;
- the cleaning glass every four weeks using water and detergent has been assumed;
- the glass recycling process as end of life treatment has been adopted.

[5] The solar factor is a parameter which indicates the ability of a transparent material to let through by solar radiation. It represents the fraction of solar energy that enters the environment, compared to the total incident.

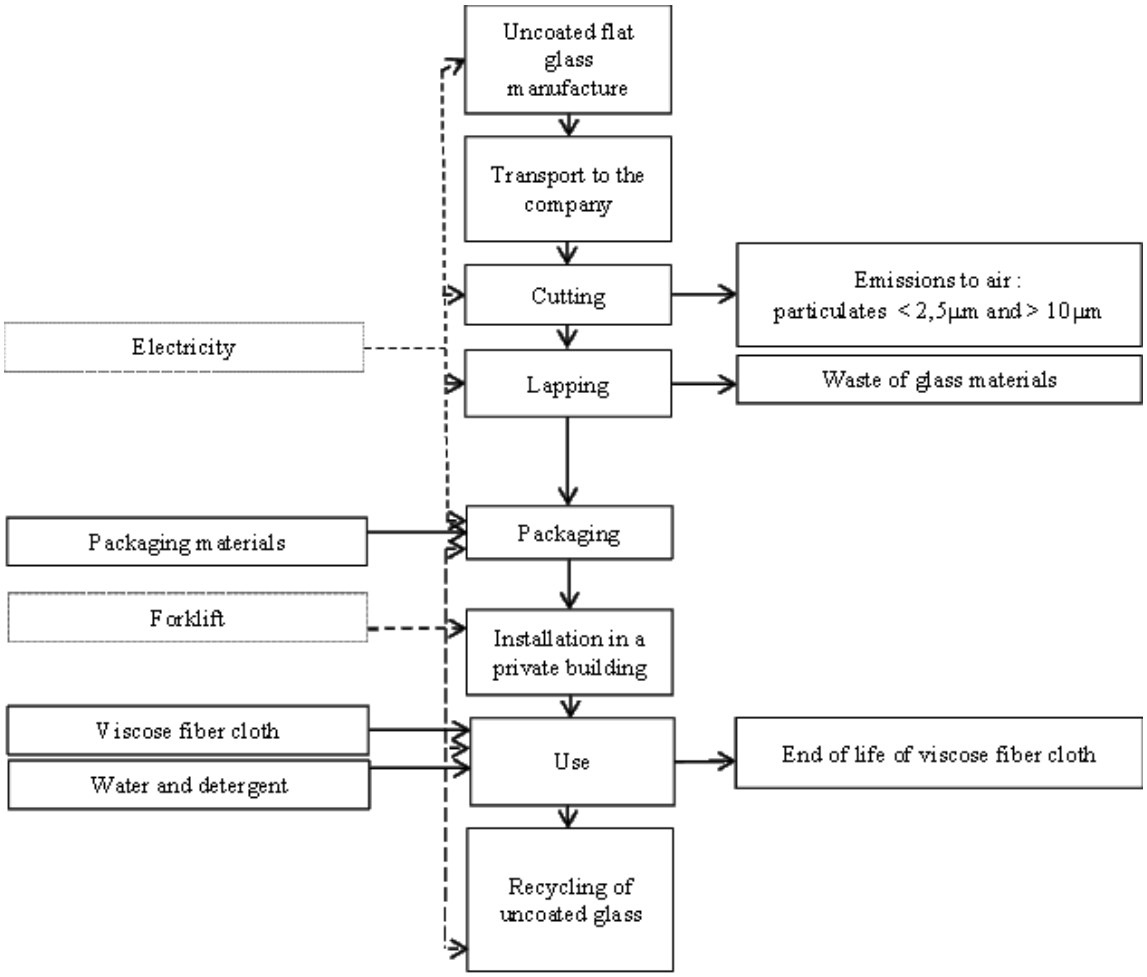


Figure 9-27 Flow chart of an uncoated flat glass

Table 40 and Figure 9.28 report the LCIA results of the comparison, considering a lifespan of 30 years, among 1 m^2 of uncoated flat glass (conventional material), 3 m^2 of nano-TiO_2 coated float glass (10 years lifetime) and 1 m^2 of nano-TiO_2 coated float glasses (30 years lifetime) re-functionalized twice (innovative materials). LCIA has been here performed by *IMPACT 2002+* modified method.

Table 40 LCIA comparison of 1 m^2 among uncoated flat glass (conventional material) and nano-TiO_2 functionalized coated float glasses (innovative materials)

Impact category	Unit	Total	**A** uncoated flat glass (30 years lifetime)	**B** nano-TiO_2 coated float glass (10 years lifetime)	**C** nano-TiO_2 coated float glass (30 years lifetime) re-functionalization
Carcinogens		7,36	1,73	2,98	2,64
Non-carcinogens	kg $C_2H_3Cl_{eq}$	4,23	5,53E-01	2,13	1,55
Respiratory inorganics	kg $PM2.5_{eq}$	2,55E-01	6,61E-02	1,24E-01	6,56E-02
Ionizing radiation	Bq $C\text{-}14_{eq}$	7,42E+03	1,55E+03	3,23E+03	2,64E+03
Ozone layer depletion	kg $CFC\text{-}11_{eq}$	1,07E-04	2,50E-05	4,30E-05	3,92E-05
Respiratory organics	kg $C_2H_{4\ eq}$	-1,10E+01	4,54E-02	-5,49E+00	-5,51
Aquatic ecotoxicity	kg TEG_{water}	4,05E+04	3,55E+03	1,99E+04	1,71E+04
Terrestrial ecotoxicity	kg TEG_{soil}	4,35E+03	3,09E+02	2,32E+03	1,72E+03
Terrestrial acid/nutri	kg $SO_{2\ eq}$	2,97	1,73	1,12	1,18E-01

Land occupation	m^2org.arable	3,31E+01	1,84E+01	9,81E+00	4,89
Aquatic acidification	kg $SO_{2\ eq}$	2,07	3,81E-01	9,82E-01	7,06E-01
Aquatic eutrophication	kg PO_4 P-lim	8,19E-02	3,33E-02	2,73E-02	2,12E-02
Global warming	kg $CO_{2\ eq}$	6,34E+02	1,67E+02	2,56E+02	2,12E+02
Non-renewable energy	MJ primary	1,12E+04	3,10E+03	4,36E+03	3,72E+03
Mineral extraction	MJ surplus	1,87E+01	2,02	9,36	7,28
Radioactive waste	kg	9,80E-03	2,13E-03	4,23E-03	3,45E-03
Carcinogens inhaled	kg	3,45E-06	-	2,24E-06	1,21E-06
Respiratory inorganics indoor	kg	-	-	-	-
Non-carcinogens indoor	CFU/pers	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	kg	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	kg	-	-	-	-

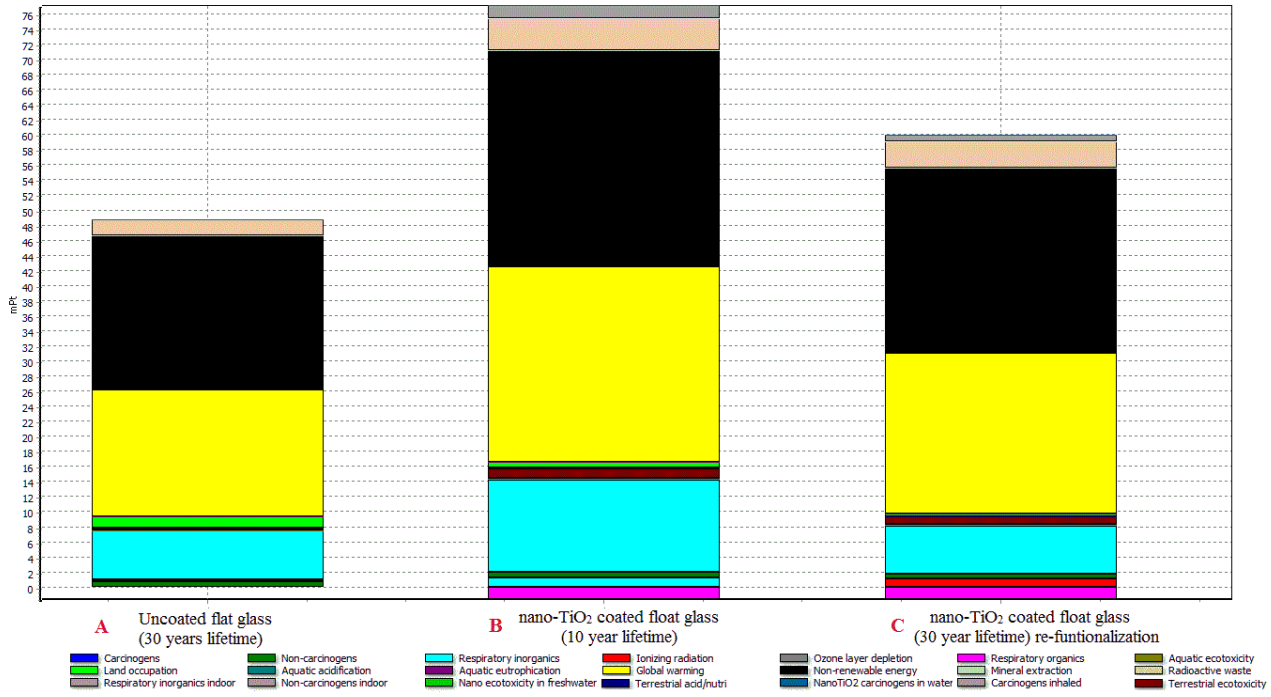


Figure 9-28 LCIA comparison by single score of 1 m^2 of conventional uncoated flat glass (conventional material) and 1 m^2 of nano-TiO_2 functionalized coated float glasses (innovative materials)

Table 41 LCIA comparison by single score of 1 m^2 of conventional uncoated flat glass (conventional material) and 1 m^2 of nano-TiO_2 functionalized coated float glasses (innovative materials)

Impact category	Unit	Total	A uncoated flat glass (30 years lifetime)	B nano-TiO_2 coated float glass (10 years lifetime)	C nano-TiO_2 coated float glass (30 years lifetime) re-functionalization
Total	mPt	1,82E+02	4,87E+01	7,55E+01	5,83E+01
Carcinogens	mPt	2,90E+00	6,84E-01	1,18E+00	1,04E+00
Non-carcinogens	mPt	1,67E+00	2,18E-01	8,42E-01	6,10E-01
Respiratory inorganics	mPt	2,52E+01	6,52E+00	1,22E+01	6,47E+00
Ionizing radiation	mPt	2,20E-01	4,59E-02	9,56E-02	7,82E-02

Ozone layer depletion	mPt	1,59E-02	3,70E-03	6,37E-03	5,80E-03
Respiratory organics	mPt	-3,29E+00	1,36E-02	-1,65E+00	-1,65E+00
Aquatic ecotoxicity	mPt	1,48E-01	1,30E-02	7,30E-02	6,25E-02
Terrestrial ecotoxicity	mPt	2,51E+00	1,78E-01	1,34E+00	9,93E-01
Terrestrial acid/nutri	mPt	2,25E-01	1,31E-01	8,51E-02	8,97E-03
Land occupation	mPt	2,63E+00	1,46E+00	7,81E-01	3,89E-01
Aquatic acidification	mPt	0,00E+00	0,00E+00	0,00E+00	0,00E+00
Aquatic eutrophication	mPt	0,00E+00	0,00E+00	0,00E+00	0,00E+00
Global warming	mPt	6,40E+01	1,68E+01	2,58E+01	2,14E+01
Non-renewable energy	mPt	7,36E+01	2,04E+01	2,87E+01	2,45E+01
Mineral extraction	mPt	1,23E-01	1,33E-02	6,16E-02	4,79E-02
Radioactive waste	mPt	9,80E+00	2,13E+00	4,23E+00	3,45E+00
Carcinogens inhaled	mPt	2,70E+00	0,00E+00	1,75E+00	9,48E-01
Respiratory inorganics indoor	mPt	-	-	-	-
Non-carcinogens indoor	mPt	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	mPt	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	mPt	-	-	-	-

Nano-TiO_2 functionalized float glass (scenario B) is the case study that produce the higher environmental damage (75.5 mPt) following by scenario C (58.3 mPt) and last scenario A (48.7 mPt). The main impact categories that mainly determine the environmental loads on all analyzed case studies are Non-renewable energy, Global warming and Respiratory inorganics impact categories. As reported in Table 41:

- In Non-renewable energy impact category, B case determines the higher impact (28.7 mPt) mainly due to *gas, natural, in ground* generated by electric energy manufacture in the production process;
- In Global warming impact category, B case determines the higher impact (25.8 mPt) mainly due to *carbon, dioxide fossil* generated by natural gas production used in the use phase for air-conditioning.
- Finally, in Respiratory inorganics impact category, B case determines the higher impact (12.2 mPt) mainly due to *particulates, < 2.5 μm* generated by lapping process in the production stage. For innovative materials (B and C case studies) *Nitrogen oxides* emission in air is reduced by photocatalytic activity of nano-TiO_2 coating generated a reduction of environmental load in this category.
- In Respiratory organics impact category, instead, B and C scenario determine a positive environmental load (50.1% and 50.3% respectively), in particular generated by the reduction of *Toluene* emission in air.

9.7 Conclusion

In conclusion, the environmental assessment, performing by *IMPACT 2002+* modified method, of LCA of four innovative building materials studied in this thesis has led to the following considerations and conclusions:

- **Indoor and Outdoor application**: only nano-TiO_2 functionalized polyurea resin application on an aluminum panel has been installed in indoor environment, in order to create a sterilized room (e.g. hospital rooms, antibacterial rooms, etc.); for all other innovative

building materials outdoor installation has been considered, in order to create glazing for nano-TiO_2 coated float glass and architectural and decorative applications for the other two materials.

- The **total damage**, expressed in eco-point (Pt), of the analyzed LCA case studies is pretty similar for nano-TiO_2 functionalized polyurea resin application on an aluminum panel (11.39 mPt), nano-TiO_2 functionalized enamel applied on an steel panel (11.8 mPt) and nano-TiO_2 functionalized porcelainized stoneware tiles (12.08 mPt), instead it increases more than double for nano-TiO_2 coated float glass (25.15 mPt).
- **Production** is the life-cycle step that determines the major environmental loads:
    1. nano-TiO_2 functionalized polyurea resin application on an aluminum panel → 93.25%
    2. nano-TiO_2 coated float glass → 65.06%
    3. nano-TiO_2 functionalized enamel applied on an steel panel → 78.5%
    4. nano-TiO_2 functionalized porcelainized stoneware tiles → 61.4%
- **Non-renewable energy** is the impact category that major afflicts nano-TiO_2 functionalized polyurea resin applied on an aluminum panel (32.04%) and nano-TiO_2 coated float glass (37.98%) case studies, in particular due to natural gas for electric energy production.
- **Global warming** is the impact category that major influences nano-TiO_2 functionalized enamel applied on an steel panel (39.5%) and nano-TiO_2 functionalized porcelainized stoneware tiles (38%) case studies, in particular caused by carbon dioxide emission released, for the first case, during firing stage and, for the latter one, during the use phase.
- Table 42 reports the **damage due to nano-TiO_2 emissions** releases to air and inhaled by human, using *IMPACT 2002+* modified method:

Table 42 Damage of nano-TiO_2 emission releases to air and inhaled by human (*IMPACT 2002+* modified method)

LCA case study	Impact category	Contribute on the total damage	Emission	Amount of emission	Main life-cycle step affected by the emission	Emission contribution on the impact category
Nano-TiO_2 functionalized polyurea resin applied on an aluminum panel	Carcinogens	2.22%	a	2.6E-6 kg	Production	80.58%
	Carcinogens inhaled	1.62%	b	2.36E-7 kg	Installation and Use phase	99.89%
Nano-TiO_2 coated float glass	Carcinogens	1.56%	a	7.26E-4 kg	Use phase	98.62%
	Carcinogens inhaled	2.32%	b	7.45E-7 kg	End of Life	68.76%
Nano-TiO_2 functionalized enamel applied on an steel panel	Carcinogens	10.9%	a	4.21E-4 kg	Use phase	94.93%
	Carcinogens inhaled	7.04%	b	1.06E-6 kg	Use phase	99.88%
Nano-TiO_2 functionalized porcelainized stoneware tiles	Carcinogens	1.85%	a	5.89E-4 kg	Use phase	98.97%
	Carcinogens inhaled	4.26%	b	6.58E-7 kg	Use phase	89.19%
	Nano-TiO_2 ecotoxicity in freshwater	7.86E-5%	c	1.89E-6 kg	Use phase	100%
	Nano-TiO_2 carcinogens in	1.58E-5%	d	1.89E-6 kg	Use phase	100%

	freshwater					

a: *particulates, < 100 nm in air* (anatase TiO_2 nanoparticles) emission to air
b*: particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles) emission inhaled by human
c: *particulates, < 100 nmin water* (anatase TiO_2 nanoparticles) emission to water
d: *nano-TiO_2 human toxicity* emission to water

The life-cycle step that mainly influences Carcinogens impact category is the use phase and for Carcinogens inhaled impact category is both use phase and end of life. The emission contribution on the impact category under study ranges from 68.76% to 99.89% and the amount of TiO_2 nanoparticles release in the "main life-cycle step affected" ranges from 2.36E-7 kg (Installation and Use phase of nano-TiO_2 functionalized polyurea resin applied on an aluminum panel) to 4.21E-4 kg (use phase of nano-TiO_2 functionalized enamel applied on an steel panel).

Nano-TiO_2 functionalized porcelainized stoneware tiles is only LCA building materials case study together with bottom-up hydrolytic synthesis of nano-TiO_2 that take into account Nano-TiO_2 ecotoxicity in freshwater and Nano-TiO_2 carcinogens in freshwater impact categories, since for the others LCA case study or no data have been available or no nano-TiO_2 releases to water occurred.

- Table 43 shows the **environmental benefits derived from nano-TiO_2 application** into/on building materials:

Table 43 Environmental benefits derived from nano-TiO_2 application into/on building materials (*IMPACT 2002+* modified method)

LCA case study	Impact category	Contribute on the total damage	Emission	Amount of emission	Main life-cycle step influenced by the emission	Emission contribution on the impact category
Nano-TiO_2 functionalized polyurea resin applied on an aluminum panel	Non-carcinogens indoor	-0.366%	e	-1.54E-2 CFU/kg	Use phase	-100%
	Respiratory inorganics indoor	-4.08%	f	-8.1E-5 kg	Use phase	-100%
Nano-TiO_2 coated float glass	Respiratory organics	-2.186%	g	-2.92 kg	Use phase	-100%
	Respiratory inorganics	16.16%	h	-9.3E-2 kg	Use phase	-331%
Nano-TiO_2 functionalized enamel applied on an steel panel	Respiratory organics	-9.479%	g	-5.84 kg	Use phase	-100%
	Respiratory inorganics	6.88%	h	1.06E-6 kg	Use phase	-154.9%
Nano-TiO_2 functionalized porcelainized stoneware tiles	Respiratory organics	-4.6%	g	5.89E-4 kg	Use phase	-100.3%
	Respiratory inorganics	13.11%	h	6.58E-7 kg	Use phase	-273.8%

e: *Escherichia Coli*
f*: Nitrogen dioxide indoor*
g: *Toluene* emission to air
h: *Nitrogen oxides* emission to air

Nano-TiO_2 functionalized polyurea resin applied on aluminum panel, due to the fact that it is installed in a room, determines indoor benefits, namely Escherichia Coli bacteria and NO_2

reduction. Nano-TiO_2 application for all other building materials, since outdoor installation has been considered, generates Toluene (VOC) and Nitrogen oxides reduction. These benefits produce environmental advantages or reduce the damage in the referred impact category.

- The **comparison** among an uncoated flat glass (conventional material) and nano-TiO_2 functionalized coated float glasses (innovative materials) showed that nano-TiO_2 functionalized building materials produce the major environmental damage due to the all auxiliary processes needed to eco-design adopting a safety approach the life-cycle of these innovative materials and in this way reducing the risk of nanoparticle releases.
- The adopted assumptions that have been taken into consideration during **eco-design** process are in summary:
  - ✓ installation, in the production phase, of HEPA (*High Efficiency Particulate Air filter*) air filter, having a efficiency of 99.97%;
  - ✓ in the nano-TiO_2 application process a closed manufacturing system has been designed;
  - ✓ use of PPE (*Personal Protective Equipment*), face mask with 95% of efficiency to protect workers from dust and nanoparticles inhalations, during coating, installation, use and end of life steps;
  - ✓ use of specific packaging to transport nanofunctionalized building materials from the company to the site of installation and then from this one to site of end of life treatment, in order limit the release of nanoparticles emissions during the transports;
  - ✓ since, no national or European regulation/guideline are now available, special waste treatment (e.g. waste inertization with concrete) has been assumed.

The environmental assessment, performing by *USEtox*^{TM} modified method, has guided to the following observations:

- regarding the **indoor and outdoor applications** and the assumptions made following the **eco-design** approach the same consideration mentioned above for *IMPACT 2002+* method have been considered;
- **Production** process is the life-cycle step that mainly affects Human toxicity, cancer, Human toxicity, non-cancer and Ecotoxicity (Table 44);

Table 44 Impact categories affected by the production process

LCA case study	Human toxicity, cancer	Human toxicity, non-cancer	Ecotoxicity
Nano-TiO_2 functionalized polyurea resin applied on an aluminum panel	95.3%	93.9%	95.5%
Nano-TiO_2 coated float glass	85.5%	80.6%	83.6%
Nano-TiO_2 functionalized enamel applied on an steel panel	92.9%	89%	92.6%
Nano-TiO_2 functionalized porcelainized stoneware tiles	79.5%	66.4%	78%

Production step mainly influences Ecotoxicity impact category for the first LCA case study and, instead, for all other studies Human toxicity, cancer impact category.

- As Table 45 shows the **damage due to nano-TiO_2 emissions** releases to air and inhaled by human, using *USEtox*^{TM} modified method, is in line with the results obtained performing by *IMPACT 2002+* modified method:

Table 45 Damage of nano-TiO_2 emission releases to air and inhaled by human (USEtox^{TM} modified method)

LCA case study	Impact category	Emission	Amount of emission	Main life-cycle step affected by the emission	Emission contribution on the impact category
Nano-TiO_2 functionalized polyurea resin applied on an aluminum panel	Human toxicity, cancer Human toxicity, non-cancer	a	2.6E-6 kg	Production	80.58%
	Human toxicity, cancer, indoor Human toxicity, non-cancer, indoor	b	2.36E-7 kg	Installation and Use phase	99.89%
Nano-TiO_2 coated float glass	Human toxicity, cancer Human toxicity, non-cancer	a	7.26E-4 kg	Use phase	98.62%
	Human toxicity, cancer, indoor Human toxicity, non-cancer, indoor	b	7.45E-7 kg	End of Life	68.76%
Nano-TiO_2 functionalized enamel applied on an steel panel	Human toxicity, cancer Human toxicity, non-cancer	a	4.21E-4 kg	Use phase	94.93%
	Human toxicity, cancer, indoor Human toxicity, non-cancer, indoor	b	1.06E-6 kg	Use phase	99.88%
Nano-TiO_2 functionalized porcelainized stoneware tiles	Human toxicity, cancer Human toxicity, non-cancer	a	5.89E-4 kg	Use phase	98.97%
	Human toxicity, cancer, indoor Human toxicity, non-cancer, indoor	b	6.58E-7 kg	Use phase	89.19%
a: *particulates, < 100 nm in air* (anatase TiO_2 nanoparticles) emission to air b: *particulates, < 100 nm inhaled* (anatase TiO_2 nanoparticles) emission inhaled by human					

The life-cycle step that mainly controls all impact categories is the use phase step. The emission contribution on the impact category under study ranges from 68.76% to 99.89% and the amount of TiO_2 nanoparticles release in the "main life-cycle step affected" ranges from 2.36E-7 kg (Installation and Use phase of nano-TiO_2 functionalized polyurea resin applied on an aluminum panel) to 4.21E-4 kg (Use phase of nano-TiO_2 functionalized enamel applied on an steel panel).

- The **comparison** among uncoated flat glass (conventional material) and nano-TiO_2 functionalized coated float glasses (innovative materials) has not been reported since the LCIA results carry out the same conclusion obtained with *IMPACT 2002+* modified method.

10 Extension of LCA to cultural heritage

The main objective of this thesis is to assess the environmental sustainability of several building materials extending their application to an historical building. The study aims to take into account the environmental and nanotoxicological aspects as well as the social, cultural and historic issues that have not ever been considered in this field. Indeed, nowadays the sustainability assessment of an historical building has not yet been investigated. In particular social, cultural and historical aspects are not still considered in the LCIA stage. Integrating these issues into the environmental assessment makes it possible to have a whole view of the benefits and impacts generated by the restoration/recovery activities of an historical building.

10.1 Social Life Cycle Assessment

In recent years, interest has grown for the inclusion of social aspects in the environmental assessment of the life cycle of products and processes leading to the development of the so-called Social Life Cycle Assessment (S-LCA). In literature there are several distinct methodological approaches in all the stages of S-LCA, and one of the main problems is the diversity in perception of the social impact of materials and processes, in addition to their quantitative determination (Jørgensen et al., 2008). Many oppure dissemination events were organized between 2004 and 2009 with organizations and experts representing key stakeholders in the field of social responsibility, in order to provide guidelines for the definition of a general code of good practice. The final version, for the S-LCA of products, was officially announced in 2009 in Canada (Benoît, C. and Mazijn, 2009). Social aspect is defined as "a social impact (and potential impact) assessment technique that aims to assess the social and socio-economic aspects of products and their potential positive and negative impacts along their life cycle". The selection of social criteria and their quantification is still one of the major challenges when implementing the concept of sustainability. As reported by (Finkbeiner et al., 2010) many efforts need to be directed to the standardization of a set of social objectives and indicators that take into account individual needs and societal goals. Currently, the large number of social sustainability indicators identified does not allow direct assignment of social indicators to products or processes. The most important criticalities of impact assessment in S-LCA are related to the need to quantitatively relate the existing indicators to the functional unit of the system, and to obtain specific data for the regionalized S-LCA. For more details, see e.g. the paper Settembre Blundo et al., 2014, which shows an innovative life cycle methodology approach for the recovery and restoration of cultural heritage.

10.2 LCA in cultural heritage field

LCA methodology has been extensively applied in the building sector for assessing the environmental performance and impact of construction materials and products throughout the entire life cycle of a construction (Ortiz-Rodriguez et al., 2010; Sharma et al., 2011). Generally, the building industry consumes a significant quantity of materials, and a lot of energy. The waste of energy in materials, not only causes a higher initial level of energy consumption during production of the building, but also determines the future consumption of energy in order to meet the demands

of heating, ventilation, and air conditioning. Moreover, historical buildings do not meet perfectly current standards in terms of energetic management and they have many restrictions in terms of construction techniques and typological and functional features. Nevertheless, historical buildings have also many sustainable characteristics: *i*) energy of realization (embodied energy) had already been spent; *ii*) saving of material resources has already been provided, since they do not need neither of a new land occupation nor the extraction, production and processing of great amount of materials; *iii*) historical buildings have morphological and technological features appropriate to environment and climate (Cinieri & Zamperini, 2013b).
Through an LCA analysis (Zabalza Bribián et al., 2011) it is possible to show that the impact of building materials can be greatly reduced by promoting the adoption of best construction practices and by partially replacing natural resources with materials from other production processes, preferably available locally. Nevertheless, the use of LCA is practically unknown in the field of cultural heritage. In fact, it is quite complex to assess an historical work of art, an architectural monument, or even a contemporary building. It is necessary to have specific tools to manage a large collection of data (Malmqvist et al., 2011). Moreover, this tool must be adapted to the various decisions made throughout the building life cycle, from building design to restoration, maintenance, and conservation (both historical and contemporary). Again, the building structure is not an independent element but exists in a context in which a variety of stakeholders operate being influenced by different factors in their activities at micro, meso, and macro economy level. Therefore, in this vein, every decision-making process aimed at defining interventions on design, recovery, and/or restoration is characterized by marked complexity due to the need of taking multiple requirements and conditions into account simultaneously (Tupenaite et al., 2011).

10.3 Restoration and conservative process

Restoration and conservation processes are based on knowledge and experience that have been developed over the years actually applied to preserve the integrity and authenticity of cultural heritage. The culture of restoration and conservation has been gradually permeated by the scientific method, based on hypotheses and testing, which induced an evolution from empirical "traditional" restoration to a more scientific and technological approach (Iaccarino Idelson, 2011).
The modern concept of conservative restoration of monuments dates back to 1794, the year when the French National Convention issued a decree for the conservation of monuments (Sette, 1996). Starting from this time a series of initiatives have been implemented that showed a change in attitude toward restoration and conservation among the intellectual class and institutions. In the mid-nineteenth century in France a so-called "stylistic" restoration approach has been proposed, theorized, and practiced by E.Viollet-le-Duc (1814-1879) and contrasting with the earlier conservative approach. It aimed at recovering the formal values of the "era and area" of origin of the monument (Hearn, 1990). "Stylistic" restoration completely ignores the passage of time and, therefore, the different historical and artistic works that may stratify the artifact, in search of an ideal (historically nonexistent) "stylistic unit" (Lamberini, 1986). Modern architectural restoration can be traced back to the approach known as "scientific" (the "third way," which goes beyond the stylistic and conservative approaches). In this case restoration is based on the awareness that it is necessary to know what is being restored before starting conservation. The study of the monument is therefore focused on a reconstruction of its historical chronology (Boito, 1883). The leading theorist of restoration in the twentieth century was Cesare Brandi (1906-1988), who postulated a

critical view based on recognition and respect for cultural heritage in terms of both historical and aesthetic authenticity (Brandi, 1977). This led to a restraint in reconstructive activity with an emphasis on conservation based on "preventive" restoration. More recently Pereira Roders (Pereira Roders, 2011) developed a design process for restoration that took into account all the necessary aspects of the process (pre-design, design, construction, use, further interventions, and demolition) and from the earliest stages also considered the reuse or recycling of all the used materials. The restoration process is the methodological moment of recognition of Cultural Heritage in its physical form and in its dual aesthetic and historical instance, for conservation, valorization, and transmission to future generations.

10.4 Sustainability in the building sector

The Brundtland Commission released the "Our Common Future", also known as the "Brundtland Report" and published in October 1987. This document coined the meaning of the term *sustainable development*. In particular, it is defined as an equilibrium between the satisfaction of the present needs and the maintenance of possibility for future generations to meet their own needs, this shall guarantee good living conditions in the long term. In 1996 the conference of Kyoto enquired directly the building sector, because of its relatively heavy environmental impact; in the same year, at Istanbul (Habitat II conference) commitments for the application of sustainability in this sector have been defined, and some aspects have already been evaluated for granted, as cultural responsibilities and training of building workers. In Italy, interventions on architectural heritage (buildings subject to protection according to Italian law - (D.Lgs. 42, 2004) are subject to authorization by the competent bodies and derogations are provided to European performance parameters. However this does not regard most of the traditional preindustrial built heritage, that is not officially declared of cultural interest according to law. For this reason laws often seem to be in contrast with actual moral needs of safeguarding, which are progressively spreading to "new patrimonies" (Cinieri & Zamperini, 2013b). Built heritage is mainly represented by the existing buildings which also consist of constructions having historical and cultural values. Commonly, historical buildings are considered as a source of energy consumption and pollution. Therefore, as the solution to environmental problems in this field is to construct new buildings; this induce to demolition or heavy refurbishment interventions, especially in the case of buildings that have no protection restrictions, even if they belong to the cultural heritage of a territory (spontaneous vernacular architecture or traditional preindustrial buildings, that are abandoned and not registered as heritage buildings, etc.). An existing building might consume a greater quantity of energy than a new building, therefore the latter could nevertheless be much more sustainable from the environmental point of view, because of its huge quantity of embodied energy has already been spent. Moreover, the preservation of existing building enables the reduction of the environmental loads, since the realization of a new building requires the demolition and reconstruction of the structure, with consequent energy consumption, pollution and creation of waste for disposal with subsequent health and pollution problems. Historical built heritage embodies the character of the local tradition and the identity of places, and it constitutes a reference point for the population. Therefore, through the maximization of permanence and the lengthening of the life time of cultural heritage, conservation of material cultural contains in itself issues of social sustainability. The preservation of historic neighborhoods and social housing should also be accompanied by the protection of the social fabric, in order to avoid a very negative social impact. A proper intervention

on existing buildings allows the preservation and perpetuation of the intangible culture heritage which produced the material evidences of historical buildings, promoting, therefore, also the cultural sustainability of refurbishment (Cinieri & Zamperini, 2013a).
For these reasons, in this thesis new indicators to assess social, cultural and historical aspects of an historical buildings have been identify and successively adopted in the impact assessment stage (LCIA) of an LCA case study on an historical building. This work belong to the ARACNE project (see chapter 9). The scope of this final LCA case study is to assess the environmental performance of the restoration process of Fiorano Modenese's Town hall (Modena, Italy) including new materials such as some of the previously discussed nano-TiO_2 functionalized building materials (glass and aluminum panel coated with polyurea resin). *Nanotoxicological* and *social, cultural and historical* aspects have been also evaluated.

10.5 Definition of indicators to assess social, cultural and historical aspects of an historical buildings in LCIA

A preliminary definition of indicators to assess social, cultural and historical aspects in LCIA stage is reported below. In particular, the goal of the present thesis is to take into account, during the impact assessment step (LCIA) of Fiorano Modenese's Town hall (historical building) restoration, special issues such as historical evidence, cultural instances, human well-being local traditions, social fabric, identification of the population in the analyzed building, and so on. This approach allows to consider not only the environmental impacts due to the refurbishment but also the social benefits that this process originates.
IMPACT 2002+ method has been modified adding new "impact" and "damage" categories for evaluating the benefits derived from social, cultural and historical aspects:

- **Cultural value of building** impact category, which refers to three new social substances:
    1. *Age of the building* with characterization factor equal to 1
    2. *Historical evidence* with characterization factor equal to 1
    3. *Aesthetic value* with characterization factor equal to 0.8

  The unit of the substances is p (pieces). The characterization factors have been outlined basing on the weight that it wants to make assume to the social substance.
  The *Age of the building* factor has been calculated in order to obtain 1 as maximum value, considering the Pyramid of Cheops as a reference, since it is considered as the oldest historical building (XXVI century b.C.).
  Maintenance of cultural assets damage category refers to Cultural value of building impact category and assumes -1 as damage assessment factor and 1/2.8 as normalization factor, where 2.8 represents the maximum value that can be attribute to this damage category. In this case it is possible to add up the characterization factors values, since the three substances can be simultaneously referred as input data. The weighting factor has been set equal to 1.

- **Human well-being** impact category, which refers to the following new social substances:
    1. *Alimentation* with characterization factor equal to 1
    2. *Sexuality* with characterization factor equal to 1
    3. *Interpersonal relationship* with characterization factor equal to 0.8
    4. *Institutional relations* with characterization factor equal to 0.8

5. *Education* with characterization factor equal to 0.8
6. *Relax* with characterization factor equal to 0.8
7. *Listening to music* with characterization factor equal to 0.5
8. *Reading* with characterization factor equal to 0.5
9. *Figurative art* with characterization factor equal to 0.5
10. *Sport* with characterization factor equal to 0.4

The unit of the substances is p (pieces). The characterization factor values have been attributed outlining a classification based on a importance order (subjective approach).

Human well-being damage category refers to Human well-being impact category and assumes -1 as damage assessment factor and 1/7.1 as normalization factor, where 7.1 represents the maximum value that can be attribute to this damage category. In this case it is possible to add up the characterization factors values, since the ten substances can be simultaneously referred as input data. The weighting factor has been set equal to 1.

- **Function** impact category, which refers to the following new social substances:
  1. *Housing* with characterization factor equal to 1
  2. *Hospital and Health building* with characterization factor equal to 0.9
  3. *Scholastic building* with characterization factor equal to 0.8
  4. *Public building* with characterization factor equal to 0.7
  5. *Religious building* with characterization factor equal to 0.7
  6. *Cultural building* with characterization factor equal to 0.6
  7. *Social building* with characterization factor equal to 0.6
  8. *Sport building* with characterization factor equal to 0.5

  The unit of the substances is p (pieces). The characterization factor values have been attributed outlining a classification in importance order (subjective approach).

  Function damage category referes to Function impact category and assumes -1 as damage assessment factor and 1/5.8 as normalization factor, where 5.8 represents the maximum value that can be attribute to this damage category. In this case it is possible to add up the characterization factors values, since the ten substances can be simultaneously referred as input data. The weighting factor has been set equal to 1.

- **Urban value** impact category, which refers to the following new social substances:
  1. *Location of the building in the inside* with characterization factor equal to 1
  2. *Location of the building in the outskirts* with characterization factor equal to 0.4
  3. *Location of the building in the outside* with characterization factor equal to 0.1

  The unit of the substances is p (pieces). The characterization factor values have been attributed outlining a classification based on a importance order (subjective approach).

  Maintenance of urban fabric damage category refers to Urban value impact category and assumes -1 as damage assessment factor and 1 as normalization factor, which represents the maximum value of characterization factors that have been attributed to the social substances of Urban value impact category. The weighting factor has been set equal to 1.

11 LCA of the restoration of historical building focusing on the usage of functionalized nanomaterials: Fiorano Modenese's Town hall

The restoration project concerns Villa Cuoghi - Vignocchi, current seat of Fiorano Modenese's Town hall, at Piazza Ciro Menotti. It was founded in 1850 as a private dimora. The commune bought it in 1929 in order to transforme the dimora into a public building. At the time of purchase, Cuoghi - Vignocchi property (Figure 11.1) was composed of a main house, lands and gardens (Risorgimento age), from which the square named Ciro Menotti has been obtained. Later, in 1939, the north side of Villa Cuoghi - Vignocchi was enlarged with a turret and new wing. In the same year the new building extension was inaugurated as Fiorano Modenese's Town hall (Figure 11.2) (function currently kept - Figure 11.3).

Figure 11-1 Villa Cuoghi Vignotti

Figure 11-2 Inauguration of Fiorano Modenese's Town hall (1939)

Figure 11-3 Current Fiorano Modenese's Town hall seat

11.1 Restoration of Fiorano Modenese's Town hall

The restoration project contemplates a significant improvement of environmental sustainability performance through a reorganization of all interior spaces mainly taking into account the following criteria:

- reduction of the electric energy consumption of lighting by adopting open spaces and installing glass walls wherever it is possible;
- elimination of architectural barriers by building an elevator and ramps, providing access to all rooms by all people including disabled people;
- introduction of rest areas to give to the employees the opportunity to relax and socialize;
- introduction per each floor of three dedicated toilettes one for women, one for men and the last one for disabled people;
- definition of a sustainable waste collection system and management within the building.

It also foresees the incorporation of new nano-TiO_2 functionalized materials studied within ARACNE project. In particular, it is assumed to replace the old single-pane windows with double-pane windows having as external glass the nano-TiO_2 functionalized float glass and as internal glass a uncoated single flat glass. Moreover, nano-TiO_2 functionalized polyurea resin applied on aluminum panels has been installed the meeting room walls (building's room with the greater influx of people) in order to reduce the indoor environmental pollutants and bacteria.

11.2 Life Cycle Assessment

11.2.1 Goal and scope definition

The aim of this LCA study is the environmental, cultural, historical and social assessment of the refurbishment of Fiorano Modenese's Town hall (Modena, Italy). The south side of the building has been built in 1850 and it was a private building. In 1939, it has been integrated in the north side with a new wing and turret. Therefore, the building has been divided in two parts one (south) referred to 1850 year and included within blue line (Fig. 11.4) and the other part (north) referred to 1939.

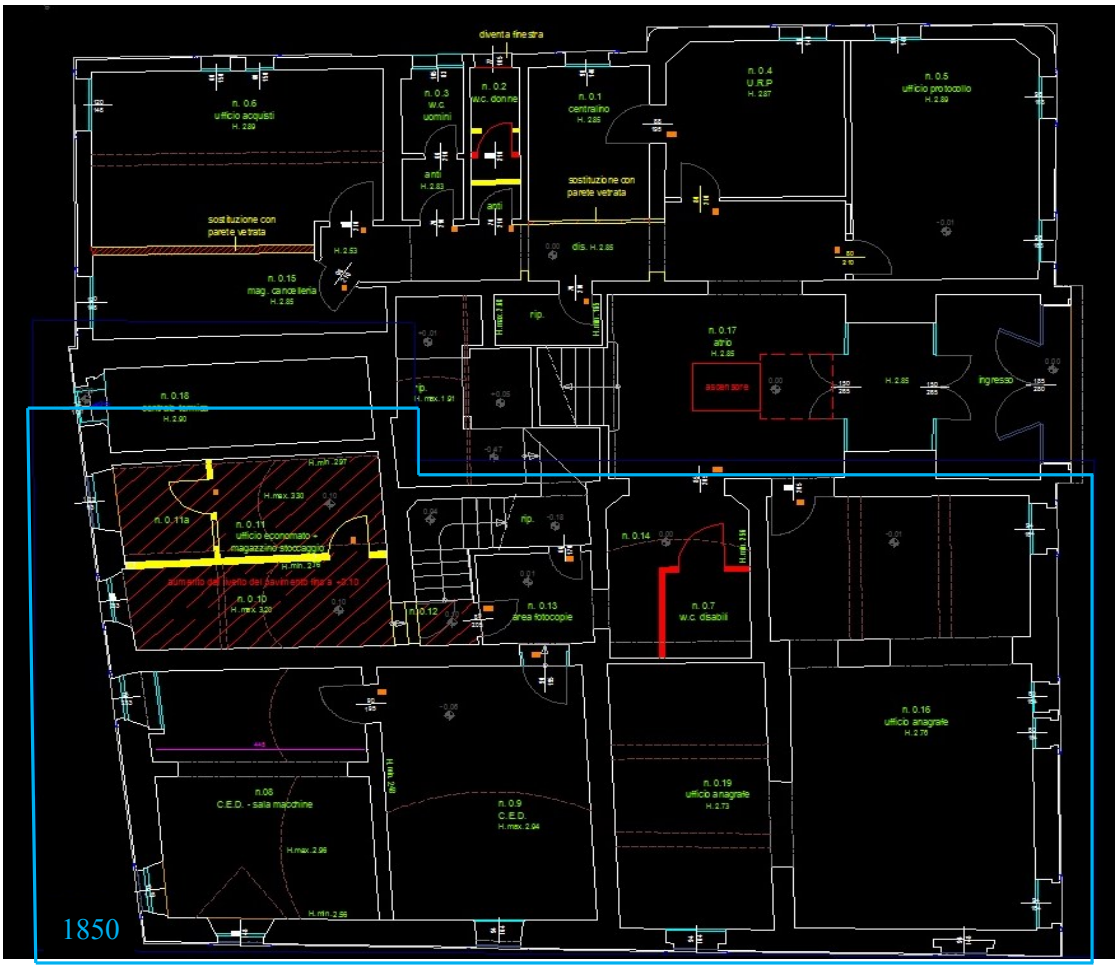


Figure 11-4 Ground floor plant of Fiorano Modenese's Town hall

11.2.2 Functional unit, function of the system and system boundaries

The function of the system is the seat of the municipal offices. The system to be studied is the restoration of Fiorano Modenese's Town hall. The functional unit is the building system (structure) used as a public building, considering a period ranging from its renovation to its disposal, therefore 1p.

It has been assumed that the refurbishment begins in 2013 and as life time of the renovated building 100 years. Referring to the building part of 1850, the life time passes until refurbishment process is equal to 163 years (=2013-1850). Instead for the part of 1939 is equal to 74 years (=2013-1939). The components/building materials of 1850 and that are maintained even after restoration have a life time of 263 years (=163+100), whereas for those of 1939 the remaining lifetime is equal to 174 years (=74+100). Therefore, in LCA study components/building materials of 1850 are allocated according to the ratio between the renovated building lifetime (100 years) and the total building lifetime: 100yrs/(100yrs+163yrs)= **0.38** and, instead, the components/building materials of 1939 are allocated according to the ratio: 100yrs/(100yrs+174yrs)= **0.5747**.

New components/building materials introduced during the restoration are allocated in LCA study with a value of **1**.

The end of life and demolition operations of components/building materials of 1850, which have to be replaced are allocated with the factor 0.38. For components/building materials of 1939, the process before mentioned are allocated with the factor 0.5747.

The boundaries of the system ranging from the supply and extraction of resources and raw materials to the disposal of each building materials, including the use phase and the maintenance operations.

11.2.3 Data quality

If available, primary data for both the components/building materials that are maintained after refurbishment process (of 1850 and 1939 years) and the new components/building materials installed in the renovation process have been used. In case these have been not available assumption and estimates have done. The LCA processes which represent these materials have been derived from Ecoinvent databases (Goedkoop & Spriensma, 2001). If missing, they have been built ad hoc.
For the use phase, heating and air conditioning have been considered as well the devices and the maintenance operations. The use phase has been schematized adopting primary data. Concerning the end of life of components/building materials, safe and environmental friendly technologies and treatment have been considered.

11.2.4 Life Cycle Inventory

Technical office personnel and people in charge of following this section of ARACNE project provided the main needs and requests to take into consideration in LCA study in order to improve building performances. The list is reported in Italian language within ANNEX I. These needs and requests has been taken into account during LCI drafting.
The number of employees which work at Fiorano Modenese's Town hall are 41.

11.2.4.1 ***Building structure, systems and devices***

The LCA of restoration of Fiorano Modenese's Town hall study has been performed evaluating the following issues:

- Definition of new layout that all rooms per each floor have to be in order to respect the criteria proposed within chapter 11.1.
- Identification of different typology of building materials of both the 1850 and the 1939, which constitute:
  - ✓ building envelope, that could be a single, double and quadruple wythe masonry wall: calculation of walling volume (height, width, thickness);
  - ✓ building roofing: calculation of covering and shingle;
  - ✓ building floorings for each floor: calculation of flooring volume (length, width, thickness).
  - ✓ internal architectural elements (walls, arches, vaults, staircases and doors): dimensions calculation;
  - ✓ windows frame and windows glass: volume calculation;

The allocation (manufacture, end of life) is equal to 0.38 for the building materials of the 1850 and 0.5747 for those of the 1939.

- Identification of different typology and size (to calculate the amount) of new building materials added during the refurbishment process in order to substitute or introduce:
  - ✓ missing building parts;
  - ✓ building parts deteriorated by the time or weathering;
  - ✓ glass walls where the internal walls have been demolished to introduce them or open space;
  - ✓ lift and the whole support structure;

- ✓ ramps (to provide easy access to all building rooms);
- ✓ new toilette for disable people or where missed;
- ✓ old single-pane windows with double-pane windows having as external glass the nano-TiO_2 functionalized float glass and as internal glass a uncoated single glass.
- ✓ nano-TiO_2 functionalized polyurea resin applied on an aluminum panels installed the walls of the meeting room (building's room with the greater influx of people) in order to reduce the indoor environmental pollutants and bacteria.

The allocation (manufacture, end of life) of these materials is equal to 1.

- Calculation of heat energy and air-conditiong demand of renovated Fiorano Modenese's Town hall in 100 years. Termotecnica-Italsoft (Italsoft, 2015) software has been used to performed these consumptions.
- Identification of materials (typology and amount) that constitute the new Heating, Ventilation, and Air-Conditioning (HVAC) system of building.
  The allocation (manufacture, end of life) of these materials is equal to 1.
- Identification of materials (typology and amount) that compose the new heating and air-conditioning devices.
  The allocation (manufacture, end of life) of these materials is equal to 1.
- Calculation of electric energy consumption for lighting of renovated Fiorano Modenese's Town hall in 100 years. Excel – Spread Sheet has been used to calculate this consumption.
- Identification of materials (typology and amount) that compose all led bulbs that have to installed in the all building rooms.
  The allocation (manufacture, end of life) of these materials is equal to 1.
- Calculation of electric energy consumption of computers, printings, photocopying, scanners and lift in 100 years.
- Identification of materials (typology and amount) that compose the computers, printings, photocopying, scanners and lift.
  The allocation (manufacture, use and end of life) of these materials is equal to 1.
- Calculation of water requirement of renovated Fiorano Modenese's Town hall in 100 years. Termotecnica-Italsoft software has been used to performed this service.
- Identification of materials (typology and amount) that compose the whole building water system.
  The allocation (manufacture, end of life) of these materials is equal to 1.
- Definition of waste collection management: identification of collection point, predisposition of specific bins, calculation of waste produced in 100 years.

11.2.4.2 *Road network for the connection between the city center and Fiorano Modenese's Town hall*

- Average weekly number of visitors and number of car and public transport needed to transport them.
- It is assumed that every day 50 visitors plus 41 employees access to the Town hall. In particular distributed as follows:
  - 45 people by bus (1 bus every 10 min) 49.5%.
    The bus travels a distance of 1 km within Fiorano Modenese's urban circuit (considering an average radius of 0.5 km).

- 11 people by bicycle 12%. Distance: 1.5 km.
- 5 people by scooter 5.5%. Distance: 2 km.
- 15 people by walk 16.5% (the distance has not been evaluated since no environmental impact are associated).
- 15 car 16.5%. Distance: 2 km.

The return has been taken into account.

- Typology and amount of materials for production and end of life of car, scooter, bicycle and public transports.
- Fuel consumptions for transport in 100 years.

11.2.4.3 ***Different scenario of the end of life treatment of nano-TiO_2 coated float glass***

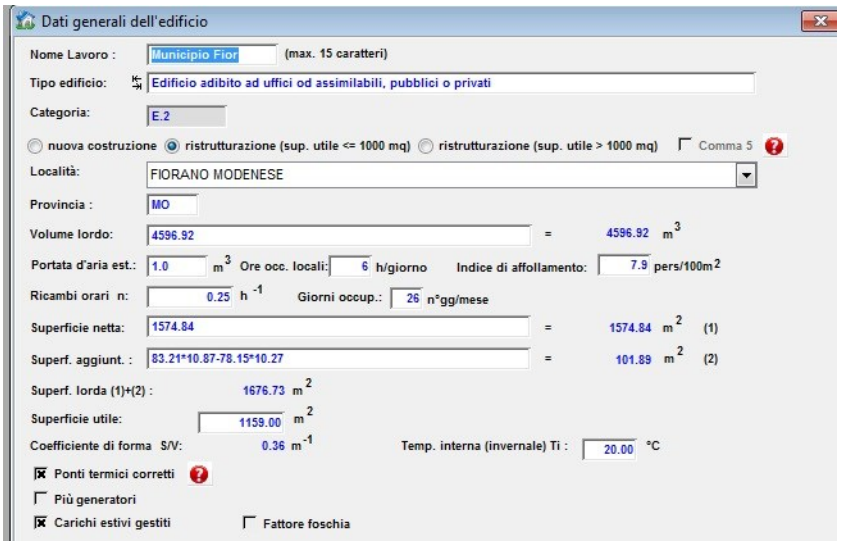
Three different scenario of and of life treatment of nano-TiO_2 coated float glass have been considered even in LCA restoration of the Fiorano Modenese's Town hall. The first scenario (**Scenario 1**) considers that glass and nano-TiO_2 coating have the same lifetime (10 years), the second one (**Scenario 2**) evaluates again the glass lifetime of 50 years and the nanocoating lifetime of 10 years, but without glass re-functionalization, during the first 10 years, 50% of nano-TiO_2 are released in air and during the following 40 years a linear decrease of benefits derived from nano-TiO_2 application and a complete release of nano-TiO_2 have been assumed. Instead, for the last one (**Scenario 3**) considers the glass lifetime of 50 years and the nanocoating lifetime of 10 years (four re-functionalization process, after every 10 years, have been needed in 50 years).
Furthermore, for the first and third scenario the inertization process with concrete has been take into account as end of life treatment, and for the second one the recycling treatment has been considered. In this LCA case study the **Scenario 3** has been adopted and in the LCIA phase has been assessed. Successively, a sensibility analysis has been carried out to compare the different environmental performance of these three different scenario.

11.2.4.4 ***Calculation of heat energy and air-conditioning demand of renovated Fiorano Modenese's Town hall***

The energy consumption for heating and air-conditioning of the building was calculated with Termotecnica-Italsoft software (Italsoft, 2015) and considering 100 years as lifetime of the renovated building.

General building data

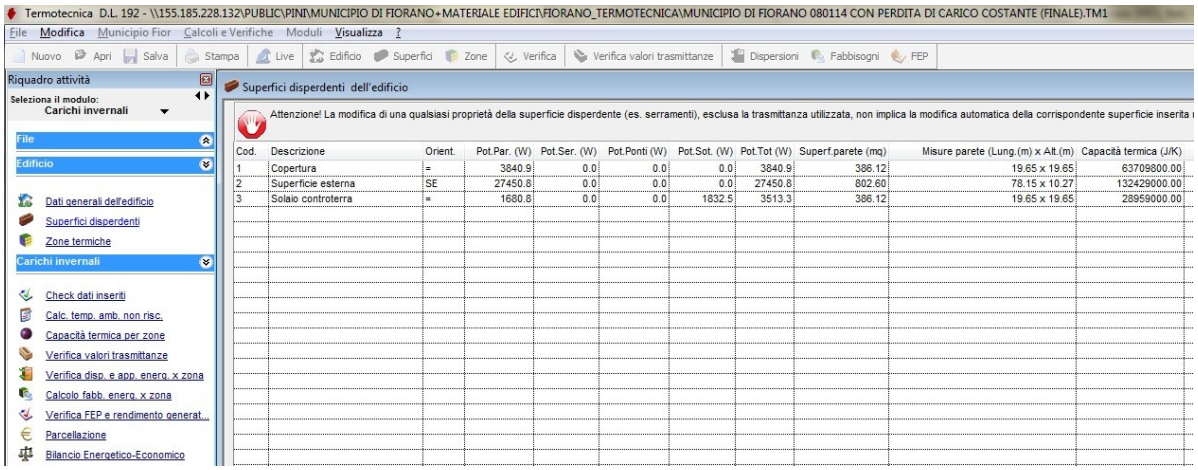
Module: Winter loads



Gross volume: area of the outer perimeter * external height = 422.9 m^2 * 10.87 m
Outer perimeter: 83.21 m
Net area per floor: 386.34 m^2 (ground floor excluded the masonry thickness)
Internal height: 10.27m
External height: 10:27 + 0.3 + 0.3 = 10.87 m (where 0.3 m is the floor dimension)
N° of people that access to the building every day: 91 (N° employees: 41. It is assumed that the building has on average 50 visitors every day).
Crowding index: 91 / (386.34 m^2 * 3) / 100 m^2 = 7.9
N° of air exchange rate: 0.5
External air flow: 1 m^3
Net outer surface: internal perimeter * internal height = 78.15 m * 10.27 m

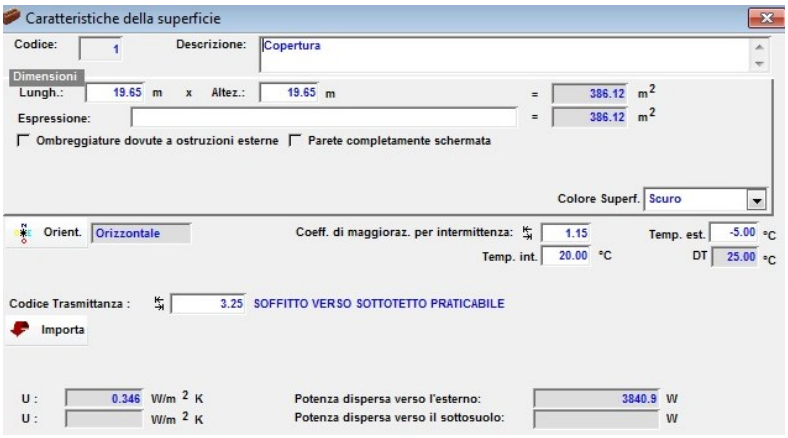
Dispersant surfaces

Termotecnica-Italsoft software version used for this study allows to outline only three building layers. Therefore only roofing, outer surfaces and slab on grade have been considered.



Roofing

Internal surface: $\sqrt{386.34\ m^2}$= 19.65 m



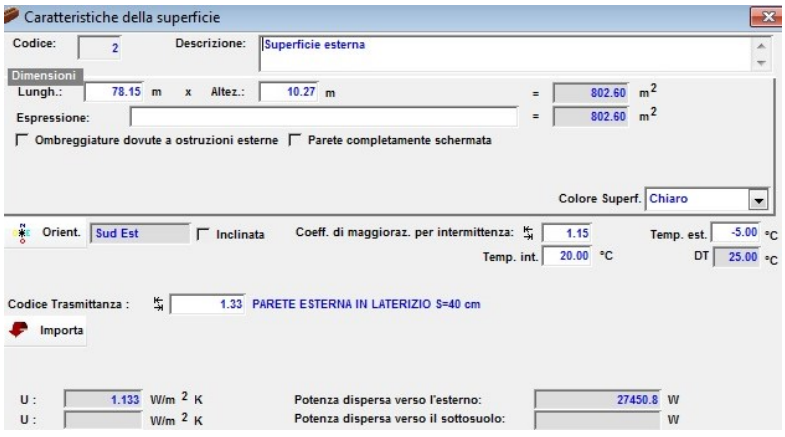
Increase coefficient for intermittence: “Radiators hot water with use of 8/12” has been selected.

New transmittance code (3.25) has been created, considering:

- gypsum plaster and lime
- brick-concrete floor
- concrete ordinary
- stoneware tiles
- still air: thickness = 1 m, conductivity = 0.1, density = 1.3 Wm^2/K = permeability 187.122E-12 kg/mPa, conductance: 0.5 m^2/K
- hollow flat tiles
- bituminous sheath
- roof tiles

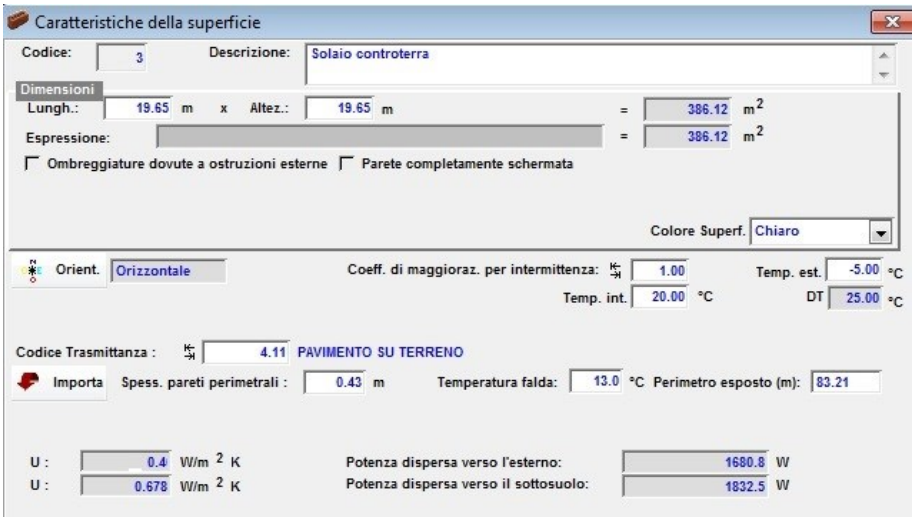
Transmittance: 0.346W $m^2/K \leq 0.4$ Wm^2/K (legislation limit).
Weight coverage: 522 kg/m^2

Outer surface



Transmittance: 1.133W $m^2/K > 0.4$ Wm^2/K. Even if, the transmittance has a value greater than legislation limit (but just a warning), Termotecnica-Italsoft software allows to continue with the analysis.
Weight coverage: 534 kg/m^2

Ground floor



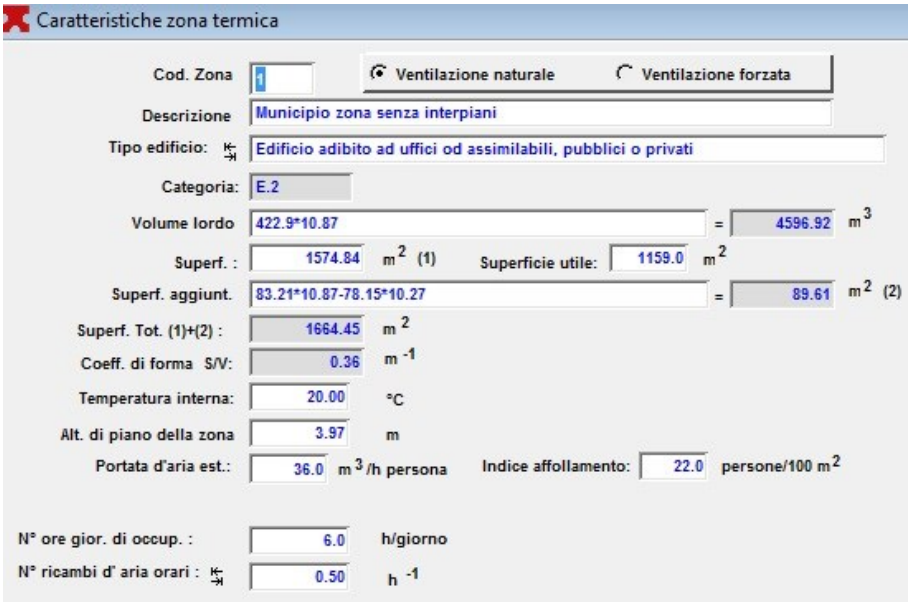
New transmittance code (4.11) has been created, considering:

- ceramic tile
- lean concrete
- screed
- ordinary concrete

Transmittance: 0.4 W m^2/K $\leq$ 0.4 Wm^2/K (legislation limit).
Weight coverage: 495 kg/m^2

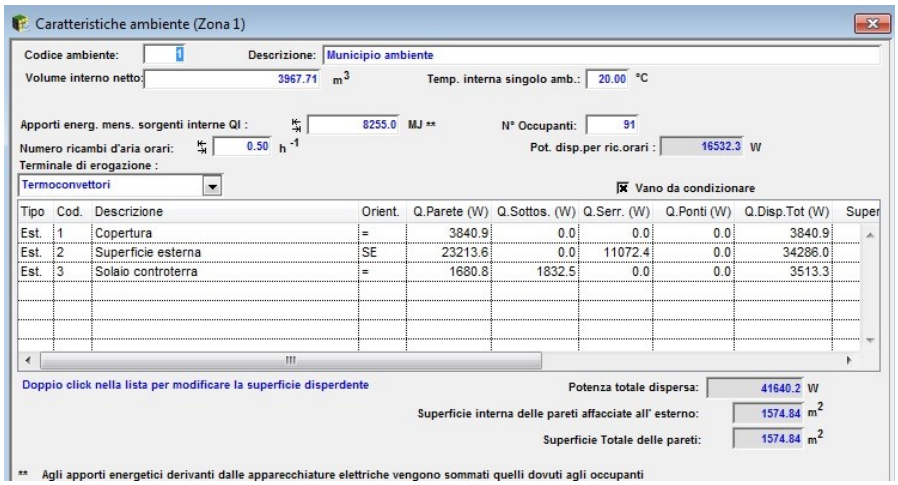
Total dispersed power from the three building layers: 34805W (this value is calculated automatically).

Thermal zone



In "Elenco zone termiche" the thermal zone shall be selected. Therefore, "Municipio ambiente" has been chosen. The three types of surfaces above described have been introduced. Doors and windows have been associated to the Outer surface.
Windows: mean area of the windows= 0.92 m * 1.71 m (calculated by a spreadsheet).

N° of windows: 63.
N° of glass door: 3.
Doors: the building has 1 entrance main door and 2 secondary entrance doors.
After introducing windows and doors into the thermal zone, its characteristics becomes:



Total dispersed power from doors and windows: 41640.2 W

Energy contributions of internal sources (computer, printer, photocopier and so on) QI: 8255MJ

Module: Summer loads

Bypass factor: n° ranks= 4, front speed= 2. This is the ratio between the weight of bypassed air, that is not coming in contact with the refractory surface, and the total weight of air cross the battery.
Outdoor air intake: 25 m^3/h.
Calculation data: it is needed indicate the period in which the calculation should be carried out, e.g. September, 22 at 9 am. Moreover, it is needed to indicate the total lighting consumption of the building.

Lighting consumption

The total lighting consumption is derived from a spreadsheet named "Doors and Windows of Fiorano Modenese's Town hall" (its immage is reported in Italian language in ANNEX II section), where per each floor and per each room the lighting consumption (i.e. electric energy consumptions for working activities, cleaning, corridors, lobbies, toilettes, fluorescent lamp) has been calculated, following the considerations below described:

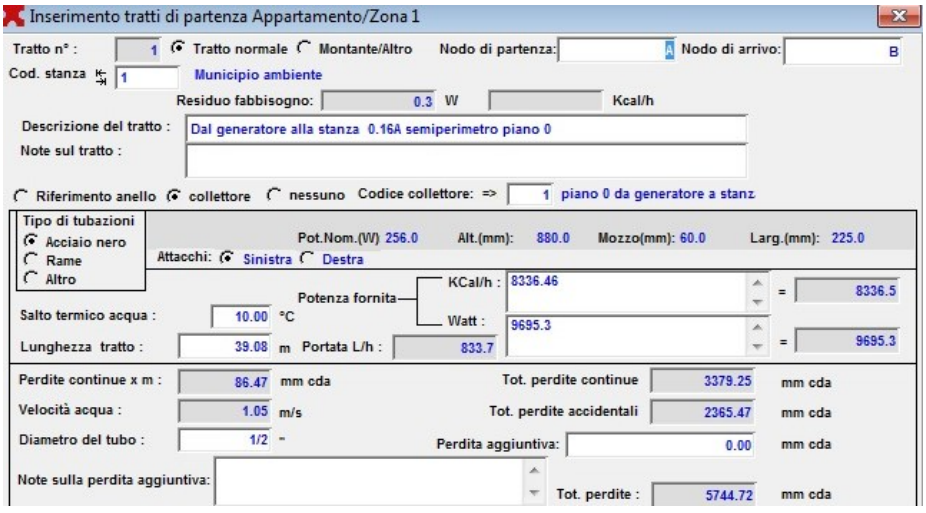
- ✓ A requirement of 350 lx for all offices, considering the maximum and minimum electric energy consumption per each room has been assumed.
- ✓ A minimum illumination from 9 am to 7 pm and no distinction between summer and winter have been considered.
- ✓ It has been evaluated a requirement of 150 lx for corridors, lobbies, toilettes.
- ✓ For all bathrooms with windows and/or blind it has been assumed that the light comes on with the entrance of a person.
- ✓ For the blind corridors the use of maximum electrical power (350 lx) has been evaluated since they needed to constant illumination.

- ✓ In case of corridors illuminated by the lighting that crosses the frosted glass walls of the adjacent office, a photocell installation (that it turns on when the lighting is not sufficient) has been considered.
- ✓ In the lighting calculation only the minimum power (150 lx) has been taken into account, since the office with glass walls and adjacent to the corridor is always illuminated in order to maintain a value of 350 lx in the office.

Total lighting consumption values: 5028 W.
Termotecnica-Italsoft software automatically calculates the total summer power consumption, which in particular is equal to 68069 W.
The heat generator has to selected from the heat generator list. *Heat pump (60kW) model Irsap with COP = 3.9* has been chosen.

Module: Sizing the Thermal system

In "Modules" section "Size of thermal system" shall be selected. In "Heating system" the apartment/thermal zone shall be taken, in this case "Municipio di Fiorano" has been chosen.
In "General data" T= 70 ° C average boiler, ΔT = 10°C, Temperature variation= 10°C / 70°C = 14.29%.
In "Tratti" the different sections of heating system have been inserted. The thermal system has been outlined considering: 6 heating system pipes + 2 pillars + 2 connectors + 1 generator.
Heating system pipes from the generator to the room: "collector" shall be selected. The power supplied has to specified considering the total dispersed power (41640.2W) and the total dispersed power due to air exchange rate (16532W) found in "Caratteristiche ambiente (Zona1)". The total amount (58172.4W) shall be divided by 3 (since it has been considered that the building is separated in 3 levels) multiplying by the number of heating system pipes per floor which is always equal to 2 (9695.3W). The radiator code: CS = 2.8 shall be indicated, after that the collector code shall be associated.



Collector: it creates the connection between the generator and the upper floors and groups pillars, namely the pipes that bring water.
Pillar: for the pillars do not need the power because they are only a link between a floor and another.

Once all collectors, pillars, heating system pipes have been outlined in the Termotecnica-Italsoft software automatically calculates the total weight of thermal system pipes, that in particulars in this case is equal to 520.056 kg.
The annual energy consumption for heating, calculated automatically by Termotecnica-Italsoft software, is equal to 196921 MJ/yr (for 100 years it is equal to 1.89480E7 MJ). Instead, the annual energy consumption for air-conditioning, calculated automatically by Termotecnica-Italsoft software, is equal to 85295.6 W (for 100 years it is equal to 9.2404E5 MJ), also in this case the pump has a yield equal to 3.9 and a consumer in his life: 1440922.19 MJ. For both cases a heat pump having a COP of 3.9 has been considered, as before mentioned.

Water network

It has been assumed that the starting collector is located outside the building of 3 m, from this point the water network departs to get to the toilets located at the ground floor and at the several floors of the building's north side. The water network for hot and cold water shall be defined and outlined. For each toilet shall be defined the number of toilet bowls, bidets and washbowls needed. Termotecnica-Italsoft software automatically shows the water capacity expressed in l/s and then the pipes diameters and number of branch point and tap.
The amount of hot water needed to supply the whole requirements of the under studied building has been calculated, 9 washbowl and 9 bidets for a total consumption of 972 l/h (automatically calculated by Termotecnica-Italsoft software) has been considered. The "coincidence factor" has been default inserted by the system and equal to 0.35 and the "correction factor" has been taken equal to 0.60. The real hot water consumption results of 972 l/h * 0.35 * 0.6 = 204.12 l/h.

Air channels for the air conditioning system

An air conditioning system constituted by three air channels, one per floor, a channel (length of 2 m) from the air inlet to the heat pump plus a channel to get to the floor. "Constant loss" and "Central air-conditioning system" have been selected. Termotecnica-Italsoft software elaborates the "Airflow calculation" which results equal to 13885.94 m^3/h.

11.2.4.5 ***Social data input***
Table 46 shows the data values (substances) inserted during the LCI draft and that have an effect on the new "impact" and "damage" categories added into *IMPACT 2002+* modified LCIA method.

Table 46 Social data input values

Social issues	Amount	Unit	Comment
Age of the building	0.0357927	p	Substance of ***Cultural value of building*** "impact" category. Building lifetime: 2013-1850. It has been taken into account the Pyramid of Cheops as the oldest historical building (2540 b. C.). Therefore, a building with the same Pyramid of Cheops' age (2540 bc+2014 ac= 4554 years) is valued equal to 1. For Fiorano Modenese's Town hall the "Age of the building" social issues values: 1/4554years = x/(2013year of restauration-1850 year of construction); x=0.035792709

Historical evidence	0,6	p	Substance of ***Cultural value of building*** "impact" category. Historical evidence of Fiorano Modenese's Town hall. It is a public building since 1939. Weighting factors: from 0 to 1. Assigned value: 0.6 (considering that the image of the building provides a limited testimony of its history).
Aesthetic value	0,5	p	Substance of ***Cultural value of building*** "impact" category. Aesthetic value of Fiorano Modenese's Town hall of fascist architecture. Weighting factors: from 0 to 1. A medium value of this period equals to 0.5 has been considered.
Institutional relations	1	p	Substance of ***Human well-being*** "impact" category. Rating from 0 to 1 of the institutional relations favored by the building. Assigned value: 1 (the town hall is the highest point of the institutional relationship between citizens and their representation).
Public building	1	p	Substance of ***Function*** "impact" category. Rating from 0 to 1 of the public building favored by the function of the building. Assigned value: 1 (the town hall is a building having a public function).
Location of the building inside the urban center	1	p	Substance of ***Urban value*** "impact" category. Rating from 0 to 1 of the location of the building inside the urban center favored by the function of the building. Assigned value: 1 (the location of the building inside the urban center corresponds to the maximum value).

11.2.5 Impact assessment

11.2.5.1 *IMPACT 2002+* modified method

Single score damage is 1161.63 Pt for 1 p of the refurbishment of Fiorano Modenese's Town hall. As Figure 11.5 shows that energy consumption for heating is the contribution which are mainly responsible for the total damage (28.28%), followed by transports (12.42%), electric energy consumption for lighting and cleaning (12.45%), and floors (11.36%), electronic equipment (9.76%).

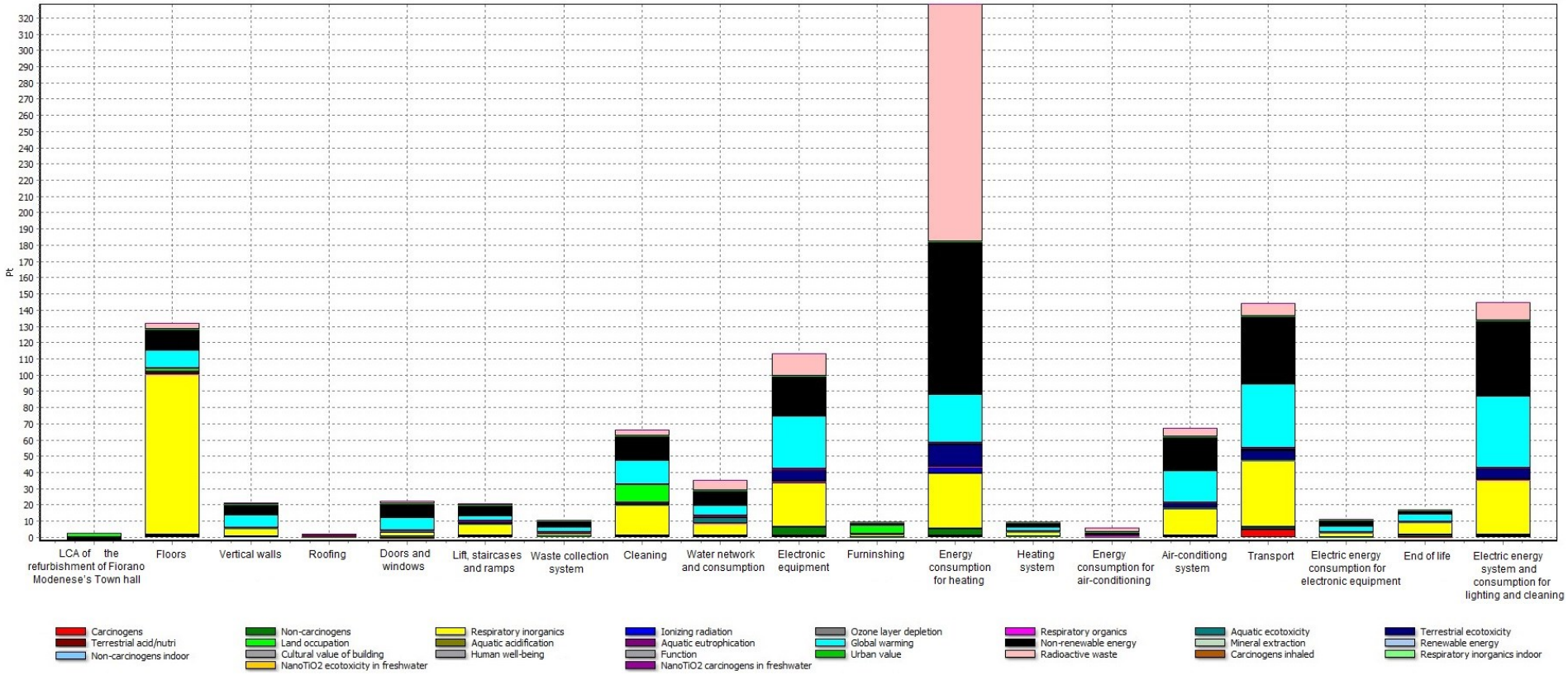


Figure 11-5 Evaluation by single score of 1 p of the refurbishment of Fiorano Modenese's Town hall

Table 47 Characterized LCIA results of 1 p of the refurbishment of Fiorano Modenese's Town hall

Impact category	Unit	Total	LCA of the refurbishment of Fiorano Modenese's Town hall	Floors	Vertical walls	Roofing	Doors and windows	Lift, staircase and ramps	Waste collection system	Cleaning	Water network and consumption	Electronic equipment
Carcinogens	kg C2H3Cl eq	2,88E+04	-	1,26E+03	5,52E+02	3,26E+01	1,01E+03	1,45E+03	5,88E+02	7,84E+02	9,68E+02	3,17E+03
Non-carcinogens	kg C2H3Cl eq	4,36E+04	-	2,28E+03	4,16E+02	2,62E+01	7,77E+02	9,58E+02	4,47E+02	1,33E+03	1,51E+03	1,34E+04
Respiratory inorganics	kg PM2.5 eq	3,14E+03	-	1,00E+03	5,10E+01	3,70E+00	2,75E+01	7,19E+01	1,78E+01	1,89E+02	7,69E+01	2,77E+02
Ionizing radiation	Bq C-14 eq	1,60E+08	-	2,96E+06	9,89E+05	8,92E+04	1,22E+06	6,92E+05	3,42E+05	3,06E+06	4,36E+06	1,01E+07
Ozone layer depletion	kg CFC-11 eq	3,42E+00	-	1,20E-02	6,27E-03	4,02E-04	1,27E-02	5,28E-03	4,15E-03	1,24E-02	3,63E-03	2,10E-02
Respiratory organics	kg C2H4 eq	1,60E+02	-	3,73E+01	2,93E+01	3,82E+00	-1,67E+03	1,84E+01	1,19E+01	8,39E+01	1,34E+01	7,81E+01
Aquatic ecotoxicity	kg TEG water	1,30E+09	-	5,95E+06	2,24E+06	1,61E+05	9,30E+06	4,76E+06	1,17E+06	2,77E+07	9,71E+08	1,13E+08
Terrestrial ecotoxicity	kg TEG soil	7,54E+07	-	2,44E+06	7,47E+05	4,94E+04	9,59E+05	2,18E+06	6,84E+05	2,33E+06	8,67E+05	1,18E+07
Terrestrial acid/nutri	kg SO2 eq	3,91E+04	-	1,63E+03	1,00E+03	7,71E+01	-7,76E+01	5,64E+02	4,04E+02	3,33E+03	9,40E+02	4,59E+03
Land occupation	m2org.arable	3,23E+05	3,63E+04	2,76E+04	1,45E+03	6,40E+03	4,68E+03	5,70E+03	3,88E+03	1,38E+05	4,17E+03	6,42E+03
Aquatic acidification	kg SO2 eq	1,06E+04	-	3,95E+02	2,33E+02	1,75E+01	2,29E+02	1,71E+02	9,24E+01	8,13E+02	3,11E+02	1,46E+03
Aquatic eutrophication	kg PO4 P-lim	1,13E+03	-	2,07E+01	7,58E+00	4,85E-01	9,17E+00	7,58E+00	5,30E+00	4,32E+01	1,93E+01	6,06E+02
Global warming	kg CO2 eq	2,32E+06	-	1,11E+05	7,56E+04	5,20E+03	7,48E+04	3,21E+04	3,31E+04	1,53E+05	6,68E+04	3,22E+05
Non-renewable energy	MJ primary	4,53E+07	-	1,89E+06	9,53E+05	6,47E+04	1,31E+06	9,92E+05	5,79E+05	2,19E+06	1,21E+06	3,61E+06
Mineral extraction	MJ surplus	4,29E+05	-	6,84E+03	2,32E+03	8,93E+01	5,38E+03	2,92E+04	1,07E+03	9,58E+03	1,80E+05	1,34E+05
Renewable energy	MJ	2,19E+07	-	5,73E+05	9,36E+04	1,17E+05	1,95E+05	1,04E+05	4,74E+04	1,45E+06	1,31E+05	3,24E+05
Cultural value of building	p	1,04E+00	1,04	-	-	-	-	-	-	-	-	-
Human well-being	p	8,00E-01	0,8	-	-	-	-	-	-	-	-	-
Function	p	7,00E-01	0,7	-	-	-	-	-	-	-	-	-
Urban value	p	1,00E+00	1	-	-	-	-	-	-	-	-	-
Radioactive waste	kg	2,08E+02	-	3,99E+00	1,34E+00	1,22E-01	1,62E+00	9,45E-01	4,62E-01	4,04E+00	6,00E+00	1,38E+01
Carcinogens inhaled	kg	3,60E-04	-	-	5,38E-05	-	3,06E-04	-	-	-	-	-
Respiratory inorganics indoor	kg	-2,35E-03	-	-	-2,35E-03	-	-	-	-	-	-	-
Non-carcinogens indoor	CFU/pers	-3,52E+00	-	-	-3,52E+00	-	-	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	kg	-	-	-	-	-	-	-	-	-	-	-

Nano-TiO_2 carcinogens in freshwater	kg		-	-	-	-	-	-	-	-	-	-

Impact category	Unit	Total	Furninshing	Energy consumption for heating	Heating system	Energy consumption for air-conditioning	Air-conditioning system	Transport	Electric energy consumption for eletronic equipment	End of life	Electric energy system and consumption for lighting and cleaning
Carcinogens	kg C2H3Cl eq	2,88E+04	1,01E+02	3,16E+03	6,21E+02	5,48E+01	1,31E+03	1,16E+04	1,10E+02	4,70E+02	1,57E+03
Non-carcinogens	kg C2H3Cl eq	4,36E+04	1,23E+02	9,93E+03	3,89E+02	1,73E+02	1,54E+03	4,03E+03	1,69E+02	3,19E+03	2,91E+03
Respiratory inorganics	kg PM2.5 eq	3,14E+03	1,60E+01	3,48E+02	2,65E+01	6,05E+00	1,69E+02	4,12E+02	2,62E+01	7,53E+01	3,38E+02
Ionizing radiation	Bq C-14 eq	1,60E+08	3,64E+05	1,14E+08	5,24E+05	1,98E+06	3,82E+06	5,98E+06	6,68E+05	4,25E+05	8,53E+06
Ozone layer depletion	kg CFC-11 eq	3,42E+00	9,12E-04	3,17E+00	2,28E-03	5,50E-02	1,72E-02	5,74E-02	3,08E-03	2,13E-03	3,92E-02
Respiratory organics	kg C2H4 eq	1,60E+02	7,70E+00	5,98E+01	5,53E+00	1,04E+00	4,01E+01	1,34E+03	6,78E+00	1,03E+01	8,74E+01
Aquatic ecotoxicity	kg TEG water	1,30E+09	6,17E+05	7,96E+07	2,08E+06	1,38E+06	1,43E+07	2,23E+07	2,40E+06	1,44E+07	3,13E+07
Terrestrial ecotoxicity	kg TEG soil	7,54E+07	2,42E+05	2,36E+07	7,81E+05	4,10E+05	5,14E+06	1,04E+07	8,62E+05	6,22E+05	1,12E+07
Terrestrial acid/nutri	kg SO2 eq	3,91E+04	2,94E+02	4,40E+03	4,08E+02	7,65E+01	2,95E+03	1,07E+04	5,16E+02	6,60E+02	6,61E+03
Land occupation	m2org.arable	3,23E+05	6,70E+04	5,49E+03	2,73E+02	9,53E+01	1,92E+03	9,73E+03	3,11E+02	3,30E+02	3,99E+03
Aquatic acidification	kg SO2 eq	1,06E+04	5,21E+01	1,46E+03	1,29E+02	2,53E+01	9,50E+02	1,84E+03	1,68E+02	1,15E+02	2,15E+03
Aquatic eutrophication	kg PO4 P-lim	1,13E+03	1,55E+00	2,33E+02	4,86E+00	4,04E+00	3,52E+01	4,26E+01	5,91E+00	3,92E+00	8,28E+01
Global warming	kg CO2 eq	2,32E+06	8,01E+03	2,99E+05	2,69E+04	5,19E+03	1,96E+05	3,91E+05	3,43E+04	4,90E+04	4,37E+05
Non-renewable energy	MJ primary	4,53E+07	1,66E+05	1,43E+07	4,36E+05	2,48E+05	3,15E+06	6,35E+06	5,53E+05	3,16E+05	7,05E+06
Mineral extraction	MJ surplus	4,29E+05	4,33E+02	1,83E+04	1,31E+03	3,17E+02	1,22E+04	9,89E+03	1,29E+03	6,90E+02	1,68E+04
Renewable energy	MJ	2,19E+07	6,36E+05	1,68E+07	3,52E+04	2,92E+05	2,72E+05	1,41E+05	4,86E+04	8,20E+03	6,19E+05
Cultural value of building	p	1,04	-	-	-	-	-	-	-	-	-
Human well-being	p	0,8	-	-	-	-	-	-	-	-	-
Function	p	0,7	-	-	-	-	-	-	-	-	-
Urban value	p	1	-	-	-	-	-	-	-	-	-
Radioactive waste	kg	2,08E+02	4,96E-01	1,46E+02	6,90E-01	2,54E+00	5,02E+00	7,84E+00	8,75E-01	5,79E-01	1,12E+01
Carcinogens inhaled	kg	3,60E-04	-	-	-	-	-	-	-	-	-
Respiratory inorganics indoor	kg	-2,35E-03	-	-	-	-	-	-	-	-	-

Non-carcinogens indoor	CFU/pers	-3,52E+00	-	-	-	-	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	kg	-	-	-	-	-	-	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	kg	-	-	-	-	-	-	-	-	-	-

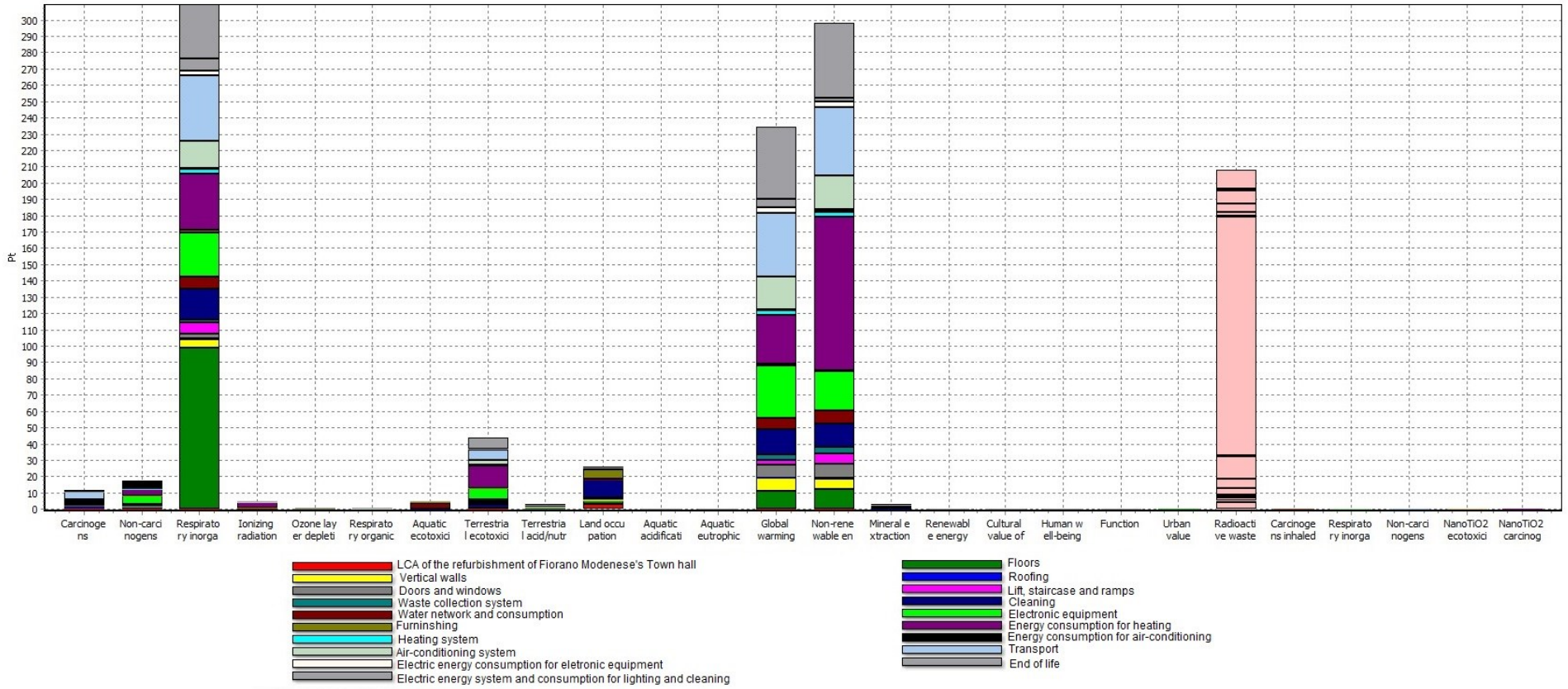


Figure 11-6 Evaluation by impact categories of 1 p of the refurbishment of Fiorano Modenese's Town hall

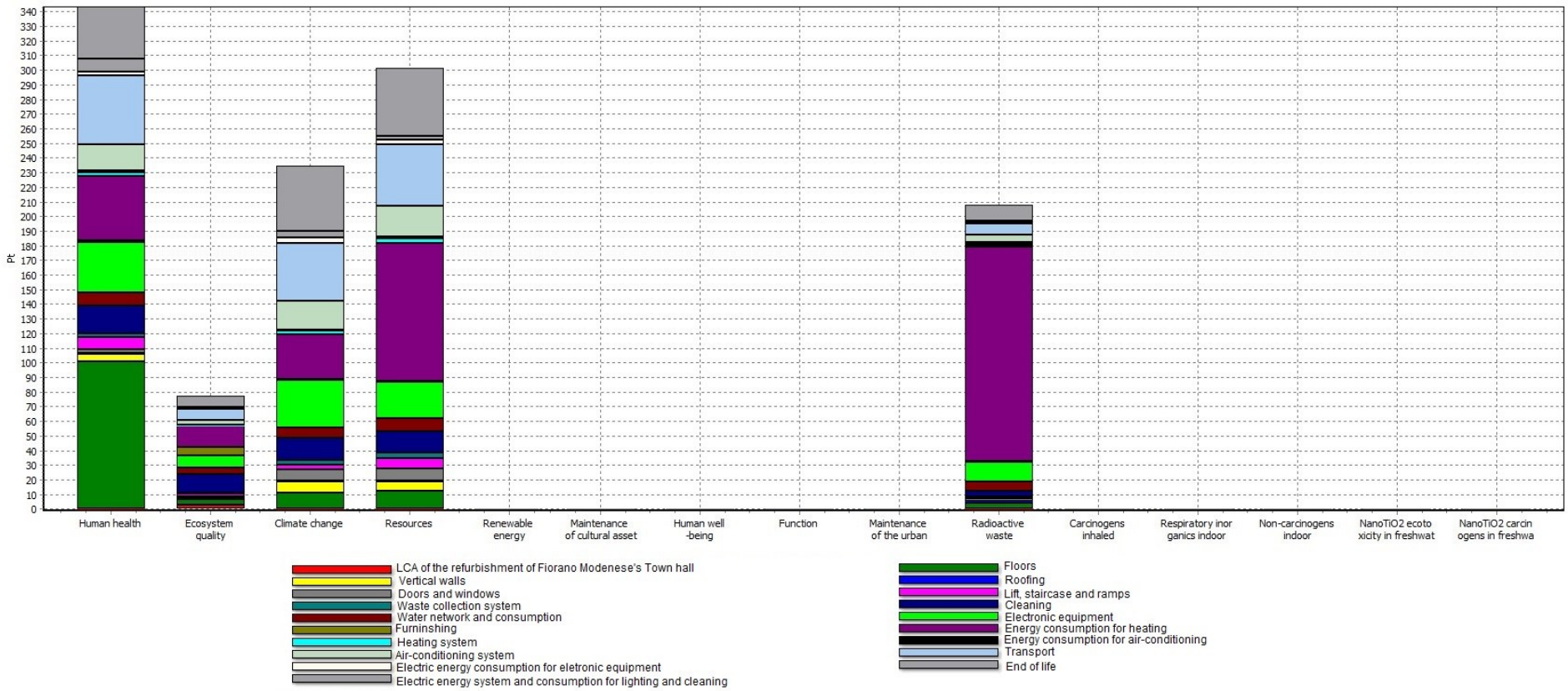


Figure 11-7 Evaluation by damage categories of 1 p of the refurbishment of Fiorano Modenese's Town hall

Table 47 and Figure 11.6 report the contributions of the main impact categories on the total damage. Therefore, highlight that the most significant contribution to the total damage is due to Respiratory inorganics (26.64%), mainly due to *Particulates, < 2.5 μm* (48.78%), *Nitrogen oxides* (23.18%) which are caused by floors (60.75%), in particular due to ceramic tile manufacture, and transport (31.33%) processes, in particular due to the transport by bus. In this impact category the total damage is balanced by the NO_x reduction (-0.6671%) of -106.89kg, in particular due to doors and windows process (-100%), where the benefits derived from nano-TiO_2 application.
Successively, the second major contribute to the total damage is generated by Non-renewable energy impact category (25.68%) which is primarily affected by *uranium, in ground* (33.83%), *gas, natural, in ground* (28.12%) and *oil crude, in ground* (23.59%) emissions. For the first emission the energy consumption for heating, in particular due to the production of copper for the heat pump, is the process that produces the major environmental load (70.99%), the latter two emissions are mainly due to the electric energy system and consumption for lighting and cleaning (28.61%, in particular due to the natural gas production, and 12.59%, in particular due to the crude oil production, respectively). In Global warming (20.17%) the major contributions are mainly determined by 88.86% of *carbon dioxide*, *fossil* caused by the electric energy system and consumption for lighting and cleaning (20.61%), in particular for the use of natural gas in the electric energy production. In Radioactive Waste impact category (17.89%), the *volume occupied by low-active radioactive waste* contributes for 67.45% due to the energy consumption for heating (71.19%), where part of the electric energy mix is made by nuclear power plants. About the Carcinogens inhaled impact category the damage is totally due to the releases in air of 3.6E-04kg of *particulates, < 100 nm inhaled* by human especially during the use phase of nano-TiO_2 coated float glass which constitutes the external part of double-pane windows installed in the building. No contributes on Nano-TiO_2 ecotoxicity in freshwater and Nano-TiO_2 carcinogens in freshwater impact categories have been assessed since no TiO_2 nanoparticles releases in water occur. In Respiratory organics (4.14E-3%) the main environmental load is caused by 891.2% of *NMVOC* emission in air, in particular due to transport process (72.32%). In this category the damage is reduced by -2498.19 kg of *Toluene* (VOC) emissions concentration derived from the benefit of nano-TiO_2 application, in particular thanks to -106.69% of nano-TiO_2 coated float glass installation in doors and windows process.
In Respiratory inorganics indoor benefit category the environmental advantage is equal to -0.009134% thanks to the reduction of -0.002354 kg of *Nitrogen dioxide indoor* concentration, due to 100% of nano-TiO_2 polyurea resin on aluminum panel applied into meeting room.
In Non-carcinogens indoor benefit category the environmental advantage is equal to -8.18E-4% thanks to the reduction of -3.5159 CFU/pers of *E. Coli* concentration, determined by 100% of nano-TiO_2 polyurea resin on aluminum panel applied into meeting room.
In Cultural value of building "impact" category the environmental advantage is equal -3.18E-2%, derived from 57.93% of *Hystorical evidence*, 38.62% of *Aesthetic value* and for 3.46% of *Age of building*, as reported in Figure 11.8

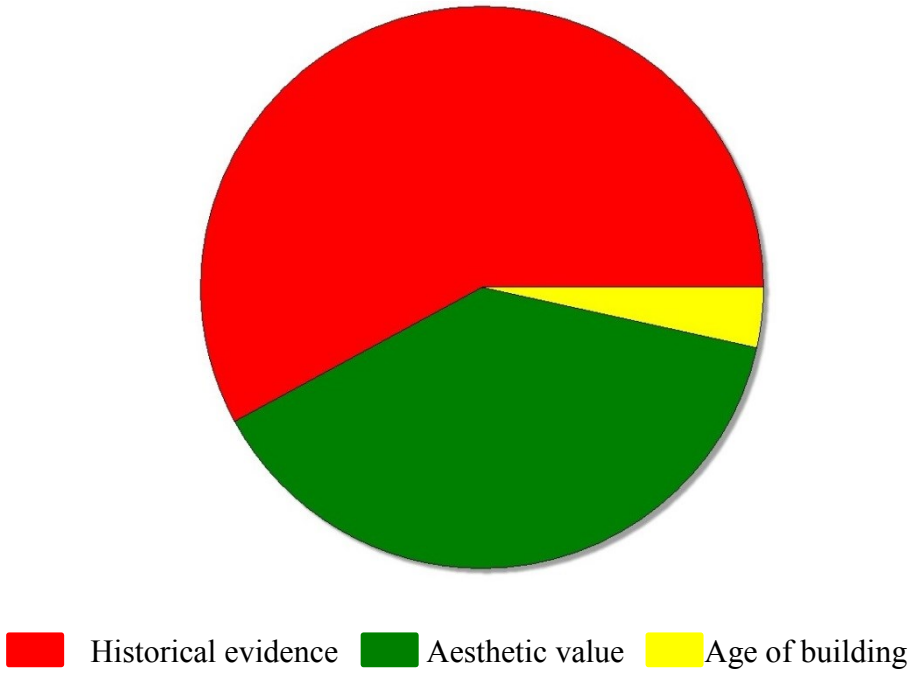


Figure 11-8 The contributes of Cultural value of building's sustances on 1 p of the refurbishment of Fiorano Modenese's Town hall

In Human well-being "impact" category the environmental advantage is equal to -9.7E-3% and is totally caused by 100% of *Institutional relations*. In Function the environmental advantage is equal to -6.03E-2% wholly due to 100% of *Public building*. In Urban value the environmental advantage is equal to -8.6E-2% and is generated by 100% of B*uilding location inside the urban center*.

Table 48 LCIA results at end-point level of 1 p of the refurbishment of Fiorano Modenese's Town hall

Damage category	Unit	Total	LCA of the refurbishment of Fiorano Modenese's Town hall	Floors	Vertical walls	Roofing	Doors and windows	Lift, staircase and ramps	Waste collection system	Cleaning	Water network and consumption	Electronic equipment
Human health	DALY	2,435	-	7,14E-1	3,87E-2	2,79E-3	2,10E-2	5,73E-2	1,55E-2	1,39E-1	6,17E-2	2,42E-1
Ecosystem quality	PDF*m2*yr	1055196	3,96E+4	5,14E+4	8,65E+3	7,46E+3	1,31E+4	2,43E+4	1,01E+4	1,73E+5	6,11E+4	1,11E+5
Climate change	kg CO2 eq	2319647,7	-	1,11E+5	7,56E+4	5,20E+3	7,48E+4	3,21E+4	3,31E+4	1,53E+5	6,68E+4	3,22E+5
Resources	MJ primary	45762653	-	1,9E+6	9,56E+5	6,48E+4	1,31E+6	1,02E+6	5,80E+5	2,2E+6	1,39E+6	3,75E+6
Renewable energy	MJ	21872490	-	5,73E+5	9,36E+4	1,17E+5	1,95E+5	1,04E+5	4,74E+4	1,45E+6	1,31E+5	3,24E+5
Maintenance of cultural assets	p	-1,036	-1,04	-	-	-	-	-	-	-	-	-
Human well-being	p	-0,8	-8,00E-1	-	-	-	-	-	-	-	-	-
Function	p	-0,7	-7,00E-1	-	-	-	-	-	-	-	-	-
Maintenance of the urban fabric	p	-1	-1	-	-	-	-	-	-	-	-	-
Radioactive waste	kg	207,85	-	3,99	1,34	1,22E-1	1,62	9,45E-1	4,62E-1	4,04	6,00E+00	1,38E+1
Carcinogens inhaled	DALY	1,99E-3	-	-	2,99E-4	-	1,70E-3	-	-	-	-	-
Respiratory inorganics indoor	DALY	-7,52E-4	-	-	-7,53E-4	-	-	-	-	-	-	-
Non-carcinogens indoor	DALY	-6,743E-5	-	-	-6,74E-5	-	-	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	PAF*m3*day	-	-	-	-	-	-	-	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	DALY	-	-	-	-	-	-	-	-	-	-	-

Damage category	Unit	Total	Furninshing	Energy consumption for heating	Heating system	Energy consumption for air-conditioning	Air-conditioning system	Transport	Electric energy consumption for eletronic equipment	End of life	Electric energy system and consumption for lighting and cleaning

Human health	DALY	2,435	1,19E-2	3,08E-1	2,15E-2	5,35E-3	1,27E-1	3,36E-1	1,93E-2	6,31E-2	2,51E-1
Ecosystem quality	PDF*m2*yr	1055196	7,52E+4	2,01E+5	7,01E+3	3,50E+3	4,65E+4	1,05E+5	7,81E+3	6,69E+3	1,02E+5
Climate change	kg CO2 eq	2319647,7	8,01E+3	2,99E+5	2,69E+4	5,19E+3	1,96E+5	3,91E+5	3,43E+4	4,90E+4	4,37E+5
Resources	MJ primary	45762653	1,66E+5	1,43E+7	4,37E+5	2,48E+5	3,16E+6	6,36E+6	5,54E+5	3,16E+5	7,07E+6
Renewable energy	MJ	21872490	6,36E+5	1,68E+7	3,52E+4	2,92E+5	2,72E+5	1,41E+5	4,86E+4	8,20E+3	6,19E+5
Maintenance of cultural assets	p	-1,036	-	-	-	-	-	-	-	-	-
Human well-being	p	-0,8	-	-	-	-	-	-	-	-	-
Function	p	-0,7	-	-	-	-	-	-	-	-	-
Maintenance of the urban fabric	p	-1	-	-	-	-	-	-	-	-	-
Radioactive waste	kg	207,85	4,96E-1	1,46E+2	6,90E-1	2,54	5,02	7,84	8,75E-1	5,79E-1	1,12E+1
Carcinogens inhaled	DALY	1,99E-3	-	-	-	-	-	-	-	-	-
Respiratory inorganics indoor	DALY	-7,52E-4	-	-	-	-	-	-	-	-	-
Non-carcinogens indoor	DALY	-6,743E-05	-	-	-	-	-	-	-	-	-
Nano-TiO_2 ecotoxicity in freshwater	PAF*m3*day	-	-	-	-	-	-	-	-	-	-
Nano-TiO_2 carcinogens in freshwater	DALY	-	-	-	-	-	-	-	-	-	-

The endpoint analysis highlights (Table 48 and Figure 11.7) that the total damage is affected by 29.56% to Human Health (343.37 Pt), 25.92% to Resources (301.12 Pt), 20.17% to Climate Change (234.28 Pt), 17.87% to Radioactive waste (207.85 Pt), 6.63% to Ecosystem Quality (77.03 Pt) and 0.0243% to Carcinogens inhaled (0.282 Pt). Moreover, the total damage is reduced by -8.18E-4% to Non-carcinogens indoor (-9.5E-3 Pt), -9.13E-3% to Respiratory inorganics indoor (-0.106 Pt) – environmental benefits derived from nano-TiO_2 applications –, -9.7E-3% to the Human well-being (-0.113 Pt), -3.18E-2% to Maintenance of cultural assets (-0.37 Pt), -6.02E-2% to Function (-0.7 Pt) and 8.61E-2% to Maintenance of the urban fabric (-1 Pt) – positive contributes resulted from social, cultural and historical aspects –.

11.2.5.2 ***USEtox^{TM} modified method***

The results of the analysis performed by a LCIA mid-point method and reported in Figure 11.9 and Table 49 show that the phases of the analyzed life cycle with the highest environmental loads are both the energy consumption for heating and electronic equipment. In particular, they contribute for:

- 23.76% and 21.53% respectively in Human toxicity, cancer;
- 27% and 27.43% respectively in Human toxicity, non-cancer;
- 22.5% and 21.73% respectively in Ecotoxicity.

The total damage of Human toxicity, cancer and Ecotoxicity impact categories is mainly due to *Chromium VI* in water (89.18% and 78.63% respectively), which is caused by the electronic equipment (23.88%). Successively, in Human toxicity, non-cancer, *Barium* in water generates major environmental load (33.26%), in particular affected by the energy consumption for heating (23.43%).

Nano-TiO_2 emissions inhaled by human (*particulates, < 100 nm inhaled*) (3.6E-4 kg) affect Human toxicity, cancer, indoor and Human toxicity, non-cancer, indoor impact categories, in particular for door and windows process (85.06%), mainly due to the use phase of nano-TiO_2 coated float glass.

Regarding nano-TiO_2 emissions released in air (*particulates, < 100 nm in air*) (6.1 kg) affect Human toxicity, cancer for 4.7E-2% and Human toxicity, non-cancer for 9.9E-3%; in particular for door and windows process (99.9%), mainly due to the use phase of nano-TiO_2 coated float glass.

For social, cultural and historical aspects, the same considerations and results obtained with *IMPACT 2002+* modified method.

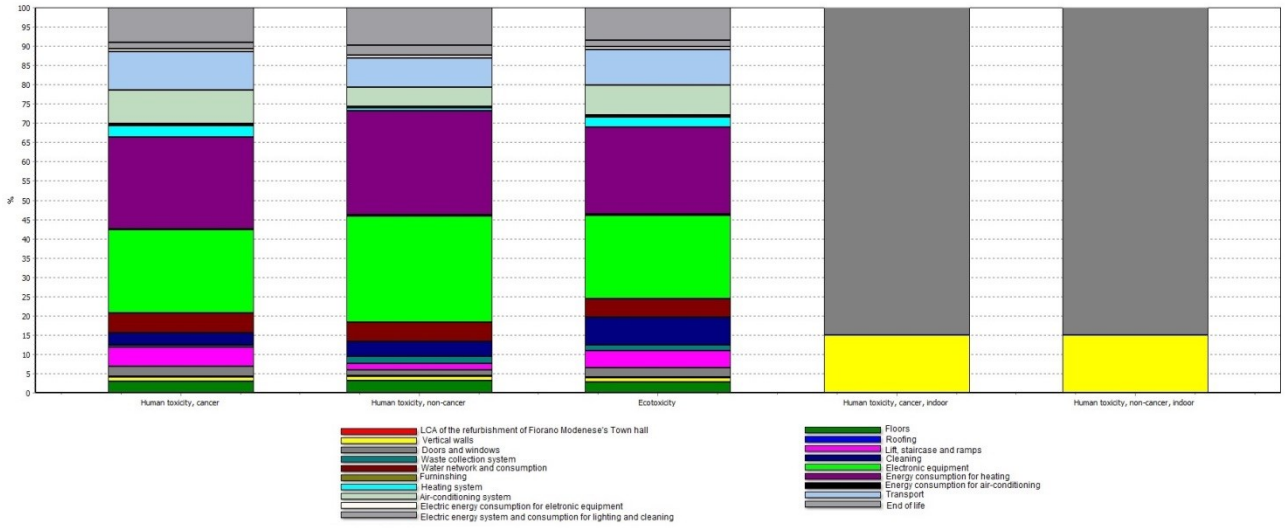


Figure 11-9 Evaluation by impact categories of 1 p of the refurbishment of Fiorano Modenese's Town hall

Table 49 Characterized LCIA results of 1 p of the refurbishment of Fiorano Modenese's Town hall

Impact category	Unit	Total	Floors	Vertical walls	Roofing	Doors and windows	Lift, staircase and ramps	Waste collection system	Cleaning	Water network and consumption	Electronic equipment
Human toxicity, cancer	CTUh[#]	2,04E-01	6,15E-03	2,33E-03	1,74E-04	5,26E-03	1,02E-02	9,94E-04	6,46E-03	1,06E-02	4,39E-02
Human toxicity, non-cancer	CTUh	1,15E-02	3,58E-04	1,39E-04	1,01E-05	1,75E-04	1,80E-04	2,18E-04	4,47E-04	5,74E-04	3,15E-03
Ecotoxicity	CTUe[§]	2,29E+06	6,51E+04	2,47E+04	1,83E+03	5,51E+04	1,03E+05	3,27E+04	1,64E+05	1,11E+05	4,98E+05
Human toxicity, cancer, indoor	CTUh	2,13E-07		3,19E-08		1,81E-07					
Human toxicity, non-cancer, indoor	CTUh	2,53E-09		3,79E-10		2,15E-09					
Impact category	Unit	Total	Furninshing	Energy consumption for heating	Heating system	Energy consumption for air-conditioning	Air-conditioning system	Transport	Electric energy consumption for electronic equipment	End of life	Electric energy system and consumption for lighting and cleaning
Human toxicity, cancer	CTUh[#]	2,04E-01	7,01E-04	4,84E-02	6,20E-03	8,42E-04	1,78E-02	2,04E-02	1,42E-03	3,49E-03	1,85E-02
Human toxicity, non-cancer	CTUh	1,15E-02	3,88E-05	3,10E-03	8,80E-05	5,38E-05	5,71E-04	8,67E-04	8,45E-05	2,92E-04	1,12E-03
Ecotoxicity	CTUe[§]	2,29E+06	7,31E+03	5,15E+05	6,23E+04	8,95E+03	1,82E+05	2,12E+05	1,50E+04	3,67E+04	1,96E+05
Human toxicity, cancer, indoor	CTUh	2,13E-07									
Human toxicity, non-cancer, indoor	CTUh	2,53E-09									
# CTUh = cases/$kg_{emitted;}$ § CTUe = PAF*m^3*yr											

11.2.6 Sensitivity analysis

11.2.6.1 *Comparison of the refurbishment of Fiorano Modenese's Town hall and the only restoration operations*

In order to evaluate the environmental damage delimited to the only restoration operations, the LCA of the only refurbishment process has been carried out. In particular, this LCA take into account only the new materials and components added during this phase and their end of life treatment.

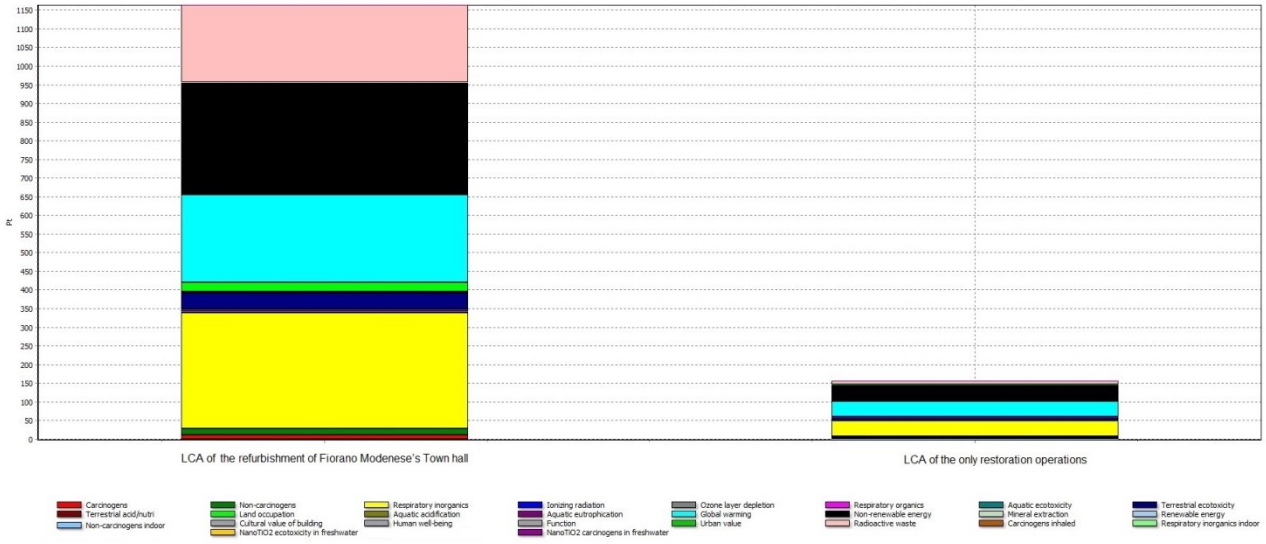


Figure 11-10 Environmental comparison of the refurbishment of Fiorano Modenese's Town hall and the only restoration operations.

The impact assessment (Figure 11.10), using *IMPACT 2002+* modified method, displays that the total damage due to the only restoration operations (156.25 Pt) represent 13.45% of the entire refurbishment of Fiorano Modenese's Town hall (1161.63 Pt). The environmental damage of the LCA of the only restoration operations is mainly caused by 42.89% to the air-conditioning system, 20.59% to the heat pump (used in winter), 12.49% to the elevator, 11.45% to doors and windows and 4.05% to end of life treatment.

11.2.6.2 *Comparison of three different scenario of the end of life treatment of nano-TiO_2 coated float glass installed in the refurbishment of Fiorano Modenese's Town hall*

The impact assessment (Figure 11.11), adopting *IMPACT 2002+* modified method, shows that the maximum damage is due to Scenario 1 (1178.78 Pt), the minimum one is due to Scenario 2 (1150.78Pt).

Figure 11-11 Environmental comparison of three different scenario of the end of life treatment of nano-TiO_2 coated float glass installed in the refurbishment of Fiorano Modenese's Town hall

In Scenario 1 the advantage of having a double-glazing functionalized does not balance the damage due to the increasing use of new materials (every 10 years the nano-functionalized external glass has to substitute with a new one). The Scenario 2 is the case that performs a minimum impact, since considers that for the entire the lifetime of the double-glazing no substitutions of functionalized glass have been made. Instead, in the Scenario 3 (1161.63 Pt), the total damage increases – compared to the total damage obtained from Scenario 2 – since four re-functionalization in 50 years and the inertization process as final end of life treatment have been considered.

11.2.7 Conclusions

Taking into consideration the environmental assessment results of the LCA of the refurbishment of Fiorano Modenese's Town hall and the sensitivity analysis results, the following conclusions can be drafted:

- *Impact 2002+* modified method: the single score damage is 1161.63 Pt and the energy consumption for heating is the contribution which are mainly responsible for the total damage (28.28%), followed by transports (12.42%), electric energy consumption for lighting and cleaning (12.45%), and floors (11.36%), electronic equipment (9.76%). The endpoint analysis highlights that the total damage is mainly affected by 29.56% to Human Health, 25.92% to Resources, 20.17% to Climate Change, 17.87% to Radioactive waste.
  Moreover, the total damage is reduced by the environmental benefits derived from nano-TiO_2 applications: -8.18E-4% to Non-carcinogens indoor, -9.13E-3% to Respiratory inorganics indoor and by the decrease in concentration of NOx (in Respiratory inorganics) and Toluene (VOcs) emissions (in Respiratory organics). Again, a positive contributes resulted from social, cultural and historical aspects: -9.7E-3% to the Human well-being, -3.18E-2% to Maintenance of cultural assets, -6.02E-2% to Function and 8.61E-2% to Maintenance of the urban fabric.
- *USEtox*^{TM} modified method: the highest environmental loads are both the energy consumption for heating and electronic equipment. In particular, they contribute for:
  - 23.76% and 21.53% respectively in Human toxicity, cancer;
  - 27% and 27.43% respectively in Human toxicity, non-cancer;

- 22.5% and 21.73% respectively in Ecotoxicity.

Door and windows process affects both Human toxicity, cancer, indoor and Human toxicity, non-cancer, indoor impact categories, for 85.06%, mainly due to the use phase of nano-TiO_2 coated float glass, where 3.6E-4 kg of nano-TiO_2 emissions have been inhaled by human. Regarding 6.1 kg of nano-TiO_2 emissions released in air, they affect Human toxicity, cancer for 4.7E-2% and Human toxicity, non-cancer for 9.9E-3%; in particular in door and windows process (99.9%), mainly due to the use phase of nano-TiO_2 coated float glass.

- Sensitivity analysis performed with *Impact 2002+* modified method:
  - the total damage due to the only restoration operations (156.25 Pt) represent 13.45% of the entire refurbishment of Fiorano Modenese's Town hall (1161.63 Pt). The environmental damage of the LCA of the only restoration operations is mainly caused by 42.89% to the air-conditioning system, 20.59% to the heat pump (used in winter), 12.49% to the elevator, 11.45% to doors and windows and 4.05% to end of life treatment.
  - the impact assessment of three different scenario of the end of life treatment of nano-TiO_2 coated float glass installed in the refurbishment of Fiorano Modenese's Town hall shows that the maximum damage is due to Scenario 1 (1178.78 Pt), which considers glass and nano-TiO_2 coating having the same lifetime (10 years). The minimum one is due to Scenario 2 (1150.78Pt), which evaluates the glass lifetime of 50 years and the nanocoating lifetime of 10 years and a linear decrease of benefits derived from nano-TiO_2 application and a complete release of nano-TiO_2 emissions during the following 40 years. On the contrary, Scenario 3 adopted in the whole LCA of the refurbishment of Fiorano Modenese's Town hall – considers the glass lifetime of 50 years and the nanocoating lifetime of 10 years (four re-functionalization process have been taken into account) and the total damage slightly increases compared to Scenario 2 being equal to 1161.63 Pt. Furthermore, for the first and third scenario the inertization process has been take into account as end of life treatment, and for the second one the recycling treatment has been considered.

Acknowledgement

I would like to acknowledge Eng. Simona Marinelli from Marche Polytechnic University for the scientific support and the technical office personnel of Fiorano Modenese's Town hall.

ANNEX I

ATTUALE PIANO TERRA
URP – ECONOMATO – CED – ANAGRAFE – PROTOCOLLO
Ufficio protocollo
da collocarsi in prossimità dell'ingresso, in maniera da essere immediatamente individuabile dai cittadini.
Spazi
Postazioni di lavoro 2 + 1 (2 impiegati + 1 messo)
Minuto archivio in cui collocare i documenti in attesa di essere smistati e ritirati
URP
Da collocarsi immediatamente all'ingresso assegnandovi anche la funzione di reception, valutare se in corrispondenza dell'URP collocare anche la postazione del centralinista (generalmente non vedente)
Spazi
Postazioni di lavoro 2 + 1 (2 impiegati + 1 postazione accessoria eventuale)
Economato
Valutare la possibilità di avvicinarlo ai servizi finanziari (ragioneria), minimo ampliamento del magazzino attuale, garantendone l'accessibilità diretta dall'esterno per il carico e scarico del materiale, individuazione di n. 2 ripostigli per lo stoccaggio del materiale per le pulizie.
Spazi
Postazioni di lavoro 2 + 1 (2 impiegati + 1 responsabile)
Magazzino per stoccaggio materiale corrente.
CED
Necessità di mantenere la sala macchine nella collocazione attuale, valutare la possibilità di creare un modesto magazzino per lo stoccaggio delle attrezzature, garantire una buona accessibilità dall'esterno per operazioni di carico e scarico.
Spazi
Postazioni di lavoro 2 + 2 (2 impiegati + 2 personale esterno)
Minuto magazzino per custodia materiale
ANAGRAFE
Spazio attuale non sufficiente e molto mal organizzato.
Servizio autonomo ed indipendente che non necessità di un collegamento diretto con gli altri servizi comunali. Si è già ipotizzato di portare questo servizio fuori dalla sede municipale
Necessita di:

- spazio di attesa dotato di sedute e di elimina code;
- spazio per la ricezione del pubblico per servizi brevi – veloci, 2 operatori in contemporanea ed utenza che attende l'erogazione del servizio in piedi, operatore separato dall'utente da vetro di sicurezza
- spazio per la ricezione del pubblico per servizi lenti , 1 o 2 operatori in contemporanea possibilità per l'utenza di sedersi, ambienti separati
- spazio per la ricezione del pubblico per servizi lentissimi, 1 operatore in ambiente separato con possibilità di sedersi per l'utenza
- Back office separato dagli altri ambienti di ricezione del pubblico, ambiente di lavoro con 2 o 3 postazioni
- Ufficio responsabile separato dagli altri ambienti
- Collocazione di n. 5 archivi rotanti

- Cassaforte
- Armadio corazzato – blindato
- N. 2 PC dedicati al collegamento permanente con il ministero dell'interno
- Accesso diretto del pubblico, senza costringere l'utenza a passare per altri ambienti
- N. 6/7 operatori complessivi
- Doppio accesso, uno per il pubblico e l'altro per il personale

ATTUALE PIANO PRIMO
UFFICIO SINDACO – SEGRETERIA DEL SIANDACO – SALA GIUNTA – SEGRETERIA GENERALE – SEGRETARIO GENERALE – VICE SEGRETARIO GENERALE – TRIBUTI – UFFICIO VICE SINDACO – CONTRATTI
Ufficio tributi
da collocarsi in prossimità dell'ufficio ragioneria – servizi finanziari, favorendo la comunicazione diretta tra i due servizi, valutare la possibilità di collocarlo al piano terra.
Postazioni di lavoro 2 + 1 (2 impiegati + 1 responsabile)
Archivio, dimensione imprecisata, quantificabile dopo il primo anno di esercizio IMU.
Ufficio Sindaco
Ufficio di rappresentanza, facilmente raggiungibile, ma non direttamente dall'utenza, spazio per accogliere più persone contemporaneamente e tavolo per piccolo riunioni.
Ufficio Segreteria Sindaco
Ufficio per n. 1 persona, ubicato adiacente all'ufficio del sindaco, con funzione di filtro – accoglienza.
Ufficio vice sindaco – assessori
Valutare la possibilità di ricavare alcuni uffici per vice sindaco ed assessori, anche se questa richiesta non è indispensabile soddisfarla.
Ufficio segreteria generale
Open space da collocarsi in prossimità dell'ufficio del segretario e vice segretario
Postazioni di lavoro 2 + 1 (2 impiegati + 1 responsabile)
Archivio, dimensione imprecisata
Sala Giunta
Attuale piccola e poco illuminata, garantire la possibilità di effettuare riunioni con un numero di almeno 10/12 persone, da individuare come ambiente di rappresentanza che permetta la possibilità di fruire di:
- punti di accesso alla rete informatica per ogni persona presente
- possibilità di utilizzare audiovisivi

Ufficio Segretario Generale e Ufficio Vice Segretario Generale
Due uffici vicini ma separati, l'ufficio del segretario generale sarà più piccolo di quello del vice, poiché la maggior parte del lavoro e la maggior presenza viene garantita dal vice segretario.
Postazioni di lavoro 1 per ufficio, possibilità di ricevere pubblico seduto.
Uffici a carattere anche di rappresentanza.
Ufficio contratti
Ufficio da collocarsi in prossimità della segreteria generale, ma separato dagli altri ambienti per questioni di riservatezza, possibilità di ricevere pubblico seduto
Postazioni di lavoro 1 + 1 (1 impiegata fissa + 1 opzionale)
Archivio, dimensione imprecisata

ATTUALE PIANO SECONDO

UFFICIO RAGIONERIA – UFFICIO PERSONALE – UFFICIO STAMPA

Ufficio ragioneria

Open space con 4/5 postazioni

3 uffici separati comunicanti però direttamente con lo spazio operativo aperto, per un operatore ciascuno.

Archivio per stoccaggio documenti finanziari anno corrente ed anno precedente.

I 3 uffici separati dovranno essere previsti anche per ricevimento di pubblico seduto, uno dei 3 dovrà essere anche di rappresentanza.

Ufficio personale

Open space con 3/4 postazioni

1 ufficio separato comunicanti però direttamente con lo spazio operativo aperto, per un operatore

Archivio per stoccaggio documenti anno corrente ed anno precedente

L'ufficio separato dovrà essere previsto anche per ricevimento di pubblico seduto.

Ufficio Stampa

n. 2 uffici separati ma comunicanti per n. 1 postazione ciascuno, con possibilità d'incremento a 2 postazioni ciascuno.

Archivio

Uffici con carattere di rappresentanza.

CONSIDERAZIONI GENERALI

Aumentare la dotazione di servizi igienici prevedendo la differenziazione per:

- servizi igienici per il pubblico da localizzare al piano terra
- servizi igienici per il personale interno
- servizi igienici divisi per genere (maschi- femmine)
- servizi igienici specifici per disabili

Aumentare la dotazione di spazi da adibire a sale riunioni per riunioni fino a 8/10 persone, sfruttando questi ambienti anche come locali archivio.

Individuare uno spazio ristoro – pausa caffè in zone non direttamente accessibili dal pubblico.

Climatizzare sia per l'estate che per l'inverno tutti gli uffici.

Rendere la pillartura completamente accessibile per disabili.

Valutare la possibilità di recuperare il terrazzo del 2° piano come volume in cui ubicare uffici di rappresentanza.

Valorizzare la stanza dell'orologio.

Valutare la possibilità di inserire una stanza da destinare ai gruppi consigliari.

ANNEX II

					Area di tutte le finestre che sono in una stanza						Superfici pareti							efficiente di assorbim				PROCEDIMENTO DESCRITTO SU "APPUNTI TEMATICHE LCA"(.doc) E "Procedimento di calcolo per l'Illuminazione negli Edifici" (.pdf)																							
PIANO	LATO	N. FINESTRA	h (altezza)	l (larghezza)	Afinestra	Afinistretot	N. STANZA	h (altezza)	la (larghezza)	lu (lunghezza)	Aovest	Asud	Aest	Anord	Asof	Apav	Astanzatot	aparint	asof	apav	p=spessore Vano finestra	h/p	l/p	L0	H	hcentrofin	(H-h)/L0	ε Fig.19.2	ψ Fig.19.1	τv Tab.1	τi	ρm	Dm [redacted]	Ill. esterna	Ill. naturale interna	ill interna minima	ill.artificiale interna	Indice i locale	Definizione Classe	hsoffitto	hsorgente	hpl	h	u (coeff. di utilizzazione Tab. pag 19 doc)	k (coeff. di manutenzione Tab. pag 19 doc)
		(riferimento in pianta)	[m]	[m]	m2	m2	(riferimento in pianta)	[m]	[m]	[m]	m2	m2	m2	m2	m2	m2	m2				m			m	m	m								lux	lux	lux	lux			m	m	m	m		
terra	sud	f1	0,94	1,48	1,3912	3,608	0,8a e 0,8 b	2,96	4,3	5,75	17,02	12,728	17,02	12,728	24,725	24,725	108,946	0,2	0,2	0,6	0,3	3,13	4,93	3,00	10,00	2,00	2,67	0,07	0,90	0,60	0,54	0,29	0,00387	12000,00	46,50	350,00	303,50	1,32	G	2,96	0,30	0,80	1,86	0,40	0,70
terra	sud	f4	0,94	1,48	1,3912	1,3912	0,16a	2,76	5	6,5	17,94	13,8	17,94	13,8	32,5	32,5	128,48	0,2	0,2	0,6	0,3	3,13	4,93	3,00	10,00	2,00	2,67	0,07	0,90	0,60	0,54	0,30	0,00122	12000,00	14,68	350,00	111,78	1,70	F	2,76	0,30	0,80	1,66	0,42	0,70
terra	sud	f2	0,94	1,64	1,5416	1,5416	0,9	2,94	4,2	5,9	17,346	12,348	17,346	12,348	24,78	24,78	108,948	0,2	0,2	0,6	0,3	3,13	5,47	3,00	10,00	2,00	2,67	0,07	0,90	0,60	0,54	0,29	0,00165	12000,00	19,85	350,00	330,15	1,33	G	2,94	0,30	0,80	1,84	0,40	0,70
terra	sud	f3	0,94	1,64	1,5416	1,5416	0,19	2,73	3,2	6,2	16,926	8,736	16,926	8,736	19,84	19,84	91,004	0,2	0,2	0,6	0,3	3,13	5,47	3,00	10,00	2,00	2,67	0,07	0,90	0,60	0,54	0,29	0,00201	12000,00	24,08	350,00	325,92	1,29	G	2,73	0,30	0,80	1,63	0,40	0,70
terra	est	f5	0,94	1,64	1,5416	1,5416	0,16a	2,76	5	6,5	17,94	13,8	17,94	13,8	32,5	32,5	128,48	0,2	0,2	0,6	0,3	3,13	5,47	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,30	0,00813	12000,00	97,58			1,70	F	2,76	0,30	0,80	1,66	0,42	0,70
terra	est	f6	0,60	1,64	0,984	0,984	0,16a	2,76	5	6,5	17,94	13,8	17,94	13,8	32,5	32,5	128,48	0,2	0,2	0,6	0,3	2,00	5,47	50,00	10,00	2,00	0,16	0,42	0,91	0,60	0,54	0,30	0,00525	12000,00	62,98			1,70	F	2,76	0,30	0,80	1,66	0,42	0,70
terra	est	f7	0,60	1,64	0,984	0,984	0,16a	2,76	5	6,5	17,94	13,8	17,94	13,8	32,5	32,5	128,48	0,2	0,2	0,6	0,3	2,00	5,47	50,00	10,00	2,00	0,16	0,42	0,91	0,60	0,54	0,30	0,00525	12000,00	62,98			1,70	F	2,76	0,30	0,80	1,66	0,42	0,70
terra	est	f8	0,94	1,64	1,5416	1,5416	0,16b	2,76	5,4	3,7	10,212	14,904	10,212	14,904	19,98	19,98	90,192	0,2	0,2	0,6	0,3	3,13	5,47	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,29	0,01209	12000,00	145,06	350,00	204,94	1,32	G	2,76	0,30	0,80	1,66	0,40	0,70
terra	est	PORTA ingresso	2,60	3,6	9,36	9,36	0,17	2,85	4,9	4,3	12,255	13,965	12,255	13,965	21,07	21,07	94,58	0,2	0,2	0,6	0,3	8,67	12,00	50,00	10,00	1,30	0,17	0,42	0,98	0,60	0,54	0,29	0,07608	12000,00	912,99	150,00	-762,99	2,18	E	2,85	0,30	1,50	1,05	0,46	0,70
terra	est	f9	0,96	1,63	1,5648	4,5504	0,5	2,89	3,8	5,6	16,184	10,982	16,184	10,982	21,28	21,28	96,892	0,2	0,2	0,6	0,3	3,20	5,43	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,29	0,03330	12000,00	399,63	350,00	-49,63	1,26	G	2,89	0,30	0,80	1,79	0,40	0,70
terra	est	f10	0,96	1,63	1,5648		0,5	2,89	3,8	5,6	16,184	10,982	16,184	10,982	21,28	21,28	96,892	0,2	0,2	0,6	0,3	3,20	5,43	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,29		12000,00				1,26	G	2,89	0,30	0,80	1,79	0,40	0,70
terra	nord	f11	0,96	1,48	1,4208		0,5	2,89	3,8	5,6	16,184	10,982	16,184	10,982	21,28	21,28	96,892	0,2	0,2	0,6	0,3	3,20	4,93	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,29		12000,00				1,26	G	2,89	0,30	0,80	1,79	0,40	0,70
terra	nord	f12	0,96	1,48	1,4208	1,4208	0,4	2,87	3,7	4	11,48	10,619	11,48	10,619	14,8	14,8	73,798	0,2	0,2	0,6	0,3	3,20	4,93	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,28	0,01402	12000,00	168,29	350,00	181,71	1,09	H	2,87	0,30	0,80	1,77	0,37	0,70
terra	nord	f13	0,90	1,46	1,314	1,314	0,1	2,85	2,5	3,4	9,69	7,125	9,69	7,125	8,5	8,5	50,63	0,2	0,2	0,6	0,3	3,00	4,87	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,27	0,01983	12000,00	237,95	350,00	112,05	0,82	I	2,85	0,30	0,80	1,75	0,32	0,70
terra	nord	f16	0,60	1,5	0,9	0,9	0,6	2,89	6	4,1	11,849	17,34	11,849	17,34	24,6	24,6	107,578	0,2	0,2	0,6	0,3	2,00	5,00	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,29	0,00586	12000,00	70,31	350,00	186,26	1,36	G	2,89	0,30	0,80	1,79	0,40	0,70
terra	nord	f17	0,60	1,5	0,9	0,9	0,6	2,89	6	4,1	11,849	17,34	11,849	17,34	24,6	24,6	107,578	0,2	0,2	0,6	0,3	2,00	5,00	50,00	10,00	2,00	0,16	0,42	0,90	0,60	0,54	0,29	0,00586	12000,00	70,31			1,36	G	2,89	0,30	0,80	1,79	0,40	0,70
terra	ovest	f18	1,20	1,48	1,776	1,776	0,6	2,89	6	4,1	11,849	17,34	11,849	17,34	24,6	24,6	107,578	0,2	0,2	0,6	0,3	4,00	4,93	3,00	10,00	2,00	2,67	0,07	0,90	0,60	0,54	0,29	0,00193	12000,00	23,12			1,36	G	2,89	0,30	0,80	1,79	0,40	0,70
terra	ovest	f19	1,20	1,48	1,776	1,776	0,15	2,85	6	1,9	5,415	17,1	5,415	17,1	11,4	11,4	67,83	0,2	0,2	0,6	0,3	4,00	4,93	3,00	10,00	2,00	2,67	0,07	0,90	0,60	0,54	0,27	0,00333	12000,00	40,00	350,00	310,00	0,82	I	2,85	0,30	0,80	1,75	0,32	0,70
terra	ovest	f20	0,72	0,92	0,6624	0,6624	0,18	2,9	5,4	1,9	5,51	15,66	5,51	15,66	10,26	10,26	62,86	0,2	0,2	0,6	0,3	2,40	3,07	3,00	10,00	2,00	2,67	0,07	0,82	0,60	0,54	0,27	0,00123	12000,00	14,77	350,00	335,23	0,78	I	2,90	0,30	0,80	1,80	0,32	0,70
terra	ovest	f21	1,22	0,63	0,7686	0,7686	0,11 e 0,11a	2,72	5,4	2,3	6,256	14,688	6,256	14,688	12,42	12,42	66,728	0,2	0,2	0,6	0,3	4,07	2,10	3,00	10,00	2,00	2,67	0,07	0,71	0,60	0,54	0,27	0,00113	12000,00	13,52	350,00	336,48	1,00	H	2,72	0,30	0,80	1,62	0,37	0,70
terra	ovest	f22 PORTA	0,9004443	0,900444335	0,8108	0,8108	0,10	2,82	5,3	2	5,64	14,946	5,64	14,946	10,6	10,6	62,372	0,2	0,2	0,6	0,3	3,00	3,00	3,00	10,00	2,00	2,67	0,07	0,82	0,60	0,54	0,27	0,00150	12000,00	18,04	350,00	331,96	0,84	I	2,82	0,30	0,80	1,72	0,32	0,70
terra	ovest	f23 PORTA	0,9004443	0,900444335	0,8108	0,8108	0,8a e 0,8 b	2,96	4,3	5,75	17,02	12,728	17,02	12,728	24,725	24,725	108,946	0,2	0,2	0,6	0,3	3,00	3,00	3,00	10,00	2,00	2,67	0,07	0,82	0,60	0,54	0,29	0,00079	12000,00	9,52	350,00	340,48	1,32	G	2,96	0,30	0,80	1,86	0,40	0,70
terra	ovest	f24	0,95	1,48	1,406		0,8a e 0,8 b	2,96	4,3	5,75	17,02	12,728	17,02	12,728	24,725	24,725	108,946	0,2	0,2	0,6	0,3	3,17	4,93	3,00	10,00	2,00	2,67	0,07	0,90	0,60	0,54	0,29	0,00000	12000,00	0,00	350,00	350,00	1,32	G	2,96	0,30	0,80	1,86	0,40	0,70
primo	sud	f25	0,95	1,83	1,7385	5,2155	1,12	3,33	4,5	6	19,98	14,985	19,98	14,985	27	27	123,93	0,2	0,2	0,6	0,3	3,17	6,10	3,00	10,00	5,00	1,67	0,08	0,92	0,60	0,54	0,29	0,00582	12000,00	69,90	350,00	280,10	1,15	G	3,33	0,30	0,80	2,23	0,40	0,70
primo	sud	f26	0,95	1,83	1,7385	1,7385	1,13	3,3	4,2	4,5	14,85	13,86	14,85	13,86	18,9	18,9	95,22	0,2	0,2	0,6	0,3	3,17	6,10	3,00	10,00	5,00	1,67	0,08	0,92	0,60	0,54	0,28	0,00260	12000,00	31,17	350,00	318,83	0,99	H	3,30	0,30	0,80	2,20	0,37	0,70
primo	sud	f27	0,95	1,83	1,7385	1,7385	1,14	3,3	3,4	4,8	15,84	11,22	15,84	11,22	16,32	16,32	86,76	0,2	0,2	0,6	0,3	3,17	6,10	3,00	10,00	5,00	1,67	0,08	0,92	0,60	0,54	0,28	0,00289	12000,00	34,72	350,00	315,28	0,90	H	3,30	0,30	0,80	2,20	0,37	0,70
primo	sud	f28	0,95	1,83	1,7385	1,7385	1,15	3,29	5,1	6,4	21,056	16,779	21,056	16,779	32,64	32,64	140,95	0,2	0,2	0,6	0,3	3,17	6,10	3,00	10,00	5,00	1,67	0,08	0,92	0,60	0,54	0,29	0,00168	12000,00	20,10	350,00	91,66	1,30	G	3,29	0,30	0,80	2,19	0,40	0,70
primo	est	f29	0,95	1,83	1,7385	1,7385	1,15	3,1	5,1	6,4	19,84	15,81	19,84	15,81	32,64	32,64	136,58	0,2	0,2	0,6	0,3	3,17	6,10	50,00	10,00	5,00	0,10	0,42	0,92	0,60	0,54	0,30	0,00899	12000,00	107,82	350,00		1,42	F	3,10	0,30	0,80	2,00	0,42	0,70
primo	est	f30	0,60	1,83	1,098	1,098	1,15	3,29	5,1	6,4	21,056	16,779	21,056	16,779	32,64	32,64	140,95	0,2	0,2	0,6	0,3	2,00	6,10	50,00	10,00	5,00	0,10	0,42	0,90	0,60	0,54	0,29	0,00543	12000,00	65,21	350,00		1,30	G	3,29	0,30	0,80	2,19	0,40	0,70
primo	est	f31	0,60	1,83	1,098	1,098	1,15	3,29	5,1	6,4	21,056	16,779	21,056	16,779	32,64	32,64	140,95	0,2	0,2	0,6	0,3	2,00	6,10	50,00	10,00	5,00	0,10	0,42	0,90	0,60	0,54	0,29	0,00543	12000,00	65,21	350,00		1,30	G	3,29	0,30	0,80	2,19	0,40	0,70
primo	est	f32	0,95	1,83	1,7385	1,7385	1,16	3,27	5,5	3,4	11,118	17,985	11,118	17,985	18,7	18,7	95,606	0,2	0,2	0,6	0,3	3,17	6,10	50,00	10,00	5,00	0,10	0,42	0,92	0,60	0,54	0,28	0,01364	12000,00	163,64	350,00	186,36	0,97	H	3,27	0,30	0,80	2,17	0,37	0,70
primo	est	f33 PORTA	1,4232357	1,42323575	2,0256	2,0256	1,18	3,39	4,35	4,35	14,7465	14,7465	14,7465	14,7465	18,9225	18,9225	96,831	0,2	0,2	0,6	0,3	4,74	4,74	50,00	10,00	5,00	0,10	0,42	0,90	0,60	0,54	0,28	0,01535	12000,00	184,20	350,00	165,80	0,95	H	3,39	0,30	0,80	2,29	0,37	0,70
primo	est	f34	0,95	1,83	1,7385	5,1972	1,20	3,43	3,9	5,6	19,208	13,377	19,208	13,377	21,84	21,84	108,85	0,2	0,2	0,6	0,3	3,17	6,10	50,00	10,00	5,00	0,10	0,42	0,92	0,60	0,54	0,28	0,03555	12000,00	426,58	350,00	-76,58	0,99	H	3,43	0,30	0,80	2,33	0,37	0,70
primo	est	f35	0,95	1,83	1,7385		1,20	3,43	3,9	5,6	19,208	13,377	19,208	13,377	21,84	21,84	108,85	0,2	0,2	0,6	0,3	3,17	6,10	50,00	10,00	5,00	0,10	0,42	0,92	0,60	0,54	0,28		12000,00				0,99	H	3,43	0,30	0,80	2,33	0,37	0,70
primo	nord	f36	0,94	1,83	1,7202		1,20	3,43	3,9	5,6	19,208	13,377	19,208	13,377	21,84	21,84	108,85	0,2	0,2	0,6	0,3	3,13	6,10	50,00	10,00	5,00	0,10	0,42	0,92	0,60	0,54	0,28		12000,00				0,99	H	3,43	0,30	0,80	2,33	0,37	0,70
primo	nord	f37	0,94	1,83	1,7202	1,7202	1,21	3,42	3,6	3,9	13,338	12,312	13,338	12,312	14,04	14,04	79,38	0,2	0,2	0,6	0,3	3,13	6,10	50,00	10,00	5,00	0,10	0,42	0,92	0,60	0,54	0,27	0,01670	12000,00	200,41	350,00	149,59	0,81	I	3,42	0,30	0,80	2,32	0,32	0,70
primo	nord	f38	0,94	1,83	1,7202	3,4404	1,22	2,95	5,1	3,7	10,915	15,045	10,915	15,045	18,87	18,87	89,66	0,2	0,2	0,6	0,3	3,13	6,10	50,00	10,00	5,00	0,10	0,42	0,92	0,60	0,54	0,28	0,02817	12000,00	338,08	350,00	11,92	1,16	G	2,95	0,30	0,80	1,85	0,36	0,70
primo	nord	f39	0,94	1,83	1,7202		1,22	2,95	5,1	3,7	10,915	15,045	10,915	15,045	18,87	18,87	89,66	0,2	0,2	0,6	0,3	3,13	6,10	50,00	10,00	5,00	0,10	0,42	0,92	0,60	0,54	0,28		12000,00	0,00	350,00	350,00	1,16	G	2,95	0,30	0,80	1,85	0,36	0,70
primo	ovest	f43	0,97	1,83	1,7751	1,7751	1,1	3,14	4,4	3,4	10,676	13,816	10,676	13,816	14,96	14,96	78,904	0,2	0,2	0,6	0,3	3,23	6,10	3,00	10,00	5,00	1,67	0,08	0,90	0,60	0,54	0,28	0,00317	12000,00	38,05	350,00	311,95	0,94	H	3,14	0,30	0,80	2,04	0,37	0,70
primo	ovest	f44	0,95	1,83	1,7385	1,7385	1,9	3,4	4	3,6	12,24	13,6	12,24	13,6	14,4	14,4	80,48	0,2	0,2	0,6	0,3	3,17	6,10	3,00	10,00	5,00	1,67	0,08	0,90	0,60	0,54	0,27	0,00309	12000,00	37,11	350,00	312,89	0,82	I	3,40	0,30	0,80	2,30	0,32	0,70
primo	ovest	f45	0,95	1,83	1,7385	1,7385	1,10	3,43	3,8	3,1	10,633	13,034	10,633	13,034	11,78	11,78	70,894	0,2	0,2	0,6	0,3	3,17	6,10	3,00	10,00	5,00	1,67	0,08	0,90	0,60	0,54	0,27	0,00358	12000,00	42,94	350,00	307,06	0,73	I	3,43	0,30	0,80	2,33	0,32	0,70
primo	ovest	f46	0,95	1,83	1,7385		1,12	3,33	4,5	6	19,98	14,985	19,98	14,985	27	27	123,93	0,2	0,2	0,6	0,3	3,17	6,10	3,00	10,00	5,00	1,67	0,08	0,90	0,60	0,54	0,29		12000,00	0,00	350,00	350,00	1,15	G	3,33	0,30	0,80	2,23	0,40	0,70
primo	ovest	f47	0,95	1,83	1,7385		1,12	3,33	4,5	6	19,98	14,985	19,98	14,985	27	27	123,93	0,2	0,2	0,6	0,3	3,17	6,10	3,00	10,00	5,00	1,67	0,08	0,90	0,60	0,54	0,29		12000,00	0,00	350,00	350,00	1,15	G	3,33	0,30	0,80	2,23	0,40	0,70
secondo	sud	f48	0,95	1,85	1,7575	5,2725	2,6	2,98	4,5	4	11,92	13,41	11,92	13,41	18	18	86,66	0,2	0,2	0,6	0,3	3,17	6,17	3,00	10,00	8,50	0,50	0,27	0,90	0,60	0,54	0,28	0,02820	12000,00	338,43	350,00	11,57	1,13	G	2,98	0,30	0,80	1,88	0,40	0,70
secondo	sud	f49	0,95	1,85	1,7575	1,7575	2,5	2,98	4,2	4,7	14,006	12,516	14,006	12,516	19,74	19,74	92,524	0,2	0,2	0,6	0,3	3,17	6,17	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,29	0,00825	12000,00	99,00	350,00	251,00	1,18	G	2,98	0,30	0,80	1,88	0,40	0,70
secondo	sud	f50	0,95	1,85	1,7575	1,7575	2,7	3,3	3,5	4,85	16,005	11,55	16,005	11,55	16,975	16,975	89,06	0,2	0,2	0,6	0,3	3,17	6,17	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,28	0,00885	12000,00	106,24	350,00	243,76	0,92	H	3,30	0,30	0,80	2,20	0,37	0,70
secondo	sud	f51	0,95	1,85	1,7575	1,7575	2,8	3,25	5,1	6,5	21,125	16,575	21,125	16,575	33,15	33,15	141,7	0,2	0,2	0,6	0,3	3,17	6,17	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,29	0,00524	12000,00	62,83	350,00	15,21	1,33	G	3,25	0,30	0,80	2,15	0,40	0,70
secondo	est	f52	0,95	1,85	1,7575	1,7575	2,8	3,25	5,1	6,5	21,125	16,575	21,125	16,575	33,15	33,15	141,7	0,2	0,2	0,6	0,3	3,17	6,17	50,00	10,00	8,50	0,03	0,50	0,85	0,60	0,54	0,29	0,00970	12000,00	116,35			1,33	G	3,25	0,30	0,80	2,15	0,40	0,70
secondo	est	f53	0,60	1,85	1,11	1,11	2,8	3,25	5,1	6,5	21,125	16,575	21,125	16,575	33,15	33,15	141,7	0,2	0,2	0,6	0,3	2,00	6,17	50,00	10,00	8,50	0,03	0,50	0,90	0,60	0,54	0,29	0,00648	12000,00	77,81			1,33	G	3,25	0,30	0,80	2,15	0,40	0,70
secondo	est	f54	0,60	1,85	1,11	1,11	2,8	3,25	5,1	6,5	21,125	16,575	21,125	16,575	33,15	33,15	141,7	0,2	0,2	0,6	0,3	2,00	6,17	50,00	10,00	8,50	0,03	0,50	0,90	0,60	0,54	0,29	0,00648	12000,00	77,81			1,33	G	3,25	0,30	0,80	2,15	0,40	0,70
secondo	est	f55	0,95	1,85	1,7575	1,7575	2,9	3,31	5,5	3,5	11,585	18,205	11,585	18,205	19,25	19,25	98,08	0,2	0,2	0,6	0,3	3,17	6,17	50,00	10,00	8,50	0,03	0,50	0,85	0,60	0,54	0,28	0,01477	12000,00	177,19	350,00	172,81	0,97	H	3,31	0,30	0,80	2,21	0,37	0,70
secondo	est	f56	0,95	1,85	1,7575	7,067	2,13	3,14	7,8	5,65	17,741	24,492	17,741	24,492	44,07	44,07	172,606	0,2	0,2	0,6	0,3	3,17	6,17	50,00	10,00	8,50	0,03	0,50	0,85	0,60	0,54	0,30	0,03110	12000,00	373,21	350,00	-23,21	1,61	F	3,14	0,30	0,80	2,04	0,42	0,70
secondo	est	f57	0,95	1,85	1,7575		2,13	3,14	7,8	5,65	17,741	24,492	17,741	24,492	44,07	44,07	172,606	0,2	0,2	0,6	0,3	3,17	6,17	50,00	10,00	8,50	0,03	0,50	0,85	0,60	0,54	0,30		12000,00	0,00	350,00	350,00	1,61	F	3,14	0,30	0,80	2,04	0,42	0,70
secondo	ovest	f58	0,97	1,85	1,7945		2,13	3,14	7,8	5,65	17,741	24,492	17,741	24,492	44,07	44,07	172,606	0,2	0,2	0,6	0,3	3,23	6,17	50,00	10,00	8,50	0,03	0,50	0,85	0,60	0,54	0,30		12000,00	0,00	350,00	350,00	1,61	F	3,14	0,30	0,80	2,04	0,42	0,70
secondo	ovest	f59	0,95	1,85	1,7575		2,13	3,14	7,8	5,65	17,741	24,492	17,741	24,492	44,07	44,07	172,606	0,2	0,2	0,6	0,3	3,17	6,17	50,00	10,00	8,50	0,03	0,50	0,85	0,60	0,54	0,30		12000,00	0,00	350,00	350,00	1,61	F	3,14	0,30	0,80	2,04	0,42	0,70
secondo	ovest	f60 corridoio dell'ascensore	1,25	1,75	2,1875	4,375	2,12	2,95	3	4,3	12,685	8,85	12,685	8,85	12,9	12,9	68,87	0,2	0,2	0,6	0,3	4,17	5,83	3,00	10,00	8,50	0,50	0,27	0,90	0,60	0,54	0,27	0,03032	12000,00	363,85	150,00	-213,85	0,96	H	2,95	0,30	0,80	1,85	0,37	0,70
secondo	ovest	f61 corridoio dell'ascensore	1,25	1,75	2,1875		2,12	2,95	3	4,3	12,685	8,85	12,685	8,85	12,9	12,9	68,87	0,2	0,2	0,6	0,3	4,17	5,83	3,00	10,00	8,50	0,50	0,27	0,90	0,60	0,54	0,27		12000,00				0,96	H	2,95	0,30	0,80	1,85	0,37	0,70
secondo	ovest	f63	0,95	1,85	1,7575	3,515	2,4	2,79	4	7	19,53	11,16	19,53	11,16	28	28	117,38	0,2	0,2	0,6	0,3	3,17	6,17	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,30	0,01256	12000,00	150,75	350,00	199,25	1,51	F	2,79	0,30	0,80	1,69	0,42	0,70
secondo	ovest	f64	0,95	1,85	1,7575		2,4	2,79	4	7	19,53	11,16	19,53	11,16	28	28	117,38	0,2	0,2	0,6	0,3	3,17	6,17	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,30	0,00000	12000,00				1,51	F	2,79	0,30	0,80	1,69	0,42	0,70
secondo	ovest	f65	0,95	1,85	1,7575	3,515	2,6	2,98	4	4,5	13,41	11,92	13,41	11,92	18	18	86,66	0,2	0,2	0,6	0,3	3,17	6,17	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,28	0,01776	12000,00	213,08	350,00	136,92	1,13	G	2,98	0,30	0,80	1,88	0,40	0,70
secondo	ovest	f66	0,95	1,85	1,7575		2,6	2,98	4	4,5	13,41	11,92	13,41	11,92	18	18	86,66	0,2	0,2	0,6	0,3	3,17	6,17	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,28	0,00000	12000,00	0,00			1,13	G	2,98	0,30	0,80	1,88	0,40	0,70
primo						corridoio cieco	1,24	3,42	1,55	3,7	12,654	5,301	12,654	5,301	5,735	5,735	47,38	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,25		350,00	0,00	150,00		0,67	J	3,42	0,30	1,50	1,62	0,26	0,70
primo						corridoio con vetrata	1,23	2,97	1,2	5	0	3,564	0	0	6	6	15,564	0,2	0,2	0,6	0						0,00	0,48	1,00	0,40	0,36	0,35	1,29299	350,00	452,55	150,00		0,83	I	2,97	0,30	1,50	1,17	0,32	0,70
primo						bagno DISABILI cieco	1,6	3,14	2	1,6	5,024	6,28	5,024	6,28	3,2	3,2	29,008	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,24		350,00	0,00	150,00		0,66	J	3,14	0,30	1,50	1,34	0,26	0,70
primo						corridoio cieco	1,17	3,29	3,1	3,5	11,515	10,199	11,515	10,199	10,85	10,85	65,128	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,27		350,00	0,00	150,00		1,10	H	3,29	0,30	1,50	1,49	0,37	0,70
primo						corridoio con vetrata	1,11	3,44	1,5	16,4	56,416	5,16	56,416	5,16	24,6	24,6	172,352	0,2	0,2	0,6	0						0,00	0,48	1,00	0,40	0,36	0,26		350,00	0,00	150,00		0,84	I	3,44	0,30	1,50	1,64	0,32	0,70
primo						corridoio con vetrata	1,2	3,14	1,6	3,3	0	5,024	6,594	5,024	5,28	5,28	27,202	0,2	0,2	0,6	0						0,00	0,48	1,00	0,40	0,36	0,28	0,65857	350,00	230,50	150,00		0,80	I	3,14	0,30	1,50	1,34	0,32	0,70
primo						ascensore/atrio con lucernario	1,19	3,10	3,2	4,2	0	8,215	13,02	28,5696	13,44	13,44	76,6846	0,2	0,2	0,6	0						0,00	0,48	1,00	0,40	0,36	0,27	0,30172	350,00	105,60	150,00		1,40	F	3,10	0,30	1,50	1,30	0,42	0,70
primo						antibagno disabili 1.3	1,3	3,14	1	2	6,28	3,14	6,28	3,14	2	2	22,84	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,24		350,00	0,00	150,00		0,50	J	3,14	0,30	1,50	1,34	0,26	0,70
primo						antibagno donne 1.4	1,4	3,14	1	2,2	6,908	3,14	6,908	3,14	2,2	2,2	24,496	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,24		350,00	0,00	150,00		0,51	J	3,14	0,30	1,50	1,34	0,26	0,70
primo						antibagno uomini 1.5	1,5	3,14	1	1,5	4,71	3,14	4,71	3,14	1,5	1,5	18,7	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,23		350,00	0,00	150,00		0,45	J	3,14	0,30	1,50	1,34	0,26	0,70
primo	nord	f40 BAGNO				bagno uomini con finestra	1,8	3,14	1,45	1,6	5,024	4,553	5,024	4,553	2,32	2,32	23,794	0,2	0,2	0,6	0,3		6,10	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,24		350,00	0,00	150,00		0,37	J	3,14	0,30	0,80	2,04	0,26	0,70
primo	nord	f41 e f42 BAGNO				bagno donne con finestra	1,7	3,14	2,2	1,65	5,181	6,908	5,181	6,908	3,63	3,63	31,438	0,2	0,2	0,6	0,3		6,10	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,25		350,00	0,00	150,00		0,46	J	3,14	0,30	0,80	2,04	0,26	0,70
terra						corridoio diventato metà open space e metà con porta a vetro	0,20	2,85	10,8	1,2	3,42	30,78	0	12,483	12,96	12,96	72,603	0,2	0,2	0,6	0						0,00	0,48	1,00	0,40	0,36	0,27	0,45543	350,00	159,40	150,00		1,03	H	2,85	0,30	1,50	1,05	0,37	0,70
terra						corridoio cieco	0,14	2,84	1,1	3,7	10,508	3,124	10,508	3,124	4,07	4,07	35,404	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,25		350,00	0,00	150,00		0,82	I	2,84	0,30	1,50	1,04	0,32	0,70
terra						bagno DISABILI cieco	0,7	2,84	1,8	2	5,68	5,112	5,68	5,112	3,6	3,6	28,784	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,25		350,00	0,00	150,00		0,91	H	2,84	0,30	1,50	1,04	0,37	0,70
terra						corridoio cieco	0,13	2,61	2,3	2,1	5,481	6,003	5,481	6,003	4,83	4,83	32,628	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,26		350,00	0,00	150,00		1,36	H	2,61	0,30	1,50	0,81	0,37	0,70
terra						corridoio cieco	0,12	2,52	1	1,7	4,284	2,52	4,284	2,52	1,7	1,7	17,008	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,24		350,00	0,00	150,00		0,87	I	2,52	0,30	1,50	0,72	0,32	0,70
terra	nord	f14 BAGNO				bagno donne con finestra	0,2	3,16	1	1,4	4,424	3,16	4,424	3,16	1,4	1,4	17,968	0,2	0,2	0,6	0,3		3,50	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,23		350,00	0,00	150,00		0,43	J	3,16	0,30	1,50	1,36	0,26	0,70
terra	nord	f15 BAGNO				bagno uomini con finestra	0,3	2,83	1,25	1,9	5,377	3,5375	5,377	3,5375	2,375	2,375	22,579	0,2	0,2	0,6	0,3		2,77	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,24		350,00	0,00	150,00		0,73	I	2,83	0,30	1,50	1,03	0,32	0,70
terra						antibagno uomini 0.3	0,3a	2,83	1,2	1,9	5,377	3,396	5,377	3,396	2,28	2,28	22,106	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,24		350,00	0,00	150,00		0,71	I	2,83	0,30	1,50	1,03	0,32	0,70
terra						antibagno donne 0.2	0,2a	3,16	1	2	6,32	3,16	6,32	3,16	2	2	22,96	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,23		350,00	0,00	150,00		0,49	J	3,16	0,30	1,50	1,36	0,26	0,70
secondo						corridoio con vetrata (calcolata in quello sotto)	2,10b	3,3	1,5	3,7																																			
secondo						corridoio con vetrata	2,10a+2,10b	3,3	1,5	3,9	13,86	0	17,16	6,27	5,85	5,85	48,99	0,2	0,2	0,6	0						0,00	0,48	1,00	0,40	0,36	0,25	0,18322	350,00	64,13	150,00		0,72	I	3,30	0,30	1,50	1,50	0,32	0,70
secondo						corridoio cieco	2,2 e 2,3	3,145	1,6	4,2	13,209	5,032	13,209	5,032	6,72	6,72	49,922	0,2	0,2	0,6	0,3		0,00	3,00	10,00	8,50	0,50	0,27	0,85	0,60	0,54	0,25		350,00	0,00	150,00		0,86	I	3,15	0,30	1,50	1,35	0,32	0,70
secondo						antibagno uomini 2.15	2,15	3,32	1,6	1,7																										150,00		0,54	J	3,32	0,30	1,50	1,52	0,26	0,70
secondo						antibagno disabili 2.18	2,18	3,01	1,85	4,25																										150,00		1,07	H	3,01	0,30	1,50	1,21	0,37	0,70
secondo						antibagno donne 2.17	2,17	2,81	1,5	1,6																										150,00		0,77	I	2,81	0,30	1,50	1,01	0,32	0,70
secondo						bagno DISABILI cieco	2,11	3,01	2,3	4,2																										150,00		1,23	G	3,01	0,30	1,50	1,21	0,40	0,70
secondo	ovest	f67				bagno donne con finestra	2,14	3,32	1,5	1,75																										150,00		0,36	J	3,32	0,30	0,80	2,22	0,26	0,70
secondo	ovest	f62				bagno uomini con finestra	2,16	2,81	1,75	2,3																										150,00		0,58	J	2,81	0,30	0,80	1,71	0,26	0,70

								Superfici visibili vetri		
n . Scrivanie	A scrivania	A scrivanie	Flusso luminoso max	**Potenza elettrica max**	Flusso luminoso min	**Potenza elettrica min**	Potenza corridoio cieco	**Atot telaio in legno finestre**	**Atot visibile vetro**	**Atot PORTE IN LEGNO**
	m2	m2	lumen	**W**	lumen	**W**	W	[m²]	**[m²]**	[m²]
6	2,00	12,36	15453,13	**151,65**	13400,28	**131,50**		0,27	1,12	
8,13	2,00	16,25	19345,24	**189,85**	18534,01	**181,88**		0,27	1,12	
6,20	2,00	12,39	15487,50	**151,99**	14609,05	**143,37**		0,27	1,27	
4,96	2,00	9,92	12400,00	**121,69**	11546,92	**113,32**		0,27	1,27	
	2,00	0,00						0,27	1,27	
	2,00	0,00						0,16	0,82	
	2,00	0,00						0,16	0,82	
5,00	2,00	9,99	12487,50	**122,55**	7311,85	**71,76**		0,27	1,27	
1,00		21,07	9815,22	**96,32**	0,00	**0,00**		0,83	**8,53**	
5,32	2,00	10,64	13300,00	**130,52**	0,00	**0,00**		0,28	1,29	
	2,00	0,00						0,28	1,29	
	2,00	0,00						0,27	1,15	
3,70	2,00	7,40	10000,00	**98,14**	5191,72	**50,95**		0,27	1,15	
2,13	2,00	4,25	6640,63	**65,17**	2125,88	**20,86**		0,26	1,06	
6,15	2,00	12,30	15375,00	**150,88**	12286,54	**120,57**		0,16	0,74	
	2,00	0,00						0,16	0,74	
	2,00	0,00						0,35	1,42	
2,85	2,00	5,70	8906,25	**87,40**	7888,40	**77,41**		0,35	1,42	
2,57	2,00	5,13	8015,63	**78,66**	7677,26	**75,34**		0,19	0,47	
3,11	2,00	6,21	8391,89	**82,35**	8067,81	**79,17**		0,35	0,42	
2,65	2,00	5,30	8281,25	**81,27**	7854,34	**77,08**			0,81	2,8669
	2,00	0,00							0,81	2,8669
	2,00	0,00						0,27	1,13	
6,75	2,00	13,50	16875,00	**165,60**	13504,88	**132,53**		0,28	1,46	
4,73	2,00	9,45	12770,27	**125,32**	11631,13	**114,16**		0,28	1,46	
4,08	2,00	8,16	11027,03	**108,21**	9933,11	**97,48**		0,28	1,46	
8,16	2,00	16,32	20400,00	**200,20**	19228,32	**188,70**		0,28	1,46	
	2,00	0,00						0,28	1,46	
	2,00	0,00						0,16	0,93	
	2,00	0,00						0,16	0,93	
4,68	2,00	9,35	12635,14	**124,00**	6727,72	**66,02**		0,28	1,46	
4,73	2,00	9,46	12785,47	**125,47**	6056,50	**59,44**			2,03	1,8981
5,46	2,00	10,92	14756,76	**144,82**	0,00	**0,00**		0,28	1,46	
	2,00	0,00						0,28	1,46	
	2,00	0,00						0,27	1,45	
3,51	2,00	7,02	10968,75	**107,64**	4688,12	**46,01**		0,27	1,45	
4,72	2,00	9,44	13104,17	**128,60**	446,23	**4,38**		0,27	1,45	
	2,00	0,00						0,27	1,45	
3,74	2,00	7,48	10108,11	**99,20**	9009,16	**88,41**		0,28	1,49	
3,60	2,00	7,20	11250,00	**110,40**	10057,12	**98,70**		0,28	1,46	
2,95	2,00	5,89	9203,13	**90,32**	8074,11	**79,24**		0,28	1,46	
	2,00	0,00						0,28	1,46	
	2,00	0,00						0,28	1,46	
4,50	2,00	9,00	11250,00	**110,40**	371,99	**3,65**		0,28	1,48	
4,94	2,00	9,87	12337,50	**121,07**	8847,74	**86,83**		0,28	1,48	
4,24	2,00	8,49	11469,59	**112,56**	7988,12	**78,39**		0,28	1,48	
8,29	2,00	16,58	20718,75	**203,32**	16998,50	**166,83**		0,28	1,48	
	2,00	0,00						0,28	1,48	
	2,00	0,00						0,16	0,95	
	2,00	0,00						0,16	0,95	
4,81	2,00	9,63	13006,76	**127,64**	6421,95	**63,02**		0,28	1,48	
11,02	2,00	22,04	26232,14	**257,43**	0,00	**0,00**		0,28	1,48	
	2,00	0,00						0,28	1,48	
	2,00	0,00						0,28	1,52	
	2,00	0,00						0,28	1,48	
3,23	2,00	6,45	3735,52	**36,66**	0,00	**0,00**		0,37	1,82	
	2,00	0,00						0,37	1,82	
7,00	2,00	14,00	16666,67	**163,56**	9488,15	**93,11**		0,28	1,48	
	2,00	0,00						0,28	1,48	
	2,00	0,00	0,00	**0,00**	0,00	**0,00**		0,28	1,48	
	2,00	0,00						0,28	1,48	
		5,74	4726,65				46,39			
		6,00			8103,93	**0,00**				
		3,20	2637,36	**25,88**	disabili					
		10,85	6283,78				61,67			
		24,60				**0,00**				
		5,28			-1897,46	**0,00**				
		13,44			2029,55	**19,92**				
		2,00	1648,35	**16,18**	disabili					
		2,20	1811,19	**17,79**	donne					
		1,50	1236,26	**12,13**	uomini					
		2,32	1912,09	**18,76**	uomini			0,27	1,45	
		3,63	2991,76	**29,36**	donne			0,18	0,87	
		12,96			-470,40	**0,00**				
		4,07	2725,45				26,75			
		3,60	2084,94	**20,46**	disabili					
		4,83	2797,30				27,45			
		1,70	1138,39				11,17			
		1,40	1153,85	**11,32**	donne			0,26	1,06	
		2,38	1590,40	**15,61**	uomini			0,30	0,58	
		2,28	1526,75	**14,98**	uomini					
		2,00	1648,35	**16,18**	donne					
		11,40	7633,93		4370,31	**42,89**				
		6,72	4500,00				44,16			
		2,72	2241,76	**22,00**	uomini					
		7,86	4503,57	**44,69**	disabili					
		2,40	1607,14	**15,77**	donne					
		9,66	5175,00	**50,79**	disabili					
		2,63	2163,40	**21,23**	donne			0,22	0,66	
		4,03	3317,31	**32,55**	uomini			0,22	0,66	

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