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Simulated environmental risk estimation of engineered nanomaterials: A case of cosmetics in Johannesburg City

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Abstract

This paper attempts to quantify the potential risks posed by engineered nanomaterials (ENMs) to the aquatic and terrestrial ecosystems from cosmetic-based nanoproducts. The predicted environmental concentrations (PEC) were modelled for the silver (nAg) and titanium dioxide ($nTiO_2$) nanoparticles embedded in cosmetic nanoproducts. The Johannesburg Metropolitan City (JHB City), in South Africa, was used as the reference study area. A mathematical model was applied to compute the quantities of ENMs flows from the cosmetic nanoproducts into the JHB City aquatic and terrestrial ecosystems. The risk quotient (RQ) of the nanoscale materials were evaluated as a ratio of PEC to the predicted no effect concentrations (PNEC). RQ values showed wide variance due to factors like; the quantities of ENMs, the fate and pathways of ENMs in the aquatic and terrestrial ecosystems, efficiency of the wastewater treatment plants (WWTP) as well as the economic and demographic data for South Africa and Switzerland. For the aquatic environment, the PEC values of nAg ranged from 2.80×10^{-3} to 6.19×10^{-1} $\mu g\ L^{-1}$ whereas for $nTiO_2$ the values ranged from $2.7\ 0 \times 10^{-3}$ to 2.70×10^{-1} $\mu g\ L^{-1}$ under the realistic dilution factor of 1 with the WWTP functioning at high removal efficiency regime. The RQ values in the aquatic ecosystems were mostly >1, indicating the potential risk of both nAg and $nTiO_2$ but <<<1 in the terrestrial ecosystems. Our results provide the first quantification of ENMs potential risk into the environment Johannesburg City in a developing country's natural and technical settings.

Keywords

cosmetics, environmental risk assessment, engineered nanomaterials, predicted no effect concentrations, predicted environmental concentrations, risk quotient, nanotechnology

Introduction

Recent successes in nanotechnology development and consequent large-scale production and applications of engineered nanomaterials (ENMs) into products have inevitably resulted to their releases in diverse environmental systems as their final sinks. This implies that ENMs at different phases of nanoproducts lifecycle (e.g. production, transportation, use, etc) will enter into the environmental systems such as aquatic ecosystems, soils, and air from direct or indirect sources as well as due to disposal of industrial and domestic effluents and solid waste streams. Available scientific reviews on the nanoecotoxicological data of ENMs show they exhibit diverse and complex effects in different biological organisms.[1-7] However, only limited studies have been attempted in pursuit of quantifying the releases of ENMs into the environment[8-10] but are inadequate to support comprehensive risk assessment of chemicals with nanoscale dimensions in different environmental compartments.

One approach of addressing these data and knowledge limitations is through use of modelling tools in estimating the quantities of ENMs, and subsequently, deriving their potential risk profiles in different

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environmental compartments. Because of the wide range of nanotechnology applications and capabilities particularly towards addressing water, health and environmental problems[11-16] in the developing countries, ENMs will be introduced into the ecological systems as previously reported in the developed countries.[17-19] Until now, very few studies have been conducted[17-20] to predict the potential quantities of ENMs released into the environment in developed countries (e.g. Switzerland)[17,18,20] or other developed regions (e.g. Europe, North America, etc).[19]

However, such studies are lacking particularly in the developing countries though nanoproducts and industrial applications containing ENMs are currently in use in these countries, and are expected to increase dramatically in the coming years. In future, high use of ENMs is expected in the developing countries to address a number of critical millennium development goal-related problems (e.g. water, health, environmental cleaning, etc)[21] as well as in enhancing the quality of life through commercial and industrial applications, particularly in the middle-developed countries such as South Africa. In this study, the focus is to present risk characterization of ENMs in the environment under the developing country setting from commercial products like the cosmetics, for example, sunscreens. The ENMs are used in cosmetics to enhance the products performance, and meet the customers' needs. Presently, these products are traded both in the developed and developing countries mainly because of the global character of the cosmetic industry. Yet, the quantities of ENMs in these types of products among others (e.g. paints, pesticides, nanomedicines, etc) are expected to find widespread use in developing countries and eventually into the environment. However, they have not been quantified to date and their potential risk to the ecosystems remains largely unknown.

Therefore, several reasons motivate for closer examination of ENMs potential risks within the context of developing countries. First, present waste management practices in many developing countries are inadequate for treating conventional and hazardous waste streams generated from manufacturing, commercial, mining, agricultural, and domestic activities.[22] Among the contributing factors to this scenario include inefficient waste collection systems, inadequate waste transfer systems, institutional under capacity, poor waste disposal practices, and malfunctioning of many wastewater treatment plants in these countries. Therefore, the emergence of nanowastes in the developing country would be a likely additional burden to the already constrained institutional and technical systems. Consequently, considerable segments of the populations in developing countries succumb periodically to diseases linked to waste-related causes. Additionally, many natural ecosystems in these countries are under threat from chemical pollution from poorly managed waste streams from mining, manufacturing plants, as well as industrial and domestic sources. Lessons gained from past experiences should be used as guide in shaping policy directions that would safeguard the humans and other ecosystems from the adverse effects of chemicals or products containing ENMs.

Secondly, due to inadequate specialized skills in the field of waste management in the developing countries,[23] the management of nanowastes would be highly challenging and intractable.[24] It is the incapacity with respect to know-how regarding the full extent of the potential impacts of nanowastes that raises concerns as a result of expected increases of nanoproducts in the developing countries. Therefore, developing countries should develop mechanisms of addressing likely potential adverse effects of nanowastes before cases of human disease or ecological harm are widespread.

Thirdly, developing countries are characterized by weak, poor, or non-existent policy and legislative frameworks for addressing waste management aspects for the common industrial-, commercial-, and municipal-related waste streams.[25] Moreover, even for the developing countries with substantive waste legislative frameworks in the statutes, like South Africa, such laws are often poorly enforced. This is closely intertwined with the second factor. To avoid the present scenario, it is proposed that the developing countries initiate strategic approaches of dealing with nanowastes that are appropriate to their situations. This is because nanotechnology remains to be one of the key economic growth drivers of the 21st century which these states will be part of. Secondly, the legislations concerning waste management at different phases of the materials lifecycle needs be developed, and institutions with the necessary infrastructure and human capacity for enforcing them effectively be established.

Hence, it is likely that the same fate of poor waste management may apply to nanowaste streams. Therefore, this study seeks to estimate the potential risk of ENMs to the aquatic and terrestrial environments within the context of developing country

environmental management setting. The findings are expected to raise awareness among the authorities in these countries – as they endeavor to optimize the benefits of nanotechnology to address developmental challenges in health, energy, and water sectors – and ultimately increase their participation in global commerce, which may involve consumer products containing ENMs.

In summary, the objectives of this paper are twofold: first, to model the quantities of nano-silver (nAg) and nano-titanium dioxide ($nTiO_2$) ENMs to the aquatic and terrestrial environments potentially released from the cosmetic products in the Johannesburg City Metropolitan (hereafter referred as JHB City). Secondly, to evaluate the potential risks of ENMs they are likely to poses to different environmental compartments. This was determined by computing the ratio of the predicted environmental concentrations (PEC) to the predicted no-effect concentrations (PNEC). The risk evaluation was carried out based on the established European Council Bureau[26] chemical risk assessment procedures. The choice of the cosmetic industry was mainly for two reasons. On the one hand, according to the inventory of company declared nanoproducts developed by Woodrow Wilson International Centre for Scholars[27] (2009), cosmetic products were found to be the major category users of ENMs and these products find wide use globally including South Africa. On the other hand, the JHB City is among the top 20 cosmopolitan cities globally in terms of the industrial-base, trade and commerce, size and hosts diverse multinational cosmetic industry companies. This makes JHB City a good case study area on the dispersion of ENMs to the environment, particularly from products with wide daily usage by large populace such as cosmetics. This provides a compelling case for examining the potential impacts of the aquatic and terrestrial environments influenced by the use of cosmetics containing ENMs. However, it is noteworthy that the potential risks of counterpart metallic bulk chemicals (for Ag and TiO_2) are not considered in this study.

Problem boundary

For any model to be meaningful, the system boundaries both temporal and spatial should be well defined. This is because such system boundaries provide a contextual framework for inferring conclusions from the derived model estimates. In addition, the setting of problem boundaries allows effective selection and identification of the model inputs, the degrees of uncertainty for the input data, as well as the formulation of the model underlying assumptions. In our study, 2007 was chosen as the base year for the data used in quantifying ENMs releases from the cosmetic products into the JHB City environment, and in assessing the potential effects into the receptor environments. The input model data used in the model comprised of global production of ENMs, population of Switzerland, population of South Africa, population of JHB City, dilution factor, ENMs toxicity data in the environment, as well as other forms of economic and social data that were required in order to develop the model.

Spatially, the JHB City covers a land area of about 1 664 km^2, and served by a network of wastewater treatment plants and sewage compositing facilities. For the sludge generated from the wastewater, up to 97.6% of the total annual tonnage is processed into agricultural compost, and the rest disposed of in landfills. However, due to high non-equitable income distribution per households particularly in the South Africa context, the poor population living in the JHB City was not taken into account during the development of the model to avoid over-estimation of the most probable releases of the ENMs into the environment.

The contributions of the case study presented in this paper are twofold. Firstly, it provides the first reported insights on estimated potential environmental accumulation of ENMs in the developing countries, which in many respects are unique from the developed countries scenarios recently published[17-20] to date. For instance, previous modelling releases of ENMs into the environment were based on developed countries territorial boundaries[17,18,20] or geographical regions[19] such as Europe and USA. And secondly, in the previous studies,[17-20] the choice of territorial and regional spatial land areas introduced large uncertainties by assuming the ENMs were released into every part of the region or country. This was probably underpinned by the assumption that the entire country or regional population were consumers of particular nanotechnology-based products or applications equitably such as paints, sprays, textiles, cleaning agents, plastics, and cosmetics. However, such approach had the limitation of under-predicting the ENMs concentrations in areas (e.g. in large cities) characterized by high application rates or use of nanoproducts. Conversely, the approach is limited by the over-prediction of ENMs concentrations in regions or areas with limited or no applications of

nanotechnology-based products. In this study, this limitation was partly addressed by focusing on risk characterization of ENMs in a city region – due to expected high release of ENMs from different nanoproducts or nanotechnology-driven applications. Cosmetics containing ENMs were used to illustrate the applicability of the model.

Model assumptions

In this paper, the proposed model is based on four key assumptions. Firstly, globally there is very limited published data on the quantities of ENMs per product category in any given country or city. Therefore, it was assumed that the ENMs quantities of ENMs owing to different nanoproducts estimated based on the published data for nAg and $nTiO_2$ globally and Switzerland[17,18,28] can be modified by use of correction factors to provide reasonable insights on the potential quantities of ENMs released into the JHB City environment. Secondly, companies in the cosmetic industry sector are multi-international in character, hence, their products are the same in form, type, and formulation globally including those marketed in South Africa. As a result, the concentration of ENMs in any unit nano-based cosmetic or sunscreen product is invariant for a given company irrespective of the location of trade area globally. Examples of the ENMs concentration per unit product (e.g. in cosmetics, paints, coatings, pesticides, etc) have recently been summarized by Boxall and co-workers.[29]

Thirdly, due to limited published ENMs, ecotoxicological data for organisms in the tropical South Africa-type climate organisms, it is assumed the data currently reported in the literature mostly on tundra organisms provides a good estimate on the potential toxicological effects owing to the release of ENMs in the former's environment. And finally, after the entry of the ENMs into the environment irrespective of the emission route, they retain their nanoscale functionalities and properties as these aspects control the interactions of nanoscale materials with the receptor organisms. Such assumption is profound given that the present data is very limited in elucidating the fate and behavior of ENMs in the environment due to the abiotic factors like pH, natural organic matter, temperature, etc.[3,7,30,31]

Model scenarios

The integrity of a computer-based predictive model is dependent on the input data; however, in real world, the available and accessible data to a large extent is characterized by high degrees of uncertainties, and the same applies to the case-study presented here. Lack of available data and the inconsistency of the fate and behavior of ENMs in different ecological systems[7,24,30,32] have been acknowledged, and the use of different scenarios attempts to mitigate part of this problem. Therefore, using the technical guidelines on the assessment of chemical exposures developed by European Chemicals Bureau,[26] three most probable scenarios were developed to account for the input data uncertainties. For example, the population statistics for JHB City exhibited large variance for the year 2007 depending on the data sources.[33] Similarly, the data variance was observed in other parameters such as wastewater generated per capita, wastewater treatment plants (WWTPs) operational efficiency within the JHB City Metropolitan area, and the market penetration of cosmetic nanoproducts, among others. The model comprised of the minimum, probable, and maximum release scenarios of ENMs from the cosmetic products in JHB City.

The minimum (conservative) scenario predicts the lowest quantities of ENMs exposure to organisms in the environment due to lower releases of nanoscale structures from the cosmetic nanoproducts. Subsequently, this leads to a possibility of least undesirable effects in the ecosystems. On the other hand, maximum (worst-case) scenario signifies optimal releases of ENMs resulting to highly elevated concentrations in the environment – with the potential to cause adverse effects to the receptor organisms. The probable scenario attempts to provide realistic estimates based on the available and reliable input model data for 2007.

Model formulation

Figure 1 illustrates mass flow-route analysis of ENMs from the cosmetic products to the natural environments through four potential release pathways, namely; wastewater from the WWTPs, direct runoffs into the environment (untreated streams), solid wastes directly disposed of into the land fills after the use phase (remains in the cosmetic products containers), and use of sewage sludge for the agricultural application purposes. In the South African context, the model does not account for the releases into the air environment because of limited manufacturing activity of cosmetics containing ENMs in the country – and therefore, the cosmetic products volumes used in this

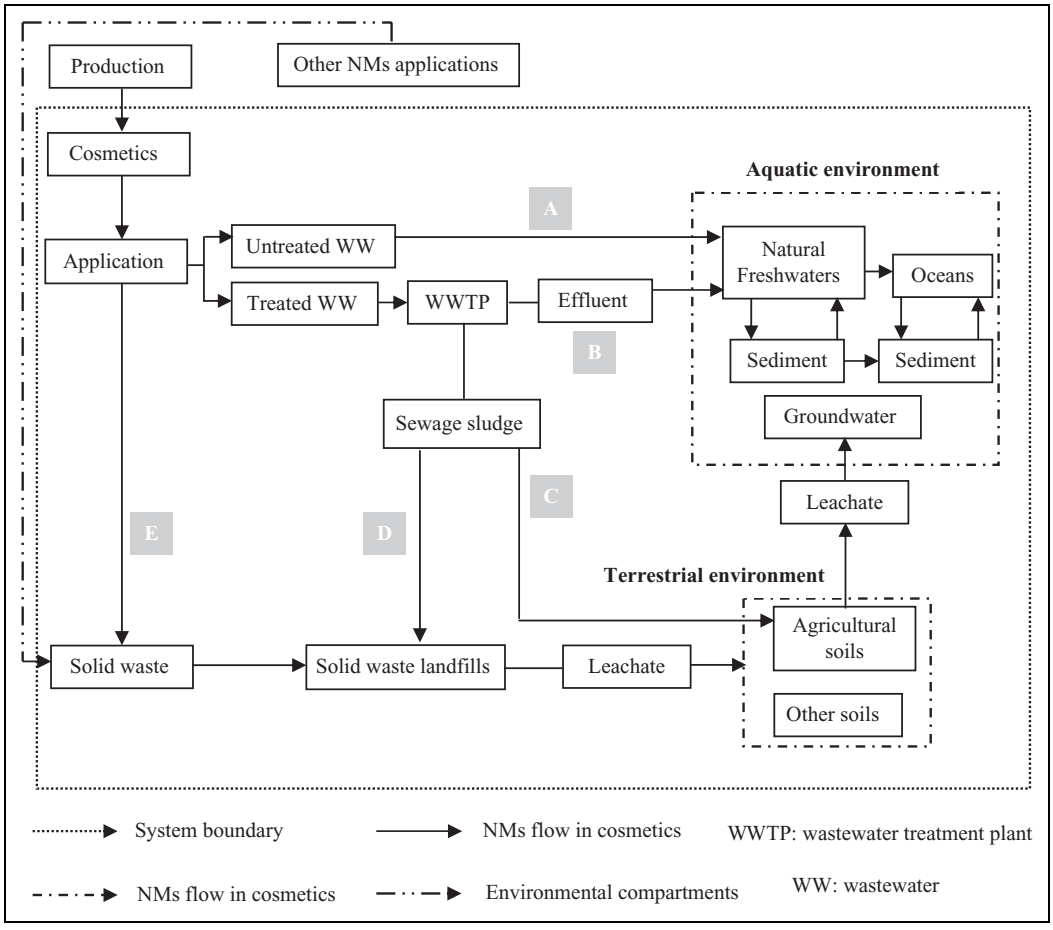

Figure 1. Schematic representation of the engineered nanomaterials (ENMs) in different environmental compartments (most likely scenario in South Africa). The ENMs flows considered include the pathways A, B, and C.

study were assumed to have been imported as finished products in South Africa. In addition, the South Africa government policy prohibits the incineration of sludge, therefore, no estimates on the quantities of ENMs releases into the air compartment from such activities are considered. This scenario dramatically contrasts the current practices in the developed countries.[17-20]

Estimation of ENMs in JHB City: aquatic and terrestrial ecosystems

To determine the ENMs environmental concentrations in the JHB City from cosmetic products, first, the Switzerland data had to be customized into South African conditions using the economic and demographic data. The economic data comprised of the gross domestic product (GDP) in reference to the income per capita for each country (Switzerland, South Africa), the JHB City's GDP contribution to the South African economy, and the nano-based cosmetic products market penetration (values used were theoretical for simulation purposes) in JHB City. The demographics data consisted of the national population for each country (Switzerland, South Africa), percentage of the low income South Africans, and the JHB population for 2007. The total quantity for each ENMs type in the cosmetic nanoproducts in the JHB City was computed using the expression:

$$\mathrm{JHB}_{\mathrm{ENM}i} = \mathrm{SW}_{\mathrm{ENM}i} \bullet \mathrm{cf}_1 \bullet \mathrm{cf}_2 \bullet \mathrm{cf}_3 \bullet \frac{\mathrm{GDP}_{\mathrm{JHB}}}{\mathrm{GDP}_{\mathrm{SA}}} \quad (1)$$

where $\mathrm{JHB}_{\mathrm{ENM}i}$ is the quantity of ENMs from cosmetic products containing ENM material i (i = nAg or $nTiO_2$), $\mathrm{GDP}_{\mathrm{JHB}}$ is the GDP for JHB City, $\mathrm{GDP}_{\mathrm{SA}}$ is the GDP for South Africa, $\mathrm{SW}_{\mathrm{ENM}i}$ the quantity of type i ENMs in Switzerland; cf_i is a correction factor, where $\mathrm{cf}_1 = \dfrac{(1-f_{\mathrm{p}}) \bullet \mathrm{POP}_{\mathrm{SA}}}{\mathrm{POP}_{\mathrm{SW}}}$ is the ratio of the South Africa population to Switzerland population (POP: population), f_{p} is percentage of the poor South

Africans (assumed to be 0.55, 0.45, 0.35 for minimum, probable, and maximum scenarios, respectively), $cf_2 = \frac{\text{GDP/capita (SA)}}{\text{GDP/capita (SW)}}$ is the correction factor as a ratio of the South Africa GDP per capita to that of Switzerland (a value of 0.391 was used as a constant under the three model scenarios), and the cf_3 represented the market penetration of cosmetic nanoproducts into the JHB City (values used were: 0.1, 0.25, and 0.45 for the minimum, probable, and maximum scenarios, correspondingly). Note that 0.1 implies about 10% of the JHB City population uses cosmetic products containing ENMs.

Estimation of the ENMs in the aquatic systems

The total ENMs released into the aquatic systems were due to the untreated run-off wastewater reaching the environment and the non-removed quantities in the effluent from the conventional WWTPs. Therefore, the total ENMs is computed using the expression:

$$\begin{aligned}\mathrm{ENM}_{\mathrm{Water,input}i} = {} & \mathrm{ENM}_{\mathrm{WW,Total}i} \bullet (1 - f_{\mathrm{WWTP}i}) \\ & + \mathrm{ENM}_{\mathrm{WW,Total}i} (f_{\mathrm{WWTP}i} - f_{\mathrm{WWTP}i} \bullet f_{\mathrm{Removal}i})\end{aligned} \tag{2}$$

where: $\mathrm{ENM}_{\mathrm{Water,input}i}$ is the total specific ENM_i in cosmetics reaching the natural waters ($t \cdot a^{-1}$); $f_{\mathrm{WWTP}i}$ is the fraction of wastewater treated in WWTPs, $f_{\mathrm{Removal}i}$ is the fraction of a given ENM_i removed during treatment through the WWTPs, and $\mathrm{ENM}_{\mathrm{WW,Total}i}$ is the total ENM_i for type i released from the cosmetic products ($t \cdot a^{-1}$).

The first part of eq. 2 determines the quantity of ENMs into the aquatic environment from run-off sources without treatment, and the second part calculates the released volume from the WWTPs due to the systems inefficiency. Algebraic simplification of Eq. 2 yields:

$$\mathrm{ENM}_{\mathrm{Water,input}i} = \mathrm{ENM}_{\mathrm{WW,Total}i} \bullet (1 - f_{\mathrm{WWTP}i} \bullet f_{\mathrm{Removal}i}) \tag{3}$$

$\mathrm{ENM}_{\mathrm{WW,Total}i}$ is estimated based on the economic and demographic data for ENM type i. Values $f_{\mathrm{WWTP}i}$ and $f_{\mathrm{Removal}i}$ parameters are dependent on the population whose effluent is treated through WWTP and the mean efficiency of treatment plants, respectively.

The concentration of ENMs in the WWTPs provide valuable insights as to whether the nanoscale materials under question poses any form of risk to the organisms in WWTPs or those in the downstream after the effluent release into the environment. The ENMs concentration in the wastewater (C_{WW}) is assumed as an equivalent of the concentration in the WWTP (C_{WWTP}), and evaluated using the expression:

$$C_{\mathrm{WW}i} = C_{\mathrm{WWTP}i} = \frac{\mathrm{ENM}_{\mathrm{WW,Total}i,\mathrm{WWTP}} \times 10^{12}}{\mathrm{WW}_{\mathrm{percapita}} \bullet f_{\mathrm{WWTP}} \bullet \mathrm{POP}} \tag{4}$$

where C_{WWTPi} is the concentration of ENMs type i in the WWTP ($\mu g \ell^{-1}$); $C_{\mathrm{WW}i}$ is the concentration of type i in wastewater ($\mu g \ell^{-1}$); $\mathrm{ENM}_{\mathrm{WW,Total}i,\mathrm{WWTP}}$ is the amount of ENM type i entering into the WWTPs ($t \cdot a^{-1}$); and $\mathrm{WW}_{\mathrm{percapita}}$ wastewater generated per person per year ($m^3 \cdot p^{-1} \cdot a^{-1}$); $f_{\mathrm{WWTP}i}$ fraction of wastewater treated in WWTPs.

Thus, the predicted environmental concentration (PEC) in the aquatic environment is evaluated as follows:

$$\begin{aligned}\mathrm{PEC}_i = {} & \frac{\mathrm{ENM}_{\mathrm{Water,input}i} \bullet 10^{12}}{\mathrm{POP} \bullet \mathrm{WW}_{\mathrm{percapita}} \bullet D_{\mathrm{k}}} = C_{\mathrm{WWTP}} \\ & \bullet \frac{\mathrm{ENM}_{\mathrm{Water,input}i}}{\mathrm{ENM}_{\mathrm{WW,Total}i,\mathrm{WWTP}}} \bullet \frac{f_{\mathrm{WWTP}}}{D_{\mathrm{k}}}\end{aligned} \tag{5}$$

where PEC_i is the concentration of ENMs type i in aquatic environment ($\mu g \ell^{-1}$), and D_{k} is the dilution factor in the receiving water.

And finally, the overall risk characterization of a given chemical – generally called risk quotient (RQ) – is computed as a ratio of the predicted environmental concentrations (PEC) to the predicted no effect concentrations (PNEC). The PNEC values for the nAg and $nTiO_2$ were evaluated using published ecotoxicological data. A risk assessment factor (AF) of 1000 was applied to account for the large data uncertainties.[26] According to ECB,[26] a value of 1000 is recommended for short-term toxicity data to provide a conservative and protective value primarily designed to ensure that substances with the potential to cause adverse effects are identified during the effects assessment. These ratios were computed for the aquatic and the terrestrial environmental compartments.

Estimation of the ENMs in the terrestrial systems

The ENM's flow into the terrestrial environmental systems occurs through agricultural application of the WWTP sludge, sludge disposal into the land fills, and from the run-off water. However, in this study, the contribution of ENMs into the terrestrial

environmental systems due to run-off will not be considered. This is because of the complexity of evaluating quantities of ENMs that result into the terrestrial environments from the run-off sources, and secondly, the paucity of data required for computing the resultant quantities into the terrestrial compartment.

The resultant ENMs into the receiving terrestrial ecosystems through the sludge from WWTP is determined by the difference between the total amount released into the treatment plant and the amount removed by the plant. The final quantity is given by:

$$\mathrm{ENM}_{\mathrm{Sludge,input}i} = \mathrm{ENM}_{\mathrm{WW,Total}i} \bullet (1 - (f_{\mathrm{WWTP}i} \bullet (1 - f_{\mathrm{Removal}i}))) \quad (6)$$

Thus, the prediction of the final concentration of ENMs in the terrestrial ecosystems due to sludge applications for the agricultural purposes is dependent on the amount of ENMs in the sludge used as fertilizer, the application rates of the sludge annually (total applied sludge per year A [$\mu g.kg^{-1}.yr^{-1}$], the bulk soil density [$RHO_{soil} = 1\ 700\ kg.m^{-3}$], and the agricultural mixing depth [$D_{soil} = 0.2$ m]).[26] Consequently, the PEC in the agricultural soils can be modelled using the equation:

$$\mathrm{PEC}_{\mathrm{soil}} = \frac{A \bullet 10^9}{\mathrm{RHO}_{\mathrm{soil}} \bullet D_{\mathrm{soil}}} \quad (7)$$

Results and discussion

Quantification of ENMs in JHB City

The global production of nAg varied from 300 tonnes (t) to 800 t by 2007 based on expert estimates and literature survey.[17] In addition, according to the Silver Institute,[34] the global production of silver was 25 620 t, with about 5% being likely available for the production of nAg as the rest was utilized in industrial applications and consumer products. This translated to 300 t, 500 t, and 1230 t as the likely minimum, probable, and maximum scenarios of global volumes of nAg, respectively. Therefore, Mueller and Nowack[17] calculated the minimum, probable, and maximum quantities of nAg for Switzerland as 2.1 t, 3.5 t, and 8.6 t, respectively. By applying eq. 1, the possible volumes of nAg in JHB City were 0.023 t, 0.085 t, and 0.263 t for the minimum, probable, and maximum scenarios, respectively, as shown in Table 1.

To characterize the risk posed by the nAg in cosmetic nanoproducts to the JHB City ecological systems, the volumes of nAg were distributed in six different applications. This resulted in the quantities for nAg used in cosmetics to be 0.008 t, 0.053 t, and 0.307 t, for the minimum, probable, and maximum scenarios, respectively, as illustrated in Table 2.

Similarly, the volumes of $nTiO_2$ were evaluated for the JHB City based on the global production volume of 5000 t according to the UNEP estimates.[35] This value has an estimated error of $\pm 40\%$ (this translates minimum volumes as 3000 t) whereas the maximum use in Switzerland industries was about 400 t – as the global production was 60 926 t.[28] Subsequently, the minimum, probable, and maximum values for $nTiO_2$ used in cosmetics in the JHB City were 0.007 t, 0.048 t, and 1.289 t, respectively (data not shown).

PEC estimations

The estimation of the PEC values for the nAg and $nTiO_2$ were derived using eq. 5. Factors influencing PEC estimates in the aquatic or terrestrial ecosystems dependent on the removal efficiency of ENMs in the WWTPs, the matrix under which the ENMs were embedded into the nanoproducts (for cosmetics it is a liquid-phase matrix), fraction of the wastewater treated in the WWTPs, dilution factor, use or disposal of the sludge, among others. As an example, the efficiency of the treatment plants for removing the ENMs could either be low or high. Preliminary findings of Westerhoff and others[36] indicated low to high WWTP removal efficiencies of different ENM types from the wastewater. For instance, the $nTiO_2$ removal efficiencies values were reported as 90% whereas for nZnO and nFe_2O_3 ENMs – also used in cosmetics –were 5% and 30%, respectively.

The nAg removal efficiency used were based on the reported values for silver in WWTP by Shafer et al.,[37] ranging from 94% to 99%, and Daxbeck et al.,[38] of 85% for the minimum, probable, and maximum scenarios, respectively. Generally, in developing countries, most WWTPs are characterized by low operational efficiencies, therefore, the values reported for $nTiO_2$[36] were regarded as 'high' (since >80%) in this study. This is because the values were derived based on experimental plant set-up in the developed countries. However, with no published data for WWTP for the JHB City, then, the high removal efficiency values in our study were assumed to be 20%–30% lower than those reported in the literature.[36-38] On the other hand, discussions with experts knowledgeable in the operations of many WWTPs in the JHB City suggested the overall removal efficiency could in practice be as low as 45% (personal

Table 1. Volumes of nAg in JHB City under the minimum, probable, and maximum scenarios[a]

Scenarios	GP[b]	Factor[d]	nAg (SW)	nAg (SA)	nAg (JHB)	MP (%)
Minimum	300	0.007	2.100	0.256	0.038	10
Probable	500	0.007	3.500	0.427	0.085	25
Maximum	1230[c]	0.007	8.600	1.050	0.263	45

Abbreviations: JHB: Johannesburg, SW: Switzerland, SA: South Africa, MP: market penetration.
[a] Values in tonnes per annum (t/a).
[b] Global production of nAg in 2007.
[c] Switzerland population in relation to that of major nanotechnology-based countries (see details in ref. 17).
[d] See statistics in refs 17 and 19 based on scenarios in Switzerland and EU, respectively.

Table 2. The distribution of nAg in six nanoproducts in Switzerland, South Africa, and JHB City[a]

Nano-based products	Switzerland			South Africa			Johannesburg		
	MIN-E_{SW}	PRO E_{SW}	MAX E_{SW}	MIN-E_{SA}	PRO-E_{SA}	MAX-E_{SA}	MIN-E_{JHG}	PRO-E_{JHB}	MAX-E_{JHB}
Plastics	0.244	0.407	1.001	0.025	0.128	0.594	0.004	0.026	0.148
Metal products	0.056	0.093	0.228	0.006	0.029	0.135	0.001	0.006	0.034
Cosmetics/ supplements	0.506	0.843	2.070	0.052	0.264	1.228	0.008	0.053	0.307
Sprays/cleaning agents	0.360	0.600	1.473	0.037	0.188	0.874	0.006	0.038	0.218
Textiles	0.222	0.371	0.911	0.023	0.116	0.540	0.003	0.023	0.135
Paint/sealings	0.712	1.187	2.917	0.073	0.372	1.730	0.011	0.074	0.432

Abbreviation: JHB: Johannesburg.
[a] Values in tonnes per annum (t/a).

communication). These values were used to develop a case of potential environmental impact when the ENM removal efficiency of the treatment plant was very low.

Other factors comprised the percentage of wastewater treated and the dilution factor. Unlike in Europe where the default dilution factor of 10 is used, in South Africa because of low precipitation, and being a water scarce country, the dilution factor was taken to be 1 or 3. In fact, during prolonged draught season, this figure is likely to be <1 because of high evaporation as well as increased use of water from the river systems for irrigation purposes. Therefore, for the JHB City, a dilution factor close or below 1 provides a more realistic estimation over the entire year.

Using the input parameters under high ENMs removal efficiency regime of the WWTPs, the quantity of nAg released into the environment from the cosmetics into the aquatic JHB City ecosystems were estimated to be 2.84 kg a^{-1}, 25.00 kg a^{-1}, and 183.18 kg a^{-1} for the minimum, probable, and maximum scenarios, respectively. On the other hand, the total quantities released into the sludge amounted to 4.93 kg a^{-1}, 27.79 kg a^{-1}, and 123.76 kg a^{-1} for the minimum, probable, and maximum scenarios, respectively. Similar values were calculated for the $nTiO_2$, and the results are summarized in Table 3. However, if the WWTPs were operating at low ENMs removal efficiency regime at 45%, 35 %, and 25% for the minimum, probable, and maximum scenarios, this yielded resultant nAg quantities into the aquatic environments as 4.97 kg a^{-1}, 39.90 kg a^{-1}, and 260.90 kg a^{-1}, respectively. Similar results were evaluated for the $nTiO_2$ (figures not shown).

The findings suggest that the environmental payload of the ENMs into a given environmental compartment (aquatic or soil) is depended on the WWTP efficiency. For example, if the WWTP efficiency changes from 'low' to 'high,' the resultant payload release into the aquatic environment decreases, and simultaneously the ENMs quantities increase in the terrestrial ecosystem through use of sludge for agricultural purposes, and disposal of unused sludge through landfills. This implies, irrespective of the removal efficiency of WWTP as low or high, the environmental concerns due to ENMs

Table 3. Calculated quantities of nAg and $nTiO_2$ in the JHB City aquatic environment at 'high' removal efficiency regime under minimum, probable, and maximum scenarios

ENM	Variable	MIN-EJHG	PRO-EJHB	MAX-EJHB
nAg	Ag_{total}: total silver released into WW (kg/a)	7.77	52.79	306.58
	f_{WWTP}: fraction of WW treated in WWTPs	0.80	0.70	0.60
	$f_{Removal}$: fraction of Ag removed in WWTPs	0.79	0.75	0.67
	Ag_{WWTP}: silver entering into WWTPs in (kg/a)	6.22	36.95	184.16
	$Ag_{WWTP,removed}$: silver removed in WWTP (Ag in sludge) (kg/a)	4.93	27.79	123.76
	$Ag_{WWTP,removed}$: silver released effluents from WWTPs (kg/a)	1.29	9.16	60.41
	$Ag_{untreated}$: silver in untreated WW (kg/a)	1.55	15.84	122.77
	Ag_{water}: silver that enters into aquatic environment (kg/a)	2.84	25.00	183.18
$nTiO_2$	$TiO2_{total}$: total TiO_2 released into WW (kg/a)	7.03	47.73	1289.38
	f_{STP}: fraction of WW treated in WWTPs	0.80	0.70	0.60
	$f_{Removal}$: fraction of TiO_2 removed in WWTPs	0.76	0.72	0.64
	TiO_{2WTTP}: TiO_2 entering into WWTPs in (kg/a)	5.62	33.41	773.63
	$TiO_{2WWTP,removed}$: TiO_2 removed in WWTP (Ag in sludge) (kg/a)	4.27	24.06	495.12
	$TiO_{2WWTP,unremoved}$: TiO_2released effluents from WWTPs (kg/a)	1.35	9.36	278.51
	$TiO_{2,\ untreated}$: TiO_2 in untreated WW (kg/a)	1.41	14.32	515.75
	TiO_{2water}: TiO_2 entering into the aquatic environment (kg/a)	2.76	23.68	794.26

Abbreviations: ENM: engineered nanomaterials, WWTP: wastewater treatment plants.

merits attention to avoid long-term unintended environmental consequences. These results confirm earlier findings[8] that the removal of ENMs (e.g. nAg) could restrict the municipal wastewater treatment facilities from trading their sludge as fertilizer for agricultural lands.

PNEC estimations

Estimated PNEC were derived from the dose-response assessment nanoecotoxicological data published in the scientific literature – and in accordance to the prescribed procedures in the Technical Guidance Document (TGD) of the European Union on risk assessment.[26] The PNEC is the ratio of the no observed effect concentration (NOEC) to the assessment factor (AF). Because of the large uncertainties of the available data on ENMs, the highest AF of 1000 was adopted in this study. Moreover, the lack of data for the NOEC values in the scientific literature either in water or soil compartments for the ENMs (nAg and $nTiO_2$) led to the use of LC_{50} and EC_{50} values as recommended by the ECB[26] in computing the PNEC values used in our model.

Table 4 summarizes PNEC values for $nTiO_2$ and nAg calculated using the limited ecotoxicological data for several relevant environmental risk assessment organisms. From the results, it shows the reported studies for nAg are largely lacking and no values were found for the NOEC, EC_{50}, or LC_{50} in the soil environment (previously lack of such data in the soil compartment had been acknowledged[17-20] – despite extensive search efforts in the scientific literature). However, the lack of standardization of NOEC, EC_{50}, or LC_{50} results in the scientific literature in addition to the limited studies reported at different trophic levels to date either in the aquatic or terrestrial organisms introduced large data uncertainties on the computed PNEC values. However, the present scenario is expected to change gradually as chronic toxicity of ENMs that are standardized and validated become available in the scientific literature.

Additional factors that influences differences in NOEC, EC_{50}, or LC_{50} values for a given ENM comprise of the production methods, medium of dispersion used during the exposure period, effects of the abiotic factors either present or absent in a given reported data set, and lack of chronic data. Therefore, in our study, the PNEC value of 1 $\mu g\ L^{-1}$ was used for the $nTiO_2$ as several available ecotoxicological data[29,42,46,47] are within this range (see Table 4). The same value was used in the studies by Mueller and Nowack.[17] In the case of nAg, a value of 1 $\mu g\ L^{-1}$ was also used as it is based on the only reported value of NOEC for nAg in the scientific literature.[40]

Risk characterization: aquatic ecosystems

Table 5 shows that the RQ for $nTiO_2$ under high removal efficiencies in the WWTP were much less than 1 for the minimum and probable scenarios irrespective of the dilution factor (D). However, for the

Table 4. Summary of calculated PNEC based on NOEC values derived from toxicity data for aquatic and terrestrial organisms[a]

ENM	Test species	Conc (mg L^{-1})	PNEC (μg L^{-1})	Reference
nAg (water)	*Ceriodaphnia dubia*	0.696 × 10^{-3} (LC_{50})	0.696 × 10^{-3}	39
	Danio rerio (Zebra fish)	1	1	40
	Danio rerio (Zebra fish)	20 (EC_{50}; ng/L)	2 × 10^{-5}	41
	E. coli & B. substilis (bacteria)	20 – 40	40	42
$nTiO_2$ (water)	*Daphnia magna*	1	1	43
	Pseudokirchneriella subcapitata	0.98	0.98	44
	Vibrio fischeri	20,000	20,000	45
	Thamnocephalus platyurus	20,000	20,000	45
	Daphnia magna	<0.1 (72 hr)	0.1	46
	Daphnia magna	<50 (48 hr)	50	46
	Daphnia magna	1	1	47
	Daphnia magna	3	3	46, 48
	Daphnia magna	250 or 500	250 or 500	49
$nTiO_2$ (soil)	*Porcellio scaber* (isopoda, Crustacea)	1025 mg/g	1025 μg/kg	50

Abbreviations: Conc.: concentrations, NOEC: no observed effect concentration, PNEC: predicted no effect concentrations.
[a] An AF of 1000 was used for NOEC, LC_{50}, EC_{50} values.

Table 5. Risk characterization of ENMs under high removal efficiency regime of the WWTP

ENM	Parameters	MIN-E_{JHG}	PRO-E_{JHB}	MAX-E_{JHB}
nAg	Concentration in STP (μg/ℓ)	7.6E-03	90.5E-03	1038.4E-03
	Dilution factor: 10 (PEC, μg/ℓ)	0.3E-03	4.3E-03	62.0E-03
	Dilution factor: 3 (PEC, μg/ℓ)	0.9E-03	14.3 E-03	206.6E-03
	Dilution factor: 1 (PEC, μg/ℓ)	2.8E-03	42.9E-03	619.7E-03
	RQ (D = 10) (no units)	2.94E-04	4.29E-03	6.20E-02
	RQ (D = 3) (no units)	9.30E-04	1.43E-02	2.07E-01
	RQ (no dilution) (no units)	2.74E-03	4.29E-02	6.20E-01
$nTiO_2$	Concentration in STP (μg/ℓ)	6.90E-03	81.80E-03	4361.90E-03
	Dilution factor: 10 (PEC, μg/ℓ)	0.30E-03	4.10E-03	268.70E-03
	Dilution factor: 3 (PEC, μg/ℓ)	0.90 E-03	13.50 E-03	895.60E-03
	Dilution factor: 1 (PEC, μg/ℓ)	2.70E-03	40.58E-03	269.9E-03
	RQ (D = 10) (no units)	2.70E-04	4.06E-03	2.69E-01
	RQ (D = 3) (no units)	9.00E-04	1.35E-02	8.96E-01
	RQ (D = 1) (no units)	2.70E-03	4.06E-02	2.69E-00

Abbreviations: JHB: Johannesburg, RQ: risk quotient, PEC: predicted environmental concentrations, WWTP: wastewater treatment plants.

maximum scenario, the RQ > 1 (2.7) or close to 1 (0.86) for D = 1 or 3. This indicates the necessity for a more thorough establishment of the potential risks of $nTiO_2$ from the cosmetic products into the aquatic environment – and merits gathering of additional data to validate our results. One way of achieving this objective is by establishing a database of well-validated NOEC values that can support environmental risk assessment. On the other hand, if a PNEC value of 0.1 μg L^{-1} (see Table 4) was used, the risk under the probable (for D =1; RQ = 0.4) and maximum scenarios (for all D values; RQ = 2.6, 8.9, 26.9) for the $nTiO_2$ suggests potential elevated risk concerns to the aquatic organisms (figures not shown).

In a previous study,[17] a PNEC value of 40 μg L^{-1} based on an EC_{50} value for nAg with *E. coli and B. substilis* as the test organisms was used. To date, only a single NOEC value of 1 mg L^{-1} for *Danio rerio* has been published, and therefore, a PNEC value of 1 μg L^{-1} was derived. It is noteworthy that if the LC_{50} value of 0.696 ng/L for *Ceriodaphnia dubia* was used,

the resultant PNEC value would be 6.96×10^{-1} μg L^{-1} (0.696 μg L^{-1}). In this study, the PNEC value derived using the *C. dubia* as a test organism was adopted primarily because it is an ideal organism for ENMs toxicity assays due to its high sensitivity to both organic and inorganic toxicants.

Secondly, *C. dubia* is a particle feeder invertebrate (particle-based diet) and this makes it an ideal candidate to accumulate high concentrations of ENMs as nanoscale materials are likely to be largely deposited in the sediment compartment of the aquatic systems. Thirdly, the results presented by Gao et al.[39] are more realistic as the ENMs were suspended directly into natural river waters through simple and gentle mechanical mixing methods as opposed to results previously obtained where drastic mixing methods such as use of ultrasound, sonication, etc, toxic solvents/surfactants (e.g., toluene, THF, SDS, SDBS), or a combination of the above techniques in the preparation of ENMS-suspensions in various results reported in the literature which lead to ideal EMNs-dispersion levels that are highly improbable to achieve in natural waters.

Under the high removal efficiency regime, the nAg risk concerns were negligible irrespective of the dilution factor for the three scenarios (minimum, probable, and maximum) if the PNEC was 40 μg L^{-1} or 1 μg L^{-1} (results shown in Table 5), which confirms our results are in agreement to previously reported findings.[17] However, considering PNEC based on the *C. dubia* as test organism as more ideal, the risk quotient would be as follows: D = 10 (0.04, 0.62, 6.16 for minimum, probable, maximum scenarios); D = 3 (0.13, 2.05, 29.7 for minimum, probable, maximum scenarios), and D = 1 (0.4, 6.16, 89.0 for minimum, probable, maximum scenarios; figures not shown). It is noteworthy that in all three dilution factors, the maximum scenario indicates high levels of risk to the environment. In addition, for the D = 1, all the three scenarios suggests elevated risk levels to the aquatic organisms and should be treated as more realistic – given they mirror more closely to the actual dilution factor throughout the year in the JHB City. Therefore, the results suggest that nAg may pose considerable risk in the JHB City area, and actual measurements are essential to validate our simulation-based results. The resultant risk would even be higher if the PNEC (of 2×10^{-5} μg L^{-1}) was calculated based on the EC_{50} value reported by Lee and colleagues[41] for *Danio rerio*. However, it should be noted that in our study, although the EC_{50} value reported by Lee and colleagues[41] are more conservative (see Table 4), they were not used in evaluating the overall risk of nAg in the aquatic environment. This is because the EC_{50} value[41] was determined using highly purified nAg and no actual environmental conditions were taken into account, for instance, in contrast to natural river water used in the case of the findings of Gao et al.[39]

The wide variation of PNEC values for a given ENM over several orders of magnitude points to the urgent need for the development of a standardized evaluation methodology for the NOEC values. This would improve the quality of data necessary for supporting meaningful risk assessment in the aquatic ecosystems. For example, the values reported by Griffitt et al.[40] and Lee et al.[41] indicate a 50,000 fold-order of magnitude difference, yet the results are based on the same species, *Danio rerio*. Furthermore, it shows the PNEC values strongly influences the final risk assessment of a given ENM. Conversely, these results may suggest that expressing the toxicity of ENMs using the mass per unit volume units may be inadequate, and an alternative or additional metric based on parameters such as surface area, surface reactivity, or surface area per unit mass, among others, should be considered in order to derive more consistent PNEC values.

Considering the risk under the low-efficiency regime, the results are summarized as follows. For the nAg if the PNEC (6.96×10^{-4} μg $L^{-}1$) was based on the *C. dubia* as test organism as more ideal, the RQ values were: for D = 10 (0.07, 0.98, 12.7 for minimum, probable, maximum scenarios); D = 3 (0.23, 3.27, 42.3 for minimum, probable, maximum scenarios), and D = 1 (0.7, 9.82, 127.0 for minimum, probable, maximum scenarios; figures not shown). Results under the maximum scenario, the RQs >10 and suggest elevated risks to the receptor organisms independent of the dilution factor. At D = 1, which reflects a realistic scenario, in JHB City depicts a high state of risk of nAg to the environment. However, for the $nTiO_2$, the results indicate a slight change of the RQ as PNEC remained at 1 μg L^{-1}, for instance, in the case of D = 1, the values for minimum, probable, and maximum scenarios were 4.41×10^{-3}, 6.18×10^{-2}, and 3.79 (figures not shown), respectively.

Risk characterization: terrestrial ecosystems

In JHB City, about 193 000 tonnes per annum (ta^{-1}) of sludge were produced in 2007 and approximately

Table 6. Calculated quantities of nAg and $nTiO_2$ in the JHB City terrestrial environment at high and lower removal efficiency regimes under minimum, probable, and maximum scenarios

		MIN-E_{JHG}		PRO-E_{JHB}		MAX-E_{JHB}	
	Parameters	LE	HE	LE	HE	LE	HE
nAg	Total nAg in sludge (kg/a)	2.80	4.93	12.90	27.79	46.00	123.76
	nAg in agricultural compost (97.6%) (kg/a)	2.24	3.94	11.46	24.68	44.90	120.79
	nAg in disposed in landfills (2.4%) (kg/a)	0.56	0.99	1.44	3.11	1.10	2.97
$nTiO_2$	Total $nTiO_2$ in sludge (kg/a)	2.50	4.27	11.70	24.06	193.40	495.12
	$nTiO_2$ in agricultural compost (97.6%)(kg/a)	2.00	3.42	10.39	21.37	188.76	483.24
	$nTiO_2$ in disposed in landfills (2.4%) (kg/a)	0.50	0.85	1.31	2.69	4.64	11.88

Abbreviations: LE: lower efficiencies in WWTP, HE: higher efficiencies in WWTP.

Table 7. PEC and RQ values for nAg and $nTiO_2$ in the terrestrial ecosystem

		MIN-EJHG		PRO-EJHB		MAX-EJHB	
ENM	Parameters	LE	HE	LE	HE	LE	HE
nAg	PEC_{soil} ($\mu g/\ell$)	5.33×10^{-6}	9.39×10^{-6}	2.21×10^{-5}	4.77×10^{-5}	7.18×10^{-5}	1.93×10^{-3}
	RQ	NA	NA	NA	NA	NA	NA
$nTiO_2$	PEC_{soil} ($\mu g/kg$)	4.76×10^{-6}	8.13×10^{-6}	2.00×10^{-5}	4.13×10^{-5}	3.02×10^{-4}	7.73×10^{-4}
	RQ	4.64×10^{-9}	7.93×10^{-9}	1.96×10^{-8}	4.03×10^{-8}	2.94×10^{-7}	2.72×10^{-4}

Abbreviations: LE: lower efficiencies in WWTP, HE: higher efficiencies in WWTP, NA: not available.

80% (minimum release) used for agricultural purposes. The remaining sludge was disposed of into the land fills. Under the maximum release of ENMs into the environment through agricultural route, 97.41% of the sludge was used for agricultural purposes. The mixing depth for agricultural land was taken as 0.2 m[26] and sludge application rate of 10 t/hectare/annum or 1 $kg/m^{-2}a^{-1}$ based on the South African sludge application standards.[51] It should be noted that the recommended sludge application rates in South Africa are double those authorized in Europe of 0.5 $kg\ m^{-2}\ a^{-1}$.[26] Additional source of ENMs flows into the terrestrial environment is from the run-off water, however, in this paper, the contribution from such sources were not considered due to lack of data. For example, there is lack of data concerning the quantity of ENMs reaching the terrestrial sources from run-off water in the JHB City. Thus, the ENMs quantities released into the terrestrial ecosystems as a result of agricultural applications and landfills leachate under the WWTP high and low removal efficiency regimes are summarized in Table 6.

In this study, risk in the terrestrial ecosystems was only evaluated for the $nTiO_2$. This is because no published NOEC, EC_{50}, or LC_{50} values for nAg were found in the scientific literature in the soil or sediment compartments. Table 7 summarizes the results for the PEC of $nTiO_2$ in the soil compartment and the RQ values. The RQ values for $nTiO_2$ appear as too low (<<<1) to cause adverse effects into the environment. However, it should be noted that the modelled values did not take into account the toxicological effects of the ENMs as a result of their inherent physicochemical properties. This means, the evaluated risk is based on the same premise as the conventional risk assessment of bulk chemicals, and therefore, limited to provide a comprehensive risk profile owing to the nanoscale characteristics of $nTiO_2$. Hence, the findings may be associated with the limitation of the model used, and therefore, it is not a confirmation for the absence of risk. Secondly, the data used was for 2007 and the accumulative effects of ENMs pre- and post the base year were not accounted for in this model. Therefore, the results indicate the necessity for experimental ecotoxicological studies to verify the absence or the presence of risks.

In summary, our paper presents the first risk assessment estimation on the potential release of ENMs into the aquatic and terrestrial environmental compartments from nanoproducts in a Metropolitan setting in a developing country – using modelling tools. The results suggest that ENMs from nanoproducts such as

cosmetics are likely to pose new challenges to the existing WWTP plants – irrespective of their operational efficiency. Experience with previous high proprietary-based industries indicates that in many cases the reported volumes of the materials used are by several orders of magnitude under-reported. Therefore, the quantities of ENMs reported for Switzerland or globally and in extension those modelled for the JHB City even under the maximum scenario potentially underestimate the current levels of risk in the aquatic and terrestrial environments.

This challenge should be addressed, for example, by developing an inventory of products in the South African market containing ENMs. And finally, numerous influencing factors together with their inherent uncertainties on the potential risk levels of ENMs in the environment, including quantities of the ENMs, dilution factor, reported toxicity (NOEC or $L(E)C_{50}$ values), economic and demographic data, the fate and behavior of ENMs in different environmental compartments, just to mention a few, need to be investigated further in order to improve the robustness of the proposed model.

Conclusions

The model results show how the potential risks of ENMs – particularly in regions of high environmental exposure, such as cities – may aid in deriving more realistic estimates rather than for an entire country or continental region. In addition, the model provides a simplified approach of utilizing the published data of ENMs quantities in nanoproducts in the developed countries scenarios to evaluate the risk these materials are likely to pose in the developing countries. Data is completely lacking in the developing countries though many are active or anticipating future active participation in the nanotechnology-driven economy. Currently, the developing countries lack primary inventory quantity data of ENMs contained in the nanoproducts being traded in their economies. Therefore, our findings highlight the need for the risk assessment of ENMs in the developing countries as the consumer nanoproducts are currently used globally – given the internationalization and globalization character of many industrial sectors such as cosmetics and paints.

Although the model provided useful insights on the risk assessment of ENMs from a modelling perspective, the results may be more coherent if a different set of metrics were used for expressing the toxicity of ENMs to minimize the wide variance observed in computing the PNEC values. Also, a fundamental modification of the model used in this study for quantifying the ENMs potential risks to the environment may be necessary. The modified model is envisaged to take into account the peculiar aspects of nanoscale materials – an aspect totally lacking in the model used in this study. This is because of the distinctive attributes of ENMs from those of counterpart bulk materials – where the later chemicals provided the basis for the development of the current model.

The poor or lack of characterization of interactions of ENMs for organisms in the soil and sediment environments limit risk assessment in such compartments. It is recommended that developing countries should also participate in hazard identification of ENMs in air, water, and soil compartments in order to achieve a more robust risk assessment as this is unachievable in the absence of validated scientific data. The author acknowledges a plausible argument that developing and middle-developing countries have more urgent socio-economic needs to direct their energies rather than to focus on nanotechnology-related risks. However, close scrutiny of the available and attractive platforms of addressing the intermittent and intractable problems in these countries such as lack of clean drinking water, urgency to cure pandemic diseases, and the restoration of highly polluted ecological systems as well as the drive for the diversification of these countries' domestic manufacturing base – nanotechnology appear to offer such a viable platform. Therefore, issues concerning potential risks related to nanotechnology-based products and materials merit attention as well in the developing countries.

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