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Experimental evidence of colloids and nanoparticles presence from 25 waste leachates

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Summary

The potential colloids release from a large pannel of 25 solid industrial and municipal waste leachates, contaminated soil, contaminated sediments and landfill leachates was studied. Standardised leaching, cascade filtrations and measurement of element concentrations in the microfiltrate (MF) and ultrafiltrate (UF) fraction were used to easily detect colloids potentially released by waste. Precautions against CO2 capture by alkaline leachates, or bacterial re-growth in leachates from wastes containing organic matter should be taken. Most of the colloidal particles were visible by transmission electron microscopy with energy dispersion spectrometry (TEM-EDS) if their elemental MF concentration is greater than 200 µg.l^{-1}. If the samples are dried during the preparation for microscopy, neoformation of particles can occur from the soluble part of the element. Size distribution analysis measured by photon correlation spectroscopy (PCS) were frequently unvalid, particularly due to polydispersity and/or too low concentrations in the leachates. A low sensitivity device is required, and further improvement is desirable in that field. For some waste leachates, particles had a zeta potential strong enough to remain in suspension. Mn, As, Co, Pb, Sn, Zn had always a colloidal form (MF concentration /UF concentration > 1.5) and total organic carbon (TOC), Fe, P, Ba, Cr, Cu, Ni are partly colloidal for more than half of the samples). Nearly all the micro-pollutants (As, Ba, Co, Cr, Cu, Mo, Ni, Pb, Sb, Sn, V and Zn) were found at least once in colloidal form greater than 100 µg.l^{-1}. In particular, the colloidal forms of Zn were always by far more concentrated than its dissolved form. The TEM-EDS method showed various particles, including manufactured nanoparticles

(organic polymer, TiO_2, particles with Sr, La, Ce, Nd). All the waste had at least one element detected as colloidal. The solid waste leachates contained significant amount of colloids different in elemental composition from natural ones. The majority of the elements were in colloidal form for wastes of packaging (3), a steel slag, a sludge from hydrometallurgy, composts (2), a dredged sediment (#18), an As contaminated soil and two active landfill leachates.

These results showed that cascade filtration and ICP elemental analysis seems valid methods in this field, and that electronic microscopy with elemental detection allows to identify particles. Particles can be formed from dissolved elements during TEM sample preparation and cross-checking with MF and UF composition by ICP is useful. The colloidal fraction of leachate of waste seems to be a significant source term, and should be taken into account in studies of emission and transfer of contaminants in the environment. Standardised cross-filtration method could be amended for the presence of colloids in waste leachates.

1. Introduction

Present waste classification and disposal guidelines have been established by hazard and the content of toxic products, which is based on conventional chemical substance's total or leachable content. Standard leaching of solid waste include a contact with water, generally at a ratio of 10 liter for 1 kg of dry matter of waste, and a cross-filtration with a membrane of nominal pore size of 0.45 µm. The chemical composition of the leachate is generally considered as soluble substances. Nevertheless, a large proportion of contaminants (40-90% or even more for the heavy metals) in aqueous natural media are believed to be adsorbed on natural colloids (Lead and Smith, 2009) of different size, which could influence the speciation, mobility and the toxicity of these pollutants (Baumann et al., 2006). In this context, it might be interesting to systematically evaluate the presence and composition of colloids in waste leachates. This may be helpful as pre-screening for selecting waste treatment methods and may be useful in the evaluation of pollutant transport in the environment. By example, in landfill leachates, the presence of carbonate minerals for binding trace metals and metalloids either by adsorption or by incorporation into their structure can be crucial for decontamination (Ettler et al., 2006).

Traditionally, a colloidal system has been defined as a dispersion of one phase in another, where the dispersed phase is in the size range of 1 nm to1 µm. Alternatively, colloids can also be defined as organic or inorganic entities, small enough to be dominated by aggregation and to

remain in a water column over reasonable timescales, but large enough to have supramolecular structure or properties e.g electric or (surface) charge (Buffle, 2006).

The nature of colloidal material is complex and several properties should be considered to characterize colloids dispersion (Hassellöv and Kaegi, 2009):

- The concentration, sometimes estimated by UV absorbance or measured as total elemental concentration by ICP (Inductively Coupled Plasma). While it is generally preferable to use molar concentrations, mass concentration is used for colloids and nanoparticles (due to the complex geometry of colloids and nanoparticles and the complexity of the mass concentration/mole ratio);
- The morphology (size, particle shape and aggregates, surface area) that can be determined by different observational techniques (atomic force microscopy, electron microscopy), analytical centrifugation (measuring the sedimentation rate in a fluid), radiation scattering (photon trajectories correlation spectroscopy) and adsorption measurements. Size distribution can be expressed in mass, volume or in number of particles;
- The chemical composition which can be determined by ICP, X-ray fluorescence spectrometry (XRF), and some analysis techniques specific to light elements;
- The physico-chemical properties including surface charge analyzed by zeta potential measurements.

Different techniques for characterisation of the colloids and nanoparticles (synthetic or natural) have been described in depth in different reviews (Lead and Wilkinson, 2006; Nowack and Bucheli, 2007; Hassellöv et al., 2008). Due to the non-specificity of each of these techniques and the low concentrations expected in wastes leachates, it is mandatory to use different techniques on the same sample. Till date there is no specifically defined method which is capable of routine monitoring the existence of such particles in the environment or in complex matrix as wastes leachates.

There are very few studies dealing with the release of colloids from solid waste. The only direct measurement is described by Koster et al. (2007) which shows release of Cu, Pb, Zn and Cr in colloidal form from a municipal solid waste incinerator's bottom ash in a laboratory column experiment. These elements were found associated with Ca, Si, Al and Fe in this study. ICP-MS was used for total elemental concentration after ultracentrifugation and Laser induced

breakdown detection (LIBD) for particle detection. Indirect indices of colloid presence in solid waste leachates were determined by computational geochemistry. Van der Sloot and Van Zommeren (2009) and Postma et al (2009) showed that leachates load of microelements (particularly Cu, Cr, Ni, Zn) of incinerator ashes, gasworks soil and waste treated wood, at different pH and filtered through 0.45 µm membrane filters, is complexed by colloidal dissolved organic carbon. They found that the ecotoxic response (Cu in waste wood) correlated well with "free" unbound concentration, without taking into account the colloidal fraction. Studies about colloids from landfill in groundwater are more frequent. Matura et al. (2010) characterized colloids from municipal landfill leachate by frontal filtration and ultrafiltration, TEM, AAS, ICP, HPLC and total organic carbon measurement (TOC). Baumann et al. (2006) showed the binding of contaminant metals and natural colloids (clay, silica, organic matter) from landfill leachate by frontal filtration, ultrafiltration and scanning electron microscopy couples with energy-dispersive X-ray spectroscopy (SEM-EDX). Jensen and Christensen (1999) studied mobility of colloids and linked transport of pollutants in landfill leachate by using frontal filtration and ultrafiltration, TOC, SEM-EDX, ASM, time-of-fly secondary ion mass spectrometry (TOF-SIMS). Backström et al (2003) used filtration and decantation to study heavy metals particles in road runoff. Colloids are studied in soil leachates by soil scientists and in particular in amended soils. For example, Karathanasis et al (2007) have percolated biosolids wastes leachates in soils at the laboratory. This practice enhanced the migration of cationic (Cd, Zn, Cu, Pb, Cr), as well as anionic metals (Mo) in subsurface soil environments up to 3 orders of magnitude over control treatments. Soil leachates were cross-filtered with 0.2 µm membrane filters, and the used filters were then assessed for colloidal fraction using acid extraction.

For manufactured nanoparticles, Kaegi et al. (2008, 2010) highlighted the issue of TiO_2 and Ag nanoparticles from cement and paint in rainwater and surface runoff. They detected TiO_2 nanoparticles up to 100 $mg.l^{-1}$ (depending on the age of the buildings and the amount of rainfall) using centrifugation, TEM, ICP-AES and ICP-MS. Kiser et al. (2009) showed the presence of TiO_2 nanoparticles in effluent of wastewater treatment plant using dead-end filtration, ICP-OES, centrifugation and TEM coupled with the X-ray microanalysis, but could not quantify with certainty. No direct observation of TiO_2 in biosolids were supplied, but adsorption of TiO_2 from water is observed, with the sewage sludges (biosolids) containing 1.1 $g.kg^{-1}$ DM of total Ti, probably being at least partly nanoparticles. Farré et al. (2010) tested 22 waste water samples in Catalonia (ES), and identified fullerenes C_{50} and C_{60} in concentrations range of 0.5 $ng.l^{-1}$ to 66 $\mu g.l^{-1}$ by liquid chromatography-mass spectrometry (LC-MS). Waste as sources of release of

manufactured nanoparticles is a potentially new problem (Brar et al., 2010). Bystrzejewska-Piotrowska et al. (2009) introduced for the first time the notion "nanowaste" and the new issues that their use/reuse implies in terms of recycling, recovery, and tracking legislation.

On the other hand, a well-known practical problem is the variability of the concentration of analytes in (cross-filtered) waste leachates according to i.e. EN 12457-1 to 4. The validation tests results of the standard (8 wastes, 9 to 11 laboratories, 4 to 5 analytes per waste) show that the median relative standard deviation (RSD) for analytical results is 3%, while for intralaboratory results it is 11% and for interlaboratory results it is 28% (calculated from EN 12457-2). At percentile 90%, the RSD are 6%, 37% and 79%, which is unsatisfactory. Possible explanations for this are the fact that different agitation conditions are allowed, but also that colloids could be retained in the filter cake which builds up during the cross-filtration of the leacheates before analysis. Another practical field that could be influenced by the presence of a fraction of colloidal contaminants is leachate transfer. The cut-off limit of 0.45 µm is considered in regulations as separation between “dissolved” and so-called “particulate” concentrations (EU Council Decision 2003/33/EC), and is frequently used in published reports of environmental assessment of waste. Regulatory values for acceptance of waste in landfills or re-use in natural environments are based on leachable content and the implicit assumption that the leachable fraction of waste is a "true" dissolved fraction and therefore potentially subject to transfer. This hypothesis could be re-evaluated at the light of the present work. The method used here further refines the so-called “dissolved” fraction in a colloidal fraction and a true dissolved fraction.

The potential emission of colloids from solid waste is not well known. The analytical methods to measure the colloids are widely used in aquatic chemistry, but not by the waste scientific community. This study aims to characterise the potential release of colloids from a large pannel of 21 solid industrial and municipal waste leachates, contaminated soil, contaminated sediments and 4 liquid wastes (bauxite residue, landfill leachates).

2. Materials and methods

2.1 Samples

The study was initially performed in 2011 on a set of 9 waste samples. Another set of 16 waste samples were studied in 2012. In total, 25 samples were studied (21 solids and 4 liquids # 9, 23, 24 and 25) (Table 1). All samples were collected from France excepted one dredged sediment coming from Belgium (# 18).

Leachate of the solid wastes was prepared as per the standard EN 12457-2, in deionized water at a liquid/solid ratio = 10 $l.kg^{-1}$ of dry matter, in closed polypropylene bottles of two liters for 24 hours. The total water volume was 1.8 L. The gas released by metallic dust sample was vented periodically. Leachates were left to stand for 15 minutes (as per standard) before filtration to allow the larger particles to settle and avoid membrane plugging during filtration. In 2012, the leachates were moreover centrigated in PTFE cups for 60 sec at 47 g, allowing particles of diameter greater than few micrometers to settle (> 6 µm for particle density of quartz, or > 4 µm for particle density of TiO_2), to prevent filter particle buildup and minimize rinsing.

2.2 Size fractionation

Waste leachates were filtered by tangential filtration with recirculation through regenerated cellulose membrane (Sartorius Sartocon 200 Hydrosart Slice) with a cut-off limit of 450 nm and 2 Kda (~ 3 nm), yielding three size fractions (Figure 1): > 450 nm, < 450 nm (microfiltrate - MF) and < 3 nm (ultrafiltrate - UF). A constant pressure of 2 bar at the input and 0.5 bar at the output of the cassette was applied. The membranes were regularly cleaned between the samples by filtering 500 ml of 1M NaOH, followed by filtration and recirculation of 500 ml of 1M NaOH for 1 hour (Sartorius protocol), and rinsing with deionized water until the filtrate pH (~ 6) and the conductivity (~15 10^{-4} $S.m^{-1}$) of deionized water was achieved. The total time for cleaning and rinsing was on an average 3.5 hrs. The first fractions of MF and UF of a sample (± 0.3 l) were diluted by the deionized water standing in the tubes, the pump and the filters, and were discarded after electrical conductivity control. For each sample, 1.2 l of settled and centrifugated leachate, 0.7 l of MF and 0.2 l of UF were finally obtained.

Neither contamination (ICP measurements) nor degradation of filtration performance (flow measurements) has been observed between one sample and another. For each element, the concentration of the element in colloidal form is assumed to be the difference between the microfiltrate (MF) and the ultrafiltrate (UF) concentrations.

2.3 Analysis

The pH, conductivity and redox potential of the leachate were measured before and after each filtration. The appropriate amounts of filtrate were collected for each analysis and properly stored (EN 16192). The zeta potential and particle size measurements (photon correlation spectroscopy PCS, Zetasizer NanoS, Malvern) were obtained within 5-7 days after filtration in 2011. Sonification before measuring was considered, but gave unconsistent size results with CeO_2 suspensions (results not shown), and has not been used. The limit of quantification of particles with a size of 100 nm is in the range of 10-100 $mg.l^{-1}$ for the device we used, which is quite high in comparison with the observed concentrations. In 2012, the measurements were obtained on same day or latest in two days using Zeta Sizer (NanoZS ZEN3600 ,Malvern). TOC was measured in 2012 only. Samples for TOC analysis were stored at -20°C until analyzed (Shimadzu TOC-6VCPH). Samples for the ICP were acidified (pH ≈ 1-2) using ultrapure HNO_3 and stored at 4°C until analysis. A microwave digestion method (EN 13656) with HCl, HNO_3 and HF acid at 205°C (in 2011) and 180°C (in 2012) for 20 minutes in bombs (MarsXpress oven) was used. After cooling down to 60°C, boric acid was added (to neutralize the hydrofluoric acid) to the solution and the samples were heated again to 160°C. The determination of the elements Al, As, Ba, Ca, Cd, Co, Cr, Cu, Fe, Hg, K, Mg, Mn, Mo, Na, Ni, P, Pb, Sb, Se, Sn,Ti, V, Zn was performed by ICP-MS (Agilent 7500 Series). Additionally, in 2012, Be and Tl were analysed as well. The limit of quantification (mean + 3 SD of filtered and digested milliQ water) was for most of the elements between < 5 $\mu g.l^{-1}$ to < 30 $\mu g.l^{-1}$, but with traces of contamination from some vessels for five elements (Hg < 50 $\mu g.l^{-1}$, Fe < 85 $\mu g.l^{-1}$, Al < 275 $\mu g.l^{-1}$, Ca < 575 $\mu g.l^{-1}$ and Na < 25000 $\mu g.l^{-1}$). The concentrations of some major elements (Na, K, Mg, Ca) were sometimes higher than the calibration range (despite dilution factor of 2000) and hence measured semi-quantitatively. Silicon was not measured, due to volatilisation by HF acid. One sample (bauxite residue) was leached, filtered and analysed in triplicate, with a mean RSD of 5% and 8% for UF and MF respectively.

The images of particles were obtained by using a TEM (Philips CM12, operated at 120 kV) coupled with element detection by EDS (Energy Dispersive Spectrometry) analysis (Oxford, model X-max), within a week after leaching and filtration. Carbon membranes of Cu TEM grids were hydrophilised by plasma discharge in air using an Emitech K100X plasma generator. A small drop (approx. 100 µL) of sample was deposited on the TEM grid and dried in air. Some samples with high salt concentration showed visible cristals in the meniscus during drying,

which could possibly hide the original particles in the samples. The grid of those samples was flushed with deionized water in 2011, and all the grids were flushed with deionized water in 2012.

2.4 Data analysis

Ratios of concentrations in the microfiltrate and the ultrafiltrate (noted MF/UF) were calculated when MF concentration was higher than the limit of quantification. When the concentration in the ultrafiltrate was below the limit of quantification, the half of the value of the limit of quantification (typically 25 $\mu g.l^{-1}$ taking into account a ten times dilution imposed by salt content) was used. Colloidal concentration is obtained by subtracting the ultrafiltrate concentration to the microfiltrate concentration (noted MF-UF), with same rule. The Wilcoxon and Mann-Whitney test was performed with XLStat version 2009.3.02 (xlstat.com).

3. Results and discussion

3.1 Elemental composition of microfiltrate and ultrafiltrate fractions

The concentration of the elements in the leachates fractions are shown in Figure 2 on a log scale. Alkaline and alkaline earth elements were present in the same concentration range, with the exception of Mg being less concentrated. The major (and less soluble) elements Al, Fe, Mn, Ti and P were present in a concentration range of 30 $mg.l^{-1}$ to 1 $mg.l^{-1}$, the iron being less concentrated. Microelements were present at lower concentration, from a maximum of 6 $mg.l^{-1}$ (Ba) to < 50 $\mu g.l^{-1}$ for Co and Hg.

Some elements were present in the microfiltrate fraction, and not in the ultrafiltrate fraction (Figure 2): Fe in APC residue bicarbonate, Pb in APC residue lime, Zn in MSWI fly ash, Ba in MSWI bottom ash, Pb in industrial APC residue, and Fe, Mn, Ba, Cr and Ni in landfill leachate. Those elements are assumed to be in particulate or colloidal form, not detectable after ultrafiltration. Zn in APC residue lime and industrial APC residue and Cu in MSWI bottom ash were present at high concentration in the MF fraction in comparison with UF. The other elements were most of the time present in slightly higher concentration in the MF fraction than in the UF fraction. Some elements were detected in lower concentration in the MF fraction than

in the UF fraction, and this is assigned to analytical error. All Be and Tl results were lower than the LOQ, and hence are not presented here.

An element has been considered as colloidal if its MF/UF ratio was greater than 1.5.

The MF/UF ratios are presented in Table 2. Some elements were always in colloidal form (MF/UF > 1.5): Mn, As, Co, Pb, Sn, Zn (see last row of the Table 2). In particular, the colloidal form of Zn (MF-UF) was always more concentrated than its dissolved form (UF). Other elements were most frequently partly colloidal (MF/UF > 1.5 for more than half of the samples): TOC, Fe, P, Ba, Cr, Cu, Ni. The major elements Ca and Mg had very frequently colloidal forms with a frequence of 48% and 47%, respectively (computed from 23 and 17 ratio respectively). Some elements were not frequently observed as colloidal: K, Ti, Mo (respectively 24%, 29% and 22%). Some elements were not observed as colloidal: Na, Al, Sb, Se, V. The elements Al and Si needs further studies (Al had a LOQ of 275 $\mu g.l^{-1}$ and Si was not measured since the digestion protocol used boric acid that volatilizes Si).

All the studied waste had at least one element detected as colloidal (Table 2, last column). The wastes of packaging (3 samples) had most > 90% of their leachable elements in colloidal form. The steel slag, the sludge from hydrometallurgy, the composts (2 samples), one dredged sediment (#18), the As contaminated soil and the two active landfill leachates had the majority of their elements in colloidal form. The other wastes had less than half or their leachable elements in colloidal form.

3.2 Particles visible by TEM-EDS

Several artifacts were observed during the analysis. For landfill leachate and sediment leachate samples, a bacterial growth occurred after filtration (Figure 3 A). For the alkaline leachates of APC residue lime, MSWI fly ash, industrial APC residue and metallic dust (all with pH > 11.2, results not shown), precipitation of calcite was observed in the contact with atmospheric CO2 (Figure 3 B). In TEM analysis, observation of copper was hampered because of Cu grids.

Selected TEM images are shown in Figure 4. We observed various patterns of particles in each leachate. By example, the particles were associated with Al in the MSWI bottom ash, to Cu in the sediment and Al and Si in industrial bottom ash and APC residue bicarbonate. Particles containing calcite, silica, aluminum and magnesium were found in landfill leachate. Industrial

APC residue contained colloids composed of carbon, sodium, potassium, calcium, silica, iron, titanium and chromium.

The particles containing Al and Si were not identified as clayey aluminosilicates and were found in APC residue bicarbonate (associated with the major elements Fe, Ca, P) and in landfill leachate (associated with Na, Ca and Mg). The particles containing Fe were found in the APC residue bicarbonate and industrial APC residue samples, and the particles containing Ti were found in industrial APC residue and MSWI BA. These major elements were associated with micro-elements. Matura et al (2010) found phyllosilicates (plate like structure with predominance of Si, Al, O and K) associated with quartz cristal (predominance of Si and O) from a closed landfill groundwater. According to Baloosha et al (2009), the main types of inorganic colloidal particles in oxygenated terrestrial and aquatic environments are aluminum phyllosilicates, oxides and hydrous oxides of iron, manganese and silicon. As a conclusion, it seems that most of the observed colloids in the waste leachates were different than the colloids of natural origin.

Manufactured nanoparticles from organic polymers and of TiO_2 have been observed (Figure 5). More, particles containing Sr, La, Ce and Nd (neodyme) were observed at Mediterranean sea harbor #1 sediment leachate (decanted and centrifugated but not microfiltrated) and Sr was observed in its MF. The particles of organic polymers were believed to be paint component. It is expected that TiO_2 will be one of the most released nanoparticles (Kiser et al. 2009).

The microscopic observations of elements in particulate form were related to the MF/UF concentration ratios of the same leachate. Elements were detected in some particles (i.e 3 particles among 20 particles analysed by TEM-EDS for one grid) that were not detected as colloidal by MF-UF ICP concentration difference and MF/UF ratio. Calculated concentration of the element in the particles (from the elemental content, the number of particles with the element related to the total number of particles that have been analysed, and the dry residue content of the leachate) were theoretically greater than the LOQ of the ICP. We think that particles grew from soluble element during preparation of the grid, probably during the drying phase, which lasted for about 4 hours on an average. The rinsing (performed on all the grids in 2012) could not fully hamper this artifact. In Figure 6, the concentrations of elements in the microfiltrate are shown as a function of the concentrations of elements in the ultrafiltrate,

separated in two groups according to the observation of elements in particles by TEM-EDS (61 data) or not (87 data). The bacteria and carbonate artifacts particles were not taken into account here. Some elements which were detected by TEM-EDS as particles have a MF/UF ratio close to 1 (hence no colloidal form), suggesting that those particles may form during the preparation of the sample for the microscopy, and probably during the drying phase, as explained above. This is also supported by the fact that the elements Na and K are frequently detected by TEM-EDS observations as particles, despite the fact that the concentrations measured by ICP in the MF and UF fractions are equal. Some particles with MF/UF ratio > 1 were not detected by the TEM-EDS (blue diamonds above the 1/1 line), mostly at MF concentrations lower than 10 000 $\mu g.l^{-1}$. Elements with MF concentration lower than 200 $\mu g.l^{-1}$ were not detected by TEM-EDS.

The elements frequently detected by cascade filtration and ICP in colloidal form and not by TEM-EDS observations were Zn, Mo, Sn, As, Mn, Ni and Ba (by decreasing order of maximum concentration). The elements detected by ICP in colloidal form and by TEM-EDS observations were Ca, Mg, P, Fe and Mn (by decreasing order of maximum concentration). The elements Mg and P detected in colloidal form by ICP were often detected by TEM-EDS observations.

3.3 Size measurements by PCS

The particles observed by PCS in the waste leachates were polydispersed in size, or settled, or were present in too low concentration to be measured, according to the calculation by the software of the apparatus, and resulting in indicative values (not presented). The artifacts formation of calcite in alkaline leachates and the presence of bacteria (re-growth after filtration) in leachates containing organic carbon may explain a part of the sedimentation and/or polydispersion observed. The valid measurements are presented at Figure 7.

3.4 Zeta potential measurements

The zeta potentials of the leachate fractions (5 - 7 days after filtration in 2011 and 1 day in 2012) are presented in Figure 8. Some samples had a poor signal due to particles sedimentation or too large polydispersion, according to the software of the apparatus. A particle with a zeta potential > | 30 mV | is considered as electrostatically stable (Hassellöv and Kaegi 2009). Six leachates had a positive zeta potential (< 8 mV) and all the others had a negative zeta potential, with four leachates indicating potential colloidal stability (< -30 mV): compost from selected

waste (# 15: -38 mV), sludges from hydrometallurgy (#10: -37 mV), packaging waste (#13: -34 mV) and bauxite residue - red mud from Al industry (#9: -30 mV). So most of the waste leachates particles studied here were probably not stable and will aggregate and settle.

The effect of pH on zeta potential is presented in Figure 9 for the three waste microfiltrates with high negative the potential at their own pH. pH-dependant charges were observed for the three samples. In particular, bauxite residue (red mud) containing iron and aluminum oxyhydroxides and zeolithes (Polcaro et al, 2000) that have positive or negative charge depending on pH (Genç et al 2003).

4. Conclusion

Standardised leaching, cascade filtrations and ICP measurement of element concentrations in the microfiltrate (MF) and ultrafiltrate (UF) fractions are good tools to detect colloids potentially released by waste. Solid waste leachates contain significant amount of colloids. Most of the colloidal particles were visible by TEM-EDS if their elemental MF concentration is greater than 200 $\mu g.l^{-1}$. If the samples are dried during the preparation for microscopy, neoformation of particles can occur from the soluble fraction of the element, and this could be checked by the ICP results. Size distribution analysis results by PCS analysis is not routine analysis yet in waste leachates. Some waste leachates had a particle electric potential that could be strong enough to form stable suspensions. All the studied waste had at least one element detected as colloidal. The compositions of particles in major element were different from natural ones. A large part (from 0 to > 99%, depending of sample and element) of the microelement emission from waste were colloidal, and this should be taken into account in studies of emission and transfer of contaminants in the environment. The transfer of colloidal contaminant in porous media will be reduced due to electrostatic adsorption and filtration effects, but the transfer of some element bound to natural colloids can be facilitated (see the classical McCarthy and Zachara 1989). The concentration limits of the European landfill decision of 2003, based on unreactive transport of landfill leachate in the aquifer, could be revisited. The cross-filtration method proposed in EU leaching standard and the development of landfill acceptance criteria could be revisited, since the filter cake buildup could reduce the <

0.45 µm concentration. A comparison with the percolation test (low speed flow, self-filtration of the eluate) is necessary.

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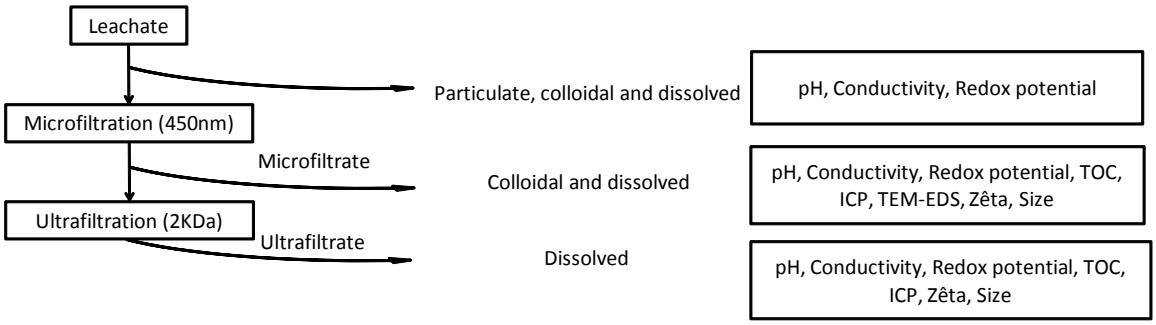

Leachate
Microfiltration (450nm)
Microfiltrate
Ultrafiltration (2KDa)
Ultrafiltrate
Particulate, colloidal and dissolved
Colloidal and dissolved
Dissolved
pH, Conductivity, Redox potential
pH, Conductivity, Redox potential, TOC, ICP, TEM-EDS, Zêta, Size
pH, Conductivity, Redox potential, TOC, ICP, Zêta, Size

Figure 1

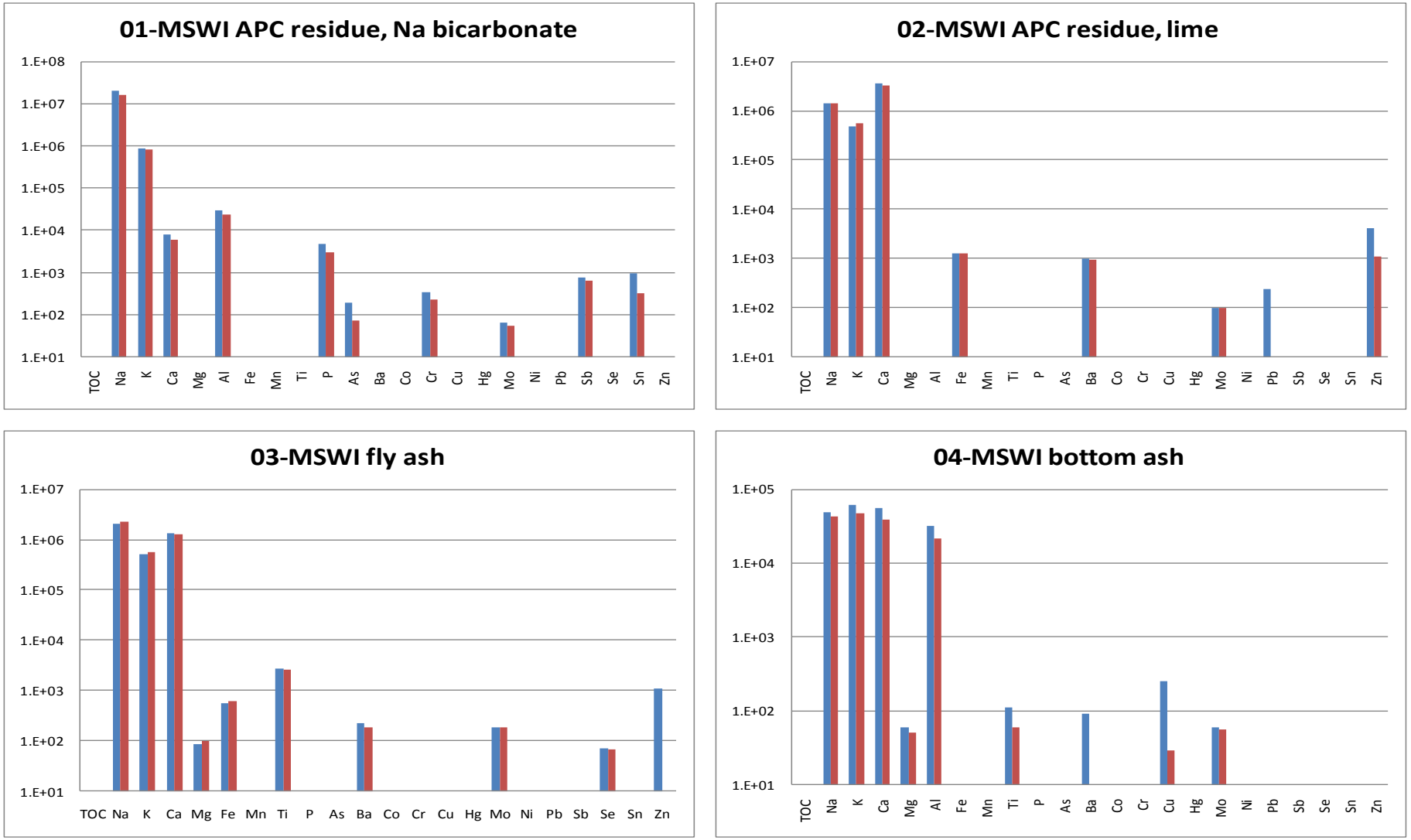
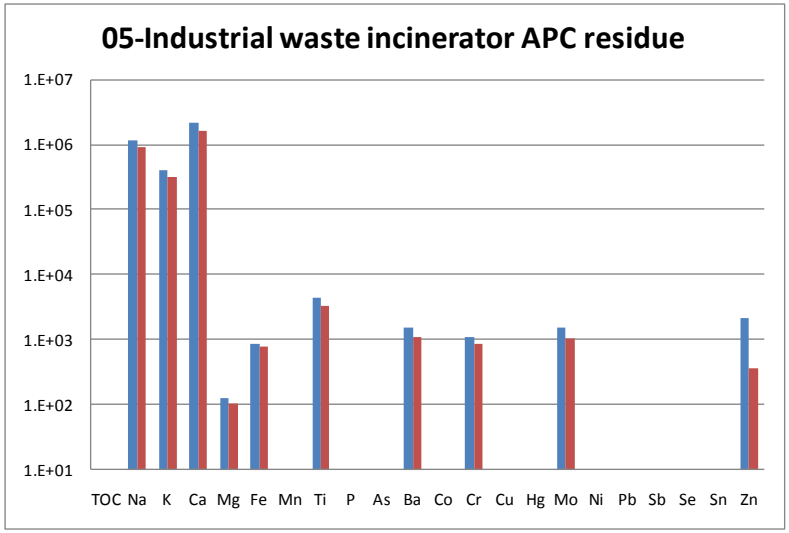
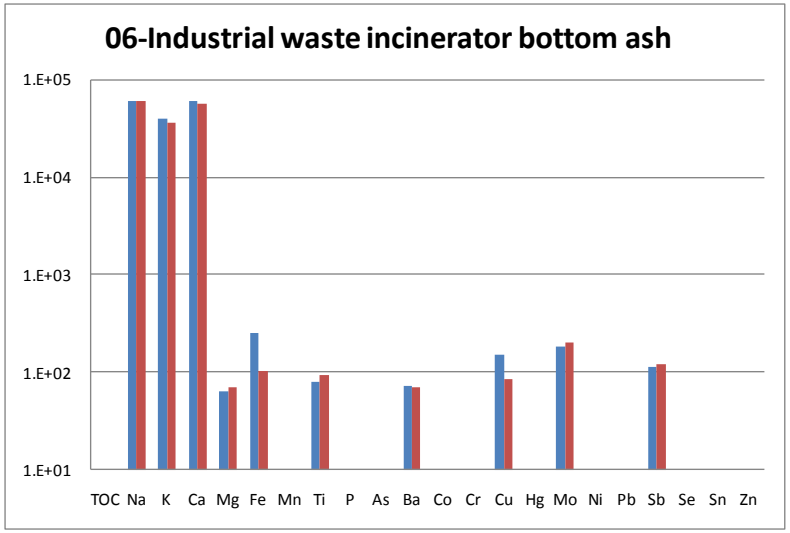
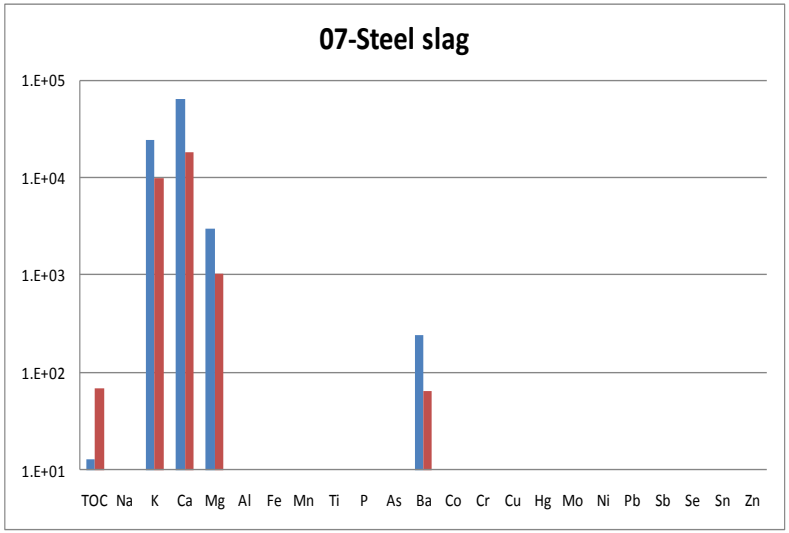
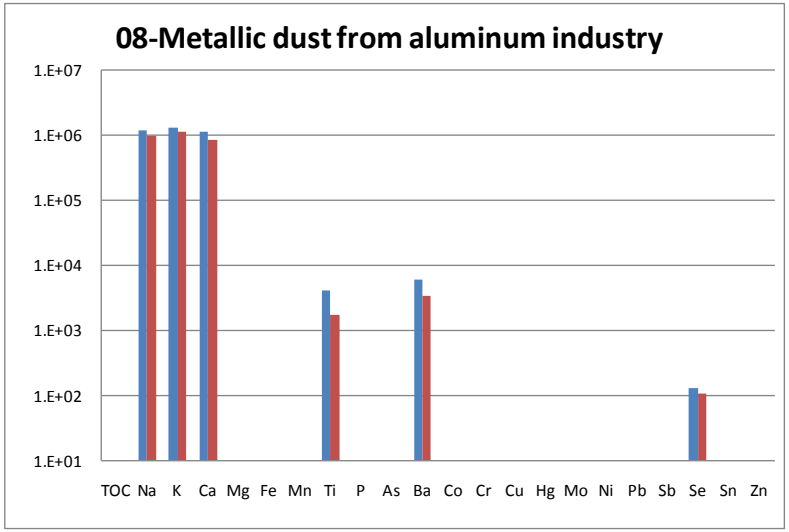

01-MSWI APC residue, Na bicarbonate
1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
TOC Na K Ca Mg Al Fe Mn Ti P As Ba Co Cr Cu Hg Mo Ni Pb Sb Se Sn Zn
02-MSWI APC residue, lime
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
TOC Na K Ca Mg Al Fe Mn Ti P As Ba Co Cr Cu Hg Mo Ni Pb Sb Se Sn Zn
03-MSWI fly ash
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
TOC Na K Ca Mg Fe Mn Ti P As Ba Co Cr Cu Hg Mo Ni Pb Sb Se Sn Zn
04-MSWI bottom ash
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
TOC Na K Ca Mg Al Fe Mn Ti P As Ba Co Cr Cu Hg Mo Ni Pb Sb Se Sn Zn

Figure 2









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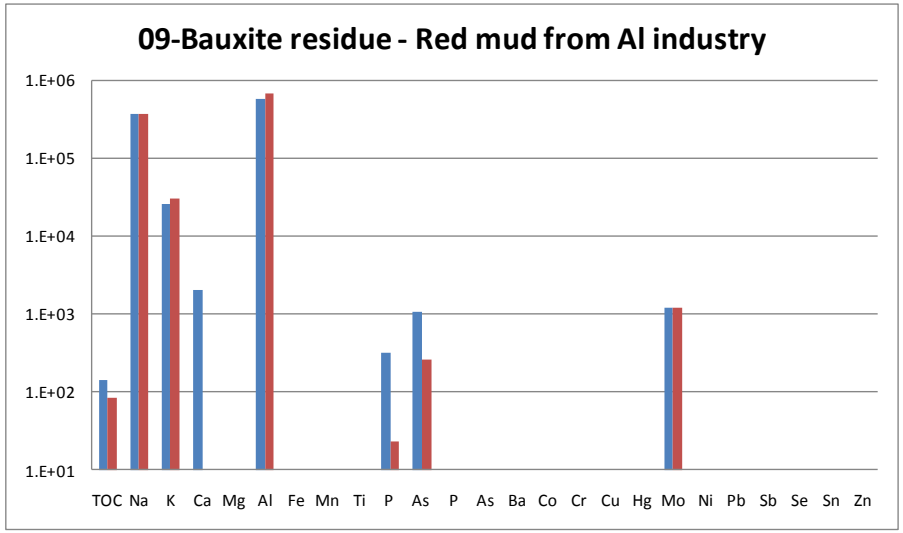

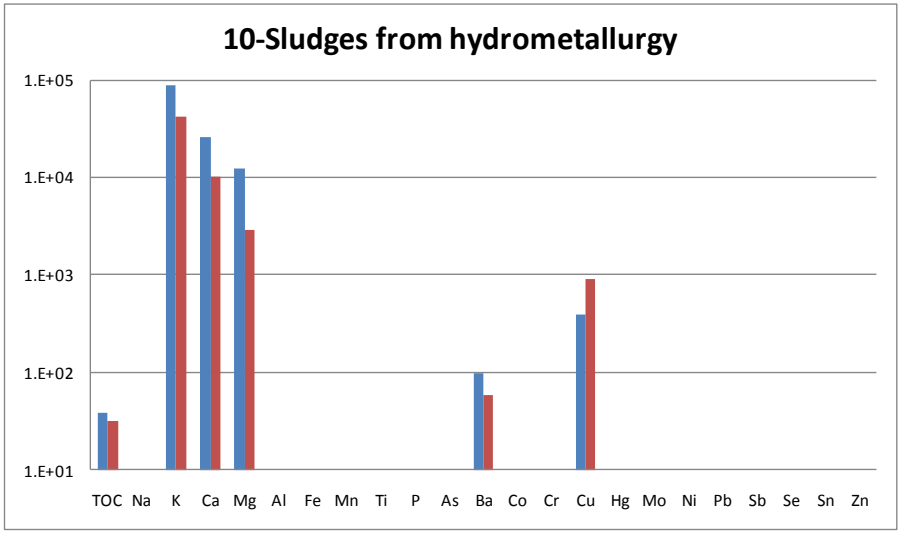

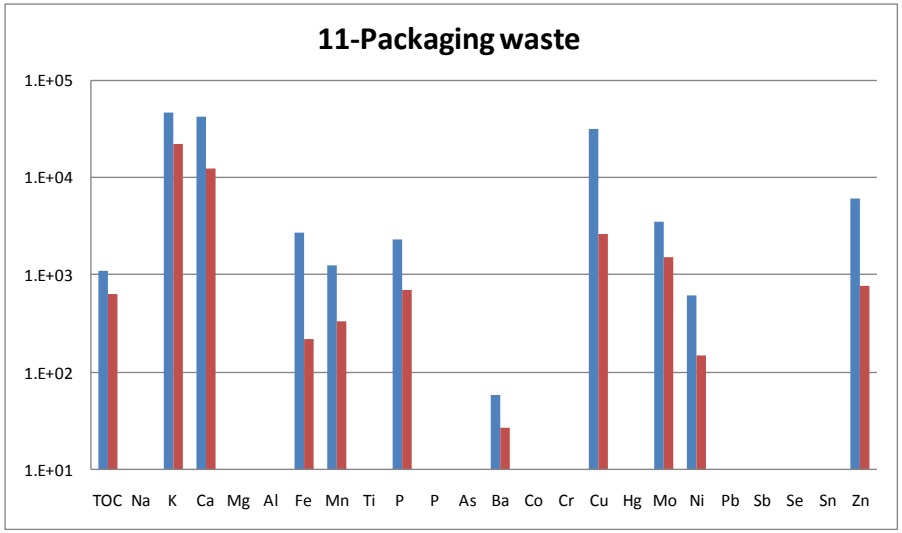

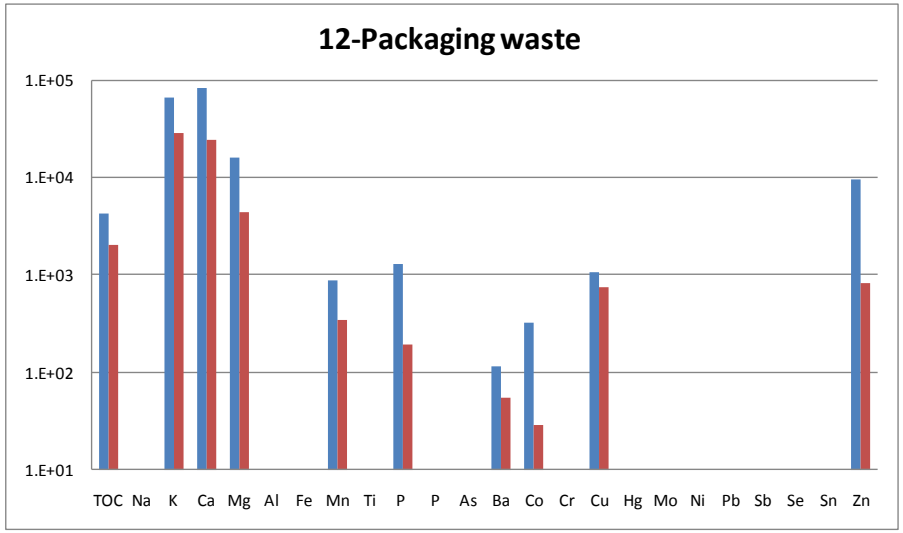

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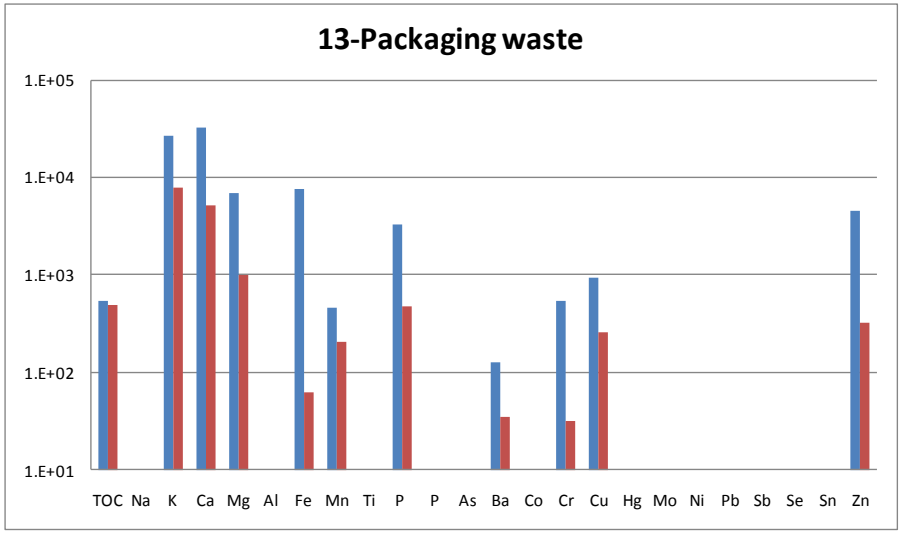

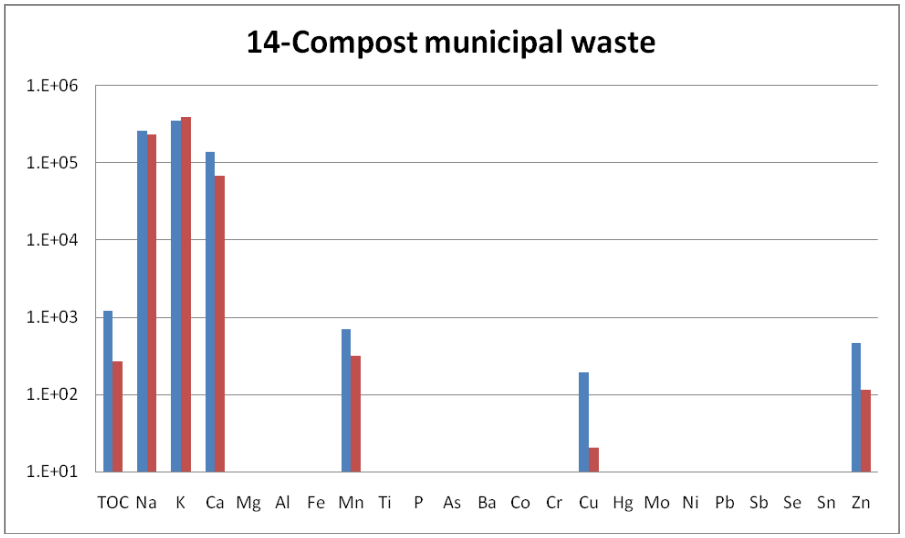

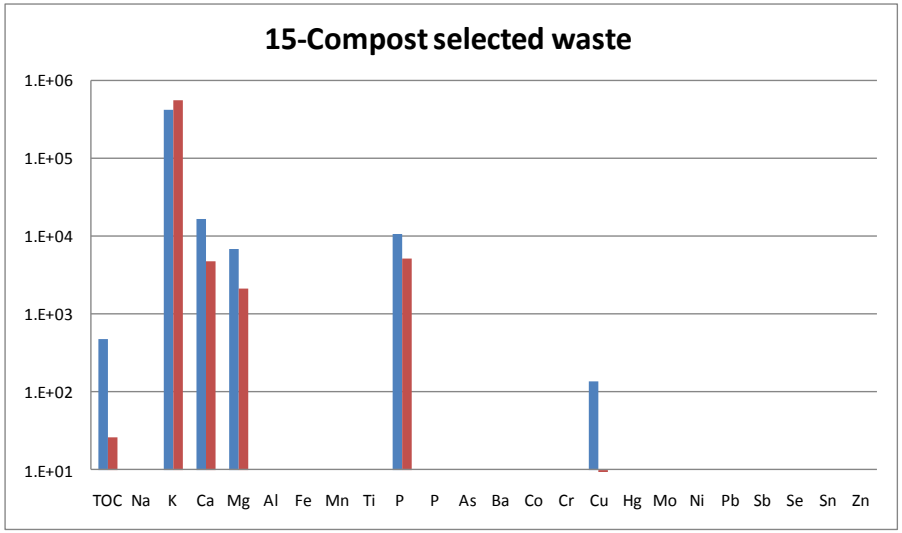

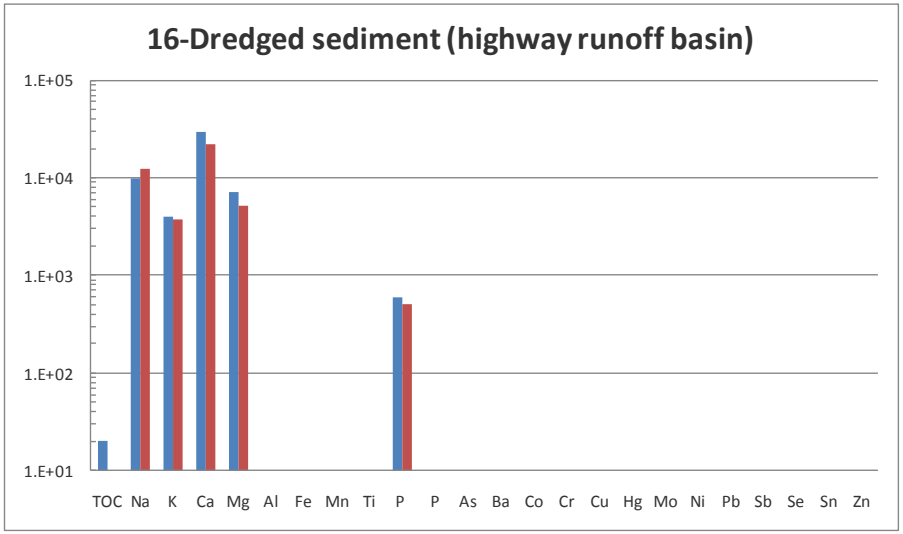

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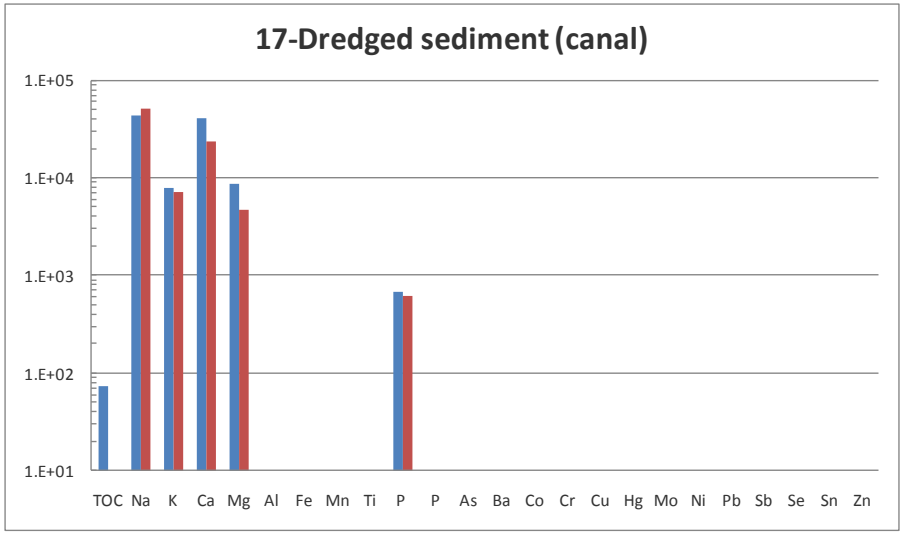

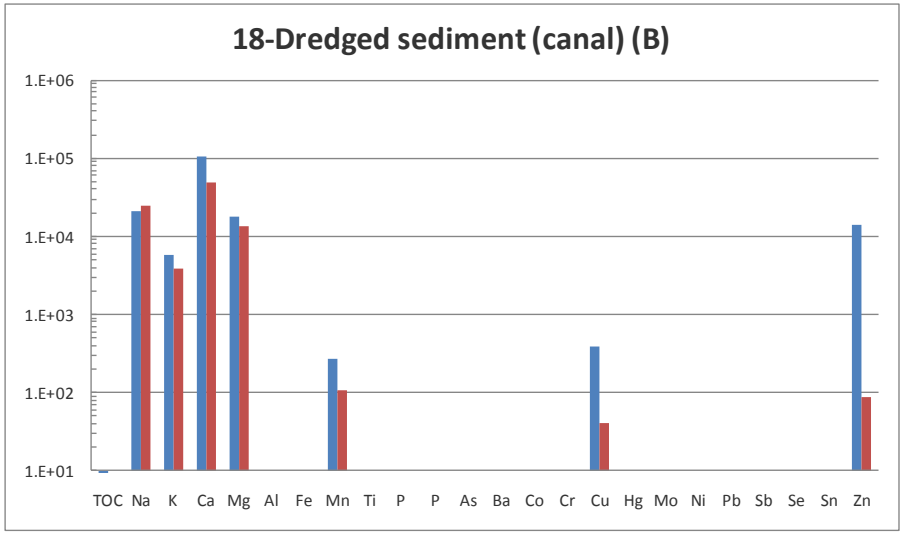

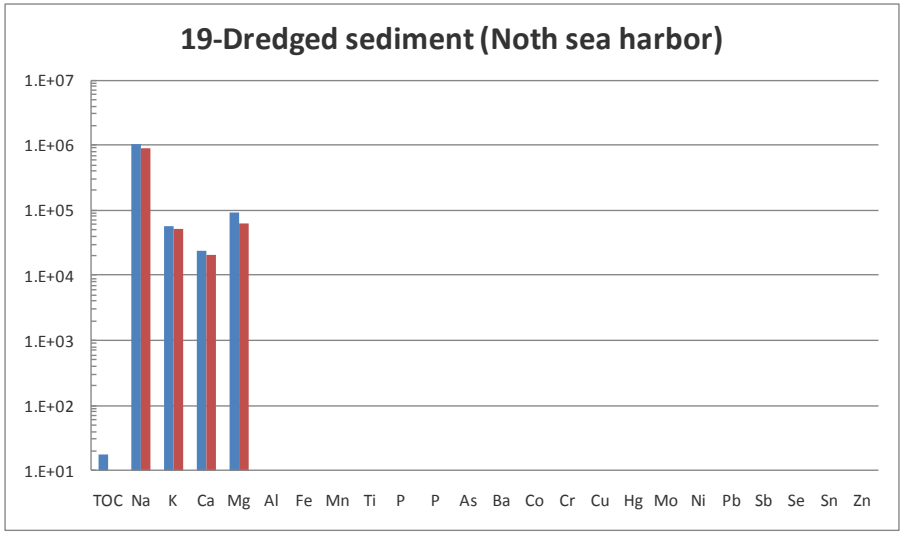

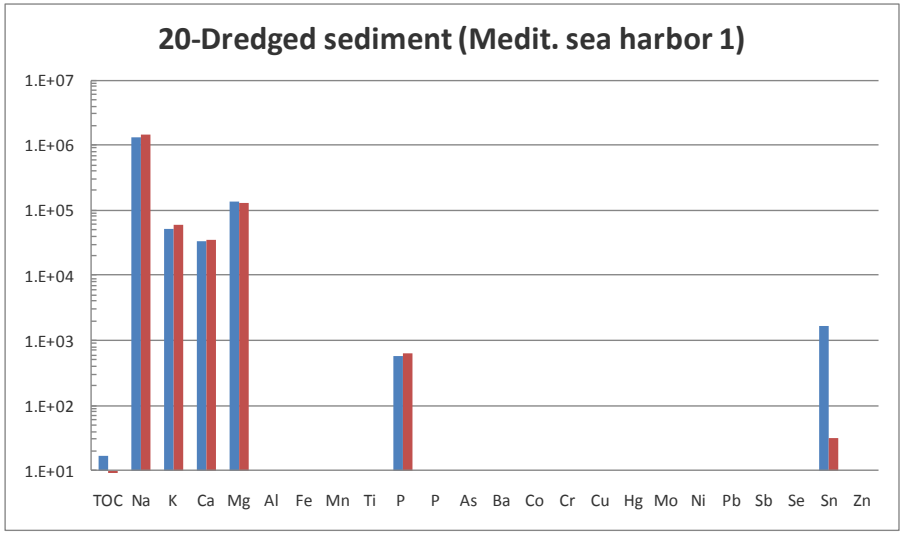

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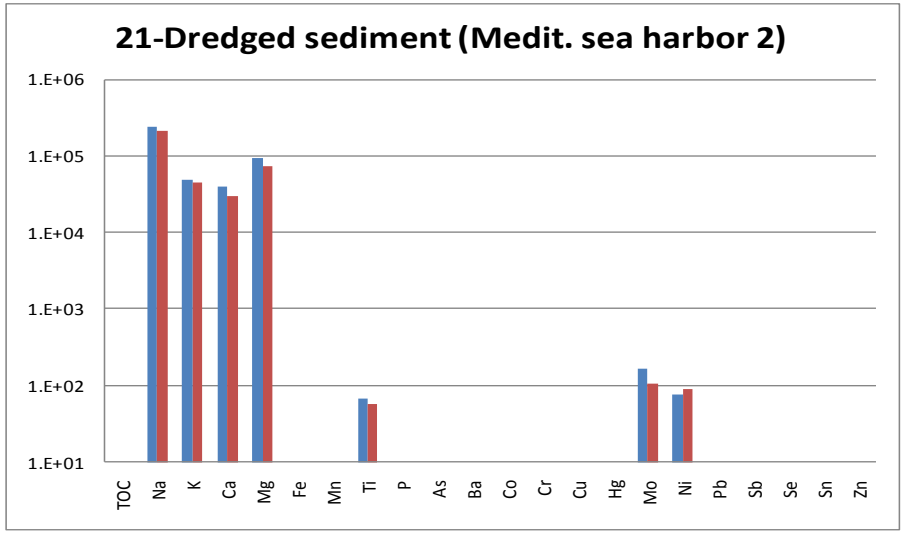

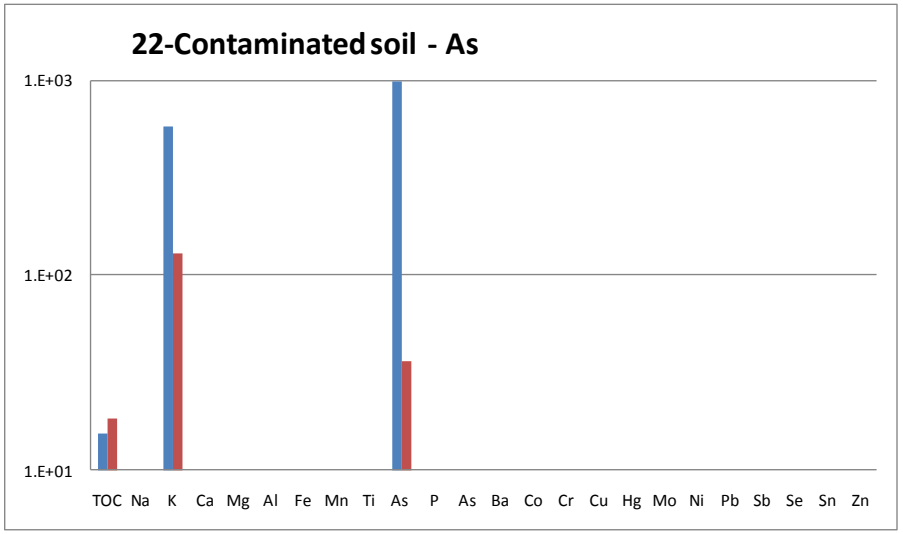

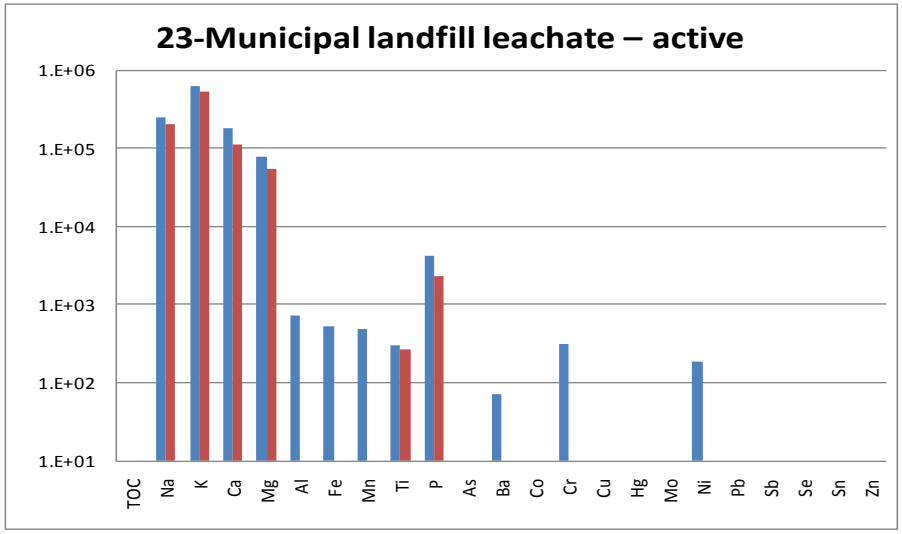

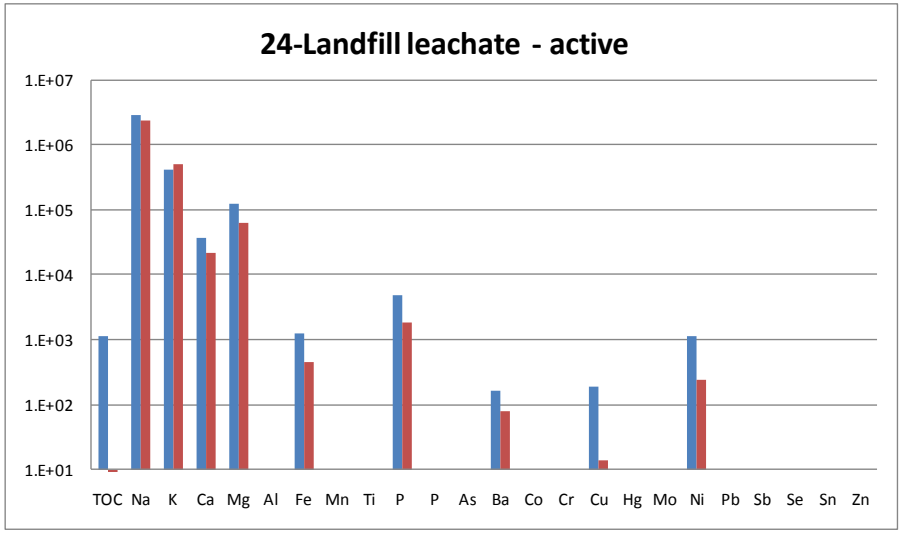

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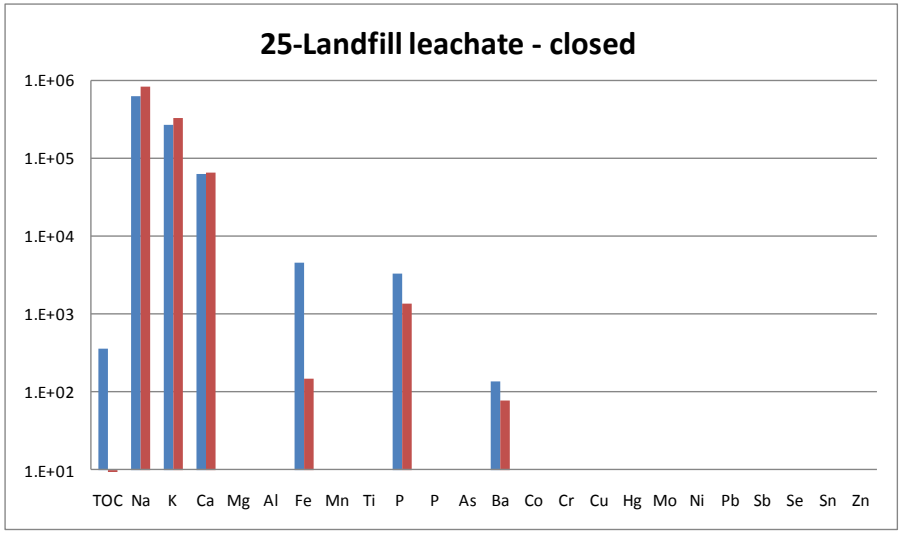

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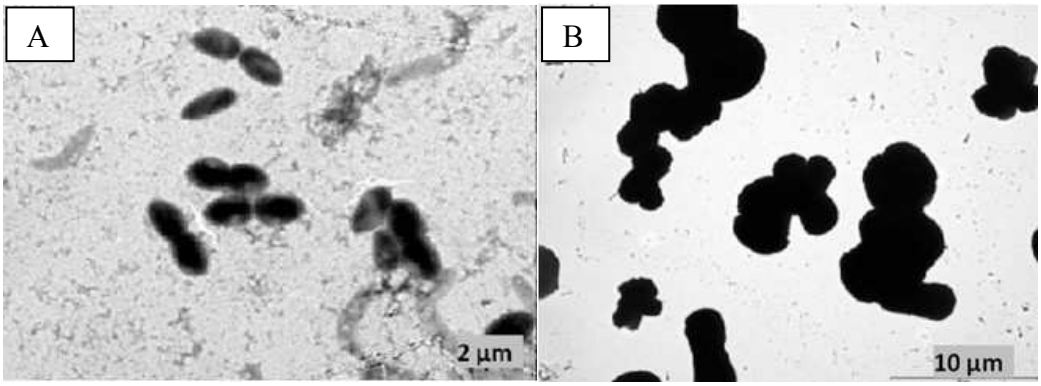


Figure 3

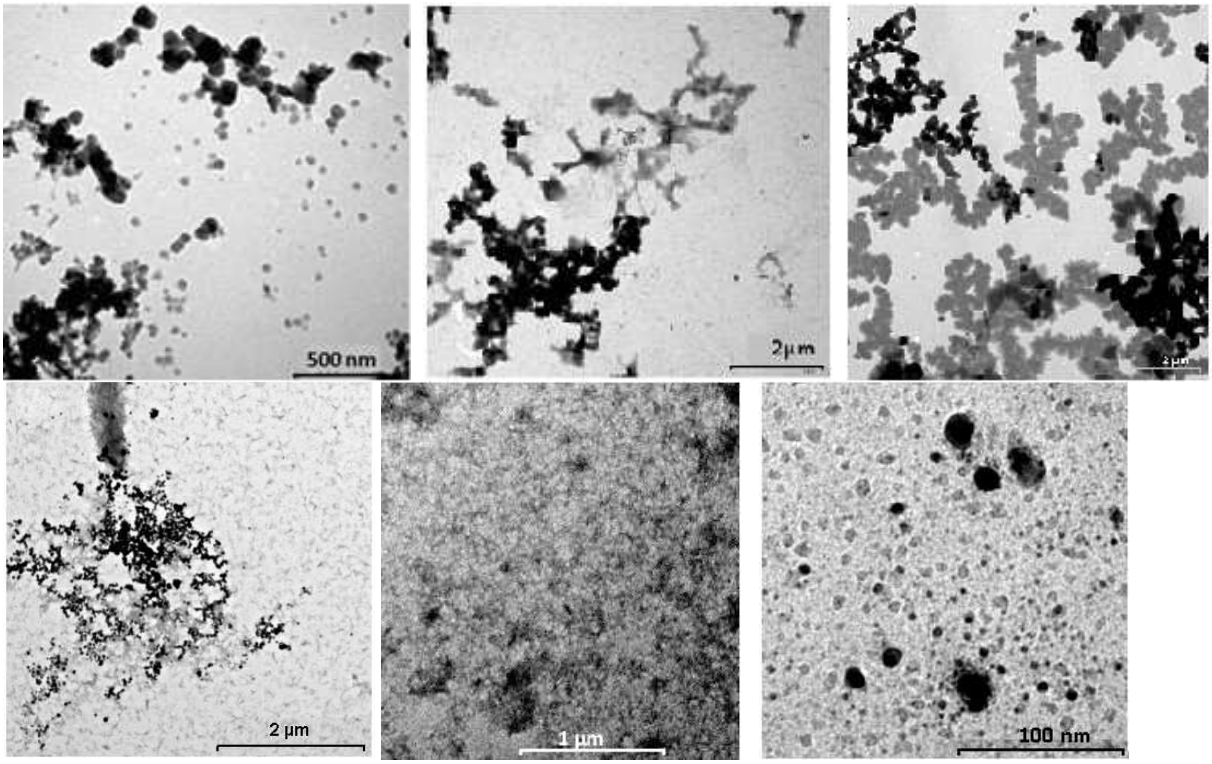
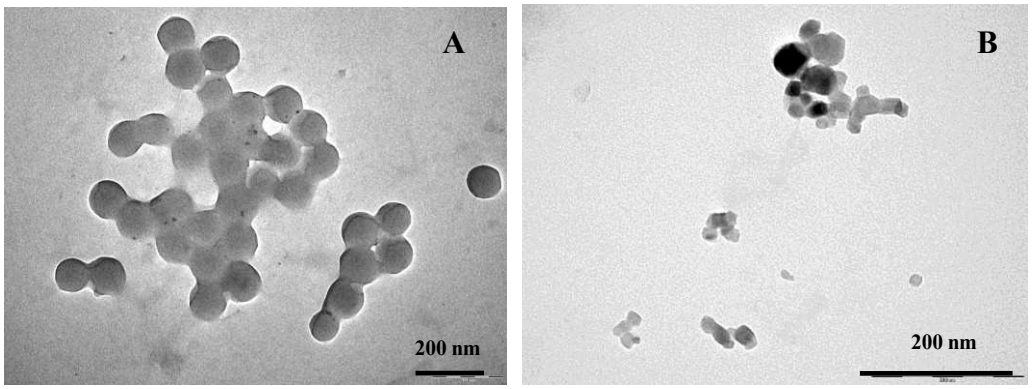


Figure 4



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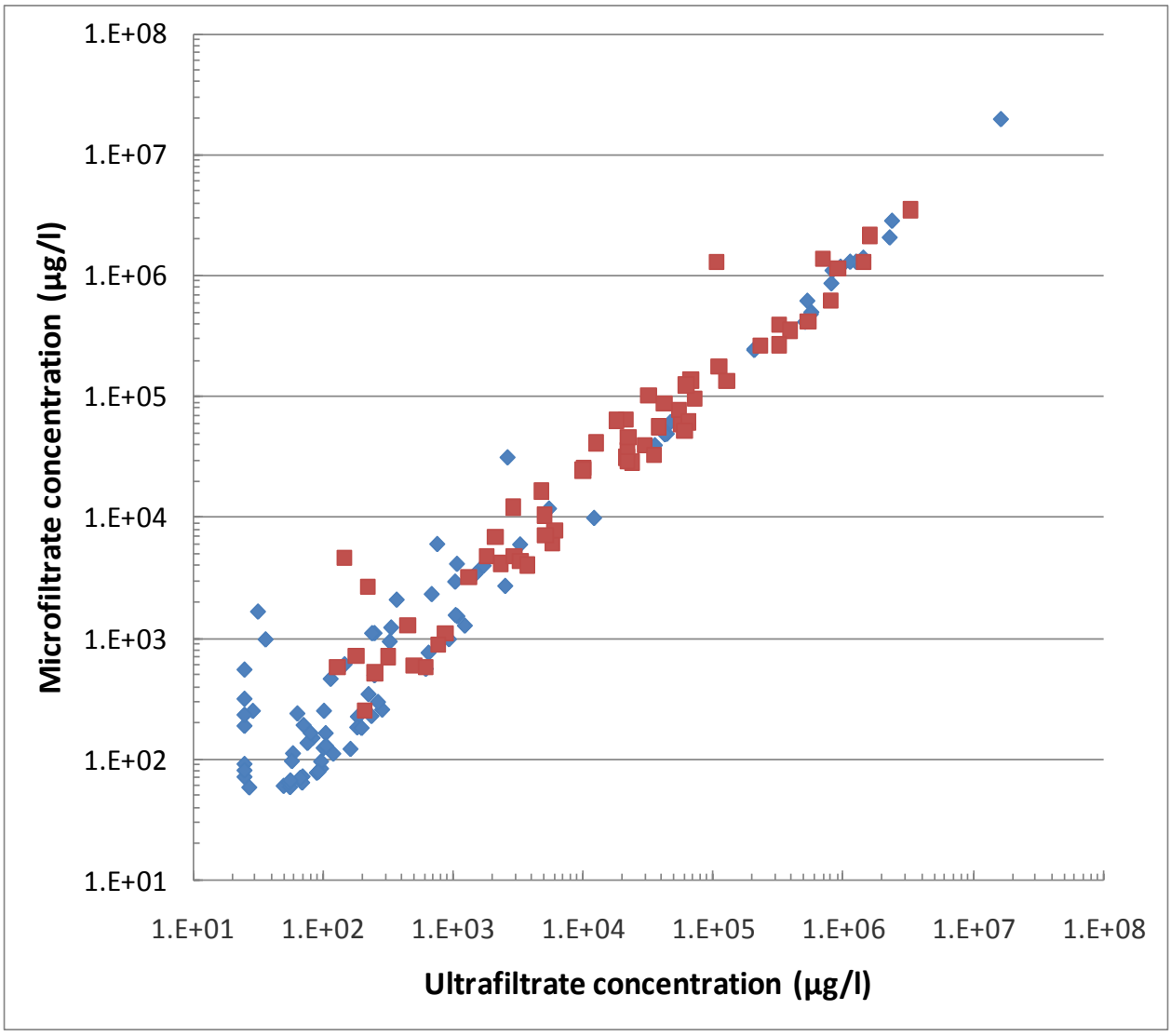
1.E+08
1.E+07
1.E+06
1.E+05
1.E+04
1.E+03
1.E+02
1.E+01
Microfiltrate concentration (µg/l)
1.E+01
1.E+02
1.E+03
1.E+04
1.E+05
1.E+06
1.E+07
1.E+08
Ultrafiltrate concentration (µg/l)

Figure 6

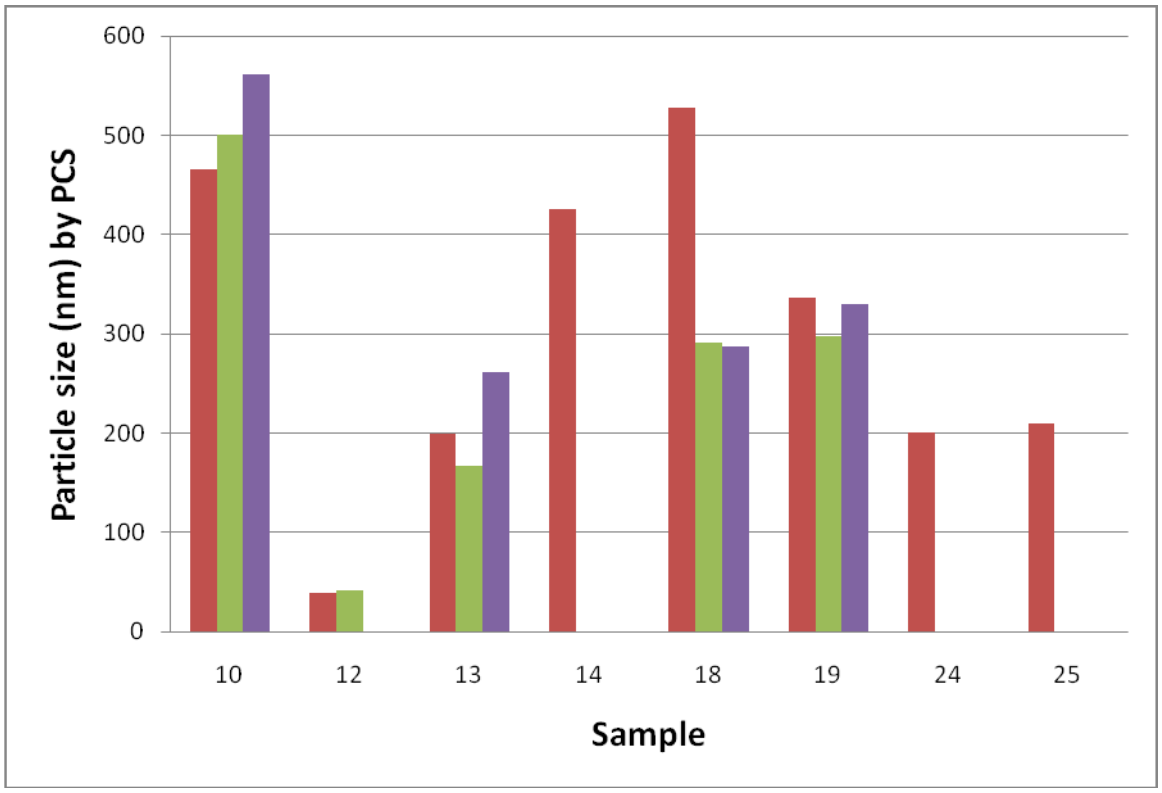
600
500
400
300
200
100
0
Particle size (nm) by PCS
10
12
13
14
18
19
24
25
Sample

Figure 7

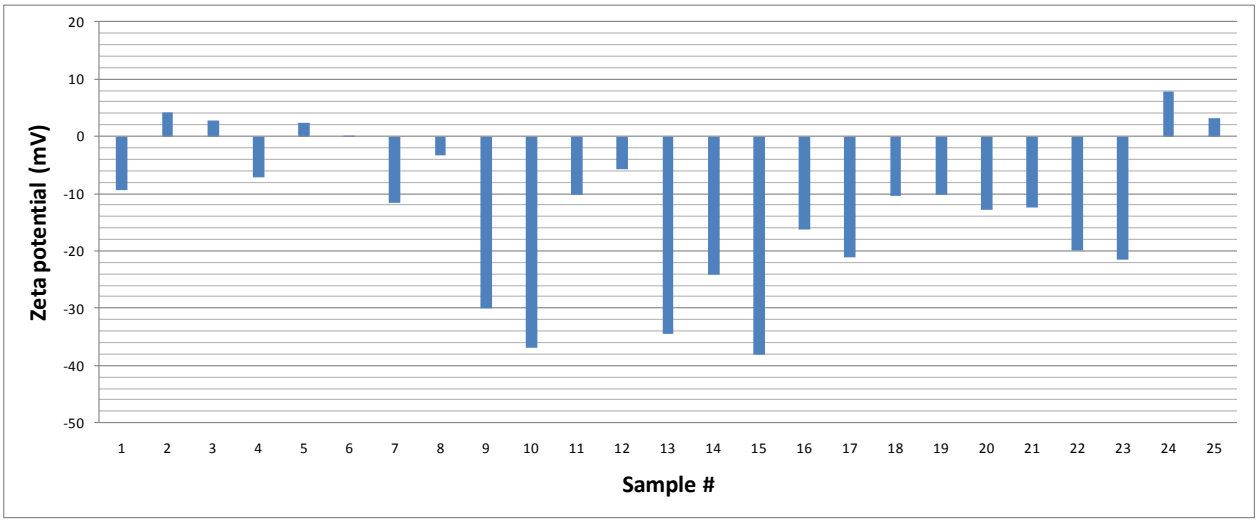
Zeta potential (mV)
20
10
0
-10
-20
-30
-40
-50
1
2
3
4
5
6
7
8
9
10
11
12
13
14
15
16
17
18
19
20
21
22
23
24
25
Sample #

Figure 8

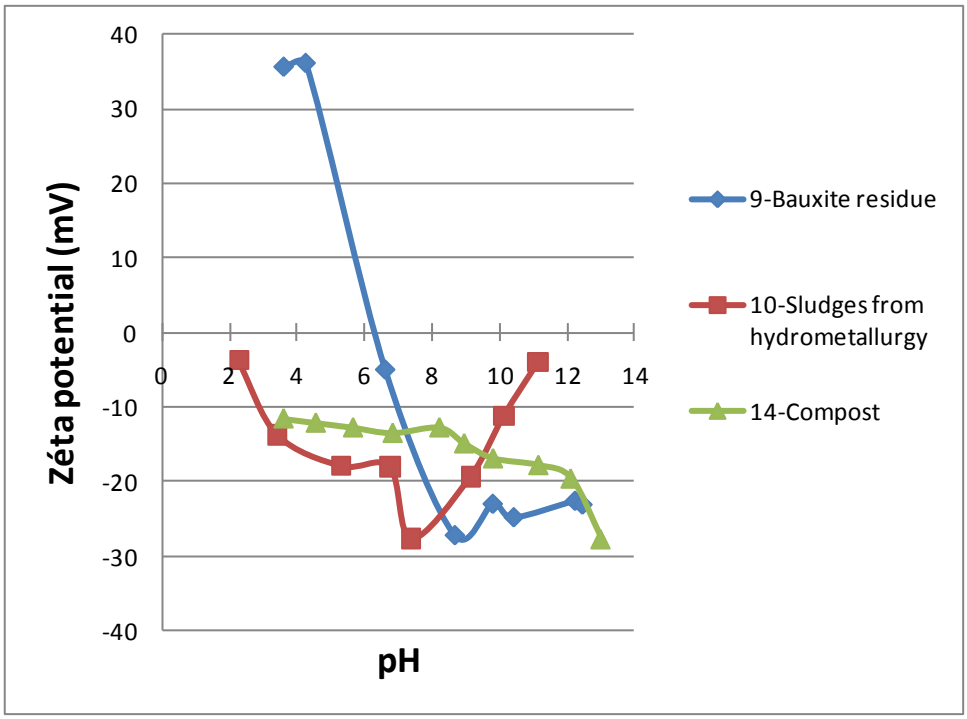
40
30
20
10
0
-10
-20
-30
-40
0
2
4
6
8
10
12
14
Zéta potential (mV)
pH
9-Bauxite residue
10-Sludges from hydrometallurgy
14-Compost

Figure 9

Tables

Table 1: Waste samples

Table 2: Ratios of microfiltrate and ultrafiltrate concentrations (MF/UF) for the elements detected in waste leachates

Table 1

#	Type	Abreviated type	European List of Waste code (*=hazardous)
1	Municipal solid waste incinerator (MSWI) Air pollution control (APC) residue, process with Na bicarbonate	APC bicarbonate	19 01 07*
2	MSWI APC residue, process with lime	APC lime	19 01 07*
3	MSWI fly ash	Fly ash	19 01 05*
4	MSWI bottom ash	Bottom ash	19 01 12
5	Industrial waste incinerator APC residue	Industrial APC	19 01 07*
6	Industrial waste incinerator bottom ash	Industrial BA	19 01 11*
7	Steel slag	Steel slag	10 02 02
8	Metallic dust from aluminum industry	Metallic dust	10 03 19*
9	Bauxite residue - Red mud from Al industry	Red Mud	01 03 09
10	Sludges from hydrometallurgy	Metal sludge	11 01 09*
11	Waste Packaging S8-GEO	Packaging 1	19 12 11*
12	Waste Packaging S8-SAR	Packaging 2	19 12 11*
13	Waste Packaging S8-SCO	Packaging 3	15 01 10*
14	Compost municipal waste	Compost 1	compost from 30 03 01
15	Compost selected waste	Compost 2	compost from 19 05 01
16	Dredged sediment – (highway runoff basin)	Sediment 1	17 05 05* or 17 05 06
17	Dredged sediment – (canal)	Sediment 2	17 05 05* or 17 05 06
18	Dredged sediment – (canal) (B)	Sediment 3	17 05 05* or 17 05 06
19	Dredged sediment – (North sea harbor)	Sediment 4	17 05 05* or 17 05 06
20	Dredged sediment – (Mediterranean sea harbor 1)	Sediment 5	17 05 05* or 17 05 06
21	Dredged sediment – (Mediterranean sea harbor 2)	Sediment 6	17 05 05*
22	Contaminated soil – As	Soil As	17 05 03*
23	Municipal landfill leachate – active	Landfill leachate 1	19 07 03
24	Municipal Landfill leachate – active	Landfill leachate 2	19 07 02* or 19 07 03
25	Municipal Landfill leachate – closed	Landfill leachate 3	19 07 02* or 19 07 03

Table 2

Sample	TOC	Na	K	Ca	Mg	Al	Fe	Ti	Mn	P	As	Ba	Co	Cr	Cu	Mo	Ni	Pb	Sb	Se	Sn	V	Zn	Nb MF/UF ratio	Nb ratio > 1.5
1		1.2	1.1	1.3		1.2				1.6	2.7			1.5		1.2			1.2		2.9			**10**	**4**
2		1.0	0.9	1.1			1.0					1.1				1.0		14.4					3.9	**8**	**2**
3		0.9	0.9	1.0	0.9		0.9	1.1				1.2				1.0				1.0			49.7	**10**	**1**
4		1.1	1.3	1.5	1.2	1.5		1.9				41.6			8.7	1.1								**9**	**3**
5		1.3	1.2	1.3	1.2		1.1	1.3				1.4		1.3		1.5							5.7	**10**	**1**
6		1.0	1.1	1.1	0.9	1.1	2.5	0.9				1.0			1.8	0.9			0.9					**11**	**2**
7	0.2		2.5	3.6	2.8							3.8												**5**	**4**
8		1.2	1.2	1.3				2.3				1.8								1.2				**6**	**2**
9	2.2	1.0	0.9			0.9				13.7	4.0					1.0						1.3		**7**	**3**
10	1.2		2.1	2.5	4.2							1.7			0.4									**6**	**4**
11	1.7		2.1	3.3			12.1		3.7	3.4		2.2			12.0	2.3	4.2						8.0	**11**	**11**
12	2.1		2.3	3.4	3.7				2.5	6.8		2.1	11.2		1.4								11.6	**10**	**9**
13	1.1		3.3	6.3	6.9		122.1		2.2	6.9		3.7		17.4	3.7								14.2	**11**	**10**
14	4.4	1.1	0.9	2.0					2.2						9.7								4.0	**7**	**5**
15	17.7		0.8	3.5	3.2					2.0					16.3									**6**	**5**
16	10.7	0.8	1.1	1.3	1.38					1.2														**5**	**1**
17	38.4	0.9	1.1	1.7	1.8					1.1														**6**	**3**
18	3.0	0.8	1.5	2.2	1.3				2.5	0.8					9.6								160.5	**9**	**5**
19	9.5	1.2	1.1	1.1	1.5					0.8														**6**	**2**
20	6.6	0.9	0.9	0.9	1.0					0.9											52.6			**7**	**2**
21		1.2	1.1	1.3	1.3			1.2								1.6	0.9							**7**	**1**
22	0.8		4.5								27.1													**3**	**2**
23		1.2	1.2	1.6	1.4		6.1	1.1	26.1	1.8		32.5					6.5							**10**	**6**
24	5.0	1.2	0.8	1.7	2.0		2.8			2.6		2.0			13.8		4.6							**10**	**8**
25	0.9	0.8	0.8	1.0			31.8			2.4		1.8												**7**	**3**
Nb ratio	**15**	**18**	**25**	**23**	**17**	**4**	**9**	**7**	**6**	**14**	**3**	**14**	**1**	**3**	**10**	**9**	**4**	**1**	**2**	**2**	**2**	**1**	**8**		
Nb ratio > 1.5	**10**	**0**	**6**	**11**	**8**	**0**	**6**	**2**	**6**	**9**	**3**	**10**	**1**	**2**	**8**	**2**	**3**	**1**	**0**	**0**	**2**	**0**	**8**		