Mineral nanoparticles in waste : potential sources (France 2014), occurrence in some engineered nanomaterials leachates, in municipal sewage sludges and in municipal landfill sludges

Pierre Hennebert, Patricia Merdy, Amandine Anderson

MINERAL NANOPARTICLES IN WASTE: POTENTIAL SOURCES (FRANCE 2014), OCCURRENCE IN SOME ENGINEERED NANOMATERIALS LEACHATES, IN MUNICIPAL SEWAGE SLUDGES AND IN MUNICIPAL LANDFILL SLUDGES

P. HENNEBERT*, P. MERDY** AND A. ANDERSON**

** INERIS-Institut National de l'Environnement Industriel et des Risques, Domaine du Petit Arbois BP33, F-13545 Aix-en-Provence, France*
*** PROTEE, Université de Toulon, BP 20132, F-83957 La Garde Cedex, France*

SUMMARY: Environmental assessment of engineered nanoparticles (ENPs) and engineered nanomaterials (ENMs) suffer of lack of data on production, emission, transfer, behaviour, toxicity, ecotoxicity and fate in natural compartments. This paper tries to bring factual data of production, content and emission of elements in a colloidal form or in an ENP form from some products, and two waste potential sinks: municipal sewage sludge and non hazardous waste landfill sludge (part of the landfill leachate decanted and concentrated to produce a liquid or solid sludge). The study is focused on mineral ENPs, since routine analytical methods are not available for organic ENPs in complex waste leachates. The declaration of production and importation of ENPs in France in 2014 (400 000 t) include carbon black (> 100 000 t/y), organic pigments (1 250 – 12 500 t/y), miscellaneous organic substances (575 – 5 750 t/y) and mineral ENPs classified here as:

· Group #1/Major elements: ENPs substances of Si (> 100 000 t/y), Ca, Ti (10 000 – 100 000 t/y), Al (2 000 – 20 000 t/y), Mg (1 100 – 11 000 t/y), Fe (300 – 3 000 t/y), Mn (10 – 100 t/y), P (1 – 10 t/y): ubiquitous in total content, ubiquitous as a colloid fraction in leachate of waste;

· Group #2/Minor elements (with soluble substances not classified as ecotoxic in the CLP regulation): ENPs substances of 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);

· Group #3/Minor elements (with soluble substances classified as ecotoxic and hazard statement code H400, H410 and H411 in the CLP regulation): ENPs substances of Ce (1 000 – 10 000 t/y), Cu, Zn (10 – 100 t/y), Ni, Sb (1 – 10 t/y), Ag, Co (0.1 - 1 kg/y).

The most "engineered" 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).

Colloidal form or ENPs of elements in leachates of 23 engineered nanomaterials have been found in a paint leachate (Si) and in three cosmetics leachates (Al, Si, and Zn). Two cosmetics have a colloidal or ENP Zn (Group # 3 element) fraction of 25 and 164 mg/kg. From 16 concrete samples, including two laboratory samples with nanosized TiO_2, one demolition concrete released Ti in colloidal form at a concentration of 1 mg/kg. No ENP of Ag, Ce, Ti and Zn in 13 municipal sewage

sludges have been found by TEM/EDS. From 10 sludges 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 on 10 a colloidal form but with a very low concentration of 0.01 mg/kg when present. From this limited research, it appears that cosmetics could be a source of ENPs, that sewage sludge could be a sink for Group #3 elements Ag and Ce since their total concentrations is significant (10 and 40 mg/kg respectively), that landfill sludges have moderate total concentration of Group #3 elements Ce, Cu, Zn, Ni, Sb, Ce, Ag and Co (46, 83, 26, 16, <10, <5 and <5 mg/kg, respectively). 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 build-up in landfill sludge) are low.

1. INTRODUCTION

Environmental assessment of engineered nanoparticles (ENPs) and engineered nanomaterials (ENMs) is an active field of research. Authors emphasized the lack of data on production, emission, transfer, behaviour, toxicity, ecotoxicity and fate in natural compartments. Are traditional waste facilities (waste water treatment plants, landfill) sinks? Will sewage sludge contaminate agricultural soils? Are NPs contained in landfills? Coming OECD papers present high quality overview of the situation, the current knowledge and gaps (OECD, 2015a to e). In absence of data, precautionary principle or attitude prevails and risks assessment (emission, transfer to a target, biological effect) are rated as potentially high. "*Health and environmental hazards have been demonstrated for a variety of manufactured nanomaterials",* however "*Not all nanomaterials induce toxic effects. Some manufactured nanomaterials have already been in use for a long time (e.g. carbon black, TiO_2) 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 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*."(SCENHIR, 2009; OECD, 2015a, 2015b).

This paper try to bring factual data of production, content and emission of elements in a colloidal form or in an ENP form from some products, and two waste potential sinks: sewage sludge and landfill sludge. The speciation between these colloidal form and NP form is not done. An analytical method for elements (successive microfiltration and ultrafiltration, and elemental analysis) is available in waste leachate (Hennebert et al., 2013a). The study is focused on mineral ENPs, since routine analytical methods are not available for organic ENPs in complex waste leachates (Nowak et al. 2015). The analysis of colloidal or NP-sized organic substances has been proposed by HPLC for fullerenes (Farré et al., 2010), and by light transmission at a wavelength of 800 nm for single wall carbon nanotubes in synthetic leachate (Lozano and Berge, 2012). For the other ENP of organic substances, a proposition could be, like for the elements, to analyse the content of the micro- and ultrafiltrate, and to calculate the colloidal fraction of the organic substance by difference.

Emission data of colloids or ENP allows to rank the elements and to further focus on ENPs that could be/are really emitted. Incineration bottom ash, sewage sludge and landfill sludge are important sinks to assess the fate of the ENPs of non hazardous ENMs as waste. These three sinks have each their specific legislation piece. In this paper, sewage sludge and landfill sludge are studied. Sewage sludge results of treatment of waste water and hard surface runoff water in municipal waste water treatment plant (WWTP). Landfill sludge results of treatment of the leachates of landfills that are mainly allowed to aerate and settle before discharge in WWTP or in

streams or rivers, or that are concentrated (press-filtering, drying) and finally that produce a liquid or solid sludge.

The annual flow of raw material is estimated to 23 t/capita.year in France in 2012 (with crop residues, excavated materials, fossil fuel for the exported manufactured goods) (JDLE, 2013). The amount of waste is 5.3 t/c.y, and the amount of waste without mineral non hazardous waste (mainly excavated material) is 1.5 t/c.y. (MEDDE, 2015). Municipal waste from households is about 0.6 t/c.y. For France (66 M inhabitants), the non mineral non hazardous waste (municipal waste) mass includes 33.7 Mt that are recycled, 19.8 Mt that are land filled, 16.2 Mt that are incinerated, and 0.8 Mt used in agriculture. The mass of non hazardous construction and demolition waste (without excavated material) is 30 Mt. The mass of municipal solid waste incinerator (MSWI) bottom ashes is 3.3 Mt, and of waste water treatment plant (WWTP) sewage sludge is 1 Mt (dry matter), including 700 kt recycled in agriculture (MEDDE, 2015; SYPREA, 2015). So the main potential "sinks" for ENPs and ENMs of non hazardous waste are landfill (rounded 20 Mt/y), recycled incinerator bottom ash for road construction (estimated rounded 2 Mt/y), and recycled sewage sludge for soil amendment (0.7 Mt/y). The amount of produced and imported ENPs in France in 2014 is 0.4 Mt/y (MEDDE, 2015), a significant quantity compared to waste fluxes.

2. MATERIAL AND METHODS

2.1 Engineered nanomaterials

The following materials have been studied:
- 8 products (claimed with nanoAg (0): dressings Mercurochrome® with Ag, flexible keyboard; claimed with TiO_2: floor tiles (from construction material dealer), medical pen Senator Antibac Ref 2645; claimed to contain NPs without further information: 4 cosmetics;
- 6 paint additives (Nanobyk 3601, 3605, 3610, 3650, 3812, 3840 containing Al_2O_3, formulated Al_2O_3, SiO_2, formulated SiO_2, CeO_2 and ZnO, all from BYK, www.byk.com) ending with 13 paint/additive/support combination;
- 3 paintings (PhotoCAL Masonry (from NANOFRANCE Technologies, http://www.photocal.fr/photocatalyst_-_photocal.html); Stophotosan and Stocolor climasan from STO, http://www.sto.fr/).

The ENPs of the 4 cosmetics have been looked for (courtesy of O. Aguerre-Chariol, INERIS). The "Eye shadow #2" contains NP ZnO (mean size 30 nm) in an inorganic phase and NP TiO_2 (mean size 80 nm) with plates containing Si, Al and K. The "Lipstick #3" contains NP ZnO (mean size 30 nm). The "Make-up #5" contains plates of Fe oxide (micrometric and nanometric), TiO_2 (micrometric and nanometric) always associated with Si (indicating potential coating of TiO_2 particles). The "Solar cream #6" contains TiO_2 (mean size 50 nm) always associated with Al, Si (probably coating of TiO_2) and Zn, and ZnO (estimated ZnO phase size 30 nm) in organic layers.

Paint additives were used following the supplier's instructions with 4 different bases (glycerophtalic, acrylic, solvent-based varnish or water-based varnish, 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, one rain occurring) in Aix-en-Provence (Figure 1). The wooden and cement plates were exposed to rain and the plaster plates were not exposed to rain. Other materials have not undergone aging.

2.2 Concretes products

Concretes manufactured at the laboratory with commercial white cement and with white cement containing TiO_2 nanoparticles, and white concrete commercial products, a cinderblock, two

concrete demolition samples and a concrete sample of Antiquity were studied in 2014. Various white cements were purchased from building material dealers. Three other cements with known nanoparticular TiO_2 content (0%, 3%, and 10%) were provided by CEREGE in limited quantities. The concrete specimens were produced in the laboratory with a mixture of commercial sand and gravel, cement (350 kg per m^3) and 8% water (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.

Three white cement outdoor products were purchased. A cinderblock with gray cement, a sample of demolition concrete of an industrial shed of about twenty years old in Aix-en-Provence (La Duranne) and the demolition concrete of an artisanal floor slab in Aix -in-Provence (Ardevie), and a sample of "Roman concrete" (mixture of sand, lime and crushed bricks, with stones of about 5 cm) from a piece fell at the foot of an aqueduct of Via Apia southeast of Rome in 2014 were studied.

2.3 Sewage sludges

Thirteen municipal sludge samples from various waste water treatment plants (WWTP) have been collected from various locations and stage of treatment in 2013 and used (Gay and Dalvai, 2014). Two raw sludges were used. Three samples from the same station at different stages of processing (thickened sludge, dewatered sludge, composted dewatered sludge) or with different process (filter pressing, liming) were used.

2.4 Landfill sludges

Ten sludges from 9 different locations in France were collected by the landfill managers (Feb-May 2015). There are 2 liquids, 2 intermediate (treated as solids) and 6 solid sludges, obtained by different process (decantation, centrifugation, filtration in press-filter after addition of $FeCl_3$ and a polymer, evaporation with the heat of biogas electric generators). The liquid sludges are discharged in municipal WWTP, and the solid sludges are discharged in the landfill or incinerated.

Figure 1 : Paints and varnished with ENPs additives, and paints containing ENPs on wood panel, plaster with cardboard, and cement plate

2.5 Analysis

2.5.1 Leachable and soluble concentration of elements in leachates (engineered nanomaterials, concrete, sewage sludges, landfill sludges)

Some samples (concrete) were broken with a hammer, crushed to 10 mm with a jaw crusher, sieved to 4 mm, the refusal was ground by step to 4 mm and sieved. Other samples were shredded with a low speed laboratory shredder (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 hours (EN 12457-2) with a net liquid/solid ratio of 10 l/kg of dry matter (DM). Leachates were successively

microfiltered and ultrafiltered at 450 nm and ±3 nm (3 KDa) 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® 3KDa, 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 2 KDa, that was used in a previous study (Hennebert et al., 2013), but much more faster (result not shown). The expensive ultrafiltration membranes can be washed in deionized water and reused without contamination. 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.

2.5.2 Size, Zeta potential (microfiltrates)

Sizes were first measured by Photon Correlation Spectroscopy (Zêtasizer, Malvern). This method is not fitted for waste due to polydispersity of the samples, and the assumptions leading to calculated size up to a few µm after a filtration at 0.45 µm (similar data in Hennebert et al., 2013). In 2015 measurements were done with Nanoparticle Track Analysis (Insight, Malvern). The zeta potential by was measured by Zêtasizer (Malvern).

2.5.3 Particle identification and composition

The presence of ENPs has been controlled in the raw cosmetic products. TEM-EDS identification and sizing of the cosmetics was done by dissolution in ethanol and TEM-EDS identification on a hydrophilised copper grid (Philips CM12, 120 kV, resolution of 0.5 nm, and Oxford X-max). About 15 pictures and dozens of EDS spectra were done per sample. NPs and elements association were looked for in three solid samples of concrete and sewage sludges by TEM-EDS (Oxford Instruments). For the same sample, several images are taken, an analysis area is chosen (rectangle with 1 – 5 µm per side, with some area up to 25 µm – 25 µm), and spectra of elements are obtained with relative concentrations in mass and number (excluding C and O) in the observed area. The method does not allow observing nanoparticles, but makes it possible to observe a frequency of occurrence and associations of elements in the analysis zone.

2.5.4 Aqua regia content of elements (sewage sludges and landfill sludges)

After pretreatment (EN 15002), the sludges 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; Hennebert et al., 2012) 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 sludges.

3. RESULTS AND DISCUSSION

3.1 Production and importation of engineered nanoparticles (ENPs) (France 2014)

The declaration of ENPs production and importation (> 100 g/year) is compulsory since 2013 in France. For the annual 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) (MEDDE, 2014). The name of a substance and the uses of the substance are published in the summary report if at least one declarer has not required

not publishing it. The exact quantities are declared and recorded but are expressed in the report as mass intervals with an amplitude of 10 factor.

The production sectors of the declarers are by decreasing frequency (sectors with >100 declarers, MEDDE, 2014): agriculture-forestry-fishing, formulation and preparations, others, machine and equipment fabrication, food industry, R&D, rubber industry, plastic industry, and fine chemicals. The declared chemicals are by decreasing frequency (chemicals with > 50 declarations, total 2 631 declarations): coatings-paints-solvents-thinners, cosmetics and personal care products, phytopharmaceuticals, fuels, polymers, others, pharmaceuticals, adhesives and sealants. The declared articles and products are by decreasing frequency (total 414 articles): rubber (99), mechanical, electrical and electronic machines (82), plastic products (56), vehicles (49), metallic articles (39), articles in stone, plaster coated with cardboard, cement, glass and ceramic (29), articles in paper (11), batteries and accumulators (3), articles in leather (1). The original report presents a Table with the amount of ENPs > 100 tons declared in 2014, and more detailed annexes. Here, the declarations were recalculated from the annexes and gathered by element (total content or leachable colloidal form, easy to analyse) and by organic substances (no routine method for analysis, i.e. black carbon, organic pigments, polymers and miscellaneous organic substances) (Table 1).

The total quantity of produced and imported ENPs is close to 400 000 t/y. The exported amount is not subtracted from that figure. The ENPs can be gathered by groups.

Table 1 : Quantities of ENPs manufactured and imported in France (declaration of 2014) by element(s) and by groups of organic substances

Elements/substances	*Declarations*	*Mass min t/y*	*Mass max t/y*	*Major substances*	*Proposed Group for elements*
Carbon Black	1	>100 000	>100 000	carbon black	
Si	38	>100 000	>100 000	SiO_2 (including food additive E551)	1
Ca	2	10 000	100 000	$CaCO_3$	1
Ti	1	10 000	100 000	TiO_2 (including food additive E171)	1
Al	4	2 010	20 100	boehmite AlOOH, Al_2O_3	1
Organic Pigments	102	1 250	12 499	synthetic organic pigments	
Polymer	13	1 141	11 412	PVC 1 000-10 000 t, various esters 121-1 210 t, nitrile 10-100 t, methylmethacrylate 10-100 t, polyacrylates 0.1-1 t, PTFE 0.1-1 t, PS 0.1-1 kg, other N.D.	
Ce	6	1 031	10 310	Reacting mixture of cerium dioxide and zirconium dioxide (additive to fuel to reduce emissions, chemical synthesis) 10 000 t, cerium dioxide and iron dioxide isostearate 11-110 t, CeO_2 10-100 t, $Ce(OH)_4$ 10-100 t	3
Si Mg	1	1 000	10 000	synthetic amorphous magnesium silicate $MgO:XSiO_2 \cdot H_2O$ (including food additive)	1
Organic substances	96	575	5 748	synthetic organic substances including pesticides	
Fe	8	302	3 022	FeOOH, Fe_2O_3, isostearate of iron oxide (including Fe(0): 10-100 kg)	1
Si Al Mg	1	100	1 000	synthetic amorphous sodium aluminosilicate $14SiO_2 \cdot Al_2O_3 \cdot Na_2O \cdot 3H_2O$ (including food additive E554)	1
Si Al Na	1	100	1 000	sodium magnesium aluminium silicate	1
Kaolinite	1	100	1 000	clay mineral $Al_2Si_2O_5(OH)_4$	1
Ba	6	21	212	$BaSO_4$, pigments	2
Cu	3	10	101	Pigments	3
Mn	3	10	101	Pigments	1
Attapulgite	1	10	100	clay mineral $(Mg,Al)_2Si_4O_{10}(OH) \cdot 4(H_2O)$	1
Zn	1	10	100	ZnO (main uses: adhesive, cosmetics, paints)	3
Bi	3	2	21	bismuth iodide oxide, bismuth bromide oxide (main uses: paints, chemical preparations)	2
Cr(III)	4	2	21	pigment, chromium iron oxide	2
Si Ca	1	1	10	silicic acid, calcium salt	1
CNT	2	1	10	carbon nanotubes, single and multi-walled	
Ca P	3	1	10	calcium hydrogenorthophosphate	1
Ni	2	1	10	nickel, 5,5'-azobis-2,4,6(1H,3H,5H)-pyrimidinetrione complexes (use: chemical preparations)	3
Sr	1	1	10	pigment	2
Sb	1	1	10	diantimony pentoxide (main use: fabrication of plastic products)	3
Zr	1	0.1	1	zirconium dioxide	2
La P	1	0.0100	0.100	lanthanum phosphate	2
Pd	1	0.0100	0.100	colloidal palladium	2
Ag	1	0.0001	0.001	silver	3
C	1	0.0001	0.001	carbon	2
Co	1	0.0001	0.001	tricobalt tetraoxide	3
Mo	1	0.0001	0.001	molybdenum	2
W	2	0.0001	0.001	tungsten trioxide	2
Y	1	0.0001	0.001	yttrium oxide	2
Au	1	N.D.	N.D.	gold nanoparticles	2
Elements	16	14	144	Other complex substances with 2 or more elements; Al P, Ba Cr Cu, Ba Ti, Ca Sr P, Co Al, Cr Sb Ti, Li Ti, Mn Fe, Mo Si, Mo W P, Pb Cr Mo, S (n.d.), Si C, Si Li Mg Na, Sr Ti, Y Zr	
Total	334	227 695	476 953		
Declared exact quantity			397 131		

3.1.1 Proposition of classification

For organic ENPs, a first group of ENP is carbon black (> 100 000 t, > 25% of the declared exact quantity, 1 declaration). It is used in tires (reinforcing filler in tires and other rubber products), and as pigment in plastic, paint and ink. Composition of tires includes 21 % of carbon black and 20-35% of carbon black and silica (Wik and Dave 2009) and particles are emitted by tire wear and found in road runoff water and sedimented in road storm basin. Shredded tires mixed with crushed limestone (to be used as fill material in embankment) have not emitted particles during one year lysimeter study (Hennebert et al., 2014). A second group are ENPs of synthetic organic pigments (referred in the colour index C.I. system; 102 declarations). The total of this group amounts 1 250 t – 12 500 t, that is 0.31% - 3.1 % of the declared exact quantity. These substances are not easily speciable in a NP form. A third group is nanosized plastic polymers (1 100 t – 11 000 t). The last group is obtained by the merging of nanosized miscellaneous organic substances including pesticides, lactose, cellulose, paraffin and waxes (575 t - 5 748 t). It includes 96 declarers.

For mineral ENPs, a first group (entitled #1 in the last column of Table 1) could be mineral ENPs of major elements Si, Ca, Ti, Mg, Fe, Mn, P with frequently natural analogues: silicon dioxide (including food 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 124 000 t – 342 000 t, that is between 31% and 86% of the declared exact quantity. The NPs of this group will be difficult to differentiate from "unintentional" or "natural" colloids in waste leachates. They are mostly similar in composition to natural minerals, but intentionally different in cristallinity, size, shape, coating or purity, all characteristics not easy to measure when the ENPs are mixed with "natural" colloids in a waste stream.

The differentiation of the ENPs of minor elements can be based on ecotoxicity of soluble substances containing these elements. The ecotoxicity hazard of substances is defined in the European chemical legislation (CLP Regulation 2008). The substances must be tested with standardised laboratory tests (chronic, acute) at different concentrations in the biota culture media, the dose/response (a measured biological effect) relationship is statistically established and the results for acute tests are expressed as the concentration producing typically 50 % of response (EC_{50}) on the population of tested organisms. The lowest EC_{50} concentration from a panel of laboratory ecotoxicological tests is used to assess the ecotoxicity of the substance. If it is below 1 mg/l, the substance is classified as acute ecotoxic with a hazard statement code (HSC) H400 (CLP 2008). For chronic ecotoxicity, longer-lasting tests are used and the result is based on the no observed effect concentration (NOEC), resulting, if lower than 1, 10 or 100 mg/l in a HSC with four levels from H410 to H413. Ecotoxicological data for the mineral substances or elements from a database (European Chemicals Agency ECHA, http://echa.europa.eu/fr/information-on-chemicals, INERIS Chemical Portal, www.ineris.fr/substances/fr/) were used here. The elements having substances with H400 and H410 hazard statement codes are Ce (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 with HSC H400 and H410 are soluble in water. Sb has a hazard statement code H411 (generic entry in classification table for most Sb substances in the CLP).

Summary tables can be found in Hennebert et al., (2015). The substances with the elements Ba, Cr(III), Sr Bi, Zr, La, Pd, Mo, Y and Au are not classified ecotoxic (ECHA portal, INERIS portal, Aug. 2015). It must be emphasized that the declared substances composing the ENPs of Ce, Cu, Zn, Ni, Sb, Ag and Co (Table 1) are not soluble at the ordinary pH of most waste. The couples ENP/ENM are: Ce/cerium dioxide, cerium hydroxide, cerium and iron isostearate, Cu/pigment, Zn/zinc oxide, Ni/organic complex, Sb/antimony pentoxide, Ag/Ag(0), 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.) should also be considered. Their eventual specific "nanoecotoxicity" seems not to be known or published in a standardized and referenced system like REACH. The classification proposed here should be updated as soon as nanoecotoxicity data are available. The elements of Table 1 that are not in the first group could then be grouped by the ecotoxicity of their soluble species.

A second group 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 could be constituted of minor elements with ecotoxic (non NP) soluble substances: Ce (1 000 – 10 000 t/y), Cu, Zn (10 – 100 t/y), Ni, Sb (1 – 10 t/y), Ag, Co (0.1 - 1 kg/y).

It can be noted that the most "new" engineered mineral NPs are not much declared: Carbon nanotubes: 1 t – 10 t, Fe(0): 10 kg – 100 kg, Ag(0): 0.1 kg – 1 kg, Au: not declared.

3.1.2 Occurrence and monitoring in waste leachates

The elements of group #1 elements are ubiquitous in waste total content and colloidal form in leachate fraction (frequently found in 25 waste leachates; Hennebert et al., 2013)

The group #2 includes four elements monitored in routine in waste samples leachate, according to the landfill acceptance criteria (EU Council Decision 2003/33/EC). 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 (Hjelmar, 2012). 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. The large quantity of cerium nanoparticulate compounds (1000 t – 10 000 t) are declared to be used in many products, substances and processes, and the part that is used as additive to fuel to reduce emissions is not clear from the summarized report of declarations. Ce, 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. Their allowed leachable concentrations for inert waste landfill are 2, 4, 0.4 and 0.06 mg/kg respectively, and for non hazardous waste landfill are 50, 50, 10 and 0.7 mg/kg respectively. Ce, Ag and Co are not monitored in routine waste characterisation.

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

3.2.1 Products

The potential emission of colloids and nanoparticles of different engineered materials or product coated with ENPs were estimated by crushing at 4 mm, leaching (EN 12457-2), settling for 15 minutes, filtering at 0.45 µm and 3 KDa, and analysing the claimed NP elements Ag, Al, Ce, Si, Ti, Zn.

Leachates of control pieces of wood, of plaster and of cement plate without paint and without additived paint had no colloidal fraction for these elements.

The size measured by PCS on the microfiltrate fraction (filtered at 450 nm) is indicative, since many calculated values are larger than the cut-off value of the filter. Another technique should be used for size measurements. The zeta potentials are all negative and greater than -30 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| are considered as electrostatically stable (Hassellöv and Kaegi, 2009).

Table 2 : Size, zeta potential and colloidal or nanoparticulate concentration of selected elements in leachate of nanomaterials

ENP	*ENM/Product/Preparation*	*Size (PCS) nm*	*Zeta potential mV*	*Ag*	*Al*	*Ce*	*Si*	*Ti*	*Zn*
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

The colloidal concentrations of the elements present in the engineered NPs are presented in the table. 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 kinds of paint (acrylic, glycerophtalic, solvent-based lasure, water-based lasure) without additive showed no colloidal fraction for the added elements. This contrasts with the findings of Kaegi et al. (2010) of emission of silver from paint during rain events, with a release of 0.5 mg/m² (30% of the applied Ag), and concentration in runoff water between 1 and 145 µg/l. From 24 samples (unweathered, unaged), there is presence of colloidal or manufactured nanoparticles in leachates of a glycero paint additived with SiO_2 (24 mg Si/ kg), a lipstick (25 mg Zn/kg), a make-up formulation (33 mg Si/kg) and a solar cream (11 mg Al/kg, 33 mg Si/kg 19 mg Ti/kg, and 164 mg Zn/kg). The other ENMs or products don't emit significant concentration of elements in colloidal or ENP form. TiO_2NPs have been found in facade and urban runoff water (Kaegi et al., 2008). The runoff rain water will flow to natural waters or to WWTP. The cosmetics form bathing water and personal wash water will to septic tank or to municipal waste water treatment plant (WWTP). The analysis of some water treatment sludges are presented later in the paper.

3.2.2 Concrete with and without TiO2 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 are

classical for concrete, with a lower value for the Roman concrete sample, which has a pH close to the pH of limestone. The contents of leachable Ti are very low. The laboratory samples # 8 and 9 (unweathered, unaged) with cement containing 3% and 10% of ENP TiO_2 have no significant release of colloidal or NP Ti. The demolition concrete of an industrial shed has a leachable colloidal or NP Ti content of 1 mg/kg, a low value. The Ti concentration in this solid sample was studied with electron microscopy probe. In total 15 spectra were recorded, focusing on particles visually different of the mass of the sample.

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

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	0.020	
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	8.80	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 TiO2	12.8	12.2	8.85	0.018	
8	Concrete with cement CER 3% NP TiO2	12.7	12.2	6.16	0.012	
9	Concrete with cement CER 10% NP TiO2	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	12.0	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	1.020	0.999
15	Demolition concrete from artisanal outdoor slab	12.0	12.3	2.47	0.012	
16	Roman concrete from Via Apia Roma 2014	8.5	9.2	0.66	0.059	0.010

The detection of elements in these records is presented at Table 4, by decreasing order of occurrence.

The matrix of this demolition concrete contains Ca, K, Si, Fe and Al (most frequently detected cations), and secondarily Na and Mg with accompanying anions (S Cl) and other elements present in lower concentration (Cr, Ti, Cu, Zn, Br and P) (Table 4). Titanium is present in 3 cases of 15 observations of the sample #14. It is each time associated with Al, Ca, Fe, K and Si, and two times out of three Cl, Mg and Na. It therefore seems 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).

Table 4 : Presence and relative concentrations of elements in microscopy observation of concrete sample #14

Element	*N observation /15*	*Mean concentration %*	*Min Cc %*	*Max Cc %*
Ca	15	36.23	0.40	93.95
K	12	4.59	0.77	16.18
Si	12	4.47	0.10	15.48
S	12	2.53	0.11	7.95
Cl	11	11.69	0.42	38.98
Fe	9	46.77	1.46	84.32
Al	8	2.73	0.45	5.86
Na	8	10.14	1.94	30.72
Mg	6	1.67	0.17	3.76
Cr	6	9.33	0.88	14.30
Ti	3	2.14	1.35	2.76
Cu	2	42.04	29.69	54.39
Zn	1	5.34	-	-
Br	1	2.99	-	-
P	1	0.10	-	-

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

3.3.1 WWTP sludges (total content)

Since there is no available method for detecting nanoparticles in solid, except a tedious search by microscopy, which is not accessible in routine, a method of selection of solid samples is tested here. The outliers of a Gaussian distribution (samples with higher total content of the element than expected if the population was normally distributed) will be looked for by microscopy.

The elements Ag, Ce, Ti and Zn were measured after aqua regia extraction of 13 sludges (Table 5).

The mean (± 1 SD) total concentration of Ag is 10 (± 5) mg/kg sludge DM. The common range of Ag for soils is 0.01 – 5 mg/kg, with a selected average of 0.05 mg/kg (Lindsay 1979), 200 times less than the mean concentration observed in the sludges. 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 (Klee and Graedel 2004, cited in Sposito 2008). The AMF for Ag is 185. Is this high Ag level due to ENP? The declared ENP Ag(0) production and importation in France in 2014 is 0.1 kg - 1 kg (Table 1). The imported goods and the accumulated goods including NPs 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 concentration of < 1 µg Ag/kg sludge DM. This calculation at the scale of one country may not apply to a particular sludge. Kaegi et al. (2013) have found with spiking experiments that Ag-NP discharged to the wastewater stream will become sulfidized to various degrees in the sewer system and are efficiently transported to the WWTP, and will accumulate in the sewage sludge. It seems nevertheless that Ag in sewage sludge is not geogenic neither “NPgenic”. The mean concentration of Ce is 40 (± 15) mg/kg sludge DM.

The most abundant of the rare earth elements is seldom monitored in environmental studies.

The concentration in the earth crust is 46 mg/kg (https://en.wikipedia.org/wiki/Cerium). As the annual production and importation in France of Ce is 1 000 t - 10 000 t, but the use for fossil fuel is not clearly separated in the MEDDE report. The observed concentrations in the sludges seem to us quite high, and Ce should be monitored for an in-depth assessment. The mean concentration of Ti is

170 (± 120) mg/kg sludge DM, 20 times less than representative concentration in soil (4 000 mg/kg (Lindsay, 1979) or 2 400 mg/kg (Sposito, 2008)). The AMF of Ti is 1. Kiser et al., (2009) 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). The mean concentration of Zn is 1 900 (± 1 000) mg/kg sludge DM, 20 times more than representative concentration in soil (50 mg/kg (Lindsay, 1979), 48 mg/kg (Sposito, 2008), range of 10 – 100 mg/kg in soils without natural anomaly in France (Baize, 1997)). The AMF of Zn is 115. So Ag and Zn concentration in the sludges clearly originate from products rather than soil. These two elements have high AMF.

Table 5 : Concentration of pseudo-total Ag, Ce, Ti and Zn in 13 municipal waste water treatment plant sludge

Element concentration (mg/kg DM)	*Ag*	*Ce*	*Ti*	*Zn*
Sludge 1	6	36	166	985
Sludge 2	5	30	99	1877
Sludge 3	7	63	198	845
Sludge 4	8	36	86	2209
Sludge 5	4	14	80	1145
Sludge 6	9	30	50	2454
Sludge 7	14	23	74	2159
Raw Sludge #8	5	29	79	1644
Raw sludge #9	18	62	232	4851*
Thickened sludge #12	15	49	357*	2097
Digested sludge #10	15	46	383*	2100
Digested composted sludge #11	13	32	335	1875
Solid sludge #13	8	53	74	800
Mean (standard deviation)	10 (4.6)	39 (15)	170 (120)	1926 (1042)

*outliers of a Gaussian distribution

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 (samples #12 and #10, and sample #9, respectively). 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 Si Al (most frequently detected cations) and secondarily Mg K Na (Table 6). 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 phase of Ti, i.e. aggregated NP TiO_2 areas, were not found (area of observations 25 microns per side). 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 7) and Cl (5 times 7) for the raw sludge, and Al, Ca, Fe, K, P, S, Si (4 out of 4) and Cl (3 times 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 may be soil, but it is not observed in all spectra of the same sample, and, as mentioned, soils have higher concentrations of Ti. Ti can also be anthropogenic (white paints, toothpaste, certain foods, sunscreen ...) and has been found as NP in façade runoff (Kaegi et al., 2008). This study cannot discriminate between pedologic and anthropogenic (nano or non nano) Ti.

Table 6 : Presence and relative concentrations of elements in the microscopy observations of waste water sludge samples #9 and #10

	Raw sludge #9				*Digested sludge #10*			
Element	*Presence/13 obs.*	*Cc mean*	*Cc min*	*Cc max*	*Presence/9 obs.*	*Cc mean*	*Cc min*	*Cc max*
Ca	13	30.71	9.90	57.85	9	8.07	4.47	14.09
P	13	15.35	3.50	21.93	8	18.33	10.59	26.75
S	13	8.60	2.11	42.15	8	4.72	0.90	10.11
Fe	12	33.94	21.19	58.03	8	36.71	10.09	65.36
Si	12	5.88	0.89	9.15	9	18.55	0.89	55.92
Al	12	2.49	0.57	4.11	6	7.97	1.09	14.24
Mg	12	1.48	0.92	2.11	3	2.84	1.81	4.46
K	11	3.86	0.36	29.50	8	4.53	0.73	16.50
Na	11	3.66	0.41	28.39	2	17.52	1.61	33.42
Cl	8	5.93	0.12	38.60	6	6.65	0.25	33.63
Ti	7	0.91	0.63	1.16	4	1.60	1.00	2.37
Ni	1	1.96	-	-	1	8.36	-	-

Zn was not detected by the probe (no peaks in the spectra) despite a high total concentration of almost 5 g/kg. 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.

So, separate phase(s) containing Ti or Zn in outliers of a normal distribution have not been found, despite the relatively high total concentration (350 mg/kg and 5 g/kg, respectively).

3.3.2 Municipal landfill leachate sludges (analysis of total content and leachable content)

The main characteristics of the sludges are presented at Table 7. Water content, density, loss on ignition and the pH of the samples are very different. 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). 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. Anions are measured by ionic chromatography in the leachates of solid samples and in filtered liquid samples. 45 elements have been measured.

The 27 elements with at least one value > LQ are presented at Table 7 by decreasing order of mean. The other 18 elements have all values lower than LQ (< 5 mg/kg unless otherwise specified): Ag, Au, Be, Bi, Cd (LQ 0.8 mg/kg), Co, Ga, Ge, Hf, Hg (LQ 0.3 mg/kg), In (LQ 10 mg/kg), Nb, Pd, Rh, Se, Ta, Te, W.

Elements of group #3 (highlighted) are present at low total concentrations, or below the LQ. Ce, 100 or 1000 times more used as ENP that the other “classical” elements Zn, Cu, Ni and Sb (EU Landfill Decision 2003/33) (Table 1), is not found. The “classical” elements are found at concentrations following the same order than the declared ENP annual quantities, reflecting probably their general use in non NP species in non hazardous products, rather than their ENP fraction. Ag and Co, declared at quantities < 1 kg, are not found.

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 (Lindsay, 1979, Sposito, 2008, Baize, 1997). Some representative mean concentrations of Zn, Cu and Ni in soils, composts and sediments of France are presented at Table 8. It seems that landfill sludges have content comparable those three environmental compartments. Concentrations of Sb, Ag and Co are not available.

Table 7 : Main characteristics and total concentration 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.

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
LOI % DM	8.9	63.4	19.8	8.6	11.2	14.2					21.0
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.

The solid samples have been leached, as well as the liquid samples 8 and 10. Liquid samples 1 and 6 have been used as they were. The leachates were microfiltered and ultrafiltered. The distribution of particles of microfiltrates of two samples is illustrated at Figure 2.

The concentrations are between 0.5 10^9 and 5 10^9 particles/ml, and the D50 and D90 are similar for the different samples at 92 nm and 147 nm (Table 9). It has been noticed that the visible absorbance of the microfiltrate is roughly correlated with the number of particles (result not shown).

Table 8 : Concentration of Zn, Cu and Ni in agricultural soils, in compost and in sediments

Compartment	*Agricultural soils (uncontaminated) (Baize et al., 2007)*		*Compost from Household compostable waste (Zdanevitch, 2012)*		*Fluvial Sediments (Hennebert and Padox, 2010)*	
Element (mg/kg)	mean	n	mean	n	mean	n
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

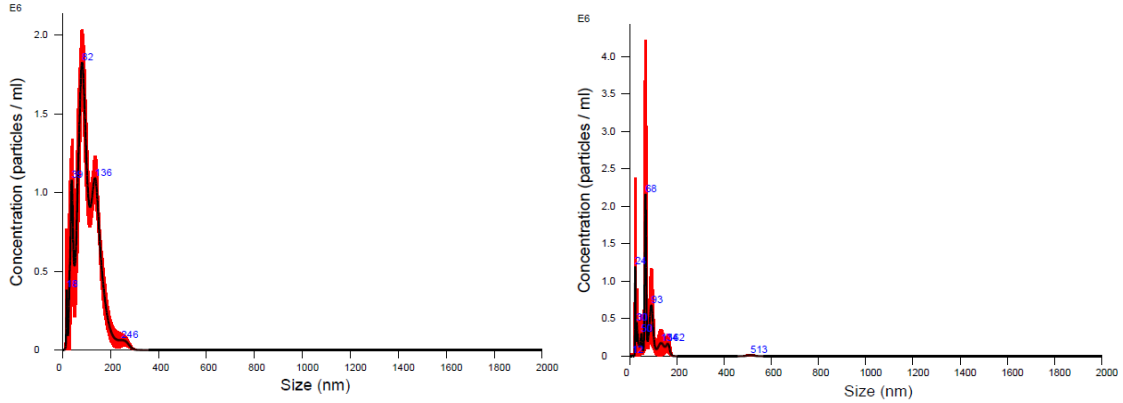

Figure 2 : Granulometry of microfiltrate of landfill sludge by Nanoparticle Track Analyzer (left: solid sample 4 after leaching, 1.6 108 particles/ml dilution 10; right: liquid sample 10, 5.0 107 particles/ml dilution 2.5)

The concentrations of colloidal or NP fraction in the leachate are presented at Table 9. Au, Bi and La have been detected neither in the microfiltrate, nor in the ultrafiltrate (LQ 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, and Ce (group #2) a maximal concentration of 10 mg/kg (in a liquid 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).

The occurrence of elements in a colloidal or ENP form (referred below as the colloidal fraction) is presented at Table 10. 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 high colloidal occurrence (between 9 and 6/10).

Elements of group #3 are highlighted in the table. Cu, Sb, Zn, Co and Ni are remarkably 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 on 10 in colloidal form, with a high colloidal/leachable fraction of 90% but with a very low concentration of 0.01 mg/kg, Table 9). Ag, the seventh element of the group, has a colloidal fraction of 100% of the leachable fraction (but in only one sample with at low concentration of 0.04 mg/kg, Table 9).

Table 9 : Colloidal or ENP leachable concentration of elements in 10 landfill sludge samples

Colloidal or ENP Concentration	*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	0.90	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)											
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	6.0	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	0.4	0.1	0.0	2.5	1.5	2.0
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	6.0	1.2	0.3	3.0	1.7	0.7	1.6
Cu	10.6	0.1	0.0	0.1	0.2	0.9	0.0	0.0	0.1	0.2	1.2
As	0.1	1.5		0.1	1.0	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	0.2	0.3	0.5
Ba	0.7	0.1	0.0	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	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 10 : Occurrence of colloidal or ENP fraction by element in 10 landfill sludge leachate samples

Occurrence as colloidal or ENP		*In case of occurrence, (Colloidal or ENP)/Leachable ratio*		
Element	*n/10*	*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			

4. CONCLUSIONS

A classification is proposed, based on the production and importation amounts of ENPs in France in 2014 (400 000 t), and on CLP classification of ecotoxicity for the soluble forms of the elements:

- Major elements (group #1): ENPs substances of Si (> 100 000 t/y), Ca, Ti (10 000 – 100 000 t/y), Al (2 000 – 20 000 t/y), Mg (1 100 – 11 000 t/y), Fe (300 – 3 000 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):
  - With production and importation > 1 t/y: ENPs substances of Ba (21 – 212 t/y), Bi, Cr(III) (2 – 21 t/y), Sr (1 – 10 t/y),
  - With production and importation < 1 t/y: ENPs substances of 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 (1 000 – 10 000 t/y), Cu, Zn (10 – 100 t/y), Ni, Sb (1 – 10 t/y), Ag, Co (0.1 - 1 kg/y).

The most "engineered" 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).

Colloidal form or ENPs of elements have been looked for at laboratory in leachates (EN 12457-2) of 23 engineered nanomaterials and have been found in a paint leachate (Si) and in three cosmetics leachates (Al, Si, and Zn). Two cosmetics have 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 Ti in colloidal form at a concentration of 1 mg/kg. The total content of Ag, Ce, Ti and Zn in 13 municipal sewage sludges showed two outliers of Gaussian distribution of Ti and Zn, but no ENPs have been found by TEM/EDS. From 10 sludges 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 on 10 a colloidal form but with a very low concentration of 0.01 mg/kg when present.

From this limited research, it appears that cosmetics could be a source of ENPs. Sewage sludge could be a sink for Ag and Ce since their total concentrations is significant (10 and 40 mg/kg respectively). Landfill sludges 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 build-up in landfill sludge) are low.

AKNOWLEDGEMENTS

The Ministère de l'Ecologie, du Développement Durable et de l'Energie (MEDDE, Paris) has funded this work (Program DRC01 and DRC54). The Centre d'Enseignement et de Recherche en Géosciences de l'Environnement (CEREGE, team Interfast, unité mixte CNRS – Aix Marseille Université) is acknowledged for the cement sample with nanoparticular TiO_2. Mr Aguerre-Chariol is thanked for information about ENPs in the cosmetic raw samples. Pauline Molina, Ismahen Samaali, Camille Malburet and Samy Vidal are thanked for their nice contribution to the laboratory work.

REFERENCES

Baize, D., Saby, N., Deslais, W. (2007). Teneurs en huit éléments en traces (Cd, Cr, Cu, Hg, Ni, Pb, Se, Zn) dans les sols agricoles en France. Résultats d'une collecte de données à l'échelon national. INRA - Orléans Unités Science du sol et InfoSol. 26 janvier 2007. http://www.gissol.fr/programme/bdetm/_rapport_anademe/rapport/03.php#3-2-2).

Baize, D. (1997). Teneurs totales en éléments traces métalliques dans les sols (France). Institut National de la recherche Agronomique - INRA. Paris. 408 pp.

CLP Regulation (2008). Regulation (EC) No 1272/2008 of the European parliament and of the Council of 16 December 2008 on Classification, Labelling and Packaging of Substances and Mixtures Regulation (CLP). 31.12.2008 Official Journal of the European Union. L 353/1. 1350 pp.

EU Landfill Decision 2003/33. Council Decision of 19 December 2002 establishing criteria and procedures for the acceptance of waste at landfills pursuant to Article 16 of and Annex II to Directive 1999/31/EC. Official Journal of the European Communities 16.1.2003, L11/27.

Gay, G., Dalvai, J. (2014). Substances émergentes dans les boues et composts de boues de stations d'épurations d'eau usées collectives – Caractérisation et évaluation des risques sanitaires. Technical report INERIS DRC - 14 - 115758 – 08437. 14.11.2014. 294 pp.

Gottschalk F., Nowack, B. (2011). The release of engineered nanomaterials to the environment. J. Environ. Monit., 13, 1145-1155.

Farré M., Pérez, S., Gajda-Schrantz, K., Osorio, V., Kantiani, L., Ginebreda A., Barceló, D. (2010). First determination of C60 and C70 fullerenes and N-methylfulleropyrrolidine C60 on the suspended material of wastewater effluents by liquid chromatography hybrid quadrupole linear ion trap tandem mass spectrometry. Journal of Hydrology 383 (2010) 44–51

Hassellöv, M., Kaegi, R. (2009). Analysis and characterization of manufactured nanoparticles in aquatic environments. In: Lead, J.R., Smith, E. (Eds.), Environmental and Human Health Impacts of Nanotechnology. Wiley, Chichester, UK, pp. 211–266.

Hennebert, P., Avellan, A., Yan, J., Aguerre-Chariol, O. (2013a). Experimental evidence of colloids and nanoparticles presence from 25 waste leachates. Waste Management 33, 1870–1881. http://dx.doi.org/10.1016/j.wasman.2013.04.014

Hennebert, P., Papin, A., Padox, J-M. (2013b). The evaluation of an analytical protocol for the determination of substances in waste for hazard classification. Waste Management 33, 1577–1588. http://dx.doi.org/10.1016/j.wasman.2013.03.013

Hennebert, P., Lambert, S., Fouillen, F., Charrasse, B. (2014). Assessing the environmental impact of shredded tires as embankment fill material. Can. Geotech. J. 51: 469–478 dx.doi.org/10.1139/cgj-2013-0194

Hennebert, P., Humez, N., Conche, I., Bishop, I., Rebischung, F. (2015). Assessment of four calculation methods proposed by the EC for waste hazard property HP 14 'Ecotoxic'. Submitted to Waste Management.

Hjelmar, O. (2012). Description of the methodology used to set the leaching criteria for acceptance of waste at landfills for inert waste, landfills for non-hazardous waste accepting stable, non-reactive hazardous waste and landfills for hazardous waste listed in Council Decision 2003/33/EC. Technical note prepared for the EU Committee for the Adaptation to Scientific and Technical Progress of EC legislation on Waste, TAC Subcommittee on Landfill. Available on request from oh@danws.dk.

JDLE (2013). http://www.journaldelenvironnement.net/article/un-francais-avale-23-tonnes-de-matieres-premieres-par-an,37654?xtor=EPR-9

Kaegi, R., Ulrich, A., Sinnet, B., Vonbank, R., Wichser, A., Zuleeg, S., Simmler, H., Brunner, S., Vonmont, H., Burkhardt, M., Boller, M. (2008). Synthetic TiO2 nanoparticle emission from exterior facades into the aquatic environment. Environmental Pollution 156 (2008) 233–239.

Kaegi, R., Sinnet, B., Zuleeg, S., Hagendorfer, H., Mueller, E., Vonbank, R., Boller, M., Burkhardt, M. (2010). Release of silver nanoparticles from outdoor facades. Environmental Pollution 158 (9), 2900–2905. http://dx.doi.org/10.1016/j.envpol.2010.06.009.

Kaegi, R., Voegelin, A., Ort, C., Sinnet, B., Thalmann, B., Krismer, J., Hagendorfer, H., Elumelu, M., Mueller, E. (2013). Fate and transformation of silver nanoparticles in urban wastewater systems. Water Research 47, 3866–3877

Kiser, M.A., Westerhoff, P., Benn, T., Wang, Y., Pérez-Rivera, J., Hristovski, K. (2009). Titanium Nanomaterial Removal and Release from Wastewater Treatment Plants. Environ. Sci. Technol. 43, 6757–6763

Klee, R.J., Graedel, T.E. (2004). Elemental cycles: a status report on human or natural dominance. Annu. Rev. Environ. Resour. 29, 69-79.

Lindsay, W.L. (1979). The chemical equilibria in soils. Wiley. 449 p.

Lozano, P., Berge, N.D. (2012). Single-walled carbon nanotube behavior in representative mature leachate. Waste Management, 32, 1699–1711

MEDDE (Ministère de l'Ecologie, du Développement durable et de l'Energie, France). (2014). Éléments issus des déclarations des substances à l'état nanoparticulaire – exercice 2014. Rapport d'étude. Novembre 2014. 40 p. http://www.developpement-durable.gouv.fr/IMG/pdf/rapport-nano-2014.pdf

MEDDE. (2015). Bilan 2012 de la production de déchets en France. Chiffres et statistiques n° 615 Mars 2015. www.statistiques.developpement-durable.gouv.fr

Nowack, B., Baalousha, M., Bornhöft, N., Chaudhry, Q., Cornelis, G. Cotterill, J., Gondikas, A., Hassellöv, M., Lead, J., Mitrano, D.M., von der Kammer, F., Wontner-Smith, T. (2015). Progress towards the validation of modeled environmental concentrations of engineered nanomaterials by analytical measurements. Environ. Sci.: Nano 2015. DOI: 10.1039/c5en00100e

OECD (Organisation for Economic Co-operation and Development). (2015°). Working Party on Resource Productivity and Waste – Nanomaterials in waste streams – Chapter 1. Draft report. S Yamaguchi and P Börkey. ENV/EPOC/WPRPW(2015)10. 19 p.

OECD (Organisation for Economic Co-operation and Development). (2015b). Working Party on Resource Productivity and Waste – Recycling of waste containing nanomaterials. Draft reflection paper - second revision. M Tellenbach. ENV/EPOC/WPRPW(2013)2/REV2. 17 p.

OECD (Organisation for Economic Co-operation and Development). (2015c). Working Party on Resource Productivity and Waste – Incineration of waste containing nanomaterials. Draft reflection paper - second revision. J Vogel and B Wiechmann with contributions from S Krause. ENV/EPOC/WPRPW(2013)/REV2. 12 p.

OECD (Organisation for Economic Co-operation and Development). (2015d). Working Party on Resource Productivity and Waste – The fate of engineered nanomaterials in sewage treatment plants and agricultural applications. Draft reflection paper - second revision. JY Bottero. ENV/EPOC/WPRPW(2013)4/REV2. 17 p.

OECD (Organisation for Economic Co-operation and Development). (2015e). Working Party on Resource Productivity and Waste – Landfilling of waste containing nanomaterials and nanowaste. Draft reflection paper. M King, J Séguin and A Loo. ENV/EPOC/WPRPW(2014)5/REV1. 23 p.

Padox JM, Hennebert P. (2010). Qualité chimique des sédiments fluviaux en France, Synthèse des bases de données disponibles. Report 03/06/2010 N° INERIS-DRC-10-105335-04971A. 99 p.

SCENIHR. (2009). "Scientific Committee on Emerging and Newly Identified Health Risks, Risk Assessment of Products of Nanotechnologies, European Commission, DG Health & Consumers, Brussels", http://ec.europa.eu/health/ph_risk/committees/04_scenihr/docs/scenihr_o_023.pdf

Sposito, G. (2008). The chemistry of soils. 2nd edition. Oxford University Press. 329 p.

SYPREA. (2015). Syndicat des professionnels du recyclage en agriculture 04/08/2015. http://syprea.org/

Wik, A., Dave, G. (2009). Occurrence and effects of tire wear particles in the environment A critical review and an initial risk assessment. Environmental pollution 157, 1-11.

XLStat. (2011). XLStat software from Addinsoft. http://www.xlstat.com

Zdanevitch, I. (2012). Etude comparative de la qualité de composts et de digestats issus de la fraction fermentescible d'ordures ménagères collectée séparément ou en mélange. Report

24/02/2012 N° INERIS DRC-12-125976-02525A. 92 pp.