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Article

Nano-TiO$_2$ Coatings for Limestone: Which Sustainability for Cultural Heritage?

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Abstract: The present study concerns the ecodesign of the application of an aqueous nano-TiO$_2$ suspension on a porous limestone used in historical monuments with a spraying system through the LCA methodology, in order to define the most critical aspects of the process and to try to minimize the environmental burden during the implementation of the application process. Because of the limited knowledge currently available regarding the effects that nano-TiO$_2$ may have on the environment or human health, a precautionary approach has been adopted in all life cycle steps, to assess the risk of having nanoparticle emissions from a nanocoating surface and for workers, who can come into contact with or inhale the nanoparticles released. The energy-intensive operations in the application stage greatly contribute to the total environmental damage, while the impact generated by nanoparticle emissions during the use phase contributes 2.9%. In addition, the self-cleaning and de-polluting transparent titania coating produces a benefit of −0.13%.

Keywords: life cycle assessment; nano-TiO$_2$ coatings; limestone; cultural heritage

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1. Introduction

Industry is rapidly developing engineered nanoparticles (ENPs) that are applied in an increasingly wider variety of consumer and industrial products. Thanks to the unique physical and chemical properties of nanoparticles, it is possible to obtain innovative applications. Nanoparticles have novel properties (chemical, mechanical, optical, magnetic, *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 innovative industrial fields, but also in traditional sectors, such as in construction. In particular, the inclusion of or coating with specific nanoparticles for building materials has been developed in order to obtain additional and superior properties (self-cleaning, antibacterial, anti-fogging, lightness, mechanical strength, durability, fire resistance, *etc.*). Among these ENPs, in the construction sector, titanium dioxide is one of the most used materials to realize self-cleaning and de-polluting coatings for cement mortars, exterior tiles, paving blocks, glasses, paints, finishing coatings, road-blocks and concrete pavements [1–3]. Its widespread use is attributed to its main features: high catalysis efficiency, chemical stability, inexpensiveness, compatibility with traditional construction materials and cultural heritage [4].

This uncontrolled growth of ENPs' employment has increased the probability of engineered nanomaterials (ENMs, accidental or incidental) being 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 the environment. However, research on the 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 the spreading of engineered nanoparticles in the environment [5,6]. The release of ENMs into the environment can potentially occur throughout their entire life cycle: from the fabrication of ENMs, to the use and end of life phases [7]. Risks from the release 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 [8]. This increases the necessity to assess the potential risks that these new materials pose with regard to human health and the environment.

Moreover, the building sector increasingly affects energy consumption, the quality and/or quantity of materials used and, consequently, the resulting environmental impacts. In this sector, a reduction of energy consumption and the regulation of non-renewable resources' exploitation are important points that need to be addressed. The design system's implementation, which takes into account both the energy and the materials (amount and typology) used during the building lifetime, together with the construction system's optimization, which allows one to obtain the greatest energy savings and to minimize the environmental burden, become essential aspects of eco-design for both the 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 time. Therefore, the environmental impacts should be analyzed in the initial steps, such as the gathering and manufacturing of raw materials, which are necessary for the production of the technological elements, and at the end of the life cycle, such as the demolition, disposal and/or recycling steps of the materials and components [9]. Nevertheless, the management of cultural heritage requires continuous conservation and restoration work, wherein different professionals are involved primarily in technical and scientific activities and exposed to different environments with materials of distinct degrees of conservation that expose the operator responsible for the protection of cultural heritage to multiple risks, such as chemical, physical and/or microbiological. Hence, the construction and restoration processes must be reviewed, adopting new bases and scenarios that take into account a complete vision over time that is able to evaluate the whole life of the building.

Life cycle assessment (LCA) is a methodology of analyzing and assessing the environmental impact of a product, process or service throughout its entire life cycle, usually from the acquisition of raw materials to final disposal. The principle is to quantify the resources consumed and the emissions released to the environment at all stages of the life cycle of the product [10]. The results are subsequently interpreted in terms of impacts on health and environment, for a range of impact categories, including global warming, eutrophication of ecosystems and others [11]. The importance of LCA lies mainly in its innovative approach, which considers all stages of the considered system to be correlated and dependent.

Although life cycle assessment has been extensively applied in the building sector for assessing the environmental performance and impacts of construction materials and products, its use is practically unknown in the field of cultural heritage, probably because it is quite complex to collect data throughout the life cycle of a historic work of art, an architectural monument, as well as a contemporary building [12].

Regarding nanomaterials, the life cycle assessment methodology has been recently recognized as a key tool for evaluating the environmental performance of nanoproducts, assessing the ENMs' releases into the environment that can potentially occur throughout their entire life cycle [13].

The present study concerns the environmental assessment of the use of nano-TiO_2-based coatings over architectural stone surfaces in order to evaluate the balance between the potential risks due to the use of engineered nanomaterials in all life cycle phases and the benefits of the self-cleaning and de-polluting properties of a transparent titania coating. In this work, an ecodesign approach has been adopted in order to minimize the environmental burdens. Because of the limited knowledge currently available regarding the effects nano-TiO_2 may have on the environment or human health [13], a safe behavior has been adopted in all life cycle steps in which workers can come into contact with or inhale nanoparticles released by a nanocoating surface. The installation of a high-efficiency particulate air filter (HEPA), a closed manufacturing system, the use of specific packaging to limit the release of nanoparticle emissions during transport, personal protective equipment (PPE) (gloves, coverall, eyewear, face mask with 95% efficiency) and a specific waste treatment have been taken into consideration. Nano-TiO_2 emissions released during production, application, use and end of life phases have been assumed, and the benefit derived from the application of nano-TiO_2 has been also assessed considering the NO_x abatement.

2. Materials and Methods

2.1. Goal and Scope Definition

The present study concerns the environmental assessment performed by the LCA methodology of a transparent nano-TiO_2 coating deposited on travertine, a porous limestone widely used in historical monuments and architectural and artistic stone elements. The aim of this study is to highlight the environmental benefits and potential risks due to the use of engineered nanomaterials in the preservation of cultural heritage.

2.2. Functional Unit and System Boundaries

The surface treatment of 3 m^2 of travertine is used as functional unit. The system function is that of a coating, designed to protect the facades of historical buildings and other architectural and monumental elements from the action of atmospheric agents. Moreover, TiO_2's photocatalytic and superhydrophilicity properties can reduce the concentrations of airborne pollutants and organic substances deposited on the material's surface and permit obtaining self-cleaning and de-polluting features. System boundaries cover the entire life cycle, including raw material extraction, production, distribution, application, use and end of life phases, thus obtaining "a cradle to grave" overview according to the LCA approach. Plants, devices, equipment, transport and energy consumptions (electricity and heat) have been also considered in the study. Emissions into the air, water and soil have been also taken into account.

2.3. Data Quality

Primary data, referring to the optimized method for the preparation of aqueous suspension of nano-TiO_2, have been collected, both directly from the authors of the patented procedure (primary data) and from the scientific literature (secondary data) [14,15]. Data related to the spray coating of TiO_2 over an architectural stone surface have been derived from the literature [4]. Where data were somehow missing, the study has been completed on the basis of secondary data obtained from the Ecoinvent database [16] and exploited them to model the background processes (land use, materials production, fuel and electricity production and transport). The following assumptions have been made:

- Installation, in the production and application processes, of HEPA (high-efficiency particulate air filter → 99.97%) air filter to minimize nanoparticle emissions to the air;
- In the application process, nano-TiO_2 emissions to the air have been assumed to be 0.1%, partly retained by a HEPA filter, then disposed in a hazardous waste incinerator and partly released into the application site and inhaled by workers;
- During the application stage, a closed spray coating system has been designed;
- PPE (personal protective equipment): face mask with 95% efficiency to protect workers from dust and nanoparticle inhalations, as indicated in the European Standard EN149 [17];
- In the use phase, the durability of titania coatings has been assumed to be 10 years during which the complete nano-TiO_2 emission to the air takes place; the end of life of the coating is therefore coincident with the use phase;
- The electricity energy supply has been assumed to be the generated by Ecoinvent.

2.4. Impact Assessment

The analysis has been performed by using the SimaPro 8.0.4 software and the IMPACT 2002+ [18,19] evaluation method to assess the environmental impacts. In order to use a more representative index of the considered system, the following additions and modification have been implemented:

- Land use has been estimated using basic indicators of Italian mixed electric energy, 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 considering some additional resources, such as silver, gravel, sand, lithium, bromine and water in the ground, derived from the category minerals of the Eco-indicator 99 method with the same characterization factors;
- The radioactive waste damage category has been added; in particular, both this kind of waste and its occupied volume have been evaluated considering the same characterization and normalization factors of the EDIP 2003 method [20]. This category allows one to take into account the possible damage from the electric energy mix, which also includes the electricity generated by nuclear plants. This latter kind of energy produces radioactive waste, which has to be safely managed and disposed;
- The carcinogens inhaled damage category has been added with a characterization factor of 1 kg and a new damage category with the calculated damage factor 5.5557 Disability Adjusted Life Years (DALY)/kg. Normalization and weighting factors remain unchanged (normalization factor: 141, weighting factor: 1).
- Nano-TiO_2 emissions to the air and inhaled by workers who handle nanomaterials during the application, use and end of life phases have been considered. In particular, particulates <100 nm substance has been added to the carcinogens impact category and particulates <100 nm inhaled substance has been introduced to a new impact category (called carcinogens inhaled) with characterization factors and damage factor respectively calculated previously [21,22]. Regarding nanoTiO_2 particles released to the air, the calculation of the damage to human health caused by the carcinogenic substance using the Ecoindicator 99 method [23] has been considered, which covers 3 main steps: fate analysis, effect analysis and damage analysis. Following this procedure, the resultant characterization factor is 1.09 kg C_2H_3Cl. For nano-TiO_2 inhaled by workers, it is assumed that the same indicators used for the calculated indoor emissions considering the concentration limit of the indoor emissions in the production room, considering the average volume of the production area, the probability of contracting lung cancer with that concentration and an average of five workers in the production room have been considered. The calculated damage assessment factor is 5.56 DALY.

2.5. Life Cycle Inventory

The inventory data have been modelled in SimaPro 8.0.4, taking the Ecoinvent database as a reference to configure the inventory of some chemicals (*i.e.*, nitric acid, titanium isopropoxide), natural gas, electricity, heat, transport, infrastructure, machinery and waste treatments. The entire life cycle is shown in Figure 1.

This comprises different stages, such as the bottom-up hydrolytic synthesis of TiO_2 nanoparticles and their dilution, transport of both the spray coating system and of the aspiration equipment to the application site, the spray coating and the use and end of life phases of the coating.

The experimental procedure and the environmental impacts of the hydrolytic sol-gel synthesis of the titanium dioxide nanoparticle suspension, produced according to the procedure patented and employed by Colorobbia Italia S.p.A. have been reported in Pini *et al*. [24].

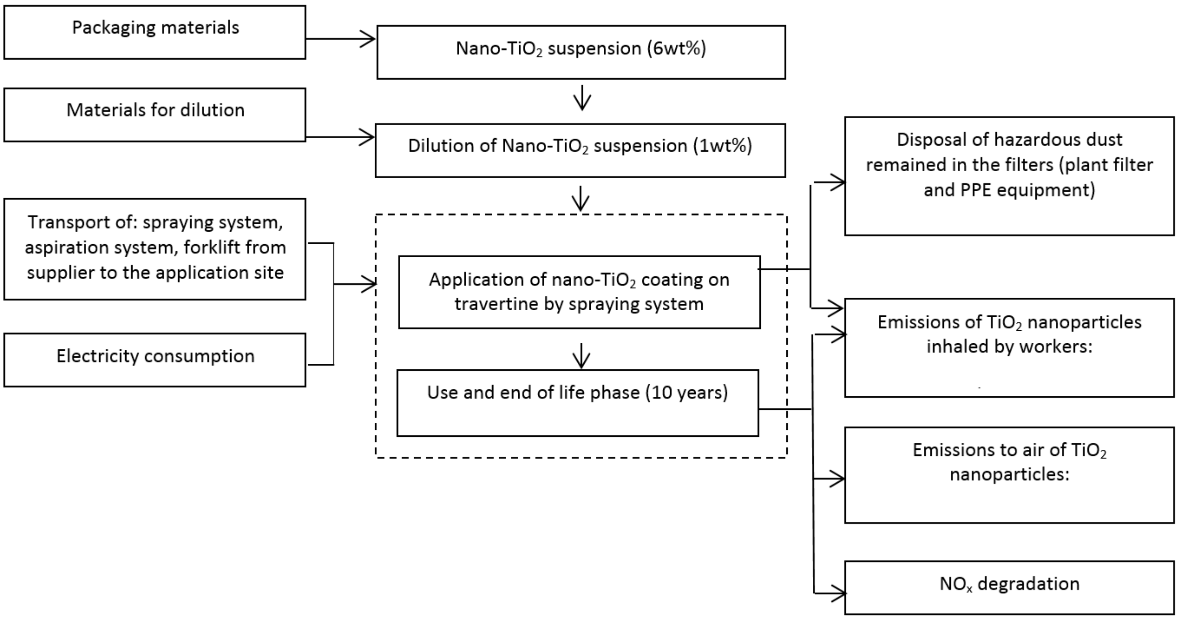

Figure 1. Flow chart of nano-TiO_2 coating on travertine.

In agreement with Quagliarini *et al.* [1,4], since the titania content of the aqueous suspension was 6 wt%, before application to the limestone surface, the suspension was further diluted with demineralized water in order to obtain a TiO_2 content of 1 wt%. Because of the limited knowledge currently available regarding the effects nano-TiO_2 may have on the environment or human health [25], a safe behavior has been adopted in the production and application steps in which there can be the risk of having the release of nanoparticles from the nanocoating surface and workers can come into contact with or inhale the released nanoparticles. Therefore, a closed suction system equipped with an aspiration and filtration device has been designed to avoid the possible release of TiO_2 nanoparticles. The spraying system has been modeled considering the primary data of industrial equipment used for polyurea resin application and assuming a system of nozzles instead of a spray gun, as well as an electrical energy reduction to one third of that used for the polyurea resin. In addition, a forklift has been considered in order to bring the worker and the spraying equipment in contact with the surface to be treated. The travertine surface (3 m^2) has been coated with a single treatment of 25 mL/m^2 of TiO_2-based suspension followed by a natural drying phase in the air. The spraying time to cover 3 m^2 of limestone is considered to equal 5 min. In the use phase, it has been assumed that TiO_2 nanoparticles are progressively released to the air over 10 years, after which the coating is considered completely removed. Titanium dioxide application on building materials and the activation by the near-UV fraction of incident solar irradiation offer a promising potential, namely the reduction of organic and inorganic pollutants. Therefore, the reduction of NO_x concentrations has been considered here for the outdoor environment. In particular, a reduction of NO emissions to the air equal to the 4.01 $mg/h\cdot m^2$ proposed by Chen *et al.* [26] due to the application of the TiO_2 coating on an architectural stone surface to obtain photocatalytic features has been taken into consideration.

For the upstream processes, the I/O data refer to the scale-up process of the nano-titania spray coating on 3 m^2 of travertine. Inventory data related to the life cycle of the bottom-up hydrolytic synthesis of nano-TiO_2 are reported by Pini *et al.* in a previous work [24]. Table 1 shows some of the most relevant I/O data.

Table 1. Inventory data of the nano-TiO_2 coating on travertine.

Life Cycle Stage	Unit	Application	Use and End of Life	Data Source
Energy input				
-Electricity consumption	kW h	1.42	–	I/O data derived from the Ecoinvent database and estimated from the literature
Material I/O				
-Input of demineralized water	kg	64.15×10^{-2}	–	Directly from the company and estimated from the literature
-Nano-TiO_2 suspension (1 wt%)	kg	0.75×10^{-1}	–	
Transport				
-Road	kg km	99.14×10^{-2}	–	Directly from the company
-Freight	kg km	4.48	–	
Waste to treatment				
-Disposal of hazardous dust retained by aspiration and mask filter	kg	7.49×10^{-7}	–	Estimated from the literature
Emissions to the air				
-Particulates, <100 nm (workers outdoor)	kg	6.75×10^{-12}	–	I/O data derived from the Ecoinvent database and estimated from the literature
-Particulates, <100 nm	kg	2.25×10^{-10}	0.75×10^{-3}	
-NO_x	mg	–	−60.77	
-HNO_3	mg	–	−83.23	

3. Life Cycle Impact Assessment

The life cycle impact assessment (LCIA) has been reported for 1 m^2 of nano-TiO_2 coating on travertine by both midpoint and endpoint assessment. LCIA results have been generated with IMPACT2002+ method using SimaPro 8.0.4, to determine the environmental impacts related to the emissions released and the resources consumed in the system under study [18,19]. 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.*) [27].

The results of the analysis at the mid-point level, reported in Table 2, show that the production and application stages have the highest environmental damage, having a significant impact on all of the considered environmental impact categories.

Table 2. Characterized life cycle impact assessment (LCIA) results of the entire life cycle of 1 m^2 of nano-TiO_2 coating on travertine.

Impact Category	Unit	Total	Production and Application	Use and End of Life Phase
Carcinogens	kg $C_2H_3Cl_{eq}$	9.38×10^{-3}	9.11×10^{-3} [97.1%]	2.73×10^{-4} [2.9%]
Non-carcinogens	kg $C_2H_3Cl_{eq}$	2.81×10^{-3}	2.81×10^{-3}	–
Respiratory inorganics	kg $PM2.5_{eq}$	2.75×10^{-4}	2.72×10^{-4} [99.06%]	-2.58×10^{-6} [−0.94%]
Ionizing radiation	Bq $C\text{-}14_{eq}$	6.19	6.19	–
Ozone layer depletion	kg $CFC\text{-}11_{eq}$	5.03×10^{-8}	5.03×10^{-8}	–
Respiratory organics	kg C_2H_{4eq}	7.84×10^{-5}	7.84×10^{-5}	–
Aquatic ecotoxicity	kg TEG $_{water}$	19.02	19.02	–
Terrestrial ecotoxicity	kg TEG $_{soil}$	4.87	4.87	–
Terrestrial acid/nutri	kg SO_{2eq}	4.45×10^{-3}	4.34×10^{-3} [96.62]	-1.11×10^{-4} [−3.38%]
Land occupation	m^2 org.arable	-1.89×10^{-2}	-1.89×10^{-2}	–
Aquatic acidification	kg SO_{2eq}	1.50×10^{-3}	1.47×10^{-3} [98.11%]	-2.83×10^{-5} [−1.89%]
Aquatic eutrophication	kg PO_4 P-lim	3.91×10^{-5}	3.91×10^{-5}	–
Global warming	kg CO_{2eq}	34.22×10^{-2}	34.22×10^{-2}	–
Non-renewable energy	MJ primary	5.86	5.86	–
Mineral extraction	MJ surplus	6.73×10^{-3}	6.73×10^{-3}	–
Renewable energy	MJ	86.46×10^{-1}	86.46×10^{-1}	–
Radioactive waste	kg	1.59×10^{-5}	1.59×10^{-5}	–
Carcinogens inhaled	kg	2.25×10^{-12}	2.25×10^{-12}	–

The analysis of the results at the mid-point level highlights that the electricity of the spraying coating process plays a major role in all of the impact assessment categories, as reported in Figure 2.

Human toxicity effects derived from the application phase of the whole process are dominated by the carcinogens impact category, by the release of aromatic hydrocarbons to the air (85.09%) for natural gas production. In addition, the impact generated by nanoparticle emissions during the use phase contributes 2.9%. In the non-carcinogens category, the environmental burdens are generated by the emissions of dioxin (27.49%) for steel production used in the electric energy plant and by the release of arsenic to the air, water and soil (26.11%, 14.11% and 10.56%, respectively) and barium in water (13.73%), due to the Italian mixed electric energy production.

The respiratory inorganics category is dominated by secondary particle creating emissions of NO_x (27.72%) and SO_2 (30.19%) to the air, as well as by particle <2.5 μm emissions to the air (27.25%), in particular for electric energy production. The use phase produces a benefit of -2.58×10^{-6} kg PM2.5 due to NO_x abatement.

The global warming impact category (23.94%) is mainly influenced by 96.1% of carbon dioxide, from fossil fuels, and the production process determines the main environmental burden (88.7%), in particular for electric energy consumption. In the terrestrial ecotoxicity impact category (7.48%), the release of zinc to the air contribute 55.66%, mainly due to the application stage, in particular for the spraying system. Ionizing radiation and ozone depletion are both dominated by the electricity used in the application stage. Radon (Rn222) and carbon (C14) emissions to the air (72.7% and 25.82%, respectively) originating from electricity generation have the most relevant contribution to the ionizing radiation category. Releases of Halon 1211, Halon 1301 and CFC-114 to the air are attributable to gas transportation processes and to offshore natural gas and oil production, dominated by the ozone depletion category. For respiratory organics, the major environmental load is due to non-methane volatile organic compound (NMVOC) emission to the air (78.98% of the impact category) released from electricity generation. Aluminum emissions to the air, in water and soil together with copper emissions in soil and chromium VI in soil, related to both the consumption of hard coal and natural gas in the energy supply processes and the electricity distribution network, contribute significantly to the aquatic and terrestrial ecotoxicity categories. The benefit observed in the land use impact category comes from soybean production for the biogas used in the Italian mixed electric energy production. In particular, the IMPACT2002+ evaluation method takes into account, specifically for soybean cultivation, the transformation from an arable substance, whereas transformation to an arable one is absent. Consequently, the effects due to land transformation for anthropogenic activity are lower than those due to the recovery of the primary conditions.

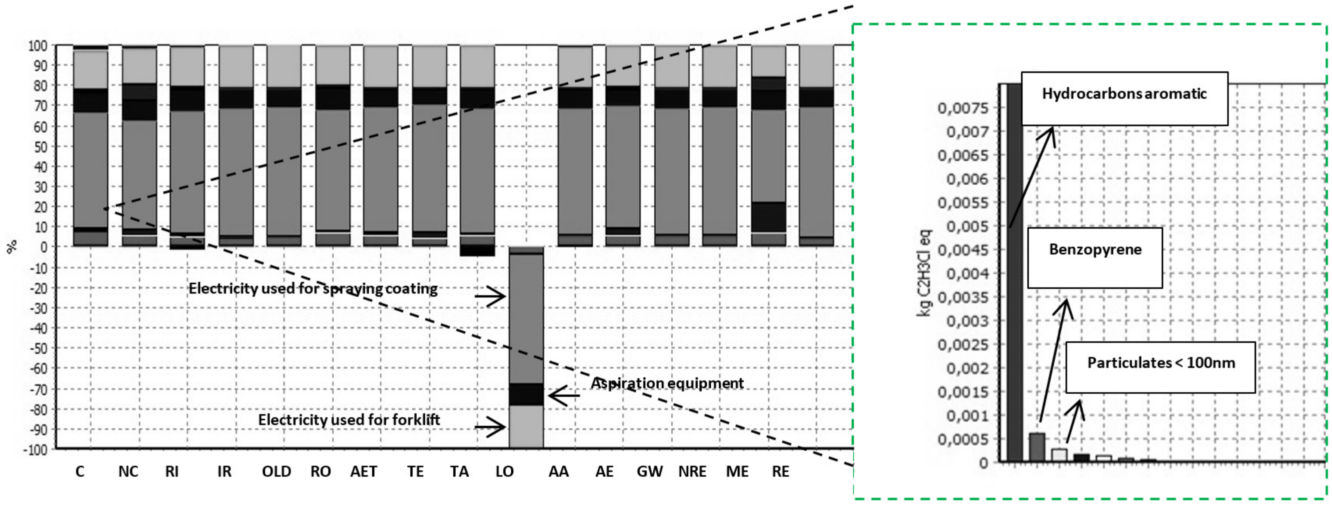

Figure 2. Evaluation by impact category of 1 m^2 of nano-TiO$_2$ coating on travertine, where: C = carcinogens; NC = non-carcinogens; RI = respiratory inorganics; IR = ionizing radiation; OLD = ozone layer depletion; RO = respiratory organics; AET = aquatic ecotoxicity; TE = terrestrial ecotoxicity; TA = terrestrial acid/nutria; LO = land occupation; AA = aquatic acidification; AE = aquatic eutrophication; GW = global warming; NRE = non-renewable energy; ME = mineral extraction. The details of the contribution of the emissions to the air for the carcinogens impact category are also reported.

Terrestrial acidification/nutrification and aquatic acidification present environmental advantages by the reduction of NO$_x$ emissions to the air during the use phase, thanks to the nano-TiO$_2$ photocatalytic properties. The most relevant contribution to global warming is mainly due to CO$_2$ emissions belonging to the combustion process of the natural gas employed in the electricity production. The greatest contribution to the eutrophication potential comes from phosphate in water (86.83%) from hard coal mining used in the electric energy mix and from Chemical Oxygen Demand (COD) emissions to water (11.02%) due to onshore Russian oil production. The environmental load to the non-renewable energy impact category is mainly due to natural gas (58.12%), hard coal (15.65%), crude oil (13.43%) and uranium (11.58) caused by the Italian mixed electric energy production. Nano-titania coating application is the subsystem contributing in total to mineral extraction, which is dominated by releases of copper in the ground (46.15%) and nickel in the ground (33.02%) from the manufacturing of machinery and infrastructure components of the spray coating system.

The energy intensive operations in the application stage greatly contribute to the depletion of non-renewable energy resources. The consumption of hydropower energy (43.5%), geothermal energy (39.43%) and biomass energy (12.47%) in the energy supply processes affects this impact category.

In the radioactive waste impact category, the volume occupied by low-active radioactive waste contributes 86.17%, mainly due to the electricity energy consumption in the application phase, where part of the electric energy mix is made by nuclear power plants.

Regarding the introduced impact category carcinogens inhaled, the damage is mainly due to emissions of titania nanoparticles (particulates <100 nm) released to the air during the application phase and inhaled by workers.

Table 3 and Figure 3 show the impact assessment findings at the endpoint level. The results of the analysis show that for all damage categories, the main environmental burdens are due to the electricity used in the spraying coating process. LCIA shows that the damage to human health is due to the effects of inorganic emissions (84.37%) caused by SO_2, particulates <2.5 mm and NO_x emissions (25.47%, 23.17% and 22.99%, respectively, of the total damage category) during the spraying coating stage (60.59%). The damage to human health is mainly due to the electricity used in the spraying coating stage (60.59%). The effects on terrestrial ecotoxicity control the overall ecosystem quality (163.82%). In this category, the damage is mainly due to land occupation (transformation to arable) of the cogeneration plant (52.04%) and to the following emissions: aluminum in soil (47.13%), copper in soil (35.18%), aluminum to the air (33.6%), chromium VI to the air (18.27%) and nitrogen oxides to the air (14.54). The damage of these substances contrasts with the advantage due to land occupation (transformation from arable) for the soybean cultivation necessary for the biogas used in the Italian mixed electric energy (−155.67%).

The damage to climate change is generated by the emissions of 0.34216 kg CO_2 (eq) due to the electricity used in the application stage (62.13%). In the resources category, the energy-intensive operations in the spraying of the nano-titania coating greatly contribute to the depletion of non-renewable energy resources (63.82%). The consumption of natural gas (58.06%), hard coal (15.63%), crude oil (13.42%) and uranium (11.57%) in the energy supply processes affects this impact category.

The volume occupied by the final repository for low-radioactive and radioactive waste determines the main impact for the radioactive waste damage category due to the electric energy consumption of the application step (63.5%). Regarding the introduced damage category carcinogens inhaled, the damage is mainly due to direct emissions of particulates <100 nm released to the air during the spraying phase and inhaled by workers.

The single score derived from the aggregation of the previous damages is 0.10709 mPt for 1 m^2 of nano-TiO_2 coating on travertine (Table 3). The damage is 31.41% due to resources, 28.1% due to climate change, 26.16% human health, 12.93 radioactive waste, 1.4% ecosystem quality and 0.0014% carcinogens inhaled.

Table 3. Characterization and evaluation of the life cycle.

Damage Category	Unit	Total	Production and Application	Use and End of Life Phase
Human health	DALY	2.28×10^{-7}	2.26×10^{-7}	-1.04×10^{-9}
Ecosystem quality	PDF·m^2·y	2.35×10^{-2}	2.34×10^{-2}	-1.16×10^{-4}
Climate change	kg CO_{2eq}	3.42×10^{-1}	3.42×10^{-1}	–
Resources	MJ primary	5.87	5.87	–
Radioactive waste	kg	1.59×10^{-5}	1.59×10^{-5}	–
Carcinogens inhaled	DALY	1.25×10^{-11}	1.25×10^{-11}	–
Single score	Pt	12.30×10^{-5}	12.28×10^{-5} [99.87%]	-1.55×10^{-7} [−0.13%]

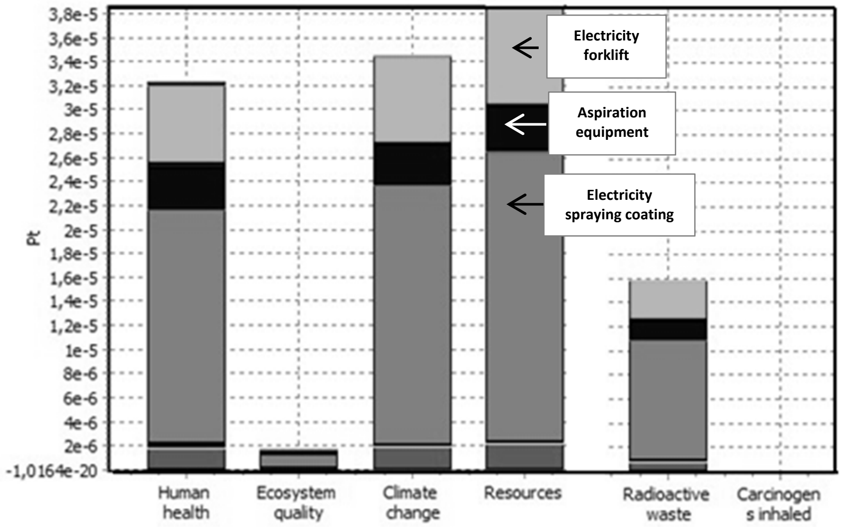

Figure 3. Evaluation by impact category of 1 m^2 of nano-TiO_2 coating on travertine.

In particular, the processing steps that mainly contribute to the total damage are the use of electricity for the spray coating (62.24%), the aspiration system (20.89%) and the bottom-up hydrolytic synthesis of nano-TiO_2 (5.42%), while the benefits produced by the self-cleaning and de-polluting of the transparent titania coating are limited to −0.13%.

From these results, it seems that the self-cleaning and depolluting properties of the nano-TiO_2 thin films result in very little gain when the total life cycle of the material is considered. However, it is necessary to point out that in order to ascertain the real sustainability of titania coatings for outdoor application, a comparison with a traditional maintenance treatment of historical building surfaces should be performed, taking into account different horizon times and primary data for the related emissions. At present, due to the lack of primary data on the durability of titania coatings and to the potentially adverse effects of TiO_2 nanoparticles on human health and the environment, a precautionary approach should be adopted, both in the design and application stages.

4. Conclusions and Recommendations

In this work, the life cycle assessment approach has been applied for the first time, to the authors' best knowledge, to evaluate the environmental sustainability of nano-TiO_2-functionalized coatings over architectural stone surfaces. In order to evaluate the balance between the potential risks due to the use of engineered nanomaterials and the benefits of the self-cleaning and de-polluting properties of nano-TiO_2-functionalized coatings, because of the limited knowledge currently available regarding the effects of nano-TiO_2 on the environment and human health, a safe behavior has been adopted in all life cycle steps.

The obtained results underline that the most important environmental loads are related to the use of electricity for the application stage: these can be easily decreased by substituting the electrical application with a manual brush application. Instead, the benefits due to the NO_x degradation during the life time of the coating are limited compared to the total damage, but it is necessary to underline that in this work, due to the lack of primary data, a comparison with traditional maintenance treatment taking into account different horizon times and primary data for the related emissions has not been performed.

Author Contributions

Federica Bondioli designed and performed the experimental section by applying nanTiO2 coatings on travertine; Martina Pini analyzed the Life Cycle Inventory data; Anna Maria Ferrari and Paolo Neri perfomed the LCA analysis and wrote the paper.

Conflicts of Interest

The authors declare no conflict of interest.

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