Speciation of organometallic compounds of Hg, Sn, and Pb in the market garden soil in Ngaoundéré (Cameroon)

Eric Noubissié^{1,2,3} · Martin Benoît Ngassoum² · Ahmed Ali³ ·
Joaquim Castro-Georgi¹ · Olivier F. X. Donard¹

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Abstract The objective of this work is to study the contamination of market garden soils by organomercury compounds (OMC), organotin compounds (OTC), and organolead compounds (OLC) using combustion debris (CD) as fertilizers. Therefore, two parcels of land used for gardening are rented on two sites. Soils were plowed and amended with CD. Samples of non-amended and amended soils were treated and then organometallic compounds of Hg, Sn, and Pb were analyzed by GC-ICP-MS. The results obtained revealed the presence of methyl-mercury (MeHg) in the soil at concentrations varying from non-detected in

non-amended soil to 171.6 µg/kg in amended soil. Among the OLC identified, tetra-ethyl-lead (TEtPb) is the most represented in the soil with concentrations ranging from 18.45 to 44,612 µg/kg. OTC has also been identified with a predominance of mono-butyl-tin (MBT) followed by trimethyl-tin (TMT) and di-methyl-tin (DMT). Soil treatments to CD have a significant influence on soil contamination to OMC, OTC, and OLC. This means that a significant amount of organometallic compounds found in amended soils would come from either direct or indirect CD.

Keywords Market garden soil · Contamination · Organometallic compounds · Hg · Pb · Sn

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✉ Eric Noubissié
noubissieerik@yahoo.fr
Martin Benoît Ngassoum
ngassoum@yahoo.fr
Ahmed Ali
aliahmed_k10@yahoo.fr
Joaquim Castro-Georgi
joaquim@hotmail.com
Olivier F. X. Donard
olivier.donard@univ-pau.fr

¹ Laboratoire de Chimie Analytique Bio Inorganique et Environnement (LCABIE), UMR 5254, CNRS-Université de Pau, Hélioparc, 2 Avenue du Président Angot, 64053 Pau Cedex 9, France

² Laboratoire de Chimie Industrielle et Bioressource (LCIB), Ecole Nationale des Sciences Agro-Industrielles (ENSAI), Université de Ngaoundéré, PB 455, Ngaoundéré, Cameroon

³ Laboratoire de Génie Chimie et Environnement (LGCE), Institut Universitaire de Technologie (IUT), Université de Ngaoundéré, BP 455, Ngaoundéré, Cameroon

Introduction

Urban agriculture is still tarnished by poor agricultural practice in several countries. In the town of Ngaoundéré (Cameroon) for example, in order to amend the soil and promote the growth of vegetables, some farmers use leachates and debris from urban waste combustion originating from landfills. Indeed, farmers go to the urban landfills that are near the fields, burn the garbage, and recover combustion debris (CD) to enrich soil before growing vegetables. Therefore, the farmed soils and the vegetables harvested are directly contaminated with metals such as Cr, Cu, Ni, Zn, Co, Cd (Adjia et al. 2008; Pasquini and Alexander 2004) and with Hg, Sn, and Pb as Noubissié et al. (2016) have recently shown. However, identification and quantification of the metal in a soil is not sufficient to make a full risk assessment. This is why this first study must be supplemented by the study of speciation of metals identified in this soil. And to be complete, the study of the speciation of metals in a soil is often carried out in two

stages. The first approach of the speciation study examined the mobility of metals in the soil by using sequential extraction studies for elements such as Cd, Pb, Cu, Zn, and Cr, which demonstrated high mobilization potential in the oxydable, acido-soluble, and exchangeable forms from the soils (Noubissie et al. 2011; Mancean et al. 2000; Garra-brants and Kosson 2000). The present work, which consists of the study of organometallic compounds such as Hg, Sn, and Pb in soil, is the continuation of this previous work on market garden soil in Ngaoundéré carried out by Noubissie et al. (2016).

Different species have been selected since they can be present in the solid wastes used to amend the soil as combustion debris. These metal species in organometallic form can originate from different sources. Organomercury compounds (OMC) are naturally present in the environment (Marvin-DiPasquale et al. 2013; Hammerschmidt et al. 2004) and are very toxic (Scheuhammer et al. 2007; Mergler et al. 2007). They can be produced in the soils or in the landfill leachate via methylation reactions (abiotic or biotic) and will yield mono-methyl-mercury (MMeHg), which is the most stable species (Benoit et al. 1999; Gilmour et al. 1998; St. Louis et al. 1994). Organotin compounds (OTC) can also originate from the methylation of tin, generating methyltin compounds (Huang and Matzner 2004a), but they are much more likely present in soil from the degradation of plastics with much higher molecular weights (alkyltins such as butyltins originating from stabilizers) or phenyltins (used in agricultural practice) (Heroult et al. 2008; Yen et al. 2001; Kannan and Lee 1996; Krugh and Miles 1996). A major environmental problem of OTCs is their persistence in soil. Thus, there is a high potential that they will contaminate crops grown on such soils. For example, the half-life of tri-butyl-tin (TBT) would range from 1 day to 4.4 years and that of tri-phenyl-tin (TPhT) from 8 to 140 days (Paton et al. 2006; Yen et al. 2001). Finally, organolead compounds (OLC), such as tetra-ethyl-lead (TEtPb) and tetra-methyl lead (TMPb), are most likely to come from the petrol used to trigger and promote the burning of the wastes and can also directly result from deposition of atmospheric emissions. Indeed, a few years ago, alkyl-leads were still used as an antiknocking agent in petrol in some European countries such as Spain despite its prohibition (Encinar et al. 2001; Leal-Granadillo et al. 2000; Van Cleuvenbergen et al. 1990). The use of these alkyl-leads are also banned in some African countries such as South Africa and Morocco (Monna et al. 2006, 2011), but it is likely that these compounds are still used in most of sub-Saharan Africa. Research has been conducted on the presence of OMC (Bachand et al. 2014; Marvin-DiPasquale et al. 2013; Cattani et al.

2008; Wong et al. 2011; Huang et al. 2003) and OTC (Heroult et al. 2008; Marcic et al. 2006; Huang and Matzner 2004a; Huang et al. 2003; Bancon-Montigny et al. 2000; Hoch 2001; Schnaak et al. 1997; Barug and Vonk 1980) in soils, but very few have been conducted on OLC in soils (Winter and Gallert 2004; Huang et al. 2003; Chau et al. 1997).

In this study, we have evaluated the potential contamination of vegetable growing on soils that are consistently amended with combustion debris. The work presented here consists of the speciation study of organometallic compounds in market garden soils in Ngaoundéré and the impact of the fertilization of soil by combustion debris (CD).

Materials and methods

Experimental sites

This work is a follow-up to the study of Noubissie et al. (2016). Thus, we have reproduced the same procedures for the preparation of farmed soils as routinely practiced in situ by farmers using CD to amended market garden soils. This cultural practice is a tradition that has been operated for at least 10 years. Two of the five sites commonly exploited for urban and suburban agriculture in the town of Ngaoundéré were chosen on the basis of previous studies (Adjia et al. 2008), which have already made a preliminary assessment of metal accumulation and transfer via this practice. This study was conducted on the most contaminated sites based on the previous studies. They are located in the Bali quarter (7°19'01,22"N; 13°35'01,42"E; altitude, 1114 m) and in the Sabongari railway station quarter (7°19'55,93"N; 13°35'44,55"E; altitude, 1096 m) close to a river (in the town of Ngaoundéré). Figure 1 show the experimental setup of the soil preparation applied on both sites and the sampling points on the ridge. A typical lot of farmland per site was rented and organized into ridges of 3-m length and 0.5-m width. The initial specific amendment was done once at the beginning of study by bringing 20 l of CD from the nearby urban rubbish dumps. They were collected and spread on the ridges, and the amended ridges were irrigated for 3 weeks twice a day with water from the nearby river. We must specify that the soils from both sites were treated in the same way, so there is no reference site, but there are rather two types of soil samples of which a non-amended soil represents the reference.

Samples

Figure 2 shows the description of the different soil samples taken. Before spreading the combustion debris (CD) on the

Fig. 1 Experimental setup of the soil preparation applied on both sites and the sampling points on the ridge

Fig. 2 Description of the different soil samples taken. **a** Non-amended soil with combustion debris (CD): SnCDS1 and SnCDS2. **b** Amended soil with combustion debris (CD) after 3 weeks of irrigation: SaCDS1 and SaCDS2

soils, initial reference soil samples non-amended with CD were collected, at 20-cm depth, which represents the maximum depth reached by the roots of the vegetables on

sites 1 and 2, respectively (SnCDS1 and SnCDS2) as shown in Fig. 2a. Another sample of soil amended with CD was taken (SaCDS1 and SaCDS2) at a depth of 20 cm,

after 3 weeks of irrigation with the water from river Soum-soum, which runs through the two experimental sites (Fig. 2b). The primary sources of amendment [combustion debris (CD)] were directly sampled. These CDs are a mixture of soil and ash, which is the product of the combustion from household waste. All samples were at first characterized according to general soil parameters such as acidity, conductivity, cationic exchange capacity, organic matter, and metals content (Table 2 of supplementary materials).

Reagents and reference material

Reagents used for the extractions are of ultrapure analytical quality, like instar nitric acid—(JT BAKER) and ultrapure water of resistivity 18.2 MΩ cm (Millipore). For the analysis, the derivatization of metal species was performed with sodium tetrapropylborate (NaBPr₄). It was purchased from Merseburger Spezialchemikalien. Analytical standards of methyl-mercury (MeHg), methyl lead (MePb), tetraethyl lead (TEtPb), methyl tin (MT), butyl tin (BT), and phenyl tin (PhT) were purchased from Sigma-Aldrich (St. Louis, MO, USA).

Speciation of organometallics

Extraction of organometallic compounds

The analytical procedure for the organometallic compounds assessment was developed to simultaneously have a good estimation of the concentrations of the organometallic compounds, since they globally have similar general physico-chemical properties for a first approach of assessment of contamination. The common extractions of organometallic compounds were performed to have a first global assessment of occurrence rather than a full quantitative context. Under the basis of their physical properties, which have a fairly large spread in boiling points but overall physico-chemical properties, we have used methods previously developed in the laboratory showing that organotin and organomercury compounds can be simultaneously extracted from simple (as water and snow) or biological matrices with high confidence (Monperrus et al. 2003, 2005). We have also adapted the procedure from Lespes et al. (2009).

Since all extraction procedures are quite similar for both organometallic compounds of Hg and Sn, we have extended an investigation directly to the alkyl-leads present in the samples. The extractions on each sample were performed on an open focused microwave system (CEM discover SP-D 80) and we repeated them three times. For a sample size of 0.1 g of soil, we added 4 ml of HNO₃ (6N) and filled it up to 5 ml in the quartz tubes. The tubes were placed in the microwave system and the mixtures digested

at 70 °C for 5 min at a power of 90 W, which has been demonstrated in the laboratory to extract the organometallic compounds quantitatively. The alkyl-leads having the same physicochemical properties were simultaneously extracted and derivatized produce. After cooling, the extracts and analytes were derivatized with the addition of solution of 2.5% NaBPr₄.

Derivatization

The derivatization step was conducted following the method of Lespes et al. (2009). In a 22-ml glass tube, 5 ml of MilliQ water, 100 µl of extract, and 5 ml of acetate buffer solution (pH = 5) were mixed. After verifying that the pH of the mixture was 5.0, 1 ml isooctane and 500 µl of NaBPr₄ (2.5%) were added and the mixture was manually shaken for 5 min. The organic phase was recovered, transferred to GC vials, and analyzed by GC-ICP-MS (using the operating conditions shown in Table 1 on supplementary materials).

Analytical performance and method validation

In order to validate the method, a series of experiments was performed to assess the stability and recovery of the organometallic moieties using standard additions on a series of test samples. The three series of organometallic compounds derivatization were performed with the analytical standards solutions. In a 22-ml glass tube, 5 ml of acetate buffer solution was added to 50, 100, 200, and 400 µl of a 5 ng/ml working standard solution containing organotin species. The same volumes were used for working with standard solutions containing organolead species. However, there were 5, 10, 20, and 40 µl of a 100 ng/ml working standard solution containing MeHg which were used. The pH of each solution was adjusted to 5.0 using HCl or NH₄OH, if necessary. Next, 1 ml isooctane and 500 µl of 2.5% NaBPr₄ were added and the vial was capped and shaken for 5 min. The organic phase was then transferred to a GC vial for analysis. The blank solutions were prepared in the same manner for the determination of detection limits and to characterize any contamination likely to occur during the preparation step.

The analytical response characteristics were determined for the three organometallic compounds. The calibration curves were generated for MT, BT, PhT, TEtPb, TMePb, and MeHg compounds through triplicate injections of 2 µl across a concentration range from 0 (i.e., analytical blank) to 2 ng/g in isooctane. Good linearity and satisfactory coefficients of correlation (R^2 values) were observed for the ¹²⁰Sn, ²⁰⁸Pb, and ²⁰²Hg response functions. The limits of detections (LOD) were determined from each calibration response function, and they were in the range

Table 1 Chemical forms and retention times of organometallic compounds identified in the soils samples

Compounds	Rt (min)	LOD (ng/g)
Inorganic lead (iPb) ^a	7.25	–
Mono-methyl lead (MMPb) ^a	6.67	–
Tetra-methyl-lead (TMePb)	4.71	0.0037
Mono-ethyl-lead (MEtPb)	6.97	–
Tetra-ethyl-lead (TEtPb)	6.83	0.004
Inorganic mercury (iHg)	5.96	0.0035
Mono-methyl-mercury (MMeHg)	4.40	0.0036
Mono-methyl-tin (MMT)	3.47	0.0038
Di-methyl-tin (DMT)	5.45	0.0041
Tri-methyl-tin (TMT)	6.59	0.0043
Inorganic tin (iSn)*	7.49	0.0038
Mono-butyl-tin (MBT)	7.64	0.0039
Di-butyl-tin (DBT)	7.85	0.0036
Tri-butyl-tin (TBT)	7.92	0.0046

LOD limit of detection, Rt retention time

^a Non-analyzed compound

0.0036–0.0051 ng/g as metal. The chemical forms' retention times and LOD of organometallic compounds found in the soil are shown in Table 1.

Results

The values of Hg, Sn, and Pb totals for all samples collected were obtained in the preliminary work performed by Noubissié et al. (2016). They are displayed in Table 3 of the supplementary material. The main results obtained on all the samples analyzed show that a wide variety of organometallic compounds are present in all samples at various concentrations.

Organomercury compounds (OMC)

A typical GC–ICP/MS chromatogram is presented in Fig. 3a performed on an amended soil. This chromatogram has practically the same configuration as the chromatograms obtained on the other soil samples. It displays that the inorganic Hg species is the most abundant in all samples. The organomercurial form identified on this chromatogram is methyl-mercury (MeHg), precisely mono-methyl-mercury, but it is worth mentioning that we will not discuss the iHg concentration levels because the analytical procedure was developed to optimize the simultaneous detection of all organometallic compounds of Hg, Sn, and Pb. The levels of OMC identified in the soil samples are shown in Table 2. MeHg is identified at concentrations varying from non-detected to 20 µg/kg in non-amended soil samples. The amended soil samples display much higher levels with a

maximum of 172 µg/kg. The elevated levels of MeHg represent only 1.2% of the total Hg found in all the soil samples analyzed. This is the typical value of methylation levels in samples.

Organotin compounds (OTC)

A typical chromatogram of organotins in an amended soil is displayed in Fig. 3b. There are large arrays of the organotin family, originating most likely from different sources. The OTC identified in the soil are divided into two groups: methylated tins (MT) and butyl-tin (BT). They represent an average of 0.14% for total Sn found in the soil of the two sites. As displayed in Fig. 3b, the order of occurrence is first for methylated tins followed by butylated tins. In terms of overall abundance, the BT constitute the major groups of OTC with 51.39%. In these soils, tri methyl tin (TMT) is the majority organotin with a representation of 29.97% on both sites, while tri butyl tin (TBT) represents the minority compound (0.65%). In general, the organotin levels are more abundant in the amended soils. In Fig. 4, a treatment effect can be observed due to the increase of OTC in the soil with the addition of CD. Indeed, the addition of CD to the soil globally increases the average concentration of MT and BT to 1.68 ± 0.70 and 1.92 ± 0.40 µg/kg, respectively.

Organolead compounds (OLC)

It is very interesting to see that organolead compounds can also be evidenced in amended soils; the typical chromatograms are displayed in Fig. 3c. Five peaks are generally observed, but only four could be identified based on available standards or on chromatographic retention times. Tetra-methyl-lead (TMePb) is identified as the first peak; tetra ethyl lead (TEtPb) is the second, and mono-ethyl-lead (MEtPb) is the fourth peak. The fifth peak is inorganic lead (iPb). The third peak on the OLC chromatogram in Fig. 3c was not identified based on standards, which are not available. However, using the retention time by Kovats (1958), IUPAC (2006), it would suggest that this little peak would either be a mono methyl lead (MMePb) or a di-ethyl lead (DEtPb). We decided to not follow though the third peak identification, since this peak was observed only in one sample. The levels of OLC identified in the soil are shown in Table 2. They represent an average 11.71% of total Pb found in the soil of the two sites. TEtPb is the most abundant with 99.95% of the OLC identified, followed by MEtPb (0.048%) and TMePb (0.004%). Globally, we notice a significant increase of the concentrations of the OLC on the amended soils with CD. The report previously made on the results of the total extractions of Pb (Table 5 in the supplementary materials), brings us to believe that the CD used in amending the soils could well be

Fig. 3 GC-ICP-MS chromatogram of OMC, OTC and OLC in one of amended soils sample. **a** GC-ICP-MS chromatogram of OMC: the first is mono-methyl-mercury (*MMHg*), and the second is inorganic mercury (*iHg*). **b** GC-ICP-MS chromatogram of OTC: Mono-methyl-tin (*MMT*), Di-methyl-tin (*DMT*), Tri-methyl-tin (*TMT*),

inorganic tin (*iSn*); Mono-butyl-tin (*MBT*), Di-butyl-tin (*DBT*), Tri-butyl-tin (*TBT*). **c** GC-ICP-MS chromatogram of OLC: the first is tetra-methyl-lead (*TMePb*), the second is tetra-ethyl-lead (*TEtPb*), the third is mono-methyl lead (*MMePb*), the fourth is mono-ethyl-lead (*MEtPb*), and the fifth is inorganic lead (*iPb*)

responsible for the considerable increase of the OLC in the amended soil samples (SaCD).

Discussion

The occurrence of organometallic compounds of Hg, Sn, and Pb is a critical issue to be mentioned here. Indeed, it is not surprising to find them in the different soils and more

specifically in the amended soils. Their presence may most certainly come from different origins discussed below.

Organomercury compounds

The main species of Hg in the study is methyl mercury. Its presence in the soil samples may have several origins. At first, inorganic Hg can be directly methylated in the soils naturally by bacteria. This hypothesis is likely, since it

Table 2 OMC, OLC, and OTC in non-amended soils (SnCD) and amended soils (SaCD)

Samples	OMC		Organolead compound				Organotin compounds													
	MeHg (µg/kg)		TMePb (µg/kg)		TEtPb (µg/kg)		MEtPb (µg/kg)		MMT (µg/kg)		DMT (µg/kg)		TMT (µg/kg)		MBT (µg/kg)		DBT (µg/kg)		TBT (µg/kg)	
	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max	min	max
SnCDS1	nd		0.29	0.55	13.53	23.37	0.36	0.63	0.11	0.20	0.31	0.70	0.66	1.87	2.11	2.24	0.47	0.69	0.022	0.023
SaCDS1	67.13	148.23	0.53	0.81	24.334	34.787	7.86	35.40	0.38	0.82	0.52	1.06	1.30	4.32	4.10	4.18	0.18	0.26	0.054	0.059
SnCDS2	18.74	20.40	0.51	0.74	1130	1343	1.61	2.94	0.12	0.48	1.40	1.57	0.67	1.31	2.00	2.14	nd		0.029	0.038
SaCDS2	162.38	397.18	0.57	2.32	1025	76,132	4.62	7.18	0.18	0.61	0.40	1.89	1.40	3.66	3.93	4.04	0.19	0.24	0.044	0.083

SnCDS1 soil non-amended with combustion debris on site 1, *SrCDS2* soil non-amended with combustion debris on site 2, *SaCDS2* soil amended with combustion debris on site 1, *SaCDS2* soil amended with combustion debris on site 2, *MeHg* methylmercury, *TMePb* tetra-methyl-lead, *TEtPb* tetra ethyl lead, *MMT* mono methyltin, *DMT* dimethyltin, *TMT* trimethyl tin, *MBT* mono butyl tin, *DBT* dibutyltin, *TBT* tributyltin, *nd* non-detected

probably comes from the methylation of inorganic mercury (iHg) already present in the non-amended soil (Fleck et al. 2013; Marvin-DiPasquale et al. 2013). Figure 3a certainly testifies to the importance of the amendment of combustion debris to enhance the amount of methylmercury present in the surface samples. Further, to direct methylation procedures of Hg triggered by the addition of the CD by bringing methylating agents, it is also possible that there is already a large amount of MeHg in the combustion debris and that they are directly added to the soils. Furthermore, additional alkylating agent sources or direct MeHg may also come from the irrigation system. Indeed, the amended soils were irrigated for 3 weeks with the water of the river Soum-soum running through the two sites. This irrigation would certainly create favorable physical and chemical conditions for the methylation process of inorganic Hg in amended soil (Mauro et al. 1999). Also, it is even possible that the water of the river Soum-soum directly contains MeHg or alkylating agents because this river runs through the town of Ngaoundéré and is constantly an outfall for rain water and releases from households. Knowing that different methylation processes of inorganic Hg are favorable in surface waters (Celo et al. 2006; Roulet et al. 2000; Akagi et al. 1977), it is believed that the water of this river has also contributed to the Hg contamination on the amended soils.

Finally, this remark is also valid for other organometallic moieties studied here for Sn and Pb. It is also very likely that the amount of MMeHg identified in the soil could also come from the trans-methylation process due to the high levels of methylated compounds found. Indeed, the results displayed in Table 2 and Fig. 4 show the presence of methylated forms of lead and tin in non-amended and amended soil samples. This means it is possible that the amount of MMeHg may also be the result of transfer of a molecule of CH_3^+ from TMePb, TMT, or DMT already present in the non-amended and amended soil (Chau et al. 1997).

Organotin compounds

Budget calculations show that the OTC identified in the soils represents only 0.14% of total tin (TSn) present in the samples on average on both sites (Noubissié et al. 2016). However, they display an unsuspected diversity of family of alkyl tin ranging from methylated forms to much higher boiling point compounds that are butylated forms. The heavier alkylated forms such as butyltin curiously represent 51% of organotin compounds identified while the methylated forms represent 49%.

Similar to what has been discussed above for methylated mercury species, it is probable that the methylated forms of tin have the same origin, either it is formed in situ in the

Fig. 4 Organotin compounds in non-amended (SnCD) and amended (SaCD) soil, sites 1 and 2. **a** Methyl-tin (MT); Mono-methyl-tin (MMT), Di-methyl-tin (DMT), Tri-methyl-tin (TMT), **b** Butyl-tin (BT), mono-butyl-tin (MBT), Di-butyl-tin (DBT), Tri-butyl-tin (TBT)

soil catalyzed by the amendments, or by the combustion debris. The irrigation systems may also either favor the methylation reactions or directly bring the methylated forms to the soil samples. It is believed that their presence comes for the most part from anthropogenic intrusion of OTC as a natural transformation of inorganic tin (iSn) to OTC in the soil (Pichard et al. 2005). Hence, only a minority of the OTC present in the soil samples would come from the biological methylation of inorganic tin, like MMT, DMT, and TMT (Maguire 1992; Rapsomanikis et al. 1987). Some methylated forms may also be the result of the degradation of the larger methyltin molecules. This is the case of the TMT degradation, which could release DMT or MMT in the soil (Heroult et al. 2008).

Interestingly, it is worth mentioning that for the methylated forms of Sn, the trimethylated form is dominant. This is consistent with the study of Pinel-Raffaitin et al. (2006) who identified the same series of methylated species from landfill leachates with the highest number of trimethylated forms. This could suggest in our case that the combustion debris could be the major source of these methylated species.

The spectrum presented by the other butylated species with the most abundance of monobutyltin and dibutyltin compounds certainly suggests a direct origin from the degradation of plastics. Butyltin, and most specifically these two compounds, are abundant in a large array of plastics. The presence of these two butylated forms of tin in the soils, whether modified or not, is certainly due to the degradation of the plastic waste buried in these soils or in the CDs. It is established that these two derivatives of OTC are used as stabilizers in the manufacture of polyvinyl chloride (PVC) (Lytle et al. 2003). In Cameroon, particularly in the town of Ngaoundéré, there is a real problem of plastic waste management. Ignorance and carelessness of

individuals often result in the accidental presence of plastic wastes in streets and farms. Plastics are sometimes buried during plowing. Besides, plastic wastes sometimes constitute over 12% of household wastes in Cameroon. Thus, the use of products obtained from incinerating household wastes to enrich farm soil would certainly contaminate these soils with MBT and/or DBT.

Finally, the presence of TBT could be due to the use of biocides, for instance in the pretreatment of the plants to be cultivated with herbicides and their subsequent treatment using pesticides. Such treatments are practiced regularly and certainly have consequences on the farmed soil and their harvests.

If on both sites the concentrations of methylated (MT) and butylated (BT) forms of tin increased (average to 1.7 and 1.92 µg/kg, respectively) after enrichment of soil with DC, we curiously noticed a decrease of DMT on site 2 and of DBT on site 1. The fact that this decrease has occurred only at one of the two sites makes the observation difficult to explain, but it is possible in the case expiring that these two species di-substituted of tin have been degraded by anaerobic microorganisms in the soil for the benefit of mono-substituted forms of tin. This could have caused the reduction of the dimethylated and dibutylated forms in favor of the increase of mono-methylated and mono-butylated forms of tin (Heroult et al. 2008). Indeed, several previous works have shown that under the action of anaerobic microorganisms (Bacteria), the tri-substituted and di-substituted species of tin undergo degradation in the soil to release the mono-substituted forms of tin and inorganic tin (iSn) (Schaefer 2005; Paton et al. 2006; Heroult et al. 2008). Thus, the mono-substituted forms of tin also undergo degradation in the soil to release iSn. However, the MBT form is very toxic to soil microorganisms (Harino et al. 1997; Paton et al. 2006) and its degradation is very

small. This leads to a higher persistence (half-life) of the MBT in the studied soils than all the other forms of OTC identified (Huang and Matzner 2004b; Heroult et al. 2008). This certainly explains the major presence of MBT forms in our soils.

Organolead compounds

At first, it is most surprising to find such an array of alkylleads present in the soil samples studied. Here also the amendment brings a very significant increase in the levels recorded. However, the soils themselves also display alkylleads.

There are very few studies on OLC in the soil, and specially in the agriculture soils. Huang et al. (2003) studied the speciation of OLC in the forest soils of Karlsruhe (Germany). They only found trimethyl-lead (TrMePb) with a maximum concentration of 42.5 pg/g. In our case, we were able to determine TMePb, MEtPb, and TETpB in the soil studied here. It is difficult to explain with certainty the origin of the three OLC identified in soil, but it is established that the TETpB identified with the highest concentration was formerly one of the principal anti-explosive products for fuels. The presence of TETpB in SnCD mostly has an atmospheric origin, as shown by Leal-Granadillo et al. (2000) in their work on the speciation of OLC in airborne particles in Oviedo (Spain). They identified concentrations of diethyl lead (DEtPb) to be between 5.5 and 23.5 pg/l. It was concluded that TETpB was a predominant constituent of lead fuels in Spain.

Having no information on the presence of atmospheric TETpB in the town of Ngaoundéré, but the fact that leaded gasoline is still used in Africa, the atmospheric origin of the TETpB identified in SnCD remains a likely source and would explain the presence in non-amended soils, also through the irrigation of the soils with the water from the river. On the other hand, due to the significant increase of TETpB in the soil enriched with CD, it is believed that this OLC must have been formed in the CD used here. In the soils amended with combustion debris, it is most likely that the occurrence of elevated tetra alkyl-leads originate from the practice of promoting the combustion of the household wastes and in the dumpsite by adding gasoline to support and sustain the combustion of these wastes. This is most likely because in Africa the use of cans to refuel hydrocarbons (oil, gasoline) is a common occurrence. At the end, these unnecessary cans are always found in urban rubbish dumps. Its presence in the CD can also be due to the use of gasoline to burn household wastes.

Finally, the occurrence of all the other minor Pb species such as MEtPb could be derived from the degradation of TETpB. It has been proven that at high temperature, TETpB decomposes to triethyl-lead

$[(CH_3CH_2)_3Pb]$ and ethyl radicals (Seyferth 2003). MEtPb is also derived from the biodegradation process of TETpB by microorganisms in the soil (Amouroux et al. 2000). Regarding the presence of TMePb in the soil, this is probably due to the methylation and trans-methylation of inorganic Pb (Chau et al. 1997).

Conclusions

The objective of this work was to study the potential contamination of the market garden soils by organometallic compounds, in particular in an urban and suburban agricultural context. Organomercury (MeHg), organotin (MT and BT), and organolead (MePb and EtPb) compounds were identified in the studied soils. The cultural practice of enriching the soil with combustion debris, which has been developed on both sites for more than 10 years, is responsible for the contamination of so-called “non-amended soils” by the OMC, OTC, and OLC identified in this work. Culture conditions, such as watering and sunshine, combined with soil amendment with combustion debris, have contributed positively to the significant increase in the amounts of OMC, OTC, and OLC on so-called “amended soils”. The presence of these organometallic compounds in the market garden soils will certainly result in the contamination of the vegetables grown there. In view of the recognized toxicity of organometallic compounds for living organisms, this contamination will stretch to the level of the main consumer of the crops of this culture, Man. This work therefore demonstrates the dangerous use of CD as an organic amendment on cultivable soils for consumers of vegetables produced from them. Farmers must not only stop farming on the culture soil plots already contaminated with organometallic compounds that are dangerous to health, but they must also completely change this cultural practice. For example, they could exploit the cultural practice which consists of developing the co-cultures by combining plant species that will enrich the soil with nitrogenous elements with the species they want to grow. On the other hand, contaminated soil plots must be decontaminated. Concerning this subject, it would be judicious to study the phyto-accumulation potential of the plant species grown on these soils, for pollutants such as OMC, OTC, and OLC. The objective here will be to see to what extent plant species known could be used to purify cultivated soils contaminated by these organometallic compounds. It would also be very important to study the speciation of organometallic compounds in the water of the Soum-soum River, which is regularly used by market gardeners to irrigate crops.

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Compliance with ethical standards

Conflict of interest We are the authors of the manuscript entitled “Speciation of organometallic compounds of Hg, Sn, and Pb in the market garden soil of Ngaoundéré (Cameroon)”, and we declare that no conflicts of interest exist in this work.

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