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Mineral Nanoparticles in Waste: Potential Sources, Occurrence in Some Engineered Nanomaterials Leachates, Municipal Sewage Sludges and Municipal Landfill Sludges

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Abstract

Environmental assessment of engineered nanoparticles (ENPs) currently suffers from lack of data on production, emission, behaviour and fate in natural compartments. This paper aims to bring factual data on production amounts of ENPs and emission of mineral elements in a colloidal or nanoparticulate forms stemming from products, (e.g. cosmetics, paints, concretes) and from two potential waste sinks, namely municipal sewage sludge and non-hazardous waste landfill sludge. Based on the declaration of production and importation of ENPs in France in 2014, we set out a classification of ENPs substances comprising carbon black, organic pigments, miscellaneous organic substances and mineral ENPs. These mineral ENPs were sub-classified on the basis of production and CLP ecotoxicological and hazard classifications. Major elements (Group #1) encompass ENPs substances ubiquitous in total contents, and also as a colloid fraction in waste leachates (Si, Ca, Ti, Al, Mg, Fe, Mn, P). Minor elements were divided as ENPs with soluble substances and dissolved metal ions non-classified as ecotoxic (Group #2: Ba, Bi, Cr (III), Sr, Zr, La, Pd, Mo, W, Y, Au) or with soluble substances classified as ecotoxic and hazard statement code in the CLP regulation (Group #3: Ce, Cu, Zn, Ni, Sb, Ag, Co). Paints, concrete and particularly cosmetics proved to be sources of ENPs. Colloidal forms of elements or ENPs were found in leachate obtained from paint (Si), in cosmetics leachates (Al, Si, Ti and Zn), and in one demolition concrete (Ti). No nanoparticulate forms or fraction of Ag, Ce, Ti and Zn were identified by TEM/EDS in municipal sewage sludge. However, sewage sludge could be a sink for Group #3 elements such as Ag and Ce, since their total concentrations were significant. Based on landfill leachates from municipal solid wastes, the colloidal fraction frequently contained elements of Group #3 (Ni, Zn, Cu, Co and Sb) but with low mean concentration and more rarely Ag and Ce, indicating that the fluxes of these elements from the landfill cells should be low, except for Ce. Landfills seem to not emit ENPs in their leachates. From a regulative aspect, monitoring of Ag in sewage sludge for agricultural use could be of concern.

Introduction

Environmental assessment of engineered nanoparticles (ENPs) and engineered nanomaterials (ENMs) is an active field of research. The main conclusions emphasize the lack of data on production amounts, emission, transfer mechanisms, behaviour, fate in natural compartments and toxicity. Are traditional waste facilities, including wastewater treatment plants (WWTPs), landfills and incinerators, final sinks? Do ENPs actually reach landfills? Can ENPs-containing sewage sludge contaminate agricultural soils? Papers from the Organisation for Economic Cooperation and Development (OECD) and some other studies present high quality overview of this situation, current knowledge and gaps [1-8] and with many potential occurrences and fate, many possibilities to check, but very few data. In absence of data, the precautionary principle prevails and the assessments (emission, transfer to targets, biological effects) conclude to potential high risks. However, even if health and environmental hazards have been demonstrated for a variety of ENMs, "*Not all nanomaterials induce toxic effects. Some ENMs have been used for a long time (e.g. carbon black, TiO₂) showing low toxicity. Therefore, the hypothesis that smaller means more reactive, and thus more toxic, cannot be substantiated by the published data. In this respect, nanomaterials are similar to normal (bulk) chemicals/substances in that some may be toxic and some may not. As there is not yet a generally applicable paradigm for nanomaterial hazard identification, a case-by-case approach for the risk assessment of nanomaterials is still recommended*" [1,2,9]. A recent meta-study has established a correlation between solubility (molecular concentration at equilibrium with the solid phase in water) of the elements or substances and ecotoxicity of the nanoparticles of the same elements or substances [10].

Regarding the ultimate fate of ENPs in waste streams, Mio. T incineration bottom ashes, sewage sludge and landfill sludge seem to be most important sinks to assess the fate of the ENPs in waste stream. Sewage sludge results from the treatment of wastewater and surface water runoff in municipal wastewater treatment plant (WWTP). Landfill sludge comes from the treatment of landfill leachates that are (i) mainly allowed to aerate and settle before their discharge in WWTP or in streams or rivers, or (ii) concentrated (press-filtering, drying) and finally produced in a liquid or solid sludge. Incineration bottom ashes are produced from treatment of solid wastes in municipal solid waste incinerators.

In France, with 66 million inhabitants, the non-mineral non-hazardous waste (municipal waste, 70.5 Mio. t) mass divides as 48%

(33.7 Mio. T) to recycling, 28% (19.8 Mio. T) to landfills, 23% (16.2 Mio. T) to incineration and 1% (0.8 Mio. T) recycled in agriculture. The mass of municipal solid waste incinerator (MSWI) bottom ashes is 3.3 Mio. t, and of wastewater treatment plant (WWTP) sewage sludge is 1 Mio. T (dry matter), including 700 kt that is recycled in agriculture [11,12]. So the main potential "sinks" for ENPs and ENMs of non-hazardous waste are (i) landfill (rounded 20 Mio. t/y), recycled incinerator bottom ash for road construction (rounded 2 Mio. t/y), and recycled sewage sludge for soil amendment (0.7 Mio. t/y). The amount of produced and imported ENPs in France in 2014 is 0.4 Mio t/y [11].

Regarding environmental monitoring of ENPs in waste streams, analysis in wastes is reviewed in Part et al. [8]. Currently, the differentiation between natural colloids and ENPs in wastes is not technically feasible in routine. In waste leachates, successive microfiltration and ultrafiltration accompanied by element analysis is described by Hennebert et al. [13]. More sophisticated methods include *e.g.* free flow fractionation (FFF) coupled on line to ICP-MS [14]. The analysis of colloidal or NP-sized organic substances can be achieved by HPLC for fullerenes [15] and by light transmission at a wavelength of 800 nm for single wall carbon nanotubes in synthetic leachates [16]. However, routine analytical methods are still not available for organic ENPs in complex waste leachates [7].

Data on emission of colloids or ENPs is a crucial data basis in order to rank the elements and further focusing on ENPs that could be, or are really emitted. In this study, we aimed at collecting factual data for production, content and emission of elements in a colloidal or in a nanoparticulate form for several types of products. This paper then focuses on potential emission of ENPs stemming from pristine products with ENPs, from WWTP sewage sludges and municipal landfill sludge, two potential temporal sinks for ENMs.

This paper tries to combine data on production volumes of ENPs by elements, selection of elements of ENPs by ecotoxicological approach and monitoring of leachable fraction of elements in colloidal size from nanomaterials, ordinary materials and possible receptacle of ENPs from products and waste, namely sewage sludge and landfill sludge, with representative sampling from France. Further work will include municipal incinerator bottom ashes.

Material and Methods

The materials and the methods are summarized in Table 1. Analytical methods are developed at Analysis section.

ENPs-containing consumer products

The following products were used, for further grinding to 4 mm and leaching tests:

– Two products claimed with nanoAg(0): Bandages Mercurochrome® "30 pansements technologie argent" and flexible keyboard Urban Factory;

– Two products claimed with nano-TiO_2: Floor tiles (from construction material dealer) and medical pen Senator Antibac (Ref 2645);

– Four cosmetic products coming from a public service laboratory without detailed information on composition, except that they contain ENPs. Specific research of ENPs in the raw material was done by a laboratory of INERIS, by TEM-EDS. The "Eye shadow #2" contained nano-ZnO (mean size 30 nm) in an inorganic phase and nano-TiO_2 (mean size 80 nm) with plates containing Si, Al and K. The "Lipstick #3" contained nano-ZnO (mean size 30 nm). The "Make-up #5" contained plates of Fe oxide (micrometric and nanometric), TiO_2 (micrometric and nanometric) always associated with Si (indicating potential coating of TiO_2 particles). The "Sun screen #6" contained TiO_2 (mean size 50 nm) always associated with Al, Si (probably the coating of TiO_2) and Zn, and ZnO (estimated size 30 nm) in organic layers [17];

Six paint additives (Nanobyk 3601, 3605, 3610, 3650, 3812, 3840 containing nano-Al_2O_3, formulated nano-Al_2O_3, nano-SiO_2, formulated nano-SiO_2, nano-CeO_2 and nano-ZnO, all from BYK, http://www.byk.com) ending with 13 paint/additive/support combinations. Paint additives were used following the supplier's instructions with 4 different bases (glycerophtalic Ripolin glycero blanc brillant, acrylic Ripolin eau blanc brillant, solvent-based varnish Lasure classique V33 chêne doré satiné or water-based varnish Lasure aqua-stop V33 chêne doré satiné, applied on a wooden support (particle board), plaster (plate covered with a cardboard layer) or cement (roof tile) and exposed vertically outdoor for one month (May 2013, 23°C mean temperature) in Aix-en-Provence (Figure 1). To mimic the normal use of these paints, the wooden and cement plates were exposed outside, without collection of the rain leachate and the (indoor) plaster plates were shield from rain;

One surface coating with nano-TiO_2 (PhotoCAL Masonry, from NANOFRANCE Technologies.

Two paints claimed with photoactivity by nano-TiO_2 (Stophotosan and Stocolor climasan from STO).

Concrete products

The following products were used:

– Three concrete specimens containing white cement with and without TiO_2 nanoparticles: The white cements without any claimed nanoparticle content were purchased from building material dealers (white cements CEM I 52.5 25 kg from PRB, CEM I 52.5 10 kg from Bostik, CEM I 52.5 5 kg from Vicat, CEM I 52.5 5 kg from Lafarge, CEM II 32.5 25 kg from Lafarge, and grey cement CEMV/A 32.5 25 kg from Lafarge). The cement containing TiO_2 nanoparticles with different percentages (0%, 3%, and 10% w/w in the cement binder) was provided by CEREGE. The concrete specimens were produced

Samples	Amount	Total content (aqua regia)	Leachate elemental concentration (colloidal-dissolved)	Particle leachate size	TEM-EDS
Consumer products	23	-	Ag Al Ce Si Ti Zn (claimed or added NPs)	PCS1	6 cosmetics
Concrete products	16	-	Ti (claimed for 2 laboratory samples)	PCS1	1 industrial concrete
Sewage sludge	13	Ag Ce Ti Zn	-	PCS1	2 sludges
Municipal landfill sludge	10	45 elements	34 elements	NTA2	

1 PCS Photon correlation spectroscopy
2 NTA: Nanoparticle Track Analysis

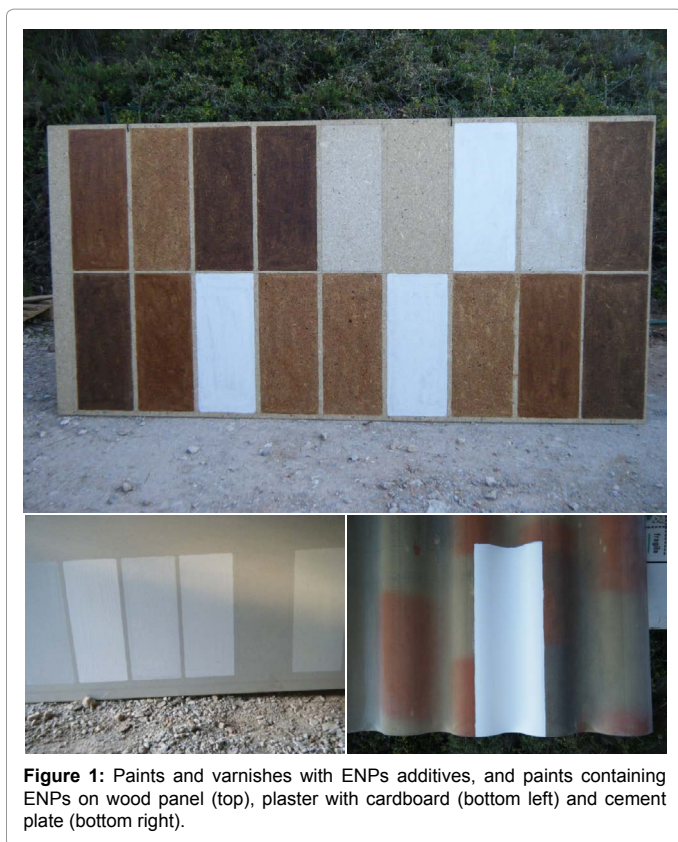**Table 1:** Samples and analysis in this study (62 samples).

Figure 1: Paints and varnishes with ENPs additives, and paints containing ENPs on wood panel (top), plaster with cardboard (bottom left) and cement plate (bottom right).

in the laboratory using a mixture of commercial sand and gravel, cement (350 kg/m³) and water (8% of the total weight of the mixture). After 28 days of curing, the specimens were removed from the moulds and followed the same treatment as other samples.

– A cinder block specimen made of white cement.

– Two demolished concrete specimens obtained from about twenty years old industrial shed in La Duranne, Aix-en-Provence and from an artisanal floor slab in Ardevie, Aix -in-Provence, respectively.

– An antique "Roman concrete" specimen (mixture of sand, lime and crushed bricks, with stones of about 5 cm) from a piece left on the floor of an aqueduct of Via Apia, southeast of Rome.

The materials without claimed ENPs and the old materials were used as controls for the presence of unintentionally-produced particles containing Ti or for presence of particles produced by leachate preparation (by crushing and/or by dissolution of the matrix during leaching).

Sewage sludges

Thirteen municipal sludge samples from various wastewater treatment plants (WWTP) were collected from various locations in France, rural (<5000 inhabitants) or urban, and with different stages of treatment in 2013 [18]. The composite samples (4 L for liquid sludge, 2 L for solid sludges in glass bottle, from 10 subsamples) were lyophilized, shredded and sieved at laboratory. Two raw sludge were used. Three samples from the same station at different stages of processing (thickened sludge, dewatered sludge, composted dewatered sludge, samples 12, 10 and 11) were used.

Municipal landfill sludges

Ten sludges were collected from nine different locations in France, by the landfill managers (February-May, 2015) in polypropylene drums of 30 L. At the laboratory, the drums were kept at 5°C before mixing and subsampling. Four were considered as liquids, and six were considered as solid sludge, obtained by different processes (decantation, centrifugation, filtration in press-filter after addition of FeCl₃ and polyacrylamide polymer, evaporation with the heat of biogas electric generators). Liquid sludge are usually discharged in municipal WWTP and solid sludge are discharged in the landfill or they are dried, sometimes stabilised with lime, and incinerated (according to the choice of the landfill manager).

Analysis

Since we investigate population of materials or waste (the samples of sewage sludge and landfill sludge are intended to be representative of the whole population), no replicates have been done.

Leachable and soluble concentration of elements in leachates (Engineered nanomaterials, concrete, sewage sludges, landfill sludge): Leaching was done with samples of particle size reduced to less than 4 mm avoiding fine shredding (EN 12457-2). Some samples (concrete) were broken with a hammer to 80 mm pieces, crushed to 10 mm with a jaw crusher, sieved to 4 mm, the refusal was ground by step to 4 mm and the sieved material was mixed and leached. Other samples (plastics, wood, plaster) were shredded with a low speed laboratory shredder (Blik, blik.fr) with 6 mm thick intersecting blades up to >90% passing a 4 mm sieve. The water content was measured and the samples were leached 24 h (EN 12457-2) with a net liquid/solid ratio of 10 l/kg of dry matter (90 g DM of waste and 900 ml of deionized water, including the water of the waste) with an agitator turning at 10 rpm (the standard method for waste acceptance in landfills, EN 12457-2).

After 15 min of settling, the leachates were successively microfiltered and ultrafiltered at 450 nm and ± 3 nm (membrane with a cutting mass of 3 KDa, corresponding approximately to a diameter of 3 nm for spheric elemental particle) with a UF stirred cell (Millipore) with 200 MPa pressure. Membranes of cellulose nitrate for microfiltration (Whatman 0.45 μm, GE Life Science) and of regenerated cellulose for ultrafiltration (Ultracel® 3 KDa, Millipore) were used. This method is statistically equivalent to tangential filtration with recirculation through regenerated cellulose membrane (Sartorius Sartocon 200 Hydrosart Slice) with a cut-off limit of 450 nm and 3 KDa, that was used in a previous study [19,20], but it is much more faster (result not shown). The statistical equivalency could indicate that no clogging occurred within the stirred cells. About 500 ml were microfiltered and from this volume, about 200 ml were ultrafiltered. The expensive ultrafiltration membranes can be washed in deionized water and reused without contamination (controlled by ICP). The filtrates were acidified to pH<2 with ultrapure 60% nitric acid. Previous tests of digestion of the acidified filtrates with aqua regia in microwave bombs (EN 13656) or on hot plate (ISO 13657) showed that this digestion was not necessary for ICP measurements (data not shown). The elements are measured by ICP in the microfiltrates (MF, leachable fraction, containing the colloidal/ENP fraction and the dissolved fraction) and in the ultrafiltrates (UF, assumed here to be the soluble fraction). The difference in content (MF-UF) is the colloidal or nanoparticulate fraction of this element in the leachate.

Average particle sizes and Zeta potential (microfiltrates): Average particle sizes were measured by Photon Correlation Spectroscopy–PCS,

also called Dynamic Light Scattering-DLS (Zetasizer, Malvern). Some measurements were done with Nanoparticle Track Analysis (NTA) (NS500, Malvern). The apparatus tracks in two directions the individual motions of a population of particles moving in a controlled flow of the sample, calculates the individual diffusion coefficient and finally the individual hydrodynamic diameter. Minor assumptions than those made for DLS make the method more robust for polydisperse samples [21]. The number of particles measured in ultrafiltered deionized water in an (uncontrolled) university laboratory environment is 3.7×10^7 particles/ml. Zeta potential was measured on a Zetasizer (Malvern) at room temperature without pH adjustment.

Particle identification and composition: Qualitative element associations per location in the matrix were targeted in three solid samples of concrete and sewage sludges by TEM-EDS (Oxford Instruments). For the same sample, several images were taken. An analysis area was chosen (rectangle of 1-5 μm × 1-5 μm, with some area up to 25 μm-25 μm) and spectra of elements were obtained with relative concentrations in mass and number (excluding C and O) in the observed area. The method does not allow for the observation of nanoparticles, but makes it possible to retrieve a frequency of occurrence and associations of elements in the analysis zone.

Total content of elements (Sewage sludge and landfill sludge): After pretreatment (according to the pretreatment standard for waste EN 15002), the sludge were digested with aqua regia (ISO 13657). Quantitative analysis with standardized methods (ISO 11885, EN 16772) of the elements was used. For landfill sludge, a screening method (AFNOR XP X30-489) [21] with ICP was used for elements other than of 12 "heavy metals or metalloids" of the EU Landfill Decision 2003/33 (As Ba Cd Cr Cu Hg Mo Ni Pb Sb Se Zn). The loss on ignition (loss of mass at 550°C ± 25°C for 1 h, EN 15169) was used as estimation for organic matter in landfill sludge. For these samples, the anions were measured by ionic chromatography in the leachates of solid samples and in filtered fraction of liquid samples.

Results and Discussion

French production and importation amounts of engineered nanoparticles (ENPs)

The declaration of ENP production and importation (>100 g/

year) has been compulsory since 2013 in France. For the annual registration period closed in June 2014, 374 declarers introduced 10 417 declarations (including 6 418 declarations with CAS number) for 319 substances representing 397 131 tons (274 667 t produced and 122 464 t imported) [22]. The name of a substance and their uses are published in the summary report, if at least one declarer has not required data confidentiality. The exact quantities are recorded but are expressed in the report as mass intervals with amplitude of factor 10. The declarations were recalculated from the annexes of the report and gathered by element and by organic substances (SI Table 1 and Figure 2). The amount that is exported is not known. Organic substances were grouped since there are no routine methods for analysis of these substances in leachates.

Proposition of classification for environmental assessment of elements of ENPs from production and ecotoxicity data: What elements should be in priority monitored to assess the impacts and the eventual risks of ENPs, particularly in waste streams? *For organic ENPs*, the most frequently used ENP is carbon black (>100000 t, >25% of the declared total quantity, 1 declaration). Carbon black is used as reinforcing filler in tires and other rubber products, and as pigment in plastics, paints and inks. Composition of tires includes 21% of carbon black and 0-15% of silica and particles are emitted by tire wear and found in road runoff water and sedimented in road storm basin [23]. Shredded tires mixed with crushed limestone (to be used as fill material in embankment) did not release particles during a one year-lysimeter study [24]. A second group are ENPs of the synthetic organic pigments (referred in the colour index C.I. system; 102 declarations). Examples are C.I. Pigment Red 48:2 (min. 1000 t), C.I. Pigment Yellow 13 (100 t), C.I. Pigment Yellow 83 (10 t), C.I. Pigment Yellow 74 (10 t), C.I. Pigment Blue 15-15:1-15:2-15:3-15:4 (10 t). The total of this group amounts to 1 250 t-12 500 t, that is 0.31%-3.1% of the declared total quantity. These substances are not easily speciable in a NP form. A third group is nanosized plastic polymers (1 100 t-11000 t). The last group is obtained by the merging of nanosized miscellaneous organic substances such as pesticides, lactose, cellulose, paraffin and waxes (575 t-5 748 t). It includes 96 declarers.

For mineral ENPs, we propose a sub-classification. A first group (Group #1) are the ENPs of major elements Si, Ca, Ti, Mg, Fe, Mn, P with frequently natural analogues: silicon dioxide (including food
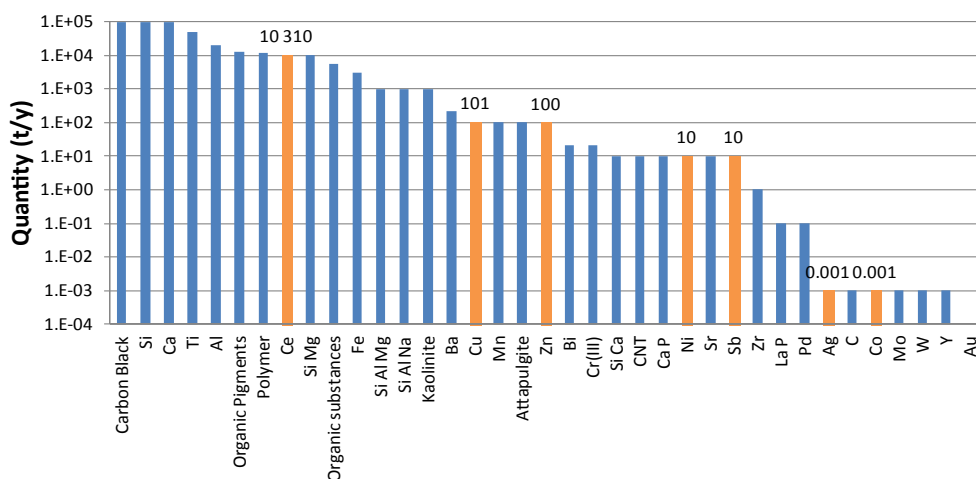

Figure 2: Higher limits of production and importation (ton/year) of nanoparticles in France in 2014. Elements in orange are classified as ecotoxic in the classification, labelling and packaging of substances and mixtures regulation (CLP regulation 2008).

additive E551), calcium carbonate, titanium dioxide (including E171), aluminium oxyhydroxides, iron oxyhydroxides, magnesium silicate (food additive), aluminosilicates (including E554), clay minerals, manganic pigments, calcium silicate, calcium hydrogenophosphate. The total of this group amounts to 124 000 t-342 000 t, which is between 31% and 86% of the declared total quantity. The ENPs of this group are difficult to differentiate from "unintentional" or "natural" colloids in waste leachates. They are mostly similar in composition to natural minerals, but intentionally different in crystallinity, size, shape, coating or purity that are challenging to measure when the ENPs are mixed with "natural" colloids in a waste stream.

One approach for considering the relative toxicity of the ENMs is to compare the species sensitivity distribution, related to the solubility of their ionic counterpart [10]. The ecotoxicity hazard of substances is defined in the European chemical legislation [25]. Ecotoxicological data for the mineral substances or elements from databases (European Chemicals Agency ECHA, http://echa.europa.eu/fr/information-on-chemicals and INERIS Chemical Portal, http://www.ineris.fr/substances/fr/) were used. The elements having substances with hazard statement codes ecotoxic acute (H400) and ecotoxic chronic of level 1 (H410) are Ce (lowest concentration with 50% of biological effect EC_{50} not known, cerium trichloride), Cu (min EC_{50}=0.041 mg/l, copper monochloride), Zn (0.032 mg/l, zinc dichloride), Ni (0.06 mg/l, nickel dichloride), Ag (EC_{50} not known, silver nitrate) and Co (0.334 mg/l, cobalt dichloride). These substances are soluble in water and generate ions. Most Sb substances have a hazard statement code ecotoxic chronic of level 2 (H411). Summary tables can be found in Hennebert et al. [26]. The substances with the elements Ba, Cr(III), Sr Bi, Zr, La, Pd, Mo, Y and Au are not classified ecotoxic. It must be emphasized that the declared substances composing the ENPs of Ce, Cu, Zn, Ni, Sb, Ag and Co (SI Table 1) are not soluble at the prevalent pH (5 to 9) of most wastes. The elements and the associated ENPs are: for Ce: cerium dioxide, cerium hydroxide, cerium and iron isostearate, for Cu: Pigment, for Zn: zinc oxide, for Ni: organic complex, for Sb: antimony pentoxide, for Ag: Ag(0) and for Co: Tricobalt tetraoxide. Their "chemical" ecotoxicity will probably be lower than the soluble substances mentioned above (EC_{50}>1 mg/l). Their potential "physical" ecotoxicity (potential accumulation in the gastro-intestinal tract, in the gills of the fishes, etc.) and their eventual specific "nanoecotoxicity" should also be considered. With 7 elements and two organic ENPs, Garner et al. [10] conclude in their meta-study that *"Few statistical differences were observed between species sensitivity distributions of an ENM and its ionic counterpart"*. The classification proposed here uses that conclusion, and it should be updated as soon as nanoecotoxicity data are available.

A second group (Group #2) could be ENPs of minor elements having non-ecotoxic (non NP) soluble substances: Ba (21-212 t/y), Bi, Cr(III) (2-21 t/y), Sr (1-10 t/y), Zr (0.1-1 t/y), La (0.01-0.1 t/y), Pd, Mo, W, Y, Au (<1 kg/y).

A third group (Group #3) could be constituted of minor elements with ecotoxic (non NP) soluble substances: Ce (1000-10000 t/y), Cu, Zn (10-100 t/y), Ni, Sb (1-10 t/y), Ag, Co (0.1-1 kg/y).

"New" engineered mineral NPs are declared in low amounts: carbon nanotubes: 1 t-10 t/y, Fe(0): 10 kg-100 kg/y, Ag(0): 0.1 kg-1 kg/y, Au: not declared.

Occurrence and monitoring of elements in waste leachates: The elements of group #1 (Si, Ca, Ti, Mg, Fe, Mn, P) are ubiquitous in waste total content and colloidal form in leachate fraction (frequently found in 25 waste leachates) [13].

The group #2 (Ba, Bi, Cr(III), Sr, Zr, La, Pd, Mo, W, Y, Au) includes four elements monitored in routine in waste samples leachate, according to the landfill acceptance criteria [26]. Currently there are no nano-specific regulations for waste. The allowed leachable concentrations of Ba, Cr(VI), Sb and Mo for inert waste landfill are 20, 0.5, 0.06 and 0.5 mg/kg respectively, and for non-hazardous waste landfill are 100, 10, 0.7 and 10 mg/kg respectively. Those values were derived from a risk assessment [27]. Leachable chromium is considered to be Cr(VI) and not Cr(III), since the substances containing Cr(III) are not soluble in water at common pH of waste. Bi, Sr, Zr, La, Pd, W, Y and Au are not monitored in routine waste characterisation.

The group #3 includes well monitored Cu, Zn, Ni and Sb. Cu and Zn are ubiquitous in waste and with Co are essential human micronutrients. Cu, Zn, Ni and Sb are monitored in waste leachates for landfill acceptance (content on the <450 nm, which consists of colloids, nanoparticles and dissolved ions). Their allowed leachable concentrations for inert waste landfill are 2, 4, 0.4 and 0.06 mg/kg, respectively and for non-hazardous waste landfills are 50, 50, 10 and 0.7 mg/kg, respectively. The large quantity of Ce nanoparticulate compounds (1000 t-10000 t) declared to be used in many products, substances and processes, and the part that used as additive to fuel to reduce emissions is not clear from the summarized report of declarations. Ce, Ag and Co is not monitored in routine waste characterisation.

Emission of colloidal/NP elements by engineered nanomaterials (analysis of leachate)

Leachates of ENPs-containing consumer products: The leachate analyses are presented at Table 2. The sizes measured by PCS on the microfiltrate fraction (filtered at 450 nm) were frequently larger than the cut-off value of the filter, and were misleading. This results from polydispersity of most of the samples and the mathematical assumptions for transformation of auto-correlation function to a distribution of size of particles μm [20]. Our conclusion was that another technique should be used for size measurements, and thus NTA was introduced into our protocol. The zeta potentials were all negative (between -30 and 0 mV) and indicate a tendency to flocculation or co-flocculation (homo- or hetero-aggregation) in natural waters or sewage, as only particles with a zeta potential >+30 mV or <-30 mV are considered as electrostatically stable [28].

The elements claimed as ENP in the products (Ag, Al, Ce, Si, Ti and Zn) and their colloidal concentration in the leachate are presented in Table 2. Other elements showed no colloidal fraction, except the major elements Ca, Mg, K and Na (data not shown). Control leachate samples of wood, plaster with cardboard and cement plate without paint and with the four types of paint (acrylic, glycerophtalic, solvent-based lasure, water-based lasure) without additives showed no colloidal fraction for the added elements. This is converse to the findings of Kaegi et al. [29,30] on emissions of silver or TiO_2 from paints during rain events. From 24 samples (unweathered, unaged), colloidal or manufactured nanoparticles were found in leachates of a glycero paint with SiO_2 additive (24 mg Si/kg), a lipstick (25 mg Zn/kg), a make-up formulation (33 mg Si/kg) and a sunscreen (11 mg Al/kg, 33 mg Si/kg 19 mg, Ti/kg, and 164 mg Zn/kg). The other ENMs or products tested did not emit concentration of elements in colloidal or ENP form greater than 10 mg/kg.

Concrete with and without TiO_2 NPs (analysis of leachate): The characteristics of concrete leachate and the contents of leachable and colloidal/NP Ti are presented in Table 3. The alkaline pH and slightly reducing redox potential (pe+pH) samples were classical for concrete, with a lower value for the Roman concrete sample, which had a pH

Declared ENP	ENM/Product/Preparation	Calculated main size (nm)	Zeta potential (mV)	Ag (mg/kg)	Al (mg/kg)	Ce (mg/kg)	Si (mg/kg)	Ti (mg/kg)	Zn (mg/kg)
Ag	Keyboard	869	-27						
	Wound dressing	256	-5.1						
Al_2O_3	Solvent-paint (lasure) on wood	205	-17				1		
	Varnish on wood	203	-11						
Al_2O_3 formulated	Acrylic-paint on wood	268	-4.9						1
	Water-paint (lasure) on wood	189	-14				5		
	Solvent-paint (lasure) on wood	148	-13				1		
	Varnish on wood	1201	-19						
CeO_2	Glycero-paint on plaster with cardboard	432	-11				6		
SiO_2 formulated	Glycero-paint on wood	9716	-24				**24**		
	Solvent-paint (lasure) on wood	1438	-12						1
	Varnish on wood	274	-7.2				3		
TiO_2	Stoneware tiles	283	-24		2		3		
	Medical pen	223	-7.1						7
	Photocatalytic indoor paint on plaster	356	-3.5				1		
	Photocatalytic coating on masonry	361	-17		2		5		
	Photocatalytic outdoor paint on cement sheet	3674	-2						
	Eye shadow #2	422	-22		1		2		
	Lipstick #3	114	-22				2		**25**
	Makeup #5	207	-14				33		
	Solar cream #6	224	-6.9		**11**		**33**	**19**	**164**
ZnO	Acrylic-paint on wood	770	-20						
	Acrylic-paint on plaster with cardboard	394	-5		1				
	Water-paint (lasure) on wood	594	-19						

Blank: <0.1 mg/kg DM

Table 2: Size (by PCS), zeta potential and colloidal or Nano particulate concentration of selected elements in leachate of nanomaterials.

n°	Sample	pH	pe+pH	CE (mS/cm)	Leachable Ti (mg/kg)	Leachable Colloidal or ENP Ti (mg/kg)
1	Concrete with white CEM I 52.5 PRB 25 kg	12.7	12.2	7.38	0.02	
2	Concrete with white CEM I 52.5 Bostik 10 kg	12.8	12.7	9.52	0.016	
3	Concrete with white CEM I 52.5 Vicat 5 kg	12.8	12.6	7.62	0.021	
4	Concrete with white CEM I 52.5 Lafarge 5 kg	12.8	12.6	9.41	0.024	0.013
5	Concrete with white CEM II 32.5 Lafarge 25 kg	12.8	12.7	8.8	0.018	
6	Concrete with grey CEMV/A 32.5 Lafarge 25 kg	12.6	11.9	4.98	0.029	
7	Concrete with cement CER 0% NP TiO_2	12.8	12.2	8.85	0.018	
8	Concrete with cement CER 3% NP TiO_2	12.7	12.2	6.16	0.012	
9	Concrete with cement CER 10% NP TiO_2	12.9	12.3	8.93	0.034	0.013
10	White concrete product - tiling	12.8	12.7	9.59	0.016	
11	White concrete product - balustrade	12.6	12.5	4.61	0.021	
12	White concrete product - edging	12.2	12	1.33	0.016	
13	Grey concrete product - cinderblock	12.1	12.3	2.21	0.015	
14	Demolition concrete from industrial structure	11.9	12.9	7.15	1.02	0.999
15	Demolition concrete from artisanal outdoor slab	12	12.3	2.47	0.012	
16	Roman concrete from Via Apia Roma 2014	8.5	9.2	0.66	0.059	0.01

Table 3: pH, redox status, conductivity, leachable Ti and colloidal or nanoparticulate leachable Ti from concrete products.

close to the pH of limestone, indicating carbonatation. The contents of leachable Ti were very low. The laboratory concrete samples # 8 and 9 (unweathered, unaged) with cement containing 3% and 10% w/w of nano-TiO_2 (4.6 and 15 kg nano-TiO_2/t concrete) had no significant release of colloidal or nanoparticulate Ti. The demolition concrete of an industrial shed (sample # 14) had a leachable colloidal or NP Ti content of 1 mg/kg. The Ti concentration of this sample was studied in the solid phase (not the leachate) with element microscopy probe using TEM. In total 15 spectra were recorded, focusing on particles visually different of the mass of the sample.

The matrix of this demolition concrete contained Ca, K, Fe, Al and Na (most frequently detected cations), Si, and secondarily Mg with accompanying anions (S Cl) and other elements present in lower concentration (Cr, Ti, Cu, Zn, Br and P) (SI Table 2). Titanium was present in 3 cases of 15 observations of the sample #14, each time associated with Al, Ca, Fe, K and Si, and two times out of three with Cl, Mg and Na. It therefore seems to be associated with this sample matrix, and does not appear as a separate phase or ENP, at this scale of observation (rectangle of 1-5 μm × 1-5 μm).

Content and emission of colloidal/NP elements by municipal sludge and landfill sludge

WWTP sludges (total content): Since there is no available method for detecting nanoparticles dispersed in the solid phase, outside of a tedious search by microscopy, which may not be routinely accessible, a method of selection of solid sample was tested here. The samples with concentration of one or more element(s) being outlier(s) of a normal distribution were selected and examined by microscopy.

The pseudo-total content of the elements Ag, Ce, Ti and Zn were measured after aqua regia extraction of 13 sludge (Table 4). According to the literature, these elements were considered to be the most relevant.

The mean (± 1 SD) total concentration of **Ag** is 10 (± 5) mg/kg dry matters (DM) of sludge. Similar or significantly higher total concentrations are found in other countries (Czech Republic (median of 14 values): 1.44 mg/kg; Germany (248 values): 3.5 mg/kg; UK (9 values): 3.6 mg/kg; Sweden (48 values): 5.4 mg/kg; South Africa (5 values): 7 mg/kg; USA (84 values): 13.6 mg/kg; Japan (14 values): 17.1 mg/kg) [31-37]. The common range of Ag for soils is 0.01-5 mg/kg, with a representative average of 0.05 mg/kg [38], 200 times less than the mean concentration observed in the sludge. The high content in the sludge is hence not from soil origin. The anthropogenic accumulation factor (AMF) is the ratio of the mass extracted annually by mining and fossil fuel production divided by the mass released annually by crustal weathering and volcanic activity [39,40]. The AMF for Ag is 185. Is this high Ag level due to ENP? A maximum UK estimation of the part of Ag NP in total Ag consumption in UK is 1.8% [41]. The declared ENP Ag(0) production and importation in France in 2014 is 0.1 kg-1 kg (Figure 1). The imported goods and the accumulated goods including ENPs are not taken into account in that figure. The production of sewage sludge in France is 1 million tons DM/year. The ratio gives a potential mean concentration of <1 µg Ag/kg sludge (assuming that that silver amount is fixed in the sludge). This calculation at the scale of one country may not apply to a particular sludge. It seems nevertheless that Ag in sewage sludge is neither geogenic nor "NPgenic". Most Ag could originate from medical products that contain Ag in bulk form. The main

sources of silver in wastewater are food, dental amalgams, cosmetics and textiles (plastics should be investigated); according to a Swedish study [42]. Silver in wastewater is immobilized in the sewage sludge to 98% [33]. An essential mechanism is the reaction of the Ag^+ ion with sulfides, producing the precipitation of Ag_2S insoluble particles [43]. Manufactured nanoparticles of metallic silver Ag(0) is also converted into surface and thus coated with a layer of Ag_2S. The free concentration of Ag^+ emitted (species that has an ecotoxicity) decreases sharply. Kaegi et al. have found with spiking experiments that Ag-NP discharged to the wastewater stream becomes sulfidized to various degrees in the sewer system and are efficiently transported to the WWTP which later accumulates in the sewage sludge as Ag_2S [44]. In conclusion, silver in products is significant and should be used only in case of real added value. The annual EU consumption is estimated to 500 tons, today lost in different waste. Silver from waste water is captured by sewage sludge, and that element should be further assessed in case of agronomic valorisation of the sludge, or for potential economic value [45].

The mean concentration of **Ce** is 40 (± 15) mg/kg sludge. The most abundant of the rare earth elements is seldom monitored in environmental studies. The available studies present total concentration of the same order of magnitude as the one we found: in Germany, the median concentration of 252 values is 16.2 mg/kg ([32], recalculated from ashes composition) and in Sweden the median of 47 values is 20 mg/kg [34]. The concentration in the earth crust is 1-50 mg/kg [38]. Three publications (Germany, USA and South Africa) show a similar distribution of rare earth elements in the local sewage sludge and in local soils and conclude to pedogenic origin [32,45,46]. The annual production and importation in France of Ce is 1000 t-10000 t. Nanoparticles of Ce dioxide, Ce oxide isostearate and (Ce oxide and Fe) isostearate are declared used in fossil fuels, but also for many industrial processes and products. The total amount of these species is 21 t/y-201 t/y. The part that is used for fuel (and could potentially end up to the WWTP) is not known. The observed concentrations in the sludges seem to us quite high, and Ce should be monitored for an in-depth assessment.

Element concentration	Ag (mg/kg DM)	Ce (mg/kg DM)	Ti (mg/kg DM)	Zn (mg/kg DM)
Sludge 1 (urban, not digested, lime)	6	36	166	985
Sludge 2 (urban, digested, dried)	5	30	99	1877
Sludge 3 (rural, not digested, lime)	7	63	198	845
Sludge 4 (urban, not digested, lime)	8	36	86	2209
Sludge 5 (rural, liquid)	4	14	80	1145
Sludge 6 (urban, digested)	9	30	50	2454
Sludge 7 (urban, not digested, dried)	14	23	74	2159
Sludge 8 (urban, raw))	5	29	79	1644
Sludge 9 (urban, raw)	18	62	232	4851*
Sludge 12 (urban, thickened)	15	49	357*	2097
Sludge 10 (urban, digested)	15	46	383*	2100
Sludge 11 (urban, digested, composted)	13	32	335	1875
Sludge 13 (urban, digested, dried)	8	53	74	800
Mean (standard deviation)	10 (4.6)	39 (15)	170 (120)	1926 (1042)
*Outliers of a Gaussian distribution				

Table 4: Concentration of (aqua regia extractible) total Ag, Ce, Ti and Zn in 13 sewage sludge from municipal waste water treatment plant.

The mean concentration of **Ti** is 170 (± 120) mg/kg sludge, 20 times less than representative concentration in soil (4000 mg/kg [31] or 2400 mg/kg [33]). The AMF of Ti is 1. Kiser et al. have observed in 8 WWTPs around the United States much higher concentrations (1800 to 6400 mg Ti/kg DM, averaging 2800 ± 1500 mg Ti/kg DM) [47].

The mean concentration of Zn is 1900 (± 1000) mg/kg sludge, 20 times more than representative concentration in soil (50 mg/kg [31], 48 mg/kg [33], range of 10-100 mg/kg in soils without natural anomaly in France [48]). The AMF of Zn is 115. The declared ENP Zn production

and importation in France in 2014 is 10-100 t/y. If this amount is reported to the annual sludge production, a concentration between 10 and 100 mg/kg sludge is obtained.

The conclusion of the comparison of concentration of these four elements in sludge and soil is that Ag and Zn in the sludge predominantly originate from non NP-products, and not from soil. These two elements have high AMF.

The research of NP form of the four elements was done by TEM-

Sludge Sample	Solid						Liquid				Mean
	2	3	4	5	7	9	1	6	8	10	(if >LQ)
Characteristics											
Water % w/w	68	65	83	81	16	55	96	96	72	70	70
Bulk density g/cm³	0.64	0.63	1.07	1.34	0.09	0.38	1	0.98	1.15	1.15	0.84
Loss on ignition % DM	8.9	63.4	19.8	8.6	11.2	14.2					21
pH (leach./liquid)	12.2	3.2	8.1	8.4	9.7	12.4	8.2	7.9	5	9.3	8.4
CE µS/cm (leach./liquid)	6910	6820	12090	2090	73600	9930	37100	5860	217000	53200	42460
Parameter mg/kg											
Cl (leach./liquid)	1744	11238	6297	1686	222208	24325	3165	402	30929	41700	34369
SO₄ (leach./liquid)	666		50313	2738	105829	1329	6462	1481	90732	15948	30611
Br (leach./liquid)	13	8	19	9	951	100	20		232	257	179
F (leach./liquid)	216	9	111	5	132	10	6		51	61	67
I (leach./liquid)	3		9	1	177	38			38	112	62
Ca	100000	2500	37500	100000	6750	100000	150	1000	1000	6750	35565
Na	375	1000	2500	2500	100000	1000	2500	1000	100000	100000	31088
S	3240	39300	39300	7170	22000	4610	2660	642	77067	8900	20489
K	1000	1000	6750	6750	37500	375	2500	375	37500	17500	11125
Si	375	150	2500	37500	375	1000	150	150	375	150	4273
Fe	6750	17500	2500	6750	150	375	13	150	150	375	3471
Mg	1000	375	2500	2500	6750	1000	150	375	1000	2500	1815
Al	150	150	1000	6750	13	150		35	35	35	924
P	1000	1000	1000	1000	150	1000	150	150	375	2500	833
B	35		15	15	375				150	1000	265
Th					150						150
Cr	90	299	213	58	22	56			21	21	98
Sr	150	13	150	150	150	35		13	35	150	94
Zn	38	251	161	153	9	39			8	8	83
Ba	22		173	119	18	23				18	62
Mn	35	13	150	150	35	35		35		35	61
Cu	23	25	42	113		26					46
Mo		17	72								44
Ni	13	100	36	17	10	18			11	6	26
Ti	35	35	13	35	13	13		13	35	35	25
Li					35				13	13	20
V		13		13	13	35			13		17
Pb			12	21							17
Zr	13	13	13	35	13				13		16
Sb		19			12						16
Sn	15	15	15								15
As		27	14	6	7	7			10		12
Ce											<10
Ag											<5
Co											<5

Quantitative data for elements As Ba Cd Cr Cu Hg Mo Ni Pb Sb Se Zn (EN ISO 11885, EN 16772), semi-quantitative data for other elements. Blank value=<5 mg/kg. Other elements with all values lower than LQ (<5 mg/kg unless otherwise specified): Au, Be, Bi, Cd (LQ 0.8 mg/kg), Ga, Ge, Hf, Hg (LQ 0.3 mg/kg), In (LQ 10 mg/kg), Nb, Pd, Rh, Se, Ta, Te, W

Table 5: Main characteristics and total concentration (xxx digestion and ICP measurement) of 45 elements in 10 landfill sludge samples (mg/kg dry matter for solid samples, mg/kg raw material for liquid samples). Elements of group #3 are highlighted.

EDS on the high-concentration outlier samples. The contents of Ag and Ce follow a normal (Gaussian) distribution, whereas the contents of Ti and Zn are not normally distributed (Shapiro-Wilk test, XLStat), with respectively 2 and 1 higher grade/outlier samples (Ti: samples #12 and #10, and Zn: sample #9). The sample #9 had also high content of Ag, Ce and Zn. The concentrations of the elements have been investigated in samples #9 and #10 with electron microscope with probe elements. The mineral matrix of the sludge contains Ca Fe Al Mg (most frequently detected cations), Si, and secondarily K Na (SI Table 3). The major anions P and S are probably part of organic compounds (C and O, unquantified) and are also present in almost all the observations of each sample. The matrix of the sludge thus appears as aggregates of aluminosilicate (probable earthy origin) and organic matter. Separate phases of Ti, i.e. aggregated NP TiO_2 areas, were not found (area of observations 25 square microns). Ti is present in half of the cases (7 of 13 observations for the raw sludge and 4 of 9 observations for the digested sludge). When present, Ti is associated with Al, Ca, Fe, K, Mg, Na, P, S, Si (7 times of 7) and Cl (5 times of 7) for the raw sludge, and Al, Ca, Fe, K, P, S, Si (4 times of 4) and Cl (3 times of 4) for the digested sludge. Concentrations (excluding C and O) are between 1 and 2%. Ti is therefore present in combination with the organo-mineral matrix sludge at this scale of observation. The origin of Ti could be anthropogenic (white paints, toothpaste, certain foods, sunscreen, façade run-off) or pedogenic, but it is not observed in all spectra of the same sample and, as mentioned, soils have higher concentrations of Ti. This study cannot discriminate between pedologic and anthropogenic (nano or non-nano) Ti. Zn was not detected by the probe (no peaks in the spectra) despite a high total concentration of almost 5 g/kg (ICP measurement). Zn is scattered in the organo-mineral matrix of the sewage sludge, as an adsorbed phase on the reactive surfaces, and probably not as a particles in these two samples. In conclusion, NPs of Ti or Zn in outliers of a normal distribution have not been found, despite their relatively high total elemental concentration in this particular sample (350 mg/kg and 5 g/kg, respectively).

Municipal landfill leachate sludges (analysis of total content and leachable content): The main characteristics of the sludge are presented at Table 5. The water content, density, loss on ignition and the pH of the samples are very different. The characteristics are published *in extenso* due to variability between samples, and scarcity of data of this kind of waste. The samples are humid, excepted one dry powder with a very low density (sample 7). The organic matter contents of the solid samples, approximated by the loss on ignition, are between 11 and 63%. The pH varies between 3.2 and 12.4. The 27 elements with at least one value greater than the limit of quantification (LOQ) are presented at Table 5 by decreasing order of mean. The other 18 elements have all values lower than LOQ (<5 mg/kg unless otherwise specified): Ag, Au, Be, Bi, Cd (LOQ 0.8 mg/kg), Co, Ga, Ge, Hf, Hg (LOQ 0.3 mg/kg), In (LOQ 10 mg/kg), Nb, Pd, Rh, Se, Ta, Te, W.

The "classical" major and minor elements are found at concentrations following the same order than the declared ENP annual quantities, reflecting probably their general use in non nanoparticulate species in non-hazardous products, rather than their ENP fraction. Comparison with representative soil concentrations indicates higher values in the landfill sludges for B and Mo, equivalent values for Cr, Zn, Cu, Ni, Li, Pb, Sn and As, and lower values for Ba, Mn, Ti, V and Zr [38,40,48].

Elements of group #3 (highlighted) are presents at low total concentrations in landfill sludges, or below the LOQ. **Ce** (declared as ENP in 1000-10000 t/y), **Ag** and **Co** (declared at quantities <1 kg) are not found. As mentioned in the discussion of sewage sludges, the concentration of Ce and Ag in the earth crust is 1-50 mg/kg and 0.05 mg/kg, respectively. The median concentration of Co in European agricultural soils is 7.5 mg/kg (n=2108) and 7.3 for grazing land (n=2023) [49]. The concentration of Sb in landfill sludges is 8 times on 10<5 mg/kg, while the concentration of **Sb** in soil is reported as baseline ranges of 0.06-0.79 mg/kg across seven soil orders in Florida soil, and up to 22 mg/kg in urban soils [50]. It can be concluded that there are probably no soil particles in the landfill sludge. On the other hand, the landfill sludge have content of **Zn**, **Cu** and **Ni** not higher than a representative population of soils, composts and sediments of France (Table 6).

The solid samples were leached at 10 l/kg DM, as well as the liquid samples 8 and 10, because they were not filterable as they were. The leachates were microfiltered and ultrafiltered. The liquid samples 1 and 6 were filtered as they were. The distribution of particles of microfiltrates of two samples is illustrated in Figure 3. The concentrations are between 5.10^8 and 5.10^9 particles/ml, and the diameter of 50% of the particles in number (D50) and the diameter of 90% of the particles in number (D90) are similar for the 10 samples at 92 nm and 147 nm (Table 7). It has been noticed that the visible absorbance of the microfiltrate is roughly correlated with the number of particles (result not shown).

The concentrations of colloidal or NP fraction in the leachate are presented in Table 7. Au, Bi and La were detected neither in the microfiltrate, nor in the ultrafiltrate (LOQ 0.05 mg/kg solid, 0.005 mg/kg liquid). The leachable mean concentration of Pd is 0.09 mg/kg, and of Y is 0.06 mg/kg, without colloidal fraction. The major elements of group #1 have the highest colloidal fraction. Ti (group #1) has a maximal colloidal concentration of 5.5 mg/kg in a solid sample. The elements of group #3 (highlighted in the table) have low concentration of colloidal fraction, between 3.2 and 0.01 mg/kg (mean value when present), except Ce with a maximal concentration of 10 mg/kg. The occurrence of elements in a colloidal or ENP form (referred below as the colloidal fraction) is presented in Table 8. The major elements of group #1 with low solubility oxides/hydroxides at neutral pH (Ti, Al, Fe and Mn, with the notable exception of Si) are totally or mostly colloidal, while cationic alkaline and alkaline-earth metals (Na, K, Mg, Ca, Sr and Ba) have very frequent colloidal occurrence (between 9 and 6 of 10 samples).

The elements of group #3 are highlighted in the table. Cu, Sb, Zn, Co and Ni are mainly in a colloidal form (between 10/10 and 8/10), with a ratio colloidal/leachable (when colloidal fraction is present) between 35 and 67% (mean value). Ce is 4 times of 10 samples in colloidal form,

Compartment	Agricultural soils (uncontaminated) (Baize et al. [48])		Compost from Household compostable waste (Zdanevitch [18])		Fluvial Sediments (Hennebert and Padox [51])	
Element	Mean (mg/kg)	Samples	Mean (mg/kg)	Samples	Mean (mg/kg)	Samples
Zn	68	11 161	230	142	446	11 053
Cu	17	11 118	66	143	49	11 072
Ni	24	11 275	17	143	27	11 498

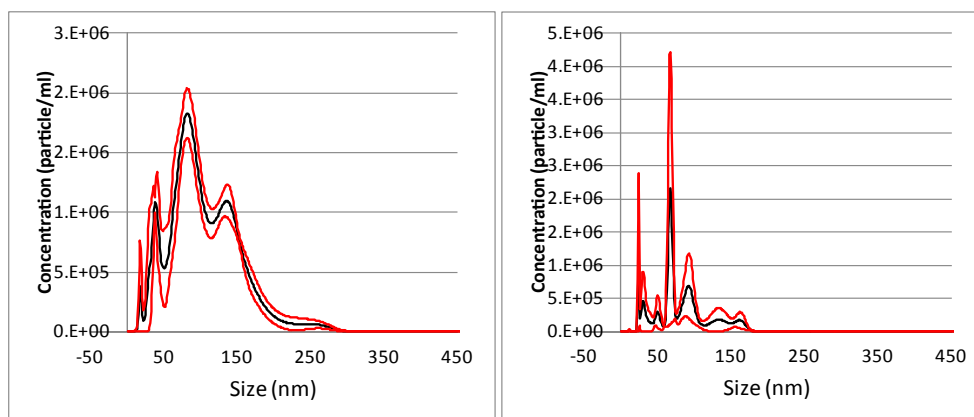**Table 6:** Concentration of Zn, Cu and Ni in agricultural soils, in compost and in sediments.

Figure 3: Granulometry of microfiltrate of landfill sludge by nanoparticle track analyzer (left: solid sample 4 after leaching, 1.6×10^8 particles/ml for the dilution 10; right: liquid sample 10, 5.0×10^7 particles/ml for the dilution 2.5).

Colloidal or ENP Concentration (>3 KDa <0.45 μm)	Solid						Liquid				Mean
Sample	2	3	4	5	7	9	1	6	8	10	
Concentration (10^9 particles/ml)	0.45	0.54	1.69	0.18	1.57	1.48	5.08	0.9	1.17	0.25	1.32
D50 (nm)	96	81	96	75	97	102	83	94	102	91	92
D90 (nm)	146	112	162	126	175	154	131	154	164	147	147
Element (mg/kg dry weight for solid, mg/kg raw for liquid) xxx											
S	180			62	1900	290	30	87	37600	1000	5144
Na	30			220		70	50	45	33100	1000	4931
K	40			60		20	70	29	16500		2787
Fe	7	8600	11	33	162	4	0	1	79	30	893
Ca	3600			84	152	1800	33	137	600	80	811
Mg				16	510	2	27	56	970	140	246
P	17	90	14	3	22	23	19	3	164	26	38
Si					4	2	1		119		31
Cr	0.1	12.4	6.3	0.6	14.6	0.6	1.5	0.3	9.3	6	5.2
Ni	5.4	3.8	2.1	0.3	9.2	1.7	0.2	0.2	5.5	3.6	3.2
Al	0.2	14	6	1	2	0	1	0.1	5	1	3
Sr	5			0.4	5	8	0.2	0.4	4	0.4	3
Zn	0.4	12.6	0.2	0.4	2	0.4	0.1	0	2.5	1.5	2
Ti	1.2	5.5	2.1	0.4	2.6	0.6	1.2	0.5	3.2	0.6	1.8
Mn	0.3		0.9	0.3	6	1.2	0.3	3	1.7	0.7	1.6
Cu	10.6	0.1	0	0.1	0.2	0.9	0	0	0.1	0.2	1.2
As	0.1	1.5		0.1	1	1.4	0.02	0.1	5.2	0.5	1.1
Zr	0.1	1.2	0.7	0.1	3.6	0.3	0.3	0.1	1.7	0.7	0.9
Co	0.8	0.1	0.2		1.9	0.7	0.1	0.1	0.6	0.6	0.6
Sb	0.1	0.8	0.3	0.04	2.9	0.1	0.1	0	0.2	0.3	0.5
Ba	0.7	0.1	0	0.3	0.5	1.9	0.1	0.1	0.3		0.4
Se	0.03	0.1	0.1		0.6	0.1	0.005		0.5	0.7	0.3
Mo		0.9		0.02	0.1	0	0.005		0.7	0.1	0.3
W		0.4					0.01		0.3		0.2
Ag					0.04						0.04
Pb					0.006			0.003		0.1	0.03
Ce		0.02				0.01	0.002		0.01		0.01
Cd	0.01	0.01	0.003		0.02	0.01	0.001	0.001	0.01	0.01	0.01
Hg					0.0005		0.0001			0.0009	0.0005
Pd											-
Y											-

Table 7: Colloidal or ENP leachable concentration of elements in 10 landfill sludge samples.

Element	Occurrence as colloidal or ENP	In case of occurrence (Colloidal or ENP)/ Leachable ratio		
	Number of samples of 10 samples	Mean	Min	Max
Ti	10	81%	53%	100%
Cr	10	72%	40%	100%
Zn	10	56%	24%	100%
Zr	9	83%	40%	100%
Co	9	67%	2%	100%
Cu	9	65%	44%	83%
Ni	9	47%	26%	73%
Sb	9	35%	11%	76%
As	9	30%	6%	58%
Se	8	54%	20%	100%
Mn	8	53%	15%	100%
P	8	32%	16%	69%
S	8	16%	1%	37%
Sr	8	15%	5%	27%
Mo	7	27%	3%	100%
Ba	7	26%	4%	48%
Mg	7	25%	7%	59%
Ca	7	23%	7%	38%
Fe	6	77%	5%	100%
K	6	8%	2%	30%
Ce	4	90%	61%	100%
Cd	4	90%	60%	100%
Al	4	68%	45%	96%
Si	4	18%	2%	31%
W	3	46%	8%	85%
Pb	3	36%	9%	54%
Hg	2	8%	5%	10%
Na	2	5%	2%	9%
Ag	1	100%	100%	100%
Pd	0			
Y	0			

Table 8: Occurrence of colloidal or ENP fraction by element in 10 landfill sludge leachate samples.

with a high colloidal/leachable fraction of 90% (but with a very low concentration of 0.01 mg/kg, Table 7). Ag is found in only one sample with at low concentration of 0.04 mg/kg but totally colloidal (Table 7).

Conclusion

Herein, a classification is proposed, based on the amounts of French ENP production and importation in 2014 (400 000 t), and on the CLP classification of ecotoxicity for the soluble forms of the elements:

– Major elements (group #1): ENPs substances of Si (>100000 t/y), Ca, Ti (10000-100000 t/y), Al (2000-20000 t/y), Mg (1100-11000 t/y), Fe (300-3000 t/y), Mn (10-100 t/y), P (1-10 t/y): Ubiquitous in total content, ubiquitous as a colloid in leachate fraction of waste ;

– Minor elements (with soluble substances not classified as ecotoxic in the CLP regulation) (group #2): Ba (21-212 t/y), Bi, Cr(III) (2-21 t/y), Sr (1-10 t/y), Zr (0.1-1 t/y), La (0.01-0.1 t/y), Pd, Mo, W, Y, Au (<1 kg/y);

– Minor elements (with soluble substances classified as ecotoxic and hazard statement code H400, H410 and H411 in the CLP regulation) (group #3): ENPs substances of Ce (1000-10000 t/y), Cu, Zn (10-100 t/y), Ni, Sb (1-10 t/y), Ag, Co (0.1-1 kg/y).

The most specific ENPs are not declared in high quantities: carbon nanotubes (1 t-10 t), Fe(0) (10 kg-100 kg), Ag(0): 0.1 kg-1 kg, Au (quantity not declared).

The colloidal (450 nm-3 nm) or ENP form of the elements were investigated at laboratory in leachates (EN 12457-2) of 23 nanoproducts and paints with pristine ENPs. These elements were found in a paint leachate (Si) and in three cosmetics leachates (Al, Si and Zn). Two cosmetics had a colloidal or ENP fraction of 25 and 164 mg/kg Zn, respectively. From 16 concrete samples, including two laboratory samples with nano-sized TiO_2, one demolition concrete released colloidal Ti at a concentration of 1 mg/kg. The total content of Ag, Ce, Ti and Zn in 13 municipal sewage sludge showed two outliers of Gaussian distribution of Ti and Zn, but ENPs were not found by TEM/EDS. From 10 sludge leachates from municipal landfill leachates, the colloidal fraction was very frequent for the elements of group #3 Ni, Zn, Cu, Co and Sb (but with low mean concentration of 3.2, 2.0, 1.2, 0.6 and 0.5 mg/kg when present) and only one time on ten for Ag (with very low concentration of 0.04 mg/kg when present). Ce had 4 times of 10 samples a colloidal form but with a very low concentration of 0.01 mg/kg when present.

From this limited research, it appears that cosmetics are important sources of ENPs. Sewage sludge could be a temporal sink for Ag and Ce since their total concentrations is high (10 and 40 mg/kg respectively) in comparison with soils and wastes, and the origin, as well as the ultimate fate after sludge treatment or use, of these elements in the sludge should be further investigated. Landfill sludge have moderate total concentration of Cu, Zn, Ni and Sb (46, 83, 26 and 16 mg/kg, respectively) and Ce, Ag and Co are not found. The concentrations of Cu, Zn and Ni are comparable to soils, composts or sediments. These concentrations could mean that the fluxes of these group #3 elements from the landfill cells (by the landfill leachate and their sedimentation in landfill sludge) are low. From a regulative aspect, monitoring of Ag in sewage sludge for agricultural use could be of concern.

Acknowledgement

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