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Assessment of the PCDD/F fate from MSWI residues used in road construction in France

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Abstract

MSWI fly ash is susceptible to contain high amount of dioxins (PCDD) and furans (PCDF). However, the use of MSWI residues for road construction started in France at period when the mixture of MSWI Bottom Ash with MSWI fly ash was used. From four old road sites, MSWI residues, road soils, reference soils and geo-textiles were sampled and their PCDD/F contents were analyzed. MSWI residues show a great heterogeneity but also high amounts of PCDD/F between 14 and 2960 ng I-TEQ.kg\(^{-1}\) DM. Road soils show less heterogeneity and contents between 0.57 et 7.23 ng I-TEQ.kg\(^{-1}\) DM lower than ordinary soils. Moreover, the specific analysis of the 17 toxic PCDD/F congeners (notably the 2,3,7,8-TetraCDD) indicates the very low noxiousness of road soils. The study also allows to assert the relation between the MSWI residue particle size and the PCDD/F content.

Keywords: incineration, ash, road, dioxin, furan, particle
1 Introduction

In many areas across the world where the high demand of construction materials compared to the availability of natural materials, as well as the lack of available space for waste disposal, are a problem, the use of by-products and wastes for road construction has been seen for a long time as an appropriate solution to reduce the amount of disposed materials and to provide at the same time alternative materials for construction. A typical case of these alternative materials is that of the Municipal Solid Waste Incinerator (MSWI) residue which is produced from the household wastes combustion and used for road and car-park construction.

In France, the use of MSWI residue in road construction is supervised since the 90’s through an order (1991) and a memorandum (1994) both from the ministry of Environment. The environmental assessment of MSWI bottom ash is based on the measurement of its unburned fraction and the leaching potential of some heavy metals, arsenic, sulfate and total organic carbon. Yet, MSWI residues may contain persistent organic pollutants (POP) such as polychlorinated dibenzo-dioxins (PCDD) and polychlorinated dibenzo-furans (PCDF). PCDD/F molecules are poorly water soluble and leaching tests are known for not being relevant toward them, nonetheless, the affinity of PCDD/F molecules for particles is also known, and such affinity may be higher toward the finest particles. As a consequence, one wonders if under the effect of rainwater infiltration into the road body, the washing of the MSWI residue layer may induce the transfer, downward, of PCDD/F molecules bound to the finest particles of the material. In such a case, on road sites, compared to some reference soils, an increase of the PCDD/F content in the soil underlying the road (called the road soil), may be observed.
In order to answer to this question, PCDD/F contents of MSWI residues sampled into old road structures, were analyzed (including an assessment of their noxiousness). The relation between the dimension of MSWI residue particles and the PCDD/F content was studied. Then MSWI residue PCDD/F contents were compared to those measured in the road soil and in neighbouring soils (local references).

As before the enforcement of the 1991 order – thus PCDD/F compounds - MSWI residues were susceptible to contain higher amounts of fly ash, the present study was focused on pre-1991 constructions. At the same time, this allows to assess the medium-term state of road soils.

2 Context of the study

2.1 Production of PCDD/F during household waste incineration

As a result of incomplete combustion, incineration of household waste produces several organic compounds such as chlorinated species (polychlorinated biphenyls (PCB), polychlorinated dibenzodioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs)). Two temperature ranges are responsible for the production of persistent organic pollutant (POP). The first one (200 to 400°C) which results from a catalysed reaction taking places on the ash particles present in combustion systems. The second one (500 to 800°C) is the result of a rearrangement of chlorinated precursors such as chlorophenols and chlorobenzenes in the gas phase (Stanmore, 2004).

Dioxin air emissions from incinerators have decreased in the last decade due to improvements in the pollution control technology and to the regulation implementation and enforcement. Two orders of 20 September, one for hazardous waste and another one for non hazardous waste, both limit the level of PCDD/F emission to 0.1 ng.m^{-3}. 

2.2 Use of MSWI residues for road construction in France

The use of MSWI residue started in France during the 1950's in the area of Paris and spread all over the country during the 1980’–1990’s, a period during which many incinerators were built (AGHTM, 1994).

As for some other alternative materials (coal fly ash, blast furnace slag…), the use of MSWI residue was codified by the ministry for public works and transports, allowing its assimilation to one of the various kinds of natural materials considered for the classical road structure design (MELT, 1997; SETRA and LCPC, 2000). The analogy is based on geo-technical responses of the MSWI residue sample to a set of usual standard mechanical tests (resistance to fragmentation and wear, sand equivalent, surface cleanliness, compactibility…).

Until the 1990’s the environmental question about the use of MSWI residue was not seen as a major concern. In 1991, an order required from the 1st of December 1992, the separating of MSWI residue into bottom ash (the fraction of the incineration residue which is collected from the incinerator grate) and fly ash (the fraction made of fine particles carried away by the flux of combustion gas which is later captured by dust collectors). While the production of MSWI bottom ash is around 250 kg per ton of incinerated residue, the production of fly ash is 20 kg per ton (AGHTM, 1994; Autret et al., 2007). Due to its high pollutant potential (notably high content in chlorides, arsenic, lead, zinc, mercury, cadmium and organic compounds), MSWI fly ash was classified as hazardous waste and has to be directed toward specific landfills for hazardous waste. Usually, the MSWI bottom ash fraction is classified as non-hazardous waste and is authorized in non-hazardous waste landfill, or also potentially authorized for road construction under specific conditions. Indeed, in 1994, a memorandum from the Ministry in charge of the Environment (French
Environment Ministry, 1994) provided recommendations for the use of MSWI bottom ash in road construction (embankment, capping layers, subgrades...). The use of MSWI bottom ash depends on its unburned fraction and on its leaching potential controlled through a standard batch leaching test (NF X 31-210, 1992). The 1994 memorandum sets maximum limit values related to the leachate: its global soluble fraction (total dissolved solids), plus specific limit values for seven chemical parameters: arsenic, cadmium, chromium VI, lead, mercury, sulfate and total organic carbon.

2.3 Knowledge about the PCDD/F fate in the road environment

The 1994 memorandum did not set any particular recommendation regarding dioxins and furans. Since the 1990’s, MSWI residue (and more specifically MSWI bottom ash) has been extensively studied in France and worldwide from the environmental point of view. This was essentially carried out with relation to its heavy metal leaching potential and poorly with relation to its organic pollutants, notably regarding PCDD/F content and release risk (Chandler et al., 1997, Bartet et al., 2001). Consequently, as opposite to heavy metals for which laboratory, lysimeter and some field studies have provided leaching data (Silvestre and Rampignon, 1995; Adam et al., 1996; Drouadaine et al., 1997; Paris et al., 1997; Drouadaine and Badreddine, 2003), very little knowledge exists today regarding the fate of PCDD/F, notably possible transfer of PCDD/F to the open environment from the use of MSWI residues in road infrastructures.

In the French context, this issue is essentially related to the effect of pre-1991 MSWI residues, as at that time bottom and fly ashes were not separated. Considering on the one hand the long term potential effect of PCDD/F, and on the other hand the infiltration of rainfall through road surface (van Ganse, 1978) and the permeability of
the MSWI residue layers (i.e. $10^{-5}$ to $10^{-4}$ m.s$^{-1}$) (François et al., 2003), understanding the fate of PCDD/F hold into old MSWI residues used in road structures has became a necessity. Indeed, due to its relatively poor mechanical properties, MSWI residue has primarily been used by road engineers mainly in the deeper layers of the road structure (SETRA and LCPC, 2000), where mechanical constraints are the lowest, immediately above the underlying natural soil. The latter (called road soil), due to its direct contact with the MSWI layer and to its ability to retain pollutants represents a major target to be considered in the context of alternative material use in road construction (Jullien and François, 2006).

3 Materials

3.1 Road site identification

In order to take advantage of the longest possible period of contact between the MSWI residue layer and the road soil, road sites for study were chosen as old as possible. However, due to the lack of written records for the oldest roads, it was only possible to go back in time as early as 20 years ago, thanks to the memory of the people who took part to the construction. For more recent sites (around 10 years old), more data was available.

The road body is a multi-layer structure. The pavement layers (surface course, base course, sub-base) are built on the pavement foundation, consisting of the natural ground after earthworks (scraped and compacted) called the subgrade, generally topped with a capping layer in the French design technique (SETRA and LCPC, 2000). Figure 1a presents the different road layers of a complete structure. In practice, depending on the physical stress expected on the road body during its use
(load due to traffic, climatic agents) and on the properties of the road materials, the number of layers in the structure and their thickness can vary. When the natural soil on which the road structure is built contains too many fine particles, this may induce a transfer of fine particles from the road soil to the upper layer. This phenomenon can induce an increase of the upper layer sensitivity to moisture variation, detrimental to its bearing capacity. This risk is usually avoided using a geo-textile; such a geo-textile was found in two of the investigated sites.

Four sites (noted A, B, C and D) were investigated from various regions in France. Sites A and B were built in the second half of the 1970’s, while sites C and D were built between 1991 and 1994. Their structure is described in Figure 1b. In both site, MSWI residues were used as 0-31.5 mm unbound graded aggregates.

Site A is the private road of a MSW incinerator plant, which essentially bears a heavy lorry traffic. The structure corresponds to a flexible pavement in which the MSWI residue was used in a thick sub-base layer (70 cm). The road soil is sandy. Built in 1978, site A was sampled at the age of 20.

Site B is an urban pavement which only undergoes light vehicle traffic. The structure is that of a flexible pavement in which the MSWI residue was used in the sub-base layer (25 cm). The underlying soil is silty. Built in 1976, Site B was sampled at the age of 22.

Site C is another urban pavement which undergoes light traffic. The structure corresponds to a semi-rigid pavement in which the MSWI residue was used in a quite thick sub-base layer (40 cm), topped with a bound layer made of blast furnace slag and coal fly ash. Due to the silt nature of the road soil, a geo-textile was laid by the
road constructor below the MSWI residue layer in order to prevent fine particles lifting towards the sub-base layer. Built in 1992, site C was sampled at the age of 9.

Site D is a public car park platform. The uncovered structure (a simple 1 cm-thick gravelling) is unusual for traditional car parks but is sometime chosen for occasionally used ones. The MSWI ash is used in the base layer (30 cm). Due to the silty nature of the road soil, a geo-textile was also laid by the road constructor below the MSWI residue layer in order to prevent fine particles lifting towards the base layer. Built in 1994, site D was sampled at the age of 9.

3.2 Material sampling

3.2.1 Sampling

On each site, the sampling operation starts by digging a trench in the pavement, down to the top of the MSWI residue layer. For safety reasons, on circulated roads, the trench is dug on the road edge side. No such consideration had to be taken into account regarding the car park. In all case, beforehand, information is collected regarding the location of buried networks (water, gas, electricity…).

Usually, the thickness of the MSWI residue layer is not known exactly; on one site it can vary by few centimeters from one point to another, which makes preferable, when possible, to dig more than one trench. A core sampler is used to collect at once the MSWI residue layer and the road soil. Then, the real thickness of the MSWI residue layer at the sampling point is measured on the core sample. The thickness of the sampled underlying soil is also measured. The core sample can then be cut in different sub-layers in order to assess the contaminant content at different depths. The upper sub-sample of the road soil, just below the MSWI residue layer, is always rather thin (usually 5 cm thick). Samples for analysis are collected in the middle of
the core section. This is a precaution avoiding peripheral contamination from the upper levels to the lower ones, as while the core sampler is pushed in, particles can move along its internal wall.

When the road site makes it easy to obtain a reference situation of the soil away from the MSWI residue road layer influence, reference samples are collected with the core sampler for analysis and comparison with the road soil. Providing data on the surrounding situation regarding PCDD/F influence on the site, the so-call reference soil makes it possible to have a view of the net impact on the road soil. For all materials, before analysis, all samples were stored in plastic bags and drums, hermetically closed.

### 3.2.2 Samples

Table 1 provides an overview of the set of samples that were analyzed, together with their codification, the numbering is for the trench (1, 2 or 3). Soil samples were collected at different depths in order to detect any vertical content variation. Depth of sampling was conditioned by the soil own-thickness.

For sites A, B and C it was possible to identify a reference soil, but not for site D. In site A, four $A_R$ samples were collected for PCDD/F content analysis (0-20 cm, 20-40 cm, 40-60 cm and 80-95 cm). In sites B, two samples were collected: 0-20 cm and 60-80 for $B_{R,}$.. In site C, the reference soil ($C_R$) was not sampled as deep as the two others: 0-5 cm and 5-15 cm.

Regarding MSWI residues, in site A, two trenches were dug into the road structure. Only one sample was collected in the first trench ($A_{M1}$) because at that point the MSWI residue layer was thin (12 cm). In the second trench ($A_{M2}$), the layer thickness was greater (65 cm) and four samples were collected in the MSWI residue ($A_{M2/14-29}$).
A\textsubscript{M2/35-45}; A\textsubscript{M2/45-65} and A\textsubscript{M2/65-85}). In site B, one trench was dug, providing one sample (B\textsubscript{M1}) of MSWI residue (35-60 cm). Similarly for site C (C\textsubscript{M1}), only one sample was collected (50-88 cm). Lastly, in site D three trenches were dug providing each one a sample (D\textsubscript{M1}, D\textsubscript{M2} and D\textsubscript{M3}) with the same geometrical characteristics (10-30 cm).

Regarding road soils, in site A, three samples were collected in the sandy road soil of trench T1 (A\textsubscript{S1}) (32-37 cm, 37-42 cm and 42-52 cm). Three road soil samples were also collected at trench T2 (A\textsubscript{S2}) (29-35 cm, 85-90 cm and 95-105 cm). Sample A\textsubscript{S2/29-35} taken from trench T2 is a thin sand layer which accidentally slid on the MSWI residue during the road work; it was not removed and has remained inserted in the MSWI residue layer since then. In site B (B\textsubscript{S1}), two samples were collected in the silty road soil (B\textsubscript{S1/60-70} and B\textsubscript{S1/70-80}). In site C, a single road soil sample (silty) was collected (C\textsubscript{S1/88-93}). In site D, three silty road soil samples were collected in trench T1 (D\textsubscript{S1/30-35}; D\textsubscript{S1/35-45} and D\textsubscript{S1/93-103}); two in trench T2 (D\textsubscript{S2/30-35} and D\textsubscript{S2/35-45}); and a single sample in trench T3 (D\textsubscript{S3/30-35}).

In sites C and D, during construction geo-textiles were laid between the MSWI residue layer and the road soil. One sample of geo-textile was collected in the trench of site C (C\textsubscript{G1}) and two geo-textile samples were collected at site D, one from trench T1 (D\textsubscript{G1}), the second from trench T2 (D\textsubscript{G2}).

4 Methods

4.1 Grading of materials

The total sample, dried at 105°C, is sieved at 2 mm. The fraction below 2 mm is sieved in a dried phase in a stainless steel sieve to separate the fractions below 1 mm and 0.5 mm. The particle size distribution of the fraction below 0.5 mm is achieved using the laser diffraction technique (Mastersizer, Malvern Instrument).
4.2 PCDD/F analysis

Determination of dry matter content was achieved by drying subsamples at 105°C following the standard EN ISO 11465.

The samples were beforehand dried at room temperature. The dried samples were treated and digested with chlorydric acid. Materials (MSWI residues and soil samples) were prepared using an accredited method, based on the standard EN 1948-2 and EN 1948-3, which consists in extracting the analyzed components with mixture of toluene and acetone. This step is followed with several stages of clean-up by chromatography on columns filled with absorbents using solvents or various elution strength. After filtration, the dioxin measurement requires a solid/liquid extraction followed with a cleaning up step. The purified extracts are reduced to a minimum volume and then mixed in a solvent compatible with the final analysis by gas chromatography.

The total eluate was prepared following the same methodology as the one used for MSWI residues.

Analyses of PCDD/F were carried out by means of a High Resolution Mass Spectrometry coupled with a High Resolution Gas Chromatography (HRMS/HRGC) VG/AutoSpec.

The analysis consisted in measuring 17 toxic congeners (7 congeners for PCDD and 10 congeners for PCDF). The seven dioxin congeners are 2,3,7,8-TetraCDD; 1,2,3,7,8-PentaCDD; 1,2,3,4,7,8-HexaCDD; 1,2,3,6,7,8-HexaCDD; 1,2,3,7,8,9-HexaCDD; 1,2,3,4,6,7,8-HeptaCDD and OctaCDD. The ten furan congeners are 2,3,7,8-TetraCDF; 1,2,3,7,8-/1,2,3,4,8-PentaCDF; 2,3,4,7,8-PentaCDF; 1,2,3,4,7,8-/1,2,3,4,7,9-HexaCDF; 1,2,3,6,7,8-HexaCDF; 1,2,3,7,8,9-HexaCDF; 1,2,3,4,6,7,8-
HeptaCDF; 1,2,3,4,7,8,9-HeptaCDF and OctaCDF. Interferences with the other 193 non toxic congeners and some other components such as Polychlorobiphenyls (PCBs), Polychloroterphenyls (PCTs), or Polychloronaphtalens (PCNs) are eliminated. The determination of congeners was realized by the isotopic dilution method using isotope as interne markers for congeners identification and quantification.

The concentration of one PCDD or PCDF congener can be converted into an International Toxic Equivalent Quantity (I-TEQ), with a Detection Limit (DL) of 1.22 nanogram I-TEQ.kg\(^{-1}\) of dry material (noted DM) and an accuracy of 4.7% on the Toxic Equivalent value. The model used for determining the I-TEQ is NATO (1998).

### 4.3 Leaching

Regarding the geo-textiles found on two sites, before chemical analyses, the recovery of particles was realized by means of leaching, intended to wash the geo-textile. The operation was renewed until the complete extraction.

Regarding MSWI residues, as PCDD/F are not water soluble compounds (Sakai et al., 2000a), the purpose of the test was not to assess their solubility but their possible residual release associated to very fine particle extraction (namely below 0.45 μm in the condition of the test due to the filter size) under the effect of water flushing. The leaching test was performed for MSWI residues from sites B and D following the EN 12457-2 standard protocol (2002). Determination of the dry matter content was made after drying of test portion at 105°C, according to the international standard ISO 11465 (1994). The liquid/solid separation is performed by means of filtration on a 0.45 μm membrane filter using a pressure filtration device. The eluate obtained after filtration was analyzed to determine PCDD/F compounds’ nature and quantity.
5 Results

Results concerning old MSWI residues are first presented. Then are those of geo-
textiles, road soils and reference soils. All material samples are defined in relation to
their depth from the surface (expressed in centimeters) and all PCDD/F contents are
expressed in nanogram of I-TEQ per kilogram of dry matter (noted ng I-TEQ.kg\(^{-1}\)
DM).

The PCDD/F congener with the greatest toxic potential, and for which the greatest
amount of toxicological data is available, is 2,3,7,8-TetraCDD (Mac Kay, 2002). Its
content in all material samples is provided (in ng.kg\(^{-1}\) DM).

Additionally, in order to assess the distribution of the different PCDD/F compounds in
the different materials the sum of the seven PCDD congeners and that of the ten
PCDF congeners was calculated (in ng.kg\(^{-1}\) DM).

5.1 MSWI residues’ characteristics

5.1.1 PCDD/F contents in MSWI residues

Results are presented in Table 2. In site A, the only one showing values below 100
ng I-TEQ.kg\(^{-1}\) DM, the PCDD/F content for the MSWI residue in trench T1 (A\(_{M1}\)) is
14.0 ng I-TEQ.kg\(^{-1}\) DM. In trench T2 (A\(_{M2}\)), it increases from the upper sample to the
third one (from 35.7 to 227 ng I-TEQ.kg\(^{-1}\) DM) and decreases in the lower sample
(63.2 ng I-TEQ.kg\(^{-1}\) DM).

In site B (B\(_{M1}\)), the PCDD/F content for the MSWI residue is 721 ng I-TEQ.kg\(^{-1}\) DM,
three time higher than the maximum value measured in site A.
In site C (C1), the PCDD/F content is similar to the maximum value found in site A
(235 ng I-TEQ.kg\(^{-1}\) DM).

The three trenches of site D (D1, D2 and D3) show, by far, the highest PCDD/F
contents. These contents are respectively 1960, 2160 and 1640 ng I-TEQ.kg\(^{-1}\) DM.

5.1.2 Relation between PCDD/F amount and particle size

A sample with a high PCDD/F content (D1), was chosen in order to assess the
possible relation between the particle size distribution of MSWI residues and their
PCDD/F load. PCDD/F contents related to fractions < 0.1 mm; 0.1-0.5 mm; 0.5-1
mm; 1-2 mm; 2-10 mm; 10-31.5 mm of the material are presented in Figure 2.

The PCDD/F contents of fractions between 2 and 31.5 mm are similar, comprised
between 733 ng I-TEQ.kg\(^{-1}\) and 888 ng I-TEQ.kg\(^{-1}\). The finest fractions and
particularly the one below 0.1 mm is 7 times higher, reaching 6590 ng I-TEQ.kg\(^{-1}\).

5.1.3 Leaching of MSWI residues

The leaching test was carried out in order to detect the proportion of PCDD/F
particles inferior to 0.45 µm. For both sites (B and D), leaching results (Table 3) show
that leachates contain a small amount of PCDD/F: 2.19 pg I-TEQ.l\(^{-1}\) for sample
B1/35-60; and 4.4.1 pg I-TEQ.l\(^{-1}\) for sample D1/10-30. Brought to the mass of dry
material involved in the leaching test, such releases are respectively equal to 0.019
ng I-TEQ. kg\(^{-1}\) DM for the first sample, and 0.041 ng I-TEQ. kg\(^{-1}\) DM for the second.

5.2 Geo-textiles’ load of PCDD/F

The load of PCDD/F on the geo-textile from site C (C1) is 175 ng I-TEQ.kg\(^{-1}\) DM
(Table 4). Site D geo-textile samples show far higher values: 754 ng I-TEQ.kg\(^{-1}\) DM
in trench T1 (D1), and 1600 ng I-TEQ.kg\(^{-1}\) DM in trench T2 (D2). The latter value is
close to the content of the MSWI residue layer above.
5.3 PCDD/F contents in road soils

For site B (B_{S1}), it varies from 7.23 to 0.57 ng I-TEQ.kg\(^{-1}\) DM from the upper to the lower sample. In site C (C_{S1/88-93}), the single sample value is 2.87 ng I-TEQ.kg\(^{-1}\) DM. In site D, from the top to the bottom of the investigated thickness in trench T1 (D_{S1}), the three values are respectively 0.86, 0.79 and 1.99 ng I-TEQ.kg\(^{-1}\) DM. In trench T2 (D_{S2}), the values are of the same order (2.22 and 0.64 ng I-TEQ.kg\(^{-1}\) DM). Lastly, trench T3 sample (D_{S3}) PCDD/F content is 2.04 ng I-TEQ.kg\(^{-1}\) DM (Table 5).

Site A presents a contrasted situation regarding its two trenches. In trench T2 (A_{S2}), the PCDD/F contents of the three samples are in the range of the previous cases B, C and D, with values evolving from 2.98 to 2.24 and 1.31 ng I-TEQ.kg\(^{-1}\) DM, from the upper to the lower sample. On the other hand, in trench T1 (A_{S1}), whereas the two first samples present low values (1.35 and 0.74 ng I-TEQ.kg\(^{-1}\) DM), the deeper sample shows a content of 24.8 ng I-TEQ.kg\(^{-1}\) DM, which is relatively high in comparison with the content of the MSWI residue layer located just above (i.e. 14.0 ng I-TEQ.kg\(^{-1}\) DM). As a consequence, this values (A_{S1/42-52}) is very uncertain and will not be considered in the interpretation.

5.4 PCDD/F contents in reference soils

Results are presented in the Table 6. In site A (A_{R}), the PCDD/F content of the reference soil decreases from 9.4 to 0.30 ng I-TEQ.kg\(^{-1}\) DM, from the surface to the deeper sample. The top sample value can be related to the atmospheric contamination in the vicinity of the incineration plant, from the chimney, at a time (the 1970’s) when fume de-pollution by means of old dust separators was not as efficient as the nowadays air pollution control systems (Chandler et al., 1997)
In site B (BR), contents are homogeneous and low (1.05 and 0.79 ng I-TEQ.kg^{-1} DM).

Contrary to site A, it seems that no particular source of pollution has an effect on the vertical profile of content.

Site C (CR) shows intermediate values between the two previous ones i.e. 5.40 and 6.49 ng I-TEQ.kg^{-1} DM for the upper and the lower samples respectively. Site C is not located in the vicinity of a particular source of PCDD/F, but it is however located in a large urban area with several potential sources.

### 5.5. Distribution of PCDD/F congeners in the road structure

Results related to the distribution of the different PCDD/F congeners (Tetra, Penta, Hexa, Hepta and Octa) in the MSWI residues, on geo-textiles samples, and in the road soils, for all sites, are illustrated by the example of site A trench T2 (Figure 3) and site C (Figure 4).

For site A, regarding the MSWI residue (AM2/14-29; AM2/35-45; AM2/45-65; AM2/65-85) they show the predominance of OctaCDD, and the secondary importance of HeptaCDD and HeptaCDF. For site C, they show the predominance of OctaCDD and OctaCDF in the MSWI residue and the secondary importance of HeptaCDD. The geo-textile of site C also show the predominance of OctaCDD and the secondary importance of HeptaCDD.

For MSWI residues, the distribution between dioxin and furan congeners is provided in Table 2. The proportion of dioxin congeners is of 50% for CM1 but it is higher for other samples: 73% for BM1; 74 to 79% for DM and 57 to 97% for AM.

The distribution between dioxin and furan congeners is provided in Table 4 for geo-textiles. In the geo-textile from site D, the proportion of dioxin congeners (74-75%) is
equivalent to that of the above MSWI residue. For site C, it is higher (69%) to that of the MSWI residue.

The distribution between dioxin and furan congeners is provided in Table 5 for road soils. For road soils, the proportion of dioxin congeners for all sites, ranges from 54 to 89%. For sites A, B and D it is comparable to the distribution observed for the MSWI residue. For site C, it is higher.

The distribution between dioxin and furan congeners is provided in Table 6 for reference soils. It is comparable to that of the respective road soils, 85% for B\textsubscript{R}; 72% for C\textsubscript{R}; 69 to 90 for A\textsubscript{R}.

The toxicity of PCDD/F varies substantially depending on the different congeners. It is generally agreed that only 17 out of the 210 dioxin and furans congeners are toxic.

The examination of is 2,3,7,8-TetraCDD content in the different samples of MSWI residue samples, geo-textiles, road soils and reference soils, reveals that its amount in road soils is very low.

For road soils (Table 5), contents range from less than 0.04 ng.kg\textsuperscript{-1} (samples A\textsubscript{S2/85-90} and D\textsubscript{S2/35-45}) to 2.35 ng.kg\textsuperscript{-1} (sample A\textsubscript{S1/42-52}), not very different from those of reference soils (Table 6), ranging from less than 0.01 ng.kg\textsuperscript{-1} (samples B\textsubscript{R/0-20 and C\textsubscript{R/0-5}) to less than 0.9 ng.kg\textsuperscript{-1} (sample A\textsubscript{R/0-20}).

As a matter of comparison, for MSWI residues (Table 2), the 2,3,7,8-TetraCDD content is below 1.5 ng.kg\textsuperscript{-1} for site A, and \leq 50 ng.kg\textsuperscript{-1} for sites B, C and samples D\textsubscript{M1} and D\textsubscript{M3}. Sample D\textsubscript{M2} content is 190 ng.kg\textsuperscript{-1}. For geo-textiles (Table 4), contents are from 6.8 to 57.5 ng.kg\textsuperscript{-1}.

6 Discussion

6.1 Characterization of MSWI residues
6.1.1 PCDD/F contents

A great heterogeneity of MSWI residue PCDD/F contents, i.e. a factor 154 from 14.0 (A_{M1}) to 2160 ng I-TEQ.kg^{-1} DM (D_{M2}) is observed between sites. A great heterogeneity can also be observed in a site such as A (a factor 16 between 14.0 and 227 ng I-TEQ.kg^{-1} DM).

The lowest recorded value (14.0 ng I-TEQ.kg^{-1} DM for A_{M1-12-24}) is in the middle of the range of values reported by Damien (1997) for bottom ash produced by recent incinerators in France in the 1990’s (4.0 to 20.6 ng I-TEQ.kg^{-1} DM). All other contents are two times to 100 times above the maximum value recorded by Damien. Such results are also well above the contents reported by Badreddine and Drouadaine (2006) on MSWI bottom ash from recent incineration and treatment facilities (i.e. around 10 ng I-TEQ.kg^{-1} DM) (Figure 5). Highest values (M_D) are even above the highest value (i.e. 1500 10 ng I-TEQ.kg^{-1} DM) reported by Sakai et al. (2000b) for Japan. A comparison showing difference between MSWI residue from the old and from recent site was proposed in figure 5.

6.1.2 Importance of the fine fraction

The analyses of size distribution of MSWI residues have shown an important proportion of the fine fraction.

The possible relation between the particle size and the PCDD/F content was postulated in an earlier study (Badreddine et al., 2003). The good relation between the PCDD/F content and the particle size demonstrates that the fine fraction is enriched with PCDD/F compounds. The sub-sample with the finest fraction (< 0.1 mm) shows by far a higher PCDD/F content (6590 ng I-TEQ.kg^{-1}), 7 times above the other particle fractions. As the fraction below 0.1 mm represents less than 10% of the
all graded aggregate (MSWI residue), this means that at least 659 ng I-TEQ.kg\(^{-1}\) (i.e. 33\%) of the 1960 ng I-TEQ.kg\(^{-1}\) of the whole material (sample D\(_{M1/30-60}\)), are included in the finest fraction.

These results confirm the assumption of the relation between the high value of the PCDD/F and the presence of fly ash mixed with bottom ash before 1991 in France. Indeed, the PCDD/F levels in fly ash are generally much higher than in bottom ash (Mac Kay, 2002). Chang and Chung (1998) reported values between 41 ng.g\(^{-1}\) and 703 ng.g\(^{-1}\) DM for MSWI fly ash).

Considering on one hand the range figures provided by Damien (1997) for MSWI bottom ash (39 to 648 ng I-TEQ.kg\(^{-1}\)) and for MSWI fly ash (765 to 4815 ng I-TEQ.kg\(^{-1}\)), and on the other hand the ratio of production between bottom ash (250 kg.ton\(^{-1}\)) and fly ash (20 kg.ton\(^{-1}\)) from incineration, one reaches the range of 67 to 814 ng I-TEQ.kg\(^{-1}\) for a theoretical mixture of bottom and fly ash. PCDD/F contents observed for MSWI residues from site A trench T2 (A\(_{M2}\)), from site B (B\(_{M1}\)) and site C (C\(_{M1}\)) are in this range. The sample from site A trench T1 is below, but those from site D are two times above the highest value of the theoretical range.

6.1.3 Mobility of PCDD/F

Very low PCDD/F releases were assert (0.0219 and 0.0441 ng I-TEQ.kg\(^{-1}\)). Compared to the total content of PCDD/F compounds in the respective MSWI residue samples (i.e. 721 ng I-TEQ.kg\(^{-1}\) DM for B\(_{M1/35-60}\) and 1960 ng I-TEQ.kg\(^{-1}\) DM D\(_{M1/10-30}\)), the released fractions are respectively 0.003 and 0.002\% of the total PCDD/F amount.

The low value recorded can be linked to the low solubility of the PCDD/F and the presence of the PCDD/F in the particles superior to 0.45 µm (Badreddine et al.,
2003). Depending on congeners, solubility values are comprised between 0.74 \times 10^{-7} and 3.75 \times 10^{-3} for PCDD (Inserm, 2000) and between 4.19 \times 10^{-4} and 1.16 \times 10^{-6} for PCDF (OMS, 1997).

6.2 Assessment of PCDD/F fate

6.2.1 PCDD/F contents of road soil

The heterogeneity among all road soil PCDD/F contents, i.e. a factor 9 between 0.74 (A_{S1}) and 7.23 ng I-TEQ.kg^{-1} DM (B_{S1}) is far lower than among MSWI residues. Such values are low in comparison to those reported by Nominé (1999) for soils of urban areas in the absence of neighbouring sources of pollution (from <1 to more than 30 ng.kg^{-1} I-TEQ.kg^{-1} DM), for soils nearby MSW incineration plants (more than 1000 ng.kg^{-1} I-TEQ.kg^{-1} DM), and even to those of soils of pasture in Europe (from <1 to 43 ng.kg^{-1} I-TEQ.kg^{-1} DM).

6.2.2 Comparison to reference soils’ contents

In order to assess the state of road soils, comparison can be made with their respective reference soils. Depending on the context (more or less potential sources of pollution in the area), the difference between them is negative (site B), negligible (site A), or even positive (site C where pollution sources affect the reference soil).

Indeed, regarding Site B, the ratio between the average contents in road soil (3.9 ng I-TEQ.kg^{-1} DM) and the reference soil (0.92 ng I-TEQ.kg^{-1} DM) is around 4.

Regarding Site A, depending on the consideration of sample A_{R/0-20} or not in the comparison, one can consider that the PCDD/F content in the road soil is lower (9 times) or slightly higher (1.04 ng I-TEQ.kg^{-1} DM in average for road soil vs 0.44 ng I-TEQ.kg^{-1} DM in average for reference soil) in trench T1. Considering trench T2, the
conclusion is the same, i.e. respectively 4 times lower, or slightly higher (2.17 ng I-TEQ.kg\(^{-1}\) DM in average for road soil vs 0.44 ng I-TEQ.kg\(^{-1}\) DM).

In the case of Site C, the content in the road soil sample (C\(_{S1/88-93}\)) is 2 times lower than in the reference soil (5.94 ng I-TEQ.kg\(^{-1}\) DM in average). Located in a large urban area, references soil of Site C can have been affected for years by several sources, which can lead to a situation similar as for Site A.

6.2.3 Comparison to MSWI residues’ contents

Some vertical profiles of PCDD/F contents in road soils (sites A and B) show decreasing values from the upper sample, downward, indication of a possible contact effect of the MSWI residue layer. Contents in the road soil are however low and the transition with the MSWI residue layer with high contents, is very well marked.

For sites A and B, where the influence of the geo-textile is not susceptible to interfere, the ratio between the road soil upper sample content and the MSWI residue layer content can serve as an indicator. Regarding Site A trench T1, this ratio (1.35 vs 14.0 ng I-TEQ.kg\(^{-1}\) DM) is 9.6%, and for trench T2 (2.98 vs 101 ng I-TEQ.kg\(^{-1}\) DM in average) it is 2.9% (the MSWI residue content is 101 ng I-TEQ.kg\(^{-1}\) DM in average). Regarding Site B, the ratio (7.23 vs 721 ng I-TEQ.kg\(^{-1}\) DM) is only 1.0%.

For sites with geo-textiles, such ratios are 1.2% for site C (2.87 vs 235 ng I-TEQ.kg\(^{-1}\) DM), or lower for site D, i.e. 0.04% for trench T1 (0.86 vs 1960 ng I-TEQ.kg\(^{-1}\) DM) and 0.1% for trench T2 (2.22 vs 2160 ng I-TEQ.kg\(^{-1}\) DM).

6.3. Role of geo-textiles

The PCDD/F load of geo-textiles compared to the content of the MSWI residue located just above is equal to 74% of the latter in the case of site C (C\(_{G1}/C_{M1}\)). For
site D, such ratios are equal to 86% in the case of trench T1 ($D_{G1}/D_{M1}$) but only 35% in the case of trench T2 ($D_{G2}/D_{M2}$).

In order to assess the role of geo-textiles toward the possible PCDD/F transfer, their load can also be compared to the content of the road soil upper sample. In the case of site C, Such ratio is 61 ($C_{G1}/C_{S1}$), and it is higher in the case of site D, 1860 for trench T1 ($D_{G1}/D_{S1}$), and 339 for trench T2 ($D_{G2}/D_{S2}$).

The role of the geo-textile inserted between the MSWI residue layer and the road soil should be clarified: may be it acts as a filter toward the transfer of fine particles downward. But may be the porosity of the road soil in itself is low enough to act as a filter, which would explain the slightly higher PCDD/F contents in some road soil upper samples.

7 Conclusion

This study shows that some MSWI residues used for road construction before the enforcement of the 1991 order can contain very high amount of PCDD/F compared to the MSWI bottom ash produced and used afterward. The heterogeneity between MSWI residues can be great from one road site to another but also on a single site. The important contribution of the fraction below 0.1 mm to the MSWI residue total contents of PCDD/F was asserted. Crossed with leaching test results, this indicates that the fraction between 0.45 and 100 μm should be investigated in more detail in order to specify the most loaded particle sizes.

As a whole, road soils PCDD/F contents are below the contents recorded for ordinary urban or rural soils, and consequently, no significant difference is observed with local
reference soils. This indicate the absence of transfer of MSWI residue to the road soil.

In addition, thanks to the very low proportion of the 2,3,7,8-TetraCDD congener, the noxiousness of road soils is reduced. In the presence of geo-textile or not, the PCDD/F content reduction between the MSWI residue and the road soil is great. The role of the geo-textile inserted between the MSWI residue layer and the road soil should be clarified.

Considering the improvements brought by the enforcement of the 1991 order regarding the fate of MSWI fly ash and those brought by the more recent air pollution control systems, the diagnosis achieved thanks to this study provides a rather positive and reassuring insight concerning the effect of today produced and used MSWI bottom ash in road construction.

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- Service d’Etudes Techniques des Routes et Autoroutes (SETRA) and Laboratoire Central des Ponts et Chaussées (LCPC), 2000. Réalisation des remblais et des couches de formes (Construction of embankments and capping layers), SETRA, Paris, France.


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### Table 1: Overview of the set of samples

<table>
<thead>
<tr>
<th>Site</th>
<th>A</th>
<th>B</th>
<th>C</th>
<th>D</th>
</tr>
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<tbody>
<tr>
<td>Material (M)</td>
<td>A&lt;sub&gt;M1&lt;/sub&gt;, A&lt;sub&gt;M2&lt;/sub&gt;</td>
<td>B&lt;sub&gt;M1&lt;/sub&gt;</td>
<td>C&lt;sub&gt;M1&lt;/sub&gt;</td>
<td>D&lt;sub&gt;M1&lt;/sub&gt;, D&lt;sub&gt;M2&lt;/sub&gt;, D&lt;sub&gt;M3&lt;/sub&gt;</td>
</tr>
<tr>
<td>Geo-textile (G)</td>
<td>-</td>
<td>-</td>
<td>C&lt;sub&gt;G1&lt;/sub&gt;</td>
<td>D&lt;sub&gt;G1&lt;/sub&gt;, D&lt;sub&gt;G2&lt;/sub&gt;</td>
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<tr>
<td>Road soil (S)</td>
<td>A&lt;sub&gt;S1&lt;/sub&gt;, A&lt;sub&gt;S2&lt;/sub&gt;</td>
<td>B&lt;sub&gt;S1&lt;/sub&gt;</td>
<td>C&lt;sub&gt;S1&lt;/sub&gt;</td>
<td>D&lt;sub&gt;S1&lt;/sub&gt;, D&lt;sub&gt;S2&lt;/sub&gt;, D&lt;sub&gt;S3&lt;/sub&gt;</td>
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<tr>
<td>Reference soil (R)</td>
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### Table 2: PCDD/F contents of MSWI residues

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<td>Sample</td>
<td>A&lt;sub&gt;M1/12-24&lt;/sub&gt;</td>
<td>A&lt;sub&gt;M2/14-19&lt;/sub&gt;</td>
<td>A&lt;sub&gt;M2/35-45&lt;/sub&gt;</td>
<td>A&lt;sub&gt;M2/45-65&lt;/sub&gt;</td>
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<td>ITE (ng I-TEQ.kg&lt;sup&gt;-1&lt;/sup&gt; DM)</td>
<td>14.0</td>
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<td>78.7</td>
<td>227</td>
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<tr>
<td>2,3,7,8-TetraCDD (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>0.79</td>
<td>1.46</td>
<td>&lt; 0.33</td>
<td>&lt; 2.15</td>
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<td>7 Dioxin congeners (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>691</td>
<td>8176</td>
<td>1643</td>
<td>3436</td>
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<tr>
<td>10 Furan congeners (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>94</td>
<td>211</td>
<td>830</td>
<td>2576</td>
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<td>Dioxin (%)</td>
<td>88</td>
<td>97</td>
<td>66</td>
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### Table 3: PCDD/F contents from eluates

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<td>Sample</td>
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<td>C&lt;sub&gt;M1/50-88&lt;/sub&gt;</td>
<td>D&lt;sub&gt;M1/10-30&lt;/sub&gt;</td>
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<tr>
<td>ITE (ng I-TEQ.kg&lt;sup&gt;-1&lt;/sup&gt; DM)</td>
<td>721</td>
<td>235</td>
<td>1960</td>
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<tr>
<td>2,3,7,8-TetraCDD (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>21.6</td>
<td>9.16</td>
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<td>7 Dioxin congeners (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
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<td>10 Furan congeners (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
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<tr>
<td>Dioxin (%)</td>
<td>73</td>
<td>50</td>
<td>75</td>
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### Table 4: PCDD/F loads of geo-textiles

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<tr>
<td>Sample</td>
<td>C_{G1}</td>
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<tr>
<td>ITE (ng I-TEQ.kg(^{-1}) DM)</td>
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<td>1600</td>
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<tr>
<td>2,3,7,8-TetraCDD (ng.kg(^{-1}))</td>
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<td>7 Dioxin congeners (ng.kg(^{-1}))</td>
<td>5346</td>
<td>74545</td>
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<tr>
<td>10 Furan congeners (ng.kg(^{-1}))</td>
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<tr>
<td>Dioxin (%)</td>
<td>69</td>
<td>74</td>
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### Table 5: PCDD/F contents of road soils

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<td>Sample</td>
<td>A_{S1/32-37}</td>
<td>A_{S1/37-42}</td>
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<td>ITE (ng I-TEQ.kg(^{-1}) DM)</td>
<td>1.35</td>
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<td>2,3,7,8-TetraCDD (ng.kg(^{-1}))</td>
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<td>7 Dioxin congeners (ng.kg(^{-1}))</td>
<td>46.2</td>
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<td>10 Furan congeners (ng.kg(^{-1}))</td>
<td>10.9</td>
<td>7.8</td>
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<td>Dioxin (%)</td>
<td>81</td>
<td>89</td>
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<td>C_{S1/88-93}</td>
<td>D_{S1/30-35}</td>
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<td>ITE (ng I-TEQ.kg(^{-1}) DM)</td>
<td>2.87</td>
<td>0.86</td>
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<td>2,3,7,8-TetraCDD (ng.kg(^{-1}))</td>
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<td>7 Dioxin congeners (ng.kg(^{-1}))</td>
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<td>10 Furan congeners (ng.kg(^{-1}))</td>
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<td>Dioxin (%)</td>
<td>70</td>
<td>87</td>
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Table 6: PCDD/F contents of reference soils

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<td>ITE (ng I-TEQ.kg&lt;sup&gt;-1&lt;/sup&gt; DM)</td>
<td>9.4</td>
<td>0.67</td>
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<td>2,3,7,8-TetraCDD (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>&lt; 0.9</td>
<td>0.05</td>
<td>&lt; 0.02</td>
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<td>7 Dioxin congeners (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>216.8</td>
<td>58.5</td>
<td>41.9</td>
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<td>10 Furan congeners (ng.kg&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>98.7</td>
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<td>7.1</td>
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<tr>
<td>Dioxin (%)</td>
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<td>89</td>
<td>86</td>
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