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MEASUREMENT OF PERSISTENT ORGANIC POLLUTANTS IN LANDFILL LEACHATES

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SUMMARY: leachates from two landfills which receive the stabilized waste (site A) and sorting refuses (site B) from mechanical biological treatment plants (MBT) have been sampled. Classical parameters, as well as organic persistent pollutants (POPs) have been measured and compared between the two sites, and to data from litterature (classical parameters and POPs) and to limit values for drinking waters, when applicable, for POPs. Though the study was limited to 3 samples, the concentrations in organic micropollutants varied, depending on the compounds and on the treatment process.

1. INTRODUCTION

Leachates from two French landfills which receive biologically stabilized municipal solid waste –MSW- have been previously studied (Zdanevitch *et al*, 2009a). Classical parameters were measured on all samples, and values were compared between leachates of the same site, and between sites. Leachates showed different behaviours depending on the measured compounds: some values were typical of young waste, while others were more representative of old, stabilized waste.

To date, there is some knowledge on the fate of organics contaminants in landfills, but more research is needed, especially on emerging compounds in leachates. Samples of leachates were taken on two landfills previously studied, for biogas emissions (Zdanevitch *et al*, 2009b) on both sites, and for leachates on site (A): Zdanevitch *et al*, 2009a. These sites receive the outputs of aerobic treatments. Materials which are landfilled are different between the two sites:

- site A has two landfill zones: the old one – K1 - received untreated MSW until 2006; the new zone – K2, organized in cells - receives waste which has been aerobically treated to stabilize the organic matter, since 2006. Leachates are collected on these two zones separately, allowing the sampling on each zone,
- site B has a high grade separation of the biodegradable fraction of MSW; this fraction is treated by a composting process. The compost is used by local farmers. The landfill receives only the refuses of sorting, which contains less biodegradable material than non-treated waste.

Leachate was sampled in the existing well at the bottom of cell 2 (C2).

2. EXPERIMENTAL

One sample of leachate was taken from each zone: site A, zone K1 and K2, and site B, cell C2. Each sample accounted for approximately 11 liters. Smaples were kept cold (4 °C) until return to the laboratory, between 24 and 48 hours. Depending on the compounds to be analyzed, sampling bottles were either made of plastic or brown glass.

The analytical Laboratory in INERIS is used to measuring POPs at trace levels in surface waters and ambient air. Yet, measuring these compounds at low concentrations in biogas or leachates (heavy polluted matrixes) is not very easy. Samples were carefully taken and quickly returned to the Laboratory. In addition, "classical" parameters (suspended matter, metals, salts...) were measured outside INERIS, in the Laboratory which already measured the leachates for the previous study. Methods used by INERIS for measuring the POPs are summarized below.

Volatile fatty acids, aldehydes, ketones were analysed by dilution of an aliquot of leachate in a DNPH (2,4-dinitrophenylhydrazine) solution, followed by direct analysis by UV/HPLC. Limit of quantification varied from 0.2 mg/L (formaldehyde) to 5.0 mg/L (volatile fatty acids).

BTX (benzene-toluene-xylenes) and HVOC (halogenated compounds): analytical methods for these compounds are standardized (NF ISO 11423-1, NF EN ISO 10301). 13 ml aliquots of leachate were taken and analyzed by:

- Headspace gas chromatography / flame ionization detector for BTX,
- Headspace gas chromatography / electron capture detector for halogenated compounds.

Quantification limits varied from 0.01 to 0.1 µg/L for most halogenated compounds, to 5 µg/L for BTX and 8 µg/L for dichloromethane.

Polycyclic aromatic compounds (PAH) were extracted with an INERIS method based on ISO 17993. Analysis was performed by HPLC with fulorimetric detection. Quantification limits were uniform: 10 ng/L.

Polychlorobiphenyl compounds (PCBs) were extracted by liquid/liquid extraction with hexane, dried on sodium sulfate, concentrated, purified on Cu and florisil cartridges, and analyzed by double GC / electron capture detector. Qunatification limits were uniform at 2 ng/L.

Polybrominated diphenyl ethers (PBDEs) and phtalates were extracted by liquid/liquid extraction, either with dichloromethane or a mixture of nC6/acetone (for solid phase of PBDEs), dried on sodium sulfate, concentrated and analyzed by GC/MS. Quantification limits were: 1 ng/kg for all PBDEs except BDE209 (10 ng/kg), 0.1 ng/g (liquid phase) and 30 ng/g (solid phase) for phtalates.

3. RESULTS AND DISCUSSION

3.1 Inorganic and global parameters

50 parameters were measured on the 3 leachates. Detailed results are not reported here but highlights are given in Table 1.

First, on site B, pH was rather acidic (value of 6.5), although leachates of site A (from both old untreated waste and stabilized waste) had a rather basic pH (7.6 to 8.6), which were more consistent with literature (Kjeldsen *et al*, Robinson *et al*).

The leachate from cell 2 of site B (receiving little organic material), though having a rather high concentration of suspended matter (970 mg/L), had much lower concentrations than leachates of site A for organic compounds, which is shown by lower values of COD, BOD5,

adsorbable organic halides (AOX)... Waste in cell 2 of site B could be considered as stabilized, as BOD5 < 100 mg/L, and COD < 1000 mg/L, beside the ratio BOD5/COD falled below 0.1 (Ravelojaona L., 2005). It was not the case for site A, though the ratio BOD5/COD was below 0.1 for both zones.

Leachate of site B had a higher content in sulphates than both samples of site A, but lower concentrations for the other salts. Therefore, the total ion contents (ion balance) of leachate B were lower than on site A. Ion balances and conductivities were similar on the two zones of site A, while conductivity was lower on leachate from site B, and the ion balance was reversed (more cations than anions).

Content of leachates in heavy metals was usually rather low for all samples, except for aluminium and iron. Manganese concentration of leachate from site B had fallen between concentrations in leachates from K1 and K2, whereas chromium, tin, nickel and zinc

Table 1. classical parameters measured on the 3 leachates

Parameter	*Units*	*Site A, K1 (old)*	*Site A, K2 (new)*	*Site B, C2*
pH		7.85	8.1	6.55
Conductivity @ 20°C	mS/cm	15.5	15.95	5.42
Suspended matter	mg/L	380	1,800	970
COD	mg O/L	3,150	14,400	736
BOD5	mg O/L	105	943	23
BOD5/COD		0.033	0.065	0.031
Sulfates	mg SO4/L	11	700	1,430
Chloride	mg/L	1,660	2,490	555
Ammonia	mg NH4/L	2,190	1,930	420
Sum anions (1)	meq/L	157	153.25	47.55
Sum cations (2)	meq/L	89	119.5	64.28
Phenol index	µg/L	97	170	<25
AOX	µg/L	1,690	1,490	120
Al	µg/L	1,200	140,000	7,600
As	µg/L	170	430	5
Cd	µg/L	<1	9.7	<1
Cr	µg/L	540	2,800	91
Cu	µg/L	<20	350	<0.02
Sn	µg/L	510	130	<100
Fe	µg/L	43,000	280,000	21,000
Hg	µg/L	<0.5	<0.5	<0.5
Mn	µg/L	630	4,000	2,300
Ni	µg/L	160	370	84
Pb	µg/L	<10	260	<10
Zn	µg/L	210	5,100	160

(1) (Cl-SO_4-NO_3-HCO_3-SiO_2)
(2) (NH_4-Na-K-Ca-Mg)

concentrations were lower in the sample from site B.

3.2 Organic pollutants

Organic compounds and persistent organic pollutants which were measured are: aromatics (benzene-toluene- xylenes) and chlorinated compounds, volatile fatty acids, aldehydes, ketones, 15 polycyclic aromatic compounds, 7 PCB, 8 PBDE, phtalates. Some of the results can be compared to limit values for drinking waters, when they exist, or to values published in other studies on landfill leachates, in particular Baun *et al* (2004): 10 Danish landfills receiving other waste as well as MSW, Oman & Junestedt (2008): 12 Swedish landfills receiving principally MSW.

3.2.1 BTX and HVOC

Table 2 presents the BTX and HVOC concentrations measured on the 3 leachates.

Benzene was not detected on either sample, which means that benzene concentration, if present, should be smaller than the detection limit (1.5 µg/L). This value is smaller than the concentrations reported by Baun *et al*: from 2.3 to 38.9 µg/L. Toluene was measured only on leachate from the old zone of site A (K1), while xylenes were measured which similar concentrations on both leachates of site A.

Most halogenated compounds were not found, or at low concentration (around the quantification limits) on the 3 samples. Only dichloromethane was measured in the leachate of the old zone K1 of site A. It should be noticed than, although trichlorethene and tetrachlorethene undergo biodegradation, they were found in lower concentrations in young leachates (K2 and C2) than in the old one: this demonstrates what we have noticed during other studies (on trace compounds in biogases for instance), that MSW which is presently collected contains less chlorinated compounds, and is therefore less toxic that it used to be. Another hypothesis is that the aerobic stabilization treatment lowers the organic content of the treated waste, and the level of contaminants which are associated to the organic matter.

Table 2. BTX and HVOC concentrations measured on the 3 leachates

Coumpound	*Units*	*Site A, K1 (old)*	*Site A, K2 (new)*	*Site B, C2*
Benzene	µg/L	ND	ND	ND
Toluene	µg/L	5	ND	ND
m,p-Xylenes	µg/L	6	5	ND
o-Xylene	µg/L	4	5	ND
Dichloromethane	µg/L	8.2	ND	ND
Chloroforme	µg/L	ND	ND	ND
Carbon tetrachloride	µg/L	ND	ND	ND
Trichlorethene	µg/L	0.06	<0.04	<0.043
Dichlorobromomethane	µg/L	ND	ND	ND
Tetrachlorethene	µg/L	0.04	0.03	0.02
Chlorodibromomethane	µg/L	0.09	ND	<0.05
Bromoforme	µg/L	<0.17	ND	ND
Hexachlorobenzene	µg/L	ND	ND	ND

ND: not detected

3.2.2 Aldehydes, ketones and volatile fatty acids

Errore. L'origine riferimento non è stata trovata. presents the measurements for aldehydes, ketones and volatile fatty acids for the 3 leachates. All the target compounds were detected on the 3 samples, but no one was quantified on either of the samples. The quantification limit of the method should be improved in order to quantify these compounds, but this may be difficult to achieve, due to the high level of all pollutants in leachates. These compounds were not studied by Baun *et al,* nor by Oman & Junestedt.

3.2.3 Polycyclic aromatic compounds (PAH)

Table 4 presents the measurements for PAHs on the 3 leachates.

Table 3. Aldehydes, ketones and volatile fatty acids contents of the 3 leachates

Coumpound	*Units*	*Site A, K1 (old)*	*Site A, K2 (new)*	*Site B, C2*
Formaldehyde	mg/L	<0.2	<0.2	<0.2
Acetaldehyde	mg/L	<0.4	<0.4	<0.4
Acroleine	mg/L	<0.7	<0.7	<0.7
Propionaldehyde	mg/L	<0.4	<0.4	<0.4
Butanal	mg/L	<1.0	<1.0	<1.0
Pentanal	mg/L	<1.4	<1.4	<1.4
Hexanal	mg/L	<1.6	<1.6	<1.6
Heptanal	mg/L	<0.5	<0.5	<0.5
Octanal	mg/L	<0.9	<0.9	<0.9
Benzaldehyde	mg/L	<0.7	<0.7	<0.7
Butanone	mg/L	<0.8	<0.8	<0.8
Pentanone	mg/L	<2.5	<2.5	<2.5
Hexanone	mg/L	<1.6	<1.6	<1.6
Heptanone	mg/L	<1.8	<1.8	<1.8
Octanone	mg/L	<2.0	<2.0	<2.0
Acetic acid	mg/L	<5.0	<5.0	<5.0
Formic acid	mg/L	<5.0	<5.0	<5.0

Table 4. Polycyclic aromatic compounds measured on the 3 leachates

Coumpound	*Units*	*Site A, K1 (old)*	*Site A, K2 (new)*	*Site B, C2*
Naphtalene	ng/L	1,986	215	270
Acenaphthene	ng/L	546	318	ND
Fluorene	ng/L	223	58	ND
Phenanthrene	ng/L	816	314	19
Antracene	ng/L	53	23	ND
Fluoranthene	ng/L	323	186	ND
Pyrene	ng/L	197	121	ND
Benzo(a)antracene	ng/L	50	30	ND
Chrysene	ng/L	83	43	ND
Benzo(b)fluoranthene (a)	ng/L	32	20	ND
Benzo(k)fluoranthene (a)	ng/L	13	<10	ND
Benzo(a)pyrene	ng/L	28	15	ND
Dibenzo(a,h)antracene	ng/L	ND	ND	ND
Benzo(g,h,i)perylene (a)	ng/L	ND	ND	ND
Indeno(1,2,3-cd)pyrene (a)	ng/L	ND	ND	ND

(a): sum of these 4 PAH must be < 100 ng/L for drinking waters (French Arrêté du 11 janvier 2007)

On site A, all the PAH which were measured were in lower concentrations on the young leachate (K2) than on the old one (K1): see in Figure 1. As for the BTX and HVOC, this could indicate that:

1) the toxic content of MSW is lower nowadays than it was some years ago, and

2) the aerobic stabilization lowers the organic content of the treated waste, and consequently, the level of contaminants which are bound to the organic matter. Also, the more volatile pollutants (such as naphthalene) may be lost by evaporation during the stabilization process.

Concentrations measured here are similar to those published by Oman & Junestedt, but much lower than those published by Baun *et al* (naphtalene ranges from 600 to 91,200 ng/L).

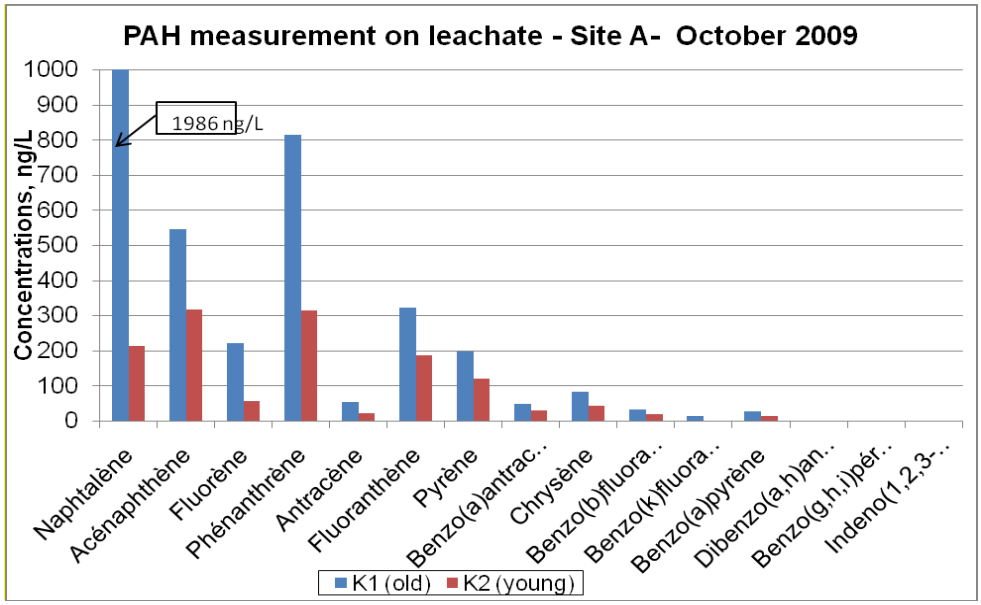

Figure 1. PAH contents for leachates of site A

On leachate of site B, except naphthalene and phenantrene, no PAH were detected.

There is a limit value for drinking waters in France (Arrêté du 11 janvier 2007): the sum of 4 PAHs (Benzo(b)fluoranthene; Benzo(k)fluoranthene; Benzo(g,h,i)perylene; Indeno(1,2,3-cd)pyrene) should be lower than 0.1µg/L (100 ng/L). All leachates fulfill this limit value (Benzo(g,h,i)perylene and Indeno(1,2,3-cd)pyrene are not detected on either of the samples).

3.2.4 Polychlorobiphenyl compounds (PCBs)

Table 5 presents the measurements for 7 PCBs on the 3 leachates. These compounds, among the 209 congeners, are assumed to represent PCB pollution as they are the most abundant, persistant and because of their toxicological properties.

All these compounds were detected and quantified in leachates of site A. Except PCB28, which showed a similar concentration between the two leachates, all the heavier PCBs are more abundant in the old leachate from K1 tant in the young one from K2: see Figure 2. PCBs are persistant. A lower concentration in the leachate from the treated waste could be due to a lower content of the waste, or to a lower leaching of these compounds, the waste being partially stabilized.

On leachate from cell 2 of site B, only 2 of the 7 PCBs were measured, and their concentrations were of the same order of magnitude as the quantification limit.

Table 5. *Polychlorobiphenyl compounds measured on the 3 leachates*

Coumpound	*Units*	*Site A, K1 (old)*	*Site A, K2 (new)*	*Site B, C2*
PCB28	ng/L	45.9	47.7	<2.0
PCB52	ng/L	55.8	35.3	2.0
PCB101	ng/L	65	23.5	3.3
PCB118	ng/L	68.1	22.5	<2.0
PCB153	ng/L	39.9	13.6	<2.0
PCB138	ng/L	48.4	17.9	<2.0
PCB180	ng/L	16.5	6.8	<2.0

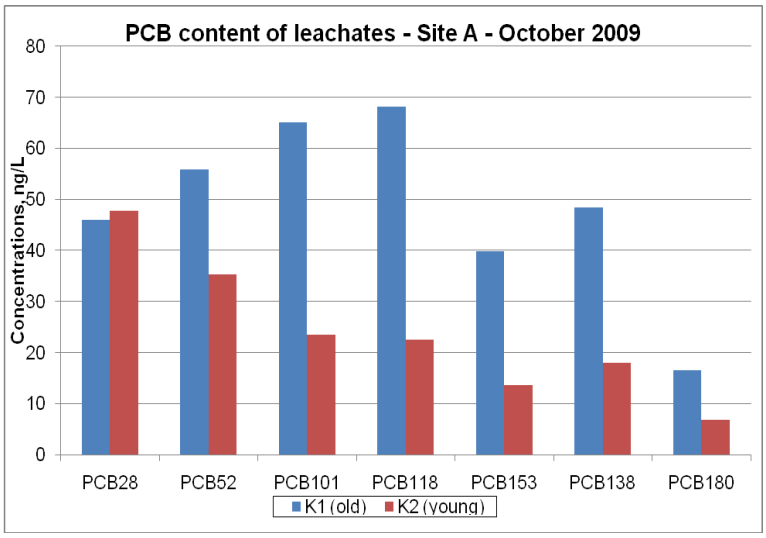

Figure 2. PCB contents for leachates of site A

3.2.5 Polybrominated diphenyl ethers (PBDEs)

PBDEs are flame retardant. They are not chemically bound to plastics, foam, fabrics, or other products in which they are used, making them more likely to leach out of these products. Analysis were done on both the liquid and solid phases, and measured on raw sample (before filtration). Table 6 presents the measurements for 8 PBDEs on the 3 leachates. Concentrations are given by weight.

For these compounds, only 5 of the 8 target compounds were detected and quantified on leachates from site A : concentrations are higher in leachates from the young zone (K2) than on the old waste (K1). One hypothesis could be that newer waste (K2 receives waste since 2006) contain more EEEW than older waste, and as PBDEs are subject to leaching, they are found in the leachates. PBDEs are reported by Oman & Jundestedt betwwen 0.002 to 7.1 μg/L (maximum for tetrabromodiphenyl ethers), depending on the compounds. None of these compounds was detected on the leachate of site B.

3.2.6 Phtalates

Phtalates are widely present in the environment. They are used in plastics and other materials to make them flexible. Table 7 presents the measurements for phtalates on the 3 leachates. As they are mostly present on the solid phase, concentrations are also reported by weight.

3 phtalates are highly abundant in the solid phase of leachate from K2 (site A), compared to the other leachates. Origin of these compounds should be explored. One phtalate (the diethylphtalate) is used as solvent and vehicle for fragrance and cosmetic ingredients.Another one (the diethylhexylphtalate) is is the most common of the class of phtalate plasticizers.

All the other compounds, and the other leachates, show no phtalates or small concentrations, similar to those reported by Oman & Jundestedt. Baun *et al* report higher concentrations, up to 340 μg/L for monoethylphtalate in one landfill leachate.

Table 6. Polybrominated diphenyl ethers contents of the 3 leachates

Coumpound	Units	Site A, K1 (old)	Site A, K2 (new)	Site B, C2
BDE28	ng/Kg	ND	ND	ND
BDE47	ng/Kg	25	38	ND
BDE99	ng/Kg	5.3	10	ND
BDE100	ng/Kg	16	40	ND
BDE153	ng/Kg	3	8	ND
BDE154	ng/Kg	9	4	ND
BDE183	ng/Kg	ND	ND	ND
BDE204	ng/Kg	ND	ND	ND

Table 7. Phtalates contents of the 3 leachates

Coumpound	Units	Site A, K1 (old)	Site A, K2 (new)**	Site B, C2
Dimethyl-phtalate	ng/g	ND	**400 (a)**	3
Diethylphtalate	ng/g	16	**7,012 (a)**	46
Dipropylphtalate	ng/g	ND	3	ND
Di-isobutyl-phtalate	ng/g	5	ND	ND
Dibutylphtalate	ng/g	4,5	5	3
Butylbenzylphtalate	ng/g	ND	ND	ND
Dicyclohexylphtalate	ng/g	ND	ND	ND
Diethylhexylphtalate	ng/g	72	**2,125 (a)**	4
Di-n-octylphtalate	ng/g	ND	ND	ND

** : analysis on both liqid and solid phases (high content in suspended matter)
(a): high phtalate content in the solid phase

Only 4 out of 8 phtalates were measured in leachate from site B, and concentrations were of the same order as the quantification limits: 0.1 ng/g (liquid phase) and 30 ng/g (solid phase).

4. CONCLUSIONS

This preliminary study was limited to 3 samples of leachates, one issued from untreated MSW, the two others coming from landfills which receive outputs of MBT. In spite of this small number of samples, different behaviours are noticeable, on “classical” parameters, and also on volatile and persistent organic pollutants.

Site A is interesting as comparison can be made between leachates from untreated and treated MSW. Leachate from the untreated waste has globally a smaller content in salts (except ammonia) and metals than the young leachate from treated waste. However, the ion balances are similar for the two leachates. Leachate from untreated waste has higher concentrations of many organic compounds, such as toluene, dichloromethane, PAHs (especially the lighter ones), and PCBs, except PCB28, which is similar on the two leachates. On the other hand, the leachate from treated waste shows higher concentrations for 4 out 5 of the measured PBDEs, and for 3 phtalates. These high concentrations prove that these compounds are probably more abundant in the actual waste than they were some years ago, and that they are not reduced by the aerobic treatment. In addition, some of those compounds are not bound to the materials in which they are added, and they are subject to leaching.

Site B, which receives only the reject of organic sorting (organic matter being valorized under a compost form), emits a rather small volume of leachate. This leachate, considering the BOD and COD values, seems to be issued from “stabilized” waste. This leachate has a very low content of most organic compounds, and intermediate values for “classical” parameters.

Aldehydes, ketones and volatile fatty acids were never detected on neither of the 3 samples.

Due to the low content in certain hazardous pollutants, the treatment of these leachates could be rather light. Nevertheless, the content in “classical” pollutants (especially salts) remains high, which implies a high grade treatment of these leachates.

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