Mineral colloids and nanoparticles in municipal solid waste incinerator bottom ashes and sunscreens leachates

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MINERAL COLLOIDS AND NANOPARTICLES IN MUNICIPAL SOLID WASTE INCINERATOR BOTTOM ASHES AND SUNSCREENS LEACHATES

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SUMMARY: This study present “real-world” potential emission of colloidal and soluble concentrations of elements from two potential sources of nanoparticles in the environment, ten representative municipal incinerator bottom ashes gathered by a professional union, and ten commercial sunscreens. The samples are leached and filtered by cascade front-filtration strirred membrane system at 0.45 μM and 3 kDa. The elements are analysed by ICP and the colloidal or nanoparticulate fraction is calculated as the difference between the 0.45 μm fraction and the 3 kDa fraction. For BA, the only elements with a colloidal concentration greater than 1 mg/kg are Ca (9 samples/10), K (4/10), Na (9/10) and Al (6/10). The other elements have lower colloidal concentrations, and for 13 elements, no colloidal fraction. For sunscreens (manufactured with nanoparticles of titanium oxide formulated with Si, Zn and/organic coatings), titanium colloidal concentrations are measured in two leachates out of ten, at low concentrations (50 mg/kg and 9 mg/kg). The same applies to silicon (17 and 23 mg/kg). The other elements of the sunscreens leachates are either low emitted and have no impact on the environment (Na, K, P) or are emitted at very low concentrations (other elements, heavy metals). The absence of the elements or the low concentrations observed in both case suggests that (i) the elements are in leachates in the form of aggregates larger than 450 nm, or (ii) homo- (sunscreen) or hetero-aggregation (MSWI-BA) actively reduces the free NP or colloidal concentrations, and hence the potential of emission of elements in a colloidal or nanoparticular form when these materials are used in contact with the environment.

1. INTRODUCTION

Numerous risk assessment studies of engineered nanoparticles hypothesize transfer coefficients from one “source” compartment of the environment to other one(s), to finally estimate the potential build-up of engineered nanoparticles (ENP) in transitory or definitive “sinks”: water bodies, sediments, (agricultural) soils, landfills, municipal solid waste incinerator bottom ash (MSWI-BA), stabilised waste… Very few “real-world” data are published.

Another difficulty in ENP studies is what ENP to look at, and if the analytical methods are available in real-world samples.

The elements of the mineral ENP of interest can be roughly known as “source” by the declarations of production and importation of engineered nanoparticles, available now in France, Belgium, Austria, and probably soon in other EU countries (Hennebert et al. 2015). A further step ranks the elements according to their ecotoxicity. In France, there are 7 elements which are declared to be used and whose soluble forms have acute or chronic ecotoxic hazard statement codes (according to the chemical regulation REACH): Ce (1 000 – 10 000 t/y), Cu, Zn (10 – 100 t/y), Ni, Sb (1 – 10 t/y), Ag, Co (< 1 t/y) (Hennebert et al. 2015).

Since 2013, a simple method for detection of potential emission of mineral NPs is proposed, by cascade tangential or stirred front filtration of leachates (EN 12457-2) of waste with microfiltration membrane (450 nm) and ultrafiltration membrane (3 kDa or about 3 nm) (Hennebert et al. 2013, Anderson et al. 2014). The difference of concentration in micro- and ultrafiltrates is the colloidal or NP concentration. TEM-EDS can be then used on the samples with significant colloidal concentrations of the elements of interest to look at ENPs.

These methods have been applied to the leachates of 10 MSWI-BA samples selected with the professional union of incinerators operators (France), and to 10 sunscreens leachates.

2. MATERIAL AND METHOD

2.1 Samples

Bottom ashes

Ten MSWI bottom ashes have been collected in 2016 and 2017, fresh or maturated, by the incinerator operators, with coordination of their professional union (SVDU). The laboratory samples have been pretreated according to EN 12457-2 (< 4 mm with a jaw crusher, with minimum production of fines), leached for 24 h at L/S 10 L/kg, and allow to settle for 15 minutes.

Sunscreens

Ten creams with a TiO2 filter were purchased in supermarkets or pharmacies in January 2017 (n ° 5 to 10). Some were rated "nano" and others were not:

- Cosmetics 1: "Lovéa" moisturizing milk Protection 50 Laboratoires Biocos
- Cosmetics 2: Solar milk "Alga Maris" Protection 50 Laboratories Biarritz
- Cosmetics 3: Sun milk kid «Alphanova sun» Protection 30 Laboratoires Alphanova Santé
- Cosmetics 4: Spray «Avène» Protection 50 Dermatological laboratories Avène Pierre Fabre
- Cosmetics 5: Mineral milk "Avène" SPF 50 Dermatological Laboratories Avene ("nano")
- Cosmetic 6: "Sheer Mineral UV Defense" SPF 50 High Protection Laboratory SkinCeuticals
- Cosmetics 7: Solar spray kid «Mustela» Protection 50 Laboratories Expanscience
- Cosmetics 8: "Spray solar SPF50" Laboratory Mixa
- Cosmetics 9: "Sunscreen UVSKI SPF 50+" Garnier ("nano")
- Cosmetics 10: «Screen Moisturizing milk 50 FPS» Laboratories Genesse («nano»)

The products were leached according to the NF EN 12457-2 standard (leaching of the waste): 20 grams of cosmetic product are stirred in 200 ml of deionized water for 24 hours.

2.2 Analysis

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® 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 3 KDa, that was used in a previous study (Hennebert et al., 2013), but it is much more faster. No apparent clogging occur with in the stirred cells. About 500 ml were microfiltrated, and from this volume, about 200 ml were ultrafiltrated. The expensive ultrafiltration membranes can be washed in deionized water and reused without contamination. The filtrates were acidified to pH < 2 with ultrapure nitric acid. The elements were 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.

3. RESULTS

3.1 Bottom ashes

The colloidal (Table 1) and soluble (Table 2) concentrations of elements (expressed in mg/kg DM) of leachates of MSWI bottom ashes are presented with pH, electric conductivity, and redox status (sum of pe and pH). The ashes are alkaline (S1 and S2 are maturated with a lower pH), mildly saline (the mean EC corresponds to about 1.3 g salt per L of leachate, or about 13 g salt/kg DM), and oxidised (pe+pH close to 15). The colloidal concentrations are very low. The only elements with a concentration greater than 1 mg/kg are Ca, K, Na and Al (9 to 4 samples of 10 with a colloidal concentration > LOQ). The other elements have lower colloidal concentrations, and for 6 elements, no colloidal fraction.

The soluble concentrations are presented in the second part of the table. The concentrations are low. They are higher than the colloidal concentrations, excepted in a few cases (coloured in yellow in the table) (Cu 4 cases / 10, Hg 3/10, Al, Fe, Sb 1/10, other elements 0/10).

Table 1: Leachable colloidal concentrations of bottom ashes, and pH, electrical conductivity and redox status (pe+pH) of the leachates (in yellow: mean concentration > 1 mg/kg)

Sample	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	Nb>LQ	Mean >LQ
pH	9.7	8.9	11.7	11.3	10.9	11.5	11.7	12.1	11.3	11.3		11.0
EC (mS/cm)	1.2	0.2	2.1	1.7	1.6	1.1	2.7	5.7	2.8	3.5		2.3
pe+pH	15.3	14.8	15.9	17.0	14.8	14.6	14.6	14.4	13.1	14.2		14.9
Conc (mg/kg)												
Al	14.0	0.3	0.7	1.4		0.2		0.2			6	2.8
Si		0.033	0.096	0.053	0.067			0.015		0.007	6	0.045
Fe	0.009		0.016	0.004							3	0.010
Mn	0.001		0.002								2	0.001

Ca	2.8	0.6	21.0	25.4	1.1	4.4		283.3	3.1	5.9	9	38.6
Mg											0	
Na		0.1	18.9	22.8	7.5	1.9	12.0	3.6	2.8	8.8	9	8.7
K		0.1	23.2						22.4	29.0	4	18.7
P	0.024		0.011			0.017			0.004		4	0.014
As											0	
Ba	0.006		0.015	0.003		0.005	0.004	0.093			6	0.021
Be											0	
Cd											0	
Ce											0	
Co											0	
Cr											0	
Cu	0.036	0.009	0.717	0.689				0.033	0.026	0.033	7	0.221
Hg	0.007		0.015	0.008	0.006	0.002					5	0.008
Mo	0.001	0.003	0.015	0.002					0.007	0.003	6	0.005
Ni											0	
Pb											0	
Sb	0.003			0.013	0.003					0.031	4	0.012
Se											0	
Sn											0	
Ti											0	
Tl											0	
V	0.002										1	0.002
Zn			0.036	0.010		0.011		0.070			4	0.032

Table 2: Leachable soluble concentrations of bottom ashes (in yellow: colloidal concentration > soluble concentration)

Sample	A1	A2	A3	A4	A5	A6	A7	A8	A9	A10	Nb>LQ	Mean >LQ
Conc (mg/kg)												
Al	35.0	0.3	42.5	82.1	21.4	45.7	9.1	5.9	129.4	24.6	10	39.6
Si		0.8	2.0	0.5	0.6	0.7	1.5	0.7	0.2	1.4	9	1.0
Fe			0.01	0.01	0.02	0.01	0.01				5	0.01
Mn		0.002			0.001			0.001			3	0.001
Ca	157.7	22.3	64.1	70.8	118.4	77.7	224.8		119.9	148.5	9	111.6
Mg	1.0	1.6	0.03	0.1	0.2	0.03	0.03		0.01	0.03	9	0.3
Na	75.1	4.3	316.2	296.4	233.8	80.6	202.0	161.2	298.0	372.5	10	204.0
K	40.1	1.3	195.8	211.4	111.0	33.9	312.9	138.2	218.9	422.5	10	168.6
P	0.07		0.05	0.17	0.24	0.10	0.03	0.05	0.06	0.05	9	0.092
As											0	
Ba	0.102	0.014	0.074	0.031	0.032	0.097	0.496	3.876	0.171	0.059	10	0.495
Be											0	
Cd											0	
Ce											0	
Co											0	
Cr			0.014	0.018	0.008	0.009				0.102	5	0.030
Cu	0.028		0.796	1.659	0.526	0.068	0.007		0.044	0.063	8	0.399
Hg	0.008	0.002	0.022	0.027	0.006	0.018	0.012		0.006		8	0.012
Mo	0.033	0.009	0.104	0.172	0.056	0.053	0.070	0.013	0.105	0.103	10	0.072
Ni											0	
Pb											0	
Sb	0.041	0.034		0.024	0.028			0.025	0.036		6	0.031

Se											0	
Sn											0	
Ti											0	
Tl											0	
V	0.007										1	0.007
Zn		0.012			0.008		0.010	0.239	0.014	0.017	6	0.050

3.2 Sunscreens

The elements which can be used in UV "filter" formulations (Ti, with possible coating of Al, Si, Zn) are present at a low leachable colloidal concentration (Table 3). Only Ti and Si have a colloidal concentration > 10 mg/kg (yellow in the table) for two sunscreens. The major elements are also present in low concentration except Na, K and P for cream 7. The elements in the soluble fraction (Table 4) at concentration > 10 mg/kg are Ti (1 sunscreen), Si (7 sunscreens) and Zn (1 sunscreen), as well as Na, K and P in some sunscreens.

The colloidal fraction is rarely greater than the dissolved fraction (Ti 3 cases /10, Si, Ca, Fe, P, Hg 2/10, Al, Mg, Be, Mo 1/10, other elements 0/10).

Table 3: Leachable colloidal concentrations of sunscreens, and pH, electrical conductivity and redox status (pe+pH) of the leachates (in yellow: concentration > 10 mg/kg)

Sample	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	Nb>LQ	Mean >LQ
pH	7.0	6.2	4.9	4.6	3.9	6.1	7.3	7.0	6.2	6.3		5.9
pe+pH	14.5	13.4	13.0	13.4	13.3	14.4	14.7	14.0	14.2	14.0		13.9
EC (mS/cm)	0.029	0.010	0.385	0.187	0.044	0.162	0.884	0.106	0.042	0.124		0.197
Conc. (mg/kg)												
Ti	1.3			50.3	0.03		0.4		0.7	9.1	6	10.3
Si			0.3	17.4	3.5	22.6	2.7	4.2	4.1	4.5	8	7.4
Zn		3.7		0.5		0.02					3	1.4
Al			2.9			0.05					2	1.5
Ca				5.9			0.4	1.0		2.9	4	2.5
Mg			0.2	1.8		5.4	4.8				4	3.0
Mn		0.005	0.005	0.035						0.003	4	0.012
Na			2.6	20.0			162.8	8.3	3.4		5	39.4
K		3.7			2.6		332.9			5.8	4	86.2
Fe			0.5	0.5			0.2	0.01		0.3	5	0.3
P	0.1		1.6	2.2		0.3	113.7		4.6	0.5	7	17.6
Ag											0	
As								0.18		0.29	2	0.24
Ba											0	
Be			0.18	0.14	0.005		0.05		0.004	0.04	6	0.07
Cd											0	
Ce											0	
Co											0	
Cr											0	
Cu				0.04						0.07	2	0.05
Hg	0.001		0.003	0.012				0.005		0.475	5	0.099
Mo								0.01		0.05	2	0.03
Ni				0.10							1	0.10

Pb											0	
Sb											0	
Se											0	
Sn								0.06	0.18		2	0.12
Tl	0.52			15.91					0.31	3.00	4	4.94
V											0	

Table 4: Leachable soluble concentrations of sunscreens (in yellow: colloidal concentration > soluble concentration)

Sample	C1	C2	C3	C4	C5	C6	C7	C8	C9	C10	Nb>LQ	Mean >LQ
Conc. (mg/kg)												
Ti	29.8			0.6				0.7	0.4	1.1	5	6.5
Si	26.6		3.9	92.7	27.1	15.2	27.2	20.3	96.0	1.8	9	34.5
Zn	0.9	20.5	2.4	2.0	0.8	0.1	0.2	0.5	0.2	0.7	10	2.8
Al			3.2	5.4	2.6	2.6					4	3.5
Ca	0.8	2.3	14.6	7.4	3.7	9.7		3.2	10.6	4.1	9	6.3
Mg			0.5	7.9	1.9	88.2	0.6		0.1	0.2	7	14.2
Mn	0.036	0.077	0.064	0.091	0.043	0.040	0.048	0.043	0.037	0.055	10	0.054
Na	9.8	9.9	774.2	421.1	42.7	186.6	2097.8	93.5	29.2	146.8	10	381.2
K			41.5	64.8		7.4	912.8			101.6	5	225.6
Fe	0.2	0.1	0.3	3.4	0.2			0.3	0.4	0.3	8	0.6
P	0.6			5.6		1.6	19.1		8.4	133.6	6	28.1
Ag											0	
As									0.15		1	0.15
Ba	0.03	0.03	0.03	0.07	0.05	0.04	0.03	0.05	0.01	0.02	10	0.03
Be	0.06		0.10	1.35	0.03			0.13	0.09	0.12	7	0.27
Cd											0	
Ce											0	
Co											0	
Cr											0	
Cu	0.09		0.07	0.31	0.11	0.05	0.21	0.44	0.21	0.19	9	0.19
Hg	0.028		0.037	0.016			0.036	0.082	0.065	0.022	7	0.041
Mo	0.03						0.03	0.02	0.03		4	0.03
Ni				0.21							1	0.21
Pb											0	
Sb											0	
Se											0	
Sn								0.18			1	0.18
Tl	8.39										1	8.39
V												

4. CONCLUSIONS

For bottom ashes, the colloidal concentrations are very low. For sunscreens (manufactured with nanoparticles of titanium oxide formulated with Si, Zn and/organic coatings), titanium colloidal concentrations are measured in two leachates out of ten, at low concentrations (50 mg/kg and 9 mg/kg). The same applies to silicon (17 and 23 mg/kg). The other elements of the sunscreens leachates are either low emitted and have no impact on the environment (Na, K, P) or are emitted at very low concentrations (other elements, heavy metals).

The absence of the elements or the low concentrations observed in both case suggests that (i) the elements are in leachates in the form of aggregates larger than 450 nm, or (ii) homo- (sunscreen) or hetero-aggregation (MSWI-BA) actively reduces the free NP or colloidal concentrations.

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REFERENCES

Anderson A, Merdy P, Villain S, Hennebert P. (2014). Analytical development dedicated to the study of the temporal evolution of waste - generated colloids. 9th ICEENN. Columbia (South Carolina, USA). 08/09/2014. 4 p.

Hennebert P, Avellan A, Yan J, Aguerre-Chariol O. (2013). Experimental evidence of colloids and nanoparticles presence from 25 waste leachates. Waste Management 33 (2013) 1870–1881.

Hennebert P, Merdy P, Anderson A. (2015). Nanoparticles in waste. Key note speech. Mineral nanoparticles in waste: potential sources (France 2014), occurrence in some engineered nanomaterials leachates, in municipal sewage sludges and in municipal landfill sludges. Proceedings Sardinia 2015 - 15th International Waste Management and Landfill Symposium. Cagliari (Italy). 05-09/10/2015.