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Kinetic monitoring of trisubstituted organotins in soil after sewage sludge application

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Organotin compounds (OTC) are widely used for their biocidal effects in various agricultural or industrial activities, leading to their environmental presence. Among the organotin species, tributyltin (TBT) and triphenyltin (TPhT) are the most used and are generally considered the most toxic. So it is important to understand their behaviour in soils and obtain data about their persistence and phytoavailability. Many works deal with OTC speciation in various matrices, but few are concerned with OTC degradation in soil. The present study focuses on kinetic monitoring of TBT and TPhT in an agricultural soil. These compounds were introduced into the soil by the way of spiked sewage sludge, simulating agricultural practice and diffuse contamination. The influence of time and initial OTC concentration on the species preservation was evaluated. TBT concentration was shown to have a positive effect on TBT preservation. Corresponding half-lives were calculated. They were 6 ± 1 days and over 39 days for TPhT and TBT, respectively. Degradation compounds, mono- and dibutyltin, and mono- and diphenyltin, were produced by both direct and successive dealkyl and dearylation processes.

Keywords: organotin; speciation; degradation; monitoring; soil; sewage sludge

Introduction

Organotin compounds (OTC) are known to be toxic and harmful for terrestrial and aquatic life.[1–3] Their toxicity depends on their chemical forms and the living organisms considered. Trisubstituted compounds, especially tributyltin (TBT) and triphenyltin (TPhT), are known to be the most toxic for numerous organisms, including humans. OTC are mainly present in the environment because of anthropogenic uses. Many of industrial or domestic products like fungicides, insecticides, bactericides, wood preservatives and PVC stabilizers have been recognized as potential sources of contamination.[4,5] Consequently, sewage sludge contains organotins in significant amounts, TBT being present with concentrations between 5 and 1500 μg (Sn) kg^{-1} in dry material.[6–8] TPhT was also found in lower concentrations [2–350 μg (Sn) kg^{-1}].[9,10] OTC concentrations in sewage sludge can vary a lot according to the season.[11] Additionally TPhT is also widely used as biocide in agriculture.[3] Consequently OTC presence in agricultural soils[12] can be due to application of sewage sludge[13] or OTC-based biocide spreading.[12,14,15] Most often, diffuse contamination leads to around 10 μg (Sn) kg^{-1} of butyl- and phenyltins in soil. However, after spreading, up to 100 μg (Sn) kg^{-1} can be found.[16]

Because of the toxicity of trisubstituted OTC and their degradation compounds [i.e. dibutyltin (DBT), monobutyltin (MBT), diphenyltin (DPhT) and monophenyltin (MPhT)], it is important to understand the behaviour of these species and evaluate their persistence in agricultural soil according to environmental conditions. This knowledge is essential with regard to soil quality, soil-to-water transfers, plant uptake and potential food risk. However some studies are about OTC degradation in soil.[3,12,16–23] They mainly concern OTC speciation at different times. Some of them deal with kinetic monitoring and half-life calculations.[16,18–21,23] The different reported half-lives range over 1 day to more than 4 years and between a few days and 140 days for TBT and TPhT, respectively.[12,16–21,23] Nevertheless, the conditions of these studies are very different (type of soil, conditions of experiment, concentration values, etc.), which explains the very different half-life values reported. Moreover, these conditions are not always totally described (e.g. temperature or oxic/anoxic conditions are not indicated) and so half-life comparison remains difficult. The OTC concentration levels studied in some of these papers [up to some mg (Sn) kg^{-1}] are also very far from those generally reported in soil in the case of diffuse contamination. However, OTC fate (including adsorption and finally degradation) depends on these levels.[8,19–21] Finally, only one study by Marcic *et al*. recently investigated sludged soil, although sludge is one of the most important sources of agricultural soil contamination.[13,22] That paper focussed on the effects of sludge amount, OTC concentration and soil pH on TBT and TPhT persistence in anoxic conditions and variable temperatures. Moreover, no kinetic monitoring in controlled conditions was made in that study. Therefore, degradation kinetics, degradation product occurrence as well as half-lives still remain unknown in sludged soil. Nevertheless, according to European legislation concerning sludge amendment and delay between sludge spreading and culture, such information appears crucial.

In a given medium, assumed to be without any organotin introduction and exportation, the OTC concentration decreasing according to time can be associated with both transformation and degradation of the involved species. Transformation is recognized to be induced by bioactivity.[3] However, although in aquatic environment methylation and hydridization processes were previously reported, such phenomena seem to be extremely limited in soil.[24,25] Degradation processes are generally admitted

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to be based on successive de-alkylations or arylations until mineral tin.[1,3] However some authors have suggested that trisubstituted species (TBT) could also be directly degraded to monosubstituted form in fresh and marine waters.[26] Despite tri-, di- and mono-organotins being generally found in soil, no information about these different transformation/degradation processes is available. Photochemical degradation appears to be the major degradation pathway in media exposed to light.[12] In darkness conditions, degradation by microorganisms and microalgaes have also been highlighted.[27–29] More recently, some authors found that at 20 °C TPhT degradation was more rapid in non-sterilized soils than in sterilized ones, whereas others did not observe such phenomena at 40 °C.[21,23] Yen *et al*. highlighted the major role of the temperature in TPhT chemical degradation in agreement with the triorganotin thermolability previously observed in solution.[23,30] Therefore, too high a temperature should have a preponderant effect on OTC chemical degradation, organotins being assumed to be mainly degraded by biotic activity in the range 10–30 °C.[16,19,20,22,23]

Toxicity was also studied in soil extracts and TPhT EC_{50} was found to be in the range 5–54 µmol l^{-1} [equivalent to 1.5–16.7 µg(Sn) l^{-1}], according to the microorganisms and pH soil.[21] TBT toxicity was estimated to be in the same order of magnitude. Unfortunately, no data is available in the case of diffuse OTC contamination observed in soil and sludged soils especially. Moreover, among the studies dealing with OTC kinetic monitoring, either all the species are present (i.e. at once tri-, di- and monosubtituted) or only one is considered (i.e. TPhT or TBT and possibly their degradation products occurring during the monitoring).[16,18–21,23] Papers considering simultaneously several organotins with their individual fate and referring to their possible co-influence being not so frequent, despite these conditions, are generally those of environmental compartments.

Finally, data relative to organotins in soil still appear very scarce. No kinetic monitoring and no information about half-life, degradation product occurrence or co-influence of triorganotin species in sludged soil is available. Therefore, the present paper focuses on the degradation kinetics of TBT and TPhT in a soil after mixing with contaminated sewage sludge. For the first time quantitative information about triorganotin degradation is provided in relation to their respective concentrations in a range representative of diffuse soil pollution, far below the toxicity level relative to microorganisms.

Materials and Methods

Experimental set-up

An experimental design was used to optimize the experiment (neither lack nor redundancy; better precision of the experimental data).[31,32] It also allowed the evaluation of studied factor influences on triorganotin persistence. Moreover, the information obtained from all the experiments could be modelled and so converted into continuous experimental information. A sequential Doehlert design was chosen in order to decrease the number of experiments as much as possible and extend the experimental field if necessary.[31] Such an approach was previously found to be convenient and reliable for environmental studies.[22]

The OTC amounts introduced into the soil were added via a spiked sludge in order to simulate common agricultural practise. The spiking TBT and TPhT concentrations were ranged over 20–50 µg(Sn) kg^{-1} of soil [corresponding to 400–1000 µg(Sn) kg^{-1} of sludge] in order to be representative of OTC sewage sludge and soil contamination previously observed.[16,33] The experiment was planned according to an initial two-factor (TBT and TPhT concentrations) Doehlert design. Time was considered as a supplementary third factor, between 0 and 53 days, according to previous studies.[22] Consequently, seven experiments with particular combination of TBT and TPhT concentrations were planned for every experimental time and five different times were considered for the design modelling. Two supplementary times (17 and 38 days) were also considered in order to validate the modelling. The effects of every factor and interaction and their respective precision were evaluated by considering least squares constraint.[32] A factor or interaction was considered as significant if the absolute value of its effect was higher than the precision. The design modelling was performed by proposing second-order polynomials with quadratic terms on the basis of influent factors and interactions. The quality of the experimental approach and modelling was evaluated by statistical calculation (precision: coefficient of determination, significance and lack of bias; variance analysis by Fisher–Snedecor tests and comparison of calculated and experimental values, in a 95% interval of confidence). All the models presented and used later on (see Results and discussion) were validated according to this approach.[32]

Spiked sewage sludge and mixture with soil

Sludge came from an urban treatment plant of 5000 equivalent inhabitants in the southwest of France. It did not contain any detectable OTC amount before spiking. Its main physicochemical characteristics are presented in Table 1(A). The studied soil sample came from a ploughed layer of a densic podzol.[34] Its physicochemical characteristics are summarized in Table 1(B).

The soil was collected in the 0–25 cm surface depth layer of a field annually cropped with maize at the INRA Pierroton Experimental Unit, near Bordeaux (France). The soil was sieved at 2 mm. Solutions of adapted concentrations of TBT and TPhT were prepared in 10 ml of Milli-Q water. These solutions were added into 70 g aliquots of sewage sludge at the same time as small quantities of water, in order to facilitate the mixing. The mixtures were homogenized for 2 h. Then, the spiked sludge aliquots were mixed with 1400 g samples of soil. The sludge–soil ratio was 5 g sludge/100 g soil. Each duplicated mixture corresponds to different TBT and TPhT concentration values defined in the experimental design. For each experiment (corresponding to particular values of TBT and TPhT concentrations), the homogenized sludged soil was shared into 12 aliquots of 50 g in order to be able to perform soil analysis at different times of experiment (according to the design experiment). Each experiment was duplicated. Each aliquot was placed into a 50 ml polyethylene capped tube. Previously, it was checked that the material of these tubes does not lead to any significant OTC adsorption or desorption. Additionally, two unspiked soil samples

Table 1. Physicochemical characteristics of sludge (A) and soil (B)

	Granulometry (g kg^{-1})			Organic carbon (g kg^{-1})	Organic Nitrogen (g kg^{-1})	pH_{water}	CEC (cmol kg^{-1})	C/N
	Clays	Silts	Sands					
A: Sludge	629	356	15	361	–	7.17	67.40	–
B: Soil	33	25	942	19.6	0.78	5.6	5.9	26

(in 12 replicates) were also prepared to be used as blanks to check the quality over the whole experiment (i.e. from set-up to analysis).

These aliquots were put into an oven at 28 °C in the dark. The pots were regularly opened and shaken to avoid anoxic conditions. At different times (between 0 and 53 days, times chosen according to the optimal criteria of experimental design), two samples corresponding to each particular design experiment were taken and put in a freezer at −80 °C until analysis.

Analysis

The OTC analysis procedure was previously developed in our laboratory and is described elsewhere.[35] Briefly, it includes three parts:

- *OTC extraction from soil*: 0.5–2 g of frozen soil was introduced into a capped 50 ml polycarbonate tube with 20 ml of glacial ethanoic acid. The sample extracting mixture was shaken for 12 h at 400 rpm in the dark, then centrifuged at 4000 rpm for 15 min.
- *Derivatisation*: 1–5 ml of the raw extract was directly introduced into a derivatization reactor. Ethylation was performed in 100 ml of sodium ethanoate–ethanoic acid buffer (pH = 4.8) with 0.5–1 ml of sodium tetraethylborate ($NaBEt_4$) (0.2%) and 1 ml of isooctane. The mixture was shaken mechanically at 400 rpm for 30 min. Then, 2 µl of the organic phase (isooctane containing ethylated OTC) was directly taken for the analysis.
- *Quantitation*: tripropyltin (TPrT) was used as internal standard (IS). The TPrT relative chromatographic responses of butyl- and phenyltin compounds were first calculated from soil–sludge mixture samples by standard additions. This previously validated quantitation approach has been shown to significantly decrease the matrix effect.[36] This quantitation method allows us to have an accurate analytical process and convenient limits of detection and quantitation (LOD and LOQ). The LOD in soil were below 0.3–2 µg(Sn) kg^{-1}.

Apparatus

Two pieces of apparatus (gas chromatograph and specific detector) were used to determine organotin concentrations: a Varian 3800 gas chromatograph (Palo Alto, CA, USA) was used with a pulsed flame photometric detector (PFPD). The separation was carried out on a capillary column (30 m × 0.255 mm i.d.) coated with polydimethylsiloxane (0.25 µm film thickness; Quadrex, New Haven, CT, USA). Nitrogen was used as carrier gas at 1 ml min^{-1}. The following temperature program had to be used to separate the organotin compounds suitably: the column temperature was held at 80 °C for the first minute, increased to 160 °C at the rate of 10 °C min^{-1}, then to 270 °C at 30 °C min^{-1} and finally held at this temperature for 2 min. The PFPD operating conditions were optimized in previous studies.[35]

An HP 6890 gas chromatograph (Hewlett-Packard, Wilmington, DE, USA) equipped with a split/splitless injection port was used as well. The capillary column was a HP5 (30 m × 0.32 mm i.d., column coated with polydimethylsiloxane). The carrier gas was helium at a flow rate of 1.4 ml min^{-1}. The temperature program was the following: 1 min at 80 °C, then increased to 280 °C at 20 °C min^{-1}. Finally the temperature was held at 280 °C for 2 min. Detection was achieved with an HP model G2350A microwave-induced plasma atomic emission detector (MIP-AES) at a Sn-characteristic wavelength (303 nm).[37]

Results and Discussion

OTC speciation

TBT and TPhT as well as organic products coming from their transformation and degradation can also significantly impact the environment because of their toxicity towards specific living organisms.[3] This is why the determination of OTC speciation in soil as a function of time is important. The corresponding monitoring is presented in Fig. 1.

As the result of the expected trisubstituted degradation, TBT and TPhT respective degradation products were found in soil. No other species, such as methylated or hydridizated tin compounds, could be observed on the corresponding chromatograms over their limits of detection [1–2 µg(Sn) kg^{-1}]. Because these species are volatile, some losses could also be considered. However, according to the results from Fig. 1, it is obvious that, if the transformation process occurs, it remains negligible in the present experimental conditions. Complementary experiments were performed in hermetically closed chambers where TBT and TPhT were incubated for 30 days either in soil or in soil solution [10 µg(Sn) of each trisubstituted compound in either 1 kg of soil or 200 ml of soil solution]. OTC were monitored by headspace solid-phase microextraction (SPME). Tetramethyl- and dimethyldiphenyltins were only detected from soil solution. Their respective amounts over the total experimental duration were 27 ± 3 and 2.5 ± 0.3 ng (Sn). These species represented less than 0.25% of the triorganotin amounts initially introduced. These results and observations suggest that biotransformation mainly occurs in wet medium. They are in agreement with those reported by Huang *et al*., suggesting that methylation of tin in soils is very

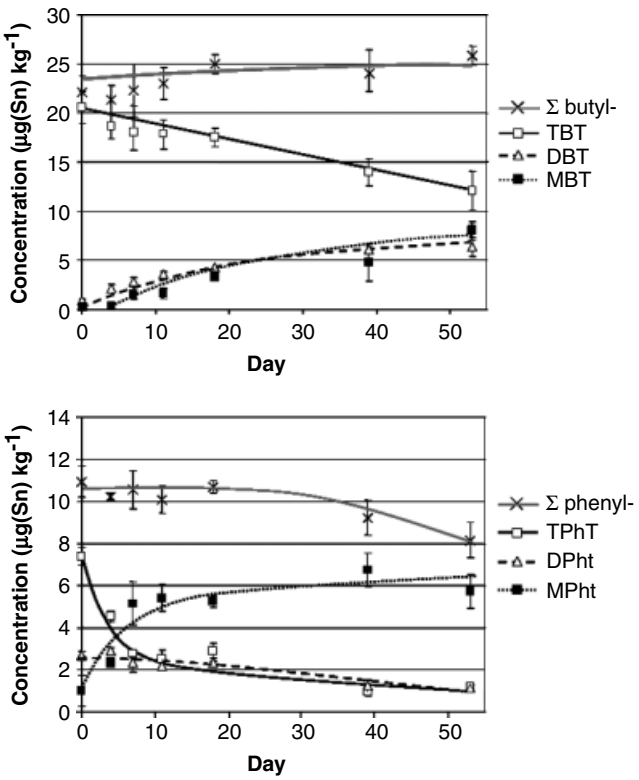

Figure 1. (A) Phenyl- and (B) butyltin speciation according to the time of incubation.

limited.[25] Therefore, it was assumed that only OTC degradation occurred in soil in the present experimental conditions.

The trisubstituted degradation process may involve either direct degradation to monosubstituted or successive debutyl- or dephenylation, leading to both di- and monosubstituted species.[1,3] In the present study, it can be noticed that TBT degradation is very low for the 10 first days of the experiment. DBT and MBT appeared after 3 and 6 days, respectively, and their concentrations increased slowly with time, according to the slow TBT degradation. Over 15 days its two degradation compounds were found to be in the same concentrations, remaining always lower than that of TBT. Consequently, according to these variations, successive debutylations may occur in the main. Unlike butyltins, DPhT and MPhT are present from the first day. Therefore, it can be assumed that some dephenylations occurred during set-up, before the start of the experiment. DPhT concentration remained constant for 40 days and decreased slowly only at the end of the experiment. At the same time, MPhT concentration quickly increased during the first 8 days before reaching a steady state, with a kinetic profile complementary to TPhT degradation. In addition, the variation of [DPhT] + [MPhT] vs [TPhT] (relative concentrations) was plotted for the whole data of the design experiments. Similarly, [MPhT] vs [TPhT] was also plotted. Both relationships appear to be significantly linear with a slope of 1.04 ± 0.07 and 1.02 ± 0.09 respectively ($r^2 = 0.845$ and 0.806). These relationships would indicate that MPhT came from TPhT degradation according to a direct process of dephenylations all through the experiment. Moreover, the kinetics of degradation appear very different according to the species, with DPhT and especially MPhT appearing to be very persistent.

Comparison of initial and final TBT and TPhT concentrations in soil

For each experiment, the aliquots corresponding to the first day of the experiment (t_0, after spiking) and 53 days later (end of experiment, t_{53}) were analysed. The corresponding initial and final concentrations of TBT and TPhT respectively are presented in Fig. 2. These data allow a first evaluation of the degradation to be made. Therefore, for TPhT, only 12% (mean value) of this compound was preserved after 53 days. Unlike TPhT, 54% of initial TBT was always present after the same time.

These values are in agreement with degradation percentages found in a recent study by Marcic *et al.*[22] In this work only 20% of TPhT was present after two months of experiments, whereas for TBT, around 50% was still in the soil after the same time. However, the experimental conditions were different since experiments were performed in 2 kg aliquots of soil in anoxic conditions, with variable temperature (most often between 15 and 30 °C, 20 °C on average) and light exposure on the soil surface, in climatic chamber or greenhouse. Therefore, the difference in physicochemical parameters such as light and temperature did not seem to significantly influence TBT and TPhT degradation inside the soil, in the corresponding experimental fields. The effect of the light appears obviously limited to the soil surface. Concerning the temperature, Yen *et al.* found this factor to be very significant, especially when it was decreased from 30 to 10 °C, TPhT being more widely preserved at 10 °C.[23] This observation can also be related to microbial activity (which is directly linked to temperature).

Influence of OTC initial concentration and experiment time on preservation

The influence of the spiking OTC concentrations in soil on their preservation was also studied by the way of their concentrations at a given time as well as the preservation index *Ic*.[38] This parameter was defined as the ratio between the concentration at *x* days and the initial one. It represents the relative concentration (after *x* days of experiment), such that a value equal to 1 corresponds to a total preservation and a 0 value to a total degradation:

$$Ic_x = \frac{[OTC]_x}{[OTC]_0}$$

where $[OTC]_x$ = OTC concentration at *x* days, $[OTC]_0$ = OTC concentration at 0 day (initial measured concentration); and Ic_x = preservation index at *x* days.

The use of *Ic* for a given triorganotin species allows the evaluation of the actual preservation of this organotin according to the experimental conditions. Owing the Doehlert design, the different concentration and *Ic* values experimentally obtained could be modelled empirically as a function of spiking OTC concentrations and time. This fitting led to the most accurate and complete information being obtained, which is the most convenient approach for the investigation presented later on.[31]

Preservation vs initial concentrations

As it is obvious that preservation depends on time; the possible influence of the initial OTC concentration was generally less studied, despite some authors having demonstrated that the

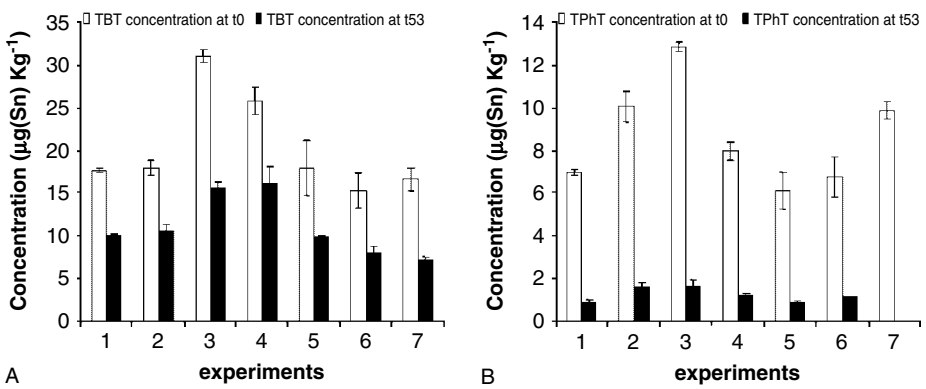

Figure 2. Comparison between concentrations of TBT (A) and TPhT (B) measured in soil initially (t_0) and at the end of experiment (t_{53}).

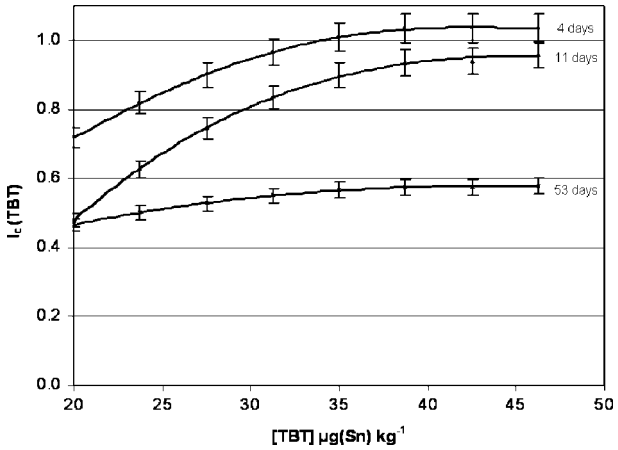

Figure 3. *Ic* variations according to TBT concentrations at 4, 11 and 53 days.

OTC behaviour and fate depend on it.[8] Consequently, the results concerning the modelling according to this parameter are first presented. TBT concentration was found to be the only parameter having a significant effect on TBT preservation in the range of studied values. Figure 3 presents the variation of *Ic* for TBT at various times of experiment.

The comparison of the different curves of this figure enhances the fact that higher initial TBT concentration leads to higher preservation (i.e. a higher *Ic*). This observation does not depend on time of experiment. As recognized in the literature, it can be assumed that, in the present experimental conditions, bioactivity could be the main process leading to triorganotin degradation.[1] Additionally, the biocide effect of TBT has to be considered. It would induce the microorganism activity to slow down and thus would explain the lower degradation of this compound. This hypothesis is in agreement with some studies dealing with the toxicity of trisubstituted organotin compounds on microorganisms.[39] Nevertheless, in the present work the triorganotin concentrations are far below the toxicity levels reported in the literature.[21] However, in the present experimental conditions the microbial activity might be modified by initial experimental set up including sludge/soil mixing and TBT presence.

From the modelling, spiking TPhT concentration was found to have no significant influence on TBT preservation, whatever the value of this concentration and experiment time. This could be partly due to the important TPhT degradation previously noticed, its degradation products occurring in the soil in significant concentrations. Moreover, despite MPhT and DPhT seeming as toxic as TPhT for soil microorganisms, the present range of phenyltin concentrations is actually far below the reported OTC toxicity level.[21] This may also explain why TPhT biodegradation was rapid and quantitative. Finally, the important dephenylation led to a very low *Ic* (TPhT) (around 0.2–0.4) at which the initial triorganotin concentrations could not be found to have any significant effect on the preservation index.

Preservation vs time

The kinetic aspect of preservation was studied by modelling the concentration over the whole experiment. Empirical models based on second-order polynomials from experimental design were proposed as previously described. Then, they were used to calculate the half-lives as precisely as possible.

From this modelling approach, the importance of the model validation on the accuracy of kinetic evaluation can be enhanced. Therefore, initially, the second-order polynomial models were statistically validated according to the procedure previously described (in Experimental setup). The comparison between experimental and calculated values was made using a set of data included in the experimental field but not considered in the design calculation (these data correspond to supplementary experiments at two different times and are represented by squares in Fig. 4). This approach allows the most robust validation as possible. Figure 4(A, B), presents the typical variations of TPhT and TBT concentrations in soil as a function of time. It can be verified for each compound that the design model satisfactorily fits the raw experimental data.

On the basis of the validated two design models, the respective TBT and TPhT half-lives were estimated to be 6 ± 1 days for TPhT and between 40 and 60 days for TBT, the half-life of

Table 2. Half-lives of TBT and TPhT in soil and main experimental conditions reported in the literature

Compound	Soil type or horizon[a]	Half-life (days)	Concentrated µg(Sn) kg^{-1}	pH	C_{org} (%)	Temperature (°C)	Oxic or anoxic/light	Reference
TBT	Silt loam	105	1000	6	1.4	20	Anoxic/dark	[19]
	Sandy loam	140	1000	7.3	2.6	20	Anoxic/dark	[19]
	Podzol (Oa horizon)	180	5	3.5	31	20	Oxic/dark	[16]
	Podzol (B/C horizon)	580	5	4.5	1.6	20	Oxic/dark	[16]
	Histosol (10–30 cm layer)	1600	5	4.6	44	20	Anoxic/dark	[16]
	Podzol (A horizon)	40–60 (estimated values)	15–30	5.6	2	28	Oxic/dark	This study
TPhT	Loam (0–5 cm layer)	140	5000–10 000	7.6	0.8–1	Not indicated	Anoxic/dark	[20]
	Podzol (0–10 cm layer)	60–70	44	3.3	1	10	Anoxic/not indicated	[18]
	Mollisol (0–10 cm layer)	139	44	4	2	10	Anoxic/not indicated	[18]
	Loam clay loam	8–16.3	15 000	4.53	1.3	30–40	Not indicated/dark	[23]
		8.3–19.4		5.11	1.1			
	Sandy loam	27–33	10 000–20 000	5.5	not indicated	20	Anoxic/light–night cycle	[21]
	Podzol (A horizon)	6 ± 1	6–13	5.6	2	28	Oxic/dark	This study

[a] The soil denominations correspond to the denomination in the original papers and are, for this reason, inhomogeneous.

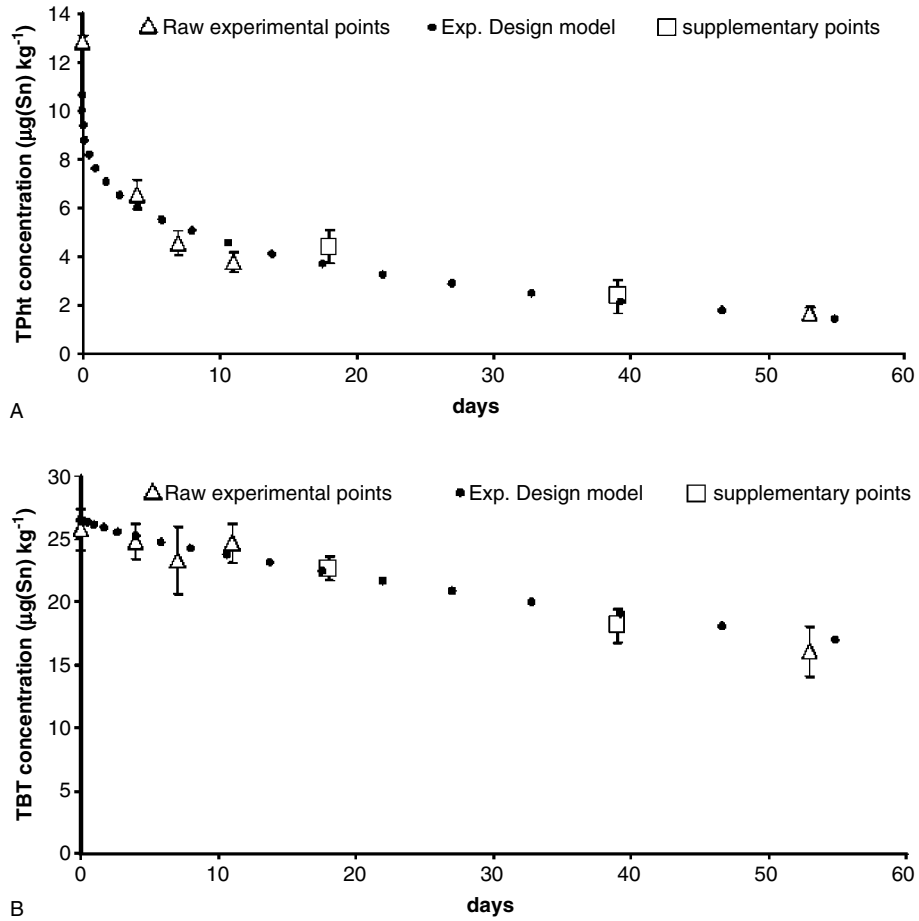

Figure 4. Experimental and calculated concentrations of (A) TPhT and (B) TBT according to time.

this last compound being found to be dependent on its initial concentration in soil. Thus, it is clear that TBT is widely less degradable than TPhT in the present experimental conditions. The different half-lives of the literature are reported in Table 2, for different soil types and experimental conditions. These values appear very different and there is no obvious relationship between the soil characteristics (texture, organic matter content, pH), other experimental conditions (temperature, oxic/anoxic conditions) and the OTC degradability. It is especially the case for TBT, no recent value being available except those from Huang and Matzner.[16] Moreover, the different half-lives are highly different for the same temperature and the same range of concentrations. This is probably due to the fact that several parameters influence TBT persistence, including the presence of sludge in soil and the method of introduction of OTC into the soil. For TPhT, and according to the data reported in the most recent papers (some of them having been recalculated for this comparison) and the present result, a significant correlation can be established between the half-lives and the temperature ($r = 0.9965$, $n = 6$). This result again enhances the important role of this parameter on TPhT persistence, in agreement with the results of Yen *et al.*[18,21,23]

Conclusion

The first conclusion of this study is that TBT is widely more persistent than TPhT. TBT initial concentration in the soil appears to be the most influential factor in TBT preservation with a clear positive effect at every time of experiment. This phenomenon could be due to the biocidal effect of TBT, this compound being possibly highly more toxic than phenyltins towards microorganisms. However, this hypothesis remains to be confirmed since the lethal concentration given in the literature is higher than the concentration involved in the present study. These first results highlight the actual TBT persistence in the terrestrial system. Moreover its degradation products, DBT as well as MBT, also appear to be persistent. TPhT degradation was found to be very rapid, with over 85% of this compound being degraded at the end of the experiment (53 days). However, it remains present for the whole duration of the experiment, at low concentrations. Furthermore, its main degradation product, MPhT, is present and appears to be more persistent. These data enhance the actual OTC persistence, even in biotic conditions favouring biodegradation. With regard to the toxicity of all these compounds, the potential risk of food contamination must be considered. This is especially important because, generally, when sludge is spread on agricultural soil, there is a latency time of some 10 days to some months between sludge application and sowing, according to plant and sludge type. In France for example, this delay varies between 21 days and 18 months. In these conditions and considering the present results, the potential OTC transfer from sludge to plant must be taken into consideration.

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