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Biogeochemistry of trimethyllead and lead in a forested ecosystem in Germany

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Abstract. Lead compounds, especially ionic organolead compounds (OLC), are highly toxic and mobile pollutants strongly affecting many ecosystems. Soil pools and fluxes with precipitation, litterfall and runoff of trimethyllead (TML), one of the dominant ionic OLC in the environment, and Pb_{total} were investigated in a forested ecosystem in NE-Bavaria, Germany. In addition, ad/desorption of TML to soils was studied in batch experiments and its degradation in soils was investigated using long term incubations. Total soil storage in the catchment was 11.56 mg Pb ha^{-1} for TML and 222 kg Pb ha^{-1} for Pb_{total}. More than 90% of the soil storage of TML was found in the wetland soils of the catchment representing only 30% of the area. Most Pb_{total} (>90%) was found in the upland soils. In upland soils, TML was only detectable in the forest floor. The annual total deposition from the atmosphere, estimated as throughfall + litterfall fluxes, amounted to 3.7 mg Pb ha^{-1} $year^{-1}$ for TML and 52 g Pb ha^{-1} $year^{-1}$ for Pb_{total}. The contribution of litterfall was 1.5 and 32%, respectively. The concentrations of TML and Pb_{total} in wet precipitation were: fog > throughfall > bulk precipitation. The annual fluxes with runoff from the catchment was 0.5 mg Pb ha^{-1} $year^{-1}$ for TML and 2.8 g Pb ha^{-1} $year^{-1}$ for Pb_{total}. TML degraded rapidly in the forest floor (Oa horizon) with a half-life ($t_{1/2}$) of 33.5 days. The degradation of TML in Fen ($t_{1/2} = 421$ days) and in the mineral soil (Bw-C horizon, $t_{1/2} = 612$ days) was much slower. Emission of tetramethyllead from wetland soils was not observed during the 1 year incubation. The adsorption affinity of TML to different soils was Fen > Oa > A ≥ Bw-C. The ratio of total soil storages to the present annual input were 3.6 years for TML. TML and Pb_{total} are still deposited in remote areas even after the use of tetraalkyllead as additives has been terminated for years. The rates of deposition are, however, much lower than in the past. Forest soils act as a sink for deposited TML and Pb_{total}. TML is accumulated mostly in wetland soils and seems to be stable under anoxic conditions for a long time. In upland soils, TML decomposes rapidly. Only small amounts of TML are transferred from soils into runoff.

Introduction

Peralkylated organolead compounds (OLC) like tetramethyllead (TTML) and tetraethyllead have been used as antiknock additives in gasoline products for several decades (Łobiński et al. 1994), but the production has been terminated for several years in Central Europe. Still these additives are used in many countries like for example, in East Europe today. In regions of high traffic density like Central Europe, past emissions of OLC during several decades have led to widespread inputs of of OLC in urban as well as rural areas (Łobiński et al. 1994) and even in high altitude alpine regions (Heisterkamp et al. 1999). The toxicity of the alkylated lead compounds varies with the degree of alkylation, with tetraalkyllead compounds being most toxic.

Tetraalkyllead compounds undergo the following decomposition in the environment:

$$R_4Pb \rightleftharpoons R_3Pb^+ \rightleftharpoons R_2Pb^{2+} \rightleftharpoons Pb^{2+}$$

Tetraalkyllead is almost insoluble in water, but di- and tri-alkyllead are water soluble and quite stable (Hempel et al. 2000). OLC emitted in the atmosphere undergo rapid photochemical decomposition (Radojevic and Harrison 1987), and OLC comprise usually only small parts of Pb_{total} in the atmosphere and precipitation (Allen et al. 1988). Studies on distribution, degradation, persistence or adsorption behaviors of OLC in soils are scarce, and are mainly focused on excessively contaminated soils in the immediate vicinity of OLC producing industrial plants (Hempel et al. 2000) or on soils experimentally contaminated with high levels of OLC (Teeling and Cypionka 1997). Thus an assessment of the environmental impacts of these compounds on natural terrestrial ecosystems like forested watersheds is still impossible due to limited data.

In case of other heavy metals like Hg, wetlands and other semiterrestrial soils have been identified as compartments of special importance for transformation reactions (Weber et al. 1998; Roulet et al. 2001). Reduction or alkylation resulting in the formation of methylmercury or volatile compounds like Hg^0 and dimethylmercury influence strongly the mobility and export of organo-Hg compounds from terrestrial catchments (Wallschläger et al. 1995; Lindberg et al. 2001). Similar processes may occur in these compartments for other organometallic compounds like OLC, but are poorly investigated yet.

In this study, we investigate the biogeochemistry of trimethyllead (TML), one of the principle ionic OLC species in the environment (Van Cleuvenbergen and Adams 1992), in a forested catchment. The aim was to determine soil pools and fluxes of TML and Pb_{total} and to gain insight into the adsorption and degradation behavior and mobility of TML in different soils.

Materials and methods

Site description

The investigation was carried out in the 'Lehstenbach' catchment (4.2 km^2 size) in the German Fichtelgebirge mountains, located at an elevation of 700–880 m a.s.l. at 50°08′N, 11°52′E (Figure 1). Mean annual air temperature is 5 °C, and mean annual precipitation is approximately 1150 mm. The catchment is dominated by Norway spruce (*Picea abies* [L.] Karst.) stands of different age. 30% of the area are covered with wetland soils of bog and fen type. Upland soils are mainly Dystric Cambisols and Haplic Podzols (FAO classification) of sandy to loamy texture, developed from deeply weathered granitic bedrock. The forest floor is a well-stratified mor type of approximately 9 cm depth. The Fichtelgebirge is a region of relative high air pollutant deposition originating from large industrial sources to the north and east (Czech Republic) and from a local brown-coal power plant about 20 km to the east.

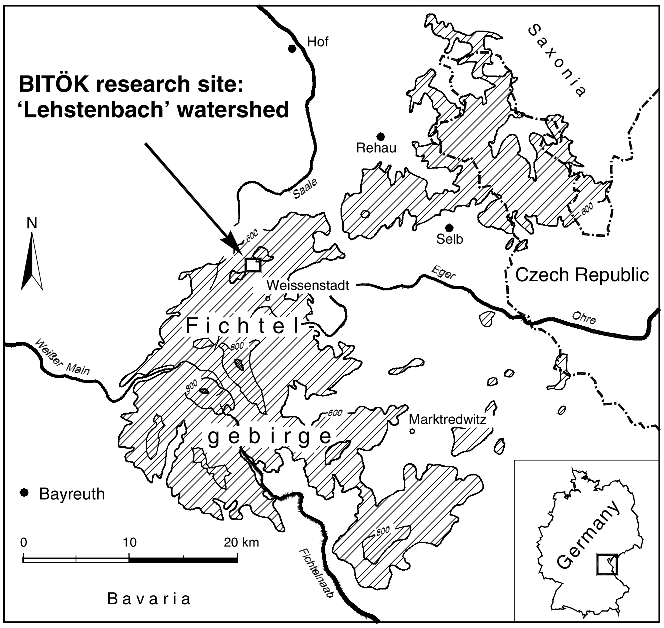

Figure 1. Location of Lehstenbach catchment in NE-Bavaria, Germany.

Materials and preparation

TML was purchased in the form of chloride with purity 95% from Alfa Aesar. Sodium tetra(*n*-propyl)borate ($NaBPr_4$), 98%, was synthesized by Dümichen, Halle. A stock solution (10 μg Pb ml^{-1}) of TML, was prepared in methanol and stored at −40 °C in the dark. A working solution with a concentration of 0.1 μg Pb ml^{-1} was prepared before each use by dilution of the stock solutions with methanol (Merck, p.a. grade). Triethyltin (TET) used as internal standard was prepared in the same way.

All glassware used was cleaned by rinsing with tap water and Milli-Q water, and put in a 10% nitric acid bath for at least 48 h. It was finally thoroughly rinsed with Milli-Q water before use.

A calibration curve for TML quantification was constructed in the range 0.01–1000 ng Pb l^{-1} ($R^2 = 0.99$) using TET as internal standard.

Precipitation sampling

Samplers for throughfall and bulk precipitation had a 200 mm diameter collector and a 5-l reservoir made of polyethylene (PE). A fine sieve made of PE was used between the collector and reservoir to prevent needles. Samplers were placed in PE tube, shield with aluminum follies to reduce sunlight, at 1 m above the ground. For throughfall sampling, three lines with three samples were installed. Samples of the same line were pooled after each sampling period. Bulk precipitation was collected with three samplers at an open site. Bulk precipitation, throughfall and runoff were sampled weekly. TML showed no appreciable adsorption on the PE container walls in preliminary experiments. Precipitation sampling was conducted from August 2001 to August 2002.

Fog sampling

Fog was sampled at a tower located close to the precipitation sampling site by a Caltech Active Strand Cloudwater Collector. More detail about the device is given by Wrzesinsky and Klemm (2000). Fog samples were stored in precleaned (double-demineralized water) HDPE bottles at $-18\,^{\circ}\mathrm{C}$ in the dark until analysis each month. Deposition of fog water was quantified by the eddy covariance method (Thalmann et al. 2002) and amounted to 88 mm from August 2001 to February 2002.

Litter sampling

Four PE funnels (35 cm diameter) were installed 1 m above ground. Inside each funnel a polytetrafluorethylene (PTFE) net was installed, to permit water flow through the funnel and to retain the litterfall. Litterfall was sampled every month from September 2001 to August 2002, freeze-dried, grounded, homogenized and stored at $2\,^{\circ}\mathrm{C}$ before analysis.

Soils sampling

Two upland soil profiles at ‘Coulissenhieb’ and ‘Weidenbrunnen’ as well as a wetland soil ‘Fen’ were sampled in fall 2001 (upland soils) and spring 2002 (wetland soils). The soil samples were then passed through a 2-mm (mineral soils) and a 5-mm (organic soils) sieve. Soil samples were homogenized and freeze-dried, since drying at higher temperatures may possibly cause losses of TML. The dried samples were ground and stored at $2\,^{\circ}\mathrm{C}$ for long-term usage.

Runoff sampling

Runoff was sampled weekly at the weir of the Lehstenbach creek from August 2001 to August 2002.

Calculation of fluxes

Fluxes with throughfall and bulk precipitation were calculated by multiplying the measured volume in the samplers with the concentrations on a weekly base.

Monthly input of fog deposition was calculated by the averaged monthly concentrations times monthly deposited amount of fog water. Annual TML and Pb_{total} fog deposition input was estimated by extrapolating the sum of 7 months measured input from August 2001 to February 2002 to 12 months. Annual TML and Pb_{total} fluxes of litterfall were calculated by multiplying the determined contents with the monthly weight of litterfall. Daily water flux with runoff of the catchment was calculated from level measurements (10 min resolution) at the weir. The annual TML and Pb_{total} fluxes with runoff were estimated by extrapolating the sum of 52 daily fluxes, which was calculated by multiplying the concentrations determined with the corresponding daily cumulative runoff water flux, to 365 days. Alewell et al. (in press) concluded that the calculation of runoff fluxes based on biweekly data resulted in errors up to 25% for time period less than 1 year. Since we used weekly data to calculate our runoff fluxes, the errors should be apparently less than 25%.

Calculation of soils storage

Calculation of the soils storages of TML and Pb_{total} to 60 cm depth was done by multiplying the contents determined with depth, soil density and percentage of fine soil material (<2 mm).

Degradation experiments

Upland soils from the Oa and Bw-C horizon in ‘Coulissenhieb’ were sieved to 5-mm and 2-mm respectively and subsequently air-dried at 20 °C. Wetland soil was sampled from 10–30 cm depth in the Fen, sieved to 5-mm and directly used for the incubation. All incubations were carried out in amber borosilica bottle (120 ml, Schott), closed gastight at 20 °C in the dark. About 10 g of both upland soils (dry weight) with 60% water content of the field capacity was incubated with 50 ng Pb TML under oxic incubation. The air in the headspace was refreshed when the CO_2 was detected over 5%. About 25 g wetland soils was incubated with 125 ng Pb TML under anoxic conditions (flushed with Argon).

Analysis of TML in soils was carried out by extraction with glacial acetic acid about monthly. Incubation bottles were merged with 30 ml glacial acetic acid and 75 ng Sn TET as internal standard, shaken horizontally for 24 h and subsequently centrifuged for 10 min (1200 g). About 2 ml of the extracting solvent was then removed into a 100 ml glass volumetric flask buffered with acetic buffer at pH 4 and diluted with Milli-Q water to 85 ml. The mixed solvent was further derivated, extracted and analyzed as described below.

For determination of TTML in the headspace, 50 ml headspace gas from the incubation bottles of wetland soils was sampled with a syringe and then passed through $NaOH_{(s)}$ filled in the pasteur pipette (150 mm length) to remove CO_2 and water. Samples were then twice trapped (ultimate tubing ID 0.53 mm and fused silica tubing ID 0.32 mm, both uncoated and methyl deactivated) at approximately −186 °C (cooled in liquid argon) and further measured by GC (HP 5890)-ICP-MS. The detection limit for TTML was 0.8 pg Pb. The recovery of this method for TTML was about 85%.

Adsorption and desorption experiment

Upland soils sampled from Oa, A and Bw-C layer and the Fen, sampled from 10–20 cm depth, were sieved to 5-mm (organic soils) and 2-mm (mineral soils) and air-dried at 20 °C. Soil samples were afterwards grounded, homogenized and stored at −40 °C before each use. The batch technique was used to determine the equilibrium concentrations of TML between the solid and solution phase. For the adsorption experiment, 1 g adsorbent was suspended with 50 ml artificial rainwater (NH_4NO_3 11.6 mg l^{-1}, K_2SO_4 7.85 mg l^{-1}, Na_2SO_4 1.11 mg l^{-1}, $MgSO_4 \cdot 7H_2O$ 1.31 mg l^{-1}, $CaCl_2$ 4.32 mg l^{-1}) in amber borosilica bottle (120 ml, Schott), closed gastight. The suspensions were spiked with TML solution to yield a concentration range from 10 to 100 ng Pb ml^{-1}. pH values were not adjusted to keep the original composition of soils as possible. The suspensions were shaken in the dark at 20 ± 1 °C for 24 h. After shaking, the samples were centrifuged (1200 g) for 20 min; 0.5–30 ml of the supernatant liquid was transferred to a 100 ml glass volumetric flask filled to 85 ml with Milli-Q water with 5 ng Sn TET as internal standard for derivatization and further analysis.

For desorption experiments, the supernatant liquid was poured off after centrifugation, and the remaining adsorbent was rinsed once with Milli-Q water before the bottle was refilled to the same volume with artificial rainwater free of TML. This mixture was shaken for 24 h under the same conditions than in the previous corresponding adsorption experiment. Sample preparation and further steps were carried out as described previously.

Analysis of trimethyllead

Derivatization of the samples was done by 10 mg sodium tetra(*n*-propyl)borate ($NaBPr_4$) in acetate buffer (pH was adjusted to 4), and extracted with 1 ml cyclopentane by vigorous shaking for 10 min. The cyclopentane extract was afterwards centrifuged (8800 g) and cleaned-up with a pasteur pipette (150 mm length) filled with approximately 0.15 g of silica gel (0.063–0.2 µm, glowed at 500 °C overnight, 5% deactivated with water) was analyzed with a coupling of a gas chromatograph (HP 6890) to an ELAN 5000 ICP-MS (Perkin-Elmer SCIEX, Thornhill, ON, Canada). More details of the coupling are described by Glindemann et al. (2002).

For quantification of TML in soils and litter, 0.5 g forest floor, wetland soil or litter and 1 g of mineral soil were extracted by 1 M $CaCl_2$, 0.1% tropolone in glacial acetic acid together with 5 ng internal standard TET in 10 ml glass centrifuge tube (Huang et al. 2003). The mixture was shaken horizontally in the dark for 24 h and subsequently centrifuged for 10 min (1300 g). The solvent was moved into 100 ml glass volumetric flask and diluted with Milli-Q water to 85 ml. The solvent was further derivated, extracted and analyzed as described above. The recoveries of all TML spiked soil samples were >90% (Huang et al. 2003).

All precipitation and runoff samples were processed within 48 h to prevent potential degradation. The samples were filtered with 1 μm glass fiber filter paper and 95 ml was moved into 100 ml glass volumetric flask with 5 ng TET as internal standard. The samples were further derivated, extracted and analyzed as described above.

Analysis of total lead

Soils and litter of about 0.5 g were digested with 3 ml distilled HNO_3 by High Pressure Accelerated Solvent (HPA-S, Anton Paar, Austria). In the 3-step program, a first heating to 80 °C, is followed by heating to 170 °C and finally to 270 °C, lasting for 90 min. The supernatant was then filtered with membrane filter, diluted to 25 ml with Milli-Q water and measured by ICP-MS (Agilent 7500 Series, Japan). For liquid samples, 10 ml samples were filtered with membrane filter and directly determined by ICP-MS. The recovery of Pb_{total} from the sediment standard LKSD-3 (Canada Centre for Mineral and Energy Technology) based on this method was 90%.

Results

In upland soils, the highest contents in forest floors were up to 0.02 ng Pb g^{-1} for TML and 160 μg Pb g^{-1} for Pb_{total} (Figure 2). Contents of TML decreased sharply with depth in the mineral soils, whereas contents of Pb_{total} enriched slightly in the Oe horizon. In the Fen soil, TML contents peaked at the depth of 10–20 cm. TML contents in wetland soils were significantly higher than in upland soils. Contents of Pb_{total} in Fen soils decreased with depth and had the highest contents around 140 μg Pb g^{-1} in the surface horizon.

Taking the soil profiles as representative, the total average soil storages in the Lehstenbach catchment were calculated as 11.6 mg Pb ha^{-1} for TML and 222 kg Pb ha^{-1} for Pb_{total} (Table 1). Most TML (35.9 mg Pb ha^{-1}) was found in wetland soils and only little (1.1 mg Pb ha^{-1}) in forest floors. No TML was detectable in mineral soils. In contrast, Pb_{total} had the highest storage in the mineral soils (>90%).

Concentrations of TML and Pb_{total} in wet precipitation were in the order: fog > throughfall > bulk precipitation and were usually under 2 ng Pb l^{-1} and 5 μg Pb l^{-1}, respectively (Table 2). Concentrations in fogs were up to 10 ng Pb l^{-1} for TML and 40 μg Pb l^{-1} for Pb_{total}. Concentrations in runoff were lower than in precipitation for TML, but were in a similar range for Pb_{total}. Contents of TML in litterfall were very low (several 10 pg Pb g^{-1}). The total annual deposition to the

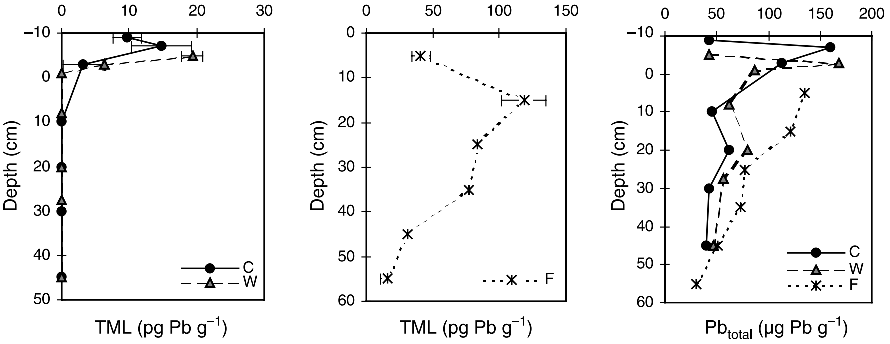

Figure 2. Contents of trimethyllead (TML) and total lead (Pb$_{total}$) in upland and wetland soils of Lehstenbach catchment. C: Coulissenhieb; W: Weidenbrunnen; F: Fen. Mean values and *SD* of three replicates extraction for TML and mean values of three replicates measurement for Pb$_{total}$ ($SD < 5\%$) were shown. Detection limits of TML: 1.09 pg Pb g^{-1} for soils and litter samples.

Table 1. Estimated storages of trimethyllead (TML) (mg Pb ha^{-1}) and total lead (kg Pb ha^{-1}) in wetland and upland soils down to 60 cm depth.

Species	Wetland soils	Forest floors	Mineral soils	Total soil storage
TML	35.9 ± 4.5	1.1 ± 0.4	0	11.6 ± 1.4
Pb$_{total}$	69.3	17.5	270	222

Table 2. Concentrations of trimethyllead (TML) and total lead in bulk precipitation (BP), throughfall (TF), for, runoff and litterfall (LF) from August 2001 to August 2002 at the catchment Lehstenbach.

	TML				Pb$_{total}$		
	Median	Average	Min-Max		Median	Average	Min-Max
BP (ng Pb l^{-1})[a]	0.08	0.12	<DL–1.45	(μg Pb l^{-1})	0.56	0.76	<DL–5.49
TF (ng Pb l^{-1})[a]	0.36	0.44	0.06–2.17	(μg Pb l^{-1})	1.92	2.07	0.57–4.98
Fog (ng Pb l^{-1})[b]	0.32	1.06	0.03–10.7	(μg Pb l^{-1})	9.48	9.61	0.48–40
LF (pg Pb g^{-1})[c]	17	21	7.7–44	(μg Pb g^{-1})	6.19	8.77	<DL–19.8
Runoff (ng Pb l^{-1})[a]	0.05	0.06	<DL–0.29	(μg Pb l^{-1})	1.09	1.28	0.09–4.32

Detection limits of TML: 10.4 pg Pb l^{-1} for water samples. <DL: below detection limits. Sample size: [a] 52; [b] 7; [c] 12.

Table 3. Annual fluxes of trimethyllead (TML) (mg Pb ha^{-1} year^{-1}) and total lead (Pb$_{total}$) (g Pb ha^{-1} year^{-1}) by bulk precipitation, throughfall, litterfall, total deposition (calculated as throughfall + litterfall) and runoff from August 2001 to August 2002 at the catchment Lehstenbach.

	Bulk precipitation	Throughfall	Fog	Litterfall	Total deposition	Runoff
TML	1.15 ± 0.12	3.64 ± 0.15	3.00 ± 0.15	0.07 ± 0.01	3.71 ± 0.15	0.51 ± 0.04
Pb$_{total}$	7.50	16.5	20.7	35.5	52.0	2.82

SD for Pb$_{total}$ were all <5%.

Table 4. Correlations between concentrations of trimethyllead (TML) and total lead (Pb_{total}) and water fluxes from August 2001 to August 2002.

	BD (mm)	BD TML	BD Pb_{total}	TF (mm)	TF TML	TF Pb_{total}	Runoff (mm)	Runoff TML	Runoff Pb_{total}
BD (mm)	XXXXX								
BD TML		XXXXX							
BD Pb_{total}			XXXXX						
TF (mm)	0.93**			XXXXX					
TF TML					XXXXX				
TF Pb_{total}	−0.36*		0.54**	−0.36*	0.45**	XXXXX			
Runoff (mm)	0.67**			0.74**		−0.32*	XXXXX		
Runoff TML				0.35*		−0.49**	0.36*	XXXXX	
Runoff Pb_{total}	0.57**			0.63**		−0.40**	0.69**	0.35*	XXXXX

$^{**}p < 0.01$. $^{*}p < 0.05$.

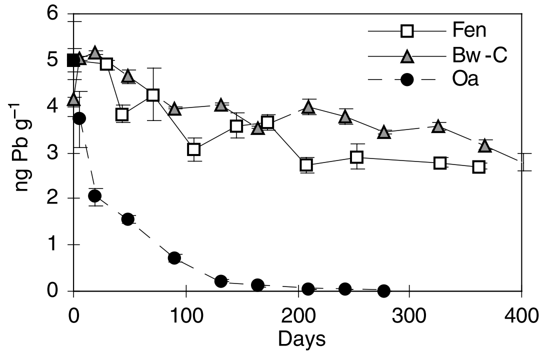

Figure 3. Degradation of trimethyllead (TML) in Oa (——●——), Bw-C (—▲—) horizons of upland soils and Fen (—□—). Mean value and *SD* of three replicates were shown.

Lehstenbach catchment was calculated as the sum of the fluxes with throughfall and litterfall and were 3.7 mg Pb ha^{-1} year^{-1} for TML and 52 g Pb ha^{-1} year^{-1} for Pb_{total}. The importance of throughfall for total deposition was different: For TML, throughfall represented 98% of total depositions, whereas for Pb total only 32% was observed (Table 3). The annual runoff fluxes from the catchment were 0.51 mg Pb ha^{-1} year^{-1} for TML 2.82 g Pb ha^{-1} year^{-1} for Pb_{total}. The output with runoff represented 14% (TML) and 5% (Pb_{total}) of the present deposition. The ratio of the average soil storage in the catchment to the present sink (annual deposition − runoff) was 3.6 years for TML.

A strong increase of TML and Pb_{total} concentrations in throughfall appeared after longer dry periods (2001-43th week, 2002-07th week and 2002-16th week). TML and Pb_{total} concentrations in bulk precipitation showed little variation below 0.2 ng Pb l^{-1} and 1 μg Pb l^{-1}. In bulk precipitation, TML concentrations peaked only in 2001-50th week (1.44 ng Pb l^{-1}, also in throughfall) and 2002-21st week (0.46 ng Pb l^{-1}) and Pb_{total} concentrations peaked in 2002-2nd week (5.49 μg Pb l^{-1}, also in throughfall) and 2002-17th week (2 μg Pb l^{-1}). Higher concentrations and fluxes of TML and Pb_{total} in runoff occurred in autumn and winter (2002-01st week – 2002-13th week).

TML and Pb_{total} concentrations in throughfall and bulk precipitation showed no correlation with the amount of precipitation (Table 4). On the contrary, the TML and Pb_{total} concentrations in runoff was positively correlated to the runoff and throughfall amount.

TML concentrations correlated with Pb_{total} concentrations in throughfall and runoff, but not in bulk precipitation. Concentrations of dissolved organic carbon (DOC) correlated significantly with TML only in throughfall ($r = 0.65$, $p = 0.001$) but with Pb_{total} in throughfall ($r = 0.76$, $p = 0$) and in runoff ($r = 0.47$, $p = 0.017$). pH in runoff correlated negatively with TML ($r = -0.60$, $p = 0.002$) and Pb_{total} ($r = -0.64$, $p = 0.001$) (Data not shown).

Half-lives and average lifetimes of TML in soils were obtained by fitting our data to first-order kinetics (with r^2>0.9 for Oa and $r^2 > 0.8$ for Bw-C and Fen) (Figure 3,

Table 5. Rate constants (k), half life ($t_{½}$) and average life (t) in first order kinetic of trimethyllead (TML) in the Oa, Bw-C horizon of upland soils and Fen.

	k (day^{-1})	$t_{½}$ (days)	t (days)
Fen	0.0021	421	607
Oa	0.0207	33.5	48.3
Bw-C	0.0011	612	884

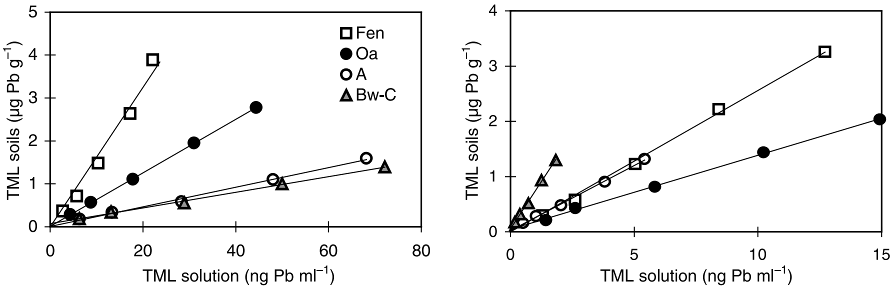

Figure 4. Adsorption (left) and desorption (right) isotherms of trimethyllead (TML) for Oa (●), A (○) and Bw-C (▲) horizons of upland soils and Fen (□). Mean values and *SD* of three replicates are shown and all $R^2 > 0.9$.

Table 6. K_d values and the percentage of adsorption (ads.) and desorption (des.) of trimethyllead (TML) in the Oa, A and Bw-C layer of upland soils and Fen. The reported results are the mean values calculated by the data points of each isotherm.

	C%	CEC (mmol$_c$ kg^{-1})	K$_d$ (ads.) (l kg^{-1})	Adsorption (%)	K$_d$ (des.) (l kg^{-1})	Desorption (%)
Fen	42.0	106.5	163	74	256	17
Oa	31.4	274.2	62.7	56	138	26
A	4.82	97.6	23.0	32	242	16
Bw-C	1.55	42.5	19.7	31	728	6

Table 5). TML decomposed very fast with 33.5 days half-life in the Oa horizon. Degradation of TML in both Bw-C and Fen was much slower with half-lives of 612 days and 421 days, respectively. No TTML was found in the headspace of the wetland soil samples during the whole investigation.

The adsorption and desorption isotherms were linear for the studied concentration range (Figure 4). TML adsorption K_d ($= [\text{TML}_{\text{sorb}}]/[\text{TML}_{\text{aq}}]$) and adsorption percentages were in the order: Fen > Oa > A > Bw-C (Table 6). All desorption K_d were higher than adsorption K_d and the amounts of TML desorbed were small (5–26% of the adsorbed).

Discussion

TML concentrations in bulk precipitation reported here were in a similar range as in other rural sites in the past (Allen et al. 1988, in UK), but much lower than in most of the past studies in urban areas (Van Cleuvenbergen and Adams 1992; Baena et al. 2000). Thus the effect of the terminated use of OLC as fuel additives is not easily visible in our data, probably because of the near border to the Czech Republic where leaded fuel is still available. The calculated rates of total deposition point to a substantial input of TML and Pb_{total} by dry and fog deposition. This is supported by the higher concentrations of TML and Pb_{total} in throughfall after longer dry periods. The calculation of total deposition as the sum of throughfall and litterfall relies on the assumption that TML and Pb_{total} in litter originates only from the atmosphere, which is very critical for Pb_{total}. The translocation of Pb from roots to leaves and needles is rather small (Adriano 2001) and the assumption seems reasonable. In case of Pb_{total}, the total deposition exceeded the input by bulk precipitation and fog, indicating additional dry deposition of Pb to the needles. In case of TML, the fog deposition and bulk precipitation almost equal the calculated total deposition. Thus the deposition behavior of TML and Pb_{total} seems different. The ratio of total deposition/bulk precipitation is about seven for Pb_{total}, but only 3 for TML. The lack of correlation between TML and Pb_{total} in bulk precipitation also suggests different behavior of the two compounds in the atmosphere. However, this cannot be proved from our data, because TML might be deposited in similar relations as Pb_{total}, followed by decomposition on the needles or re-emission to the atmosphere. Decomposition of TML on needles is likely, since in our investigations we observed a half-life of 34 days in aerobic soils. The phyllosphere is rich in microorganisms (Stadler et al. 2001) which might decompose TML on the leaves. This could also explain the very small fluxes of TML with litterfall.

The correlation between the concentrations of both Pb species in throughfall indicates similarity in the mobilization from the needle surfaces probably by complexation with dissolved organic matter (DOC) (Wang and Benoit 1996). This was confirmed by the good correlation of both TML and Pb_{total} to DOC in throughfall.

TML was adsorbed to all soil samples. The adsorption strength as indicated by the K_d value was generally much lower as those reported for Pb^{2+} (270-217000, Sauvé et al. 2000) which can be explained by the single charged TML molecule and by the specific complexation of Pb^{2+} by the soil organic matter (SOM). The adsorption of TML was stronger in Fen and Oa soils than the A and Bw-C soils, reflecting their higher cation exchange capacity and C contents. SOM is known to strongly adsorb organic metal species, like in the case of organotin compounds (Arnold et al. 1998). Therefore TML seems to be more mobile in mineral soils than in organic soils. The lower K_d (ads.) in the Oa than in the Fen soil is possibly due to the higher release of DOC from the Oa soil complexing with TML (Wang and Benoit 1996). The solutions obtained from the Oa samples during the batch experiments were strongly colored in comparison to the Fen soil, suggesting the higher release of DOC. The adsorption of TML to the different soils had in all cases a remarkable hysteresis. The K_d values for the desorption were up to 35 times higher than for the adsorption.

The degradation of TML was relatively fast in the aerobic Oa soil. The lower degradation rates of TML in the Fen soil might be attributed to lower bioactivity under anoxic condition and stabilization of TML via the stronger adsorption onto C-rich wetland soils with high CEC. Although both chemical and biological degradation of TML in soils have been demonstrated (Ou et al. 1994, 1995), the much higher TML degradation rate in forest floor than in wetland and mineral soils points to the importance of biological decay (Macaskie and Dean 1990).

Most TML stored in the catchment was found in the wetland soils. This reflects the strong TML adsorption in the Fen soil and the low rates of decomposition of TML under anoxic conditions. The maximum concentration of TML in the Fen soil was observed in 10–20 cm depth. The 0–10 cm layer is partly subjected to aerobic conditions that will increase the rate of decay. The TML maximum in the 10–20 cm layer and the TML content in the deeper layer must result from the vertical transport of TML into the deeper layers, despite the strong adsorption to the soil. Thus TML seems to be mobile to some extend in soils, if not decomposed. The depth gradients in upland soils with highest contents of TML and Pb_{total} in the forest floors point to the input of TML and Pb_{total} by precipitation and litterfall and reflect well their strong adsorption to SOM. There seems to be no significant vertical transport of TML in the upland soils, since the contents in depth >10 cm was below detection limit. This coincides with the fast decomposition of TML in upland soils.

We do not consider the methylation of Pb under anoxic conditions as a dominant process in the Fen soil, since the contents of TML were in the same order of magnitude than those observed from the Oa soil. In case of Methyl-Hg the contents were about 40 times higher in the Fen soil as compared to the Oa horizon (Schwesig et al. 1999). Furthermore, the anoxic incubation of the Fen soil did not result in the formation of TTML (as revealed by headspace analysis), which would be a sign of *in situ* methylation.

The contents of Pb_{total} in the mineral soils had a relatively flat gradient. This points to the influence of natural geogenic Pb sources from the granite (Arnaudov et al. 1977). These sources also seem to influence the Pb_{total} profile in the Fen soil, since the mineral content of the Fen is between 10 – 25%.

When comparing the calculated annual deposition of TML with the total soil storage in the catchment, the soil storage is only about 3.6 times the annual deposition, reflecting the rapid degradation of TML mainly in the upland soils.

The average concentrations of TML in runoff are only about 10% of those in throughfall which supports our findings on the degradation of TML in upland soils and the strong retention in wetland soils. Thus, the mobility of TML in the catchment and the risk of TML transfer from the soils to the runoff seems very low. The runoff concentration of Pb_{total} is about 50% of the one in througfall, and most of the deposited Pb is stored in the catchment.

Elevated TML and Pb_{total} concentrations in runoff, especially Pb_{total}, during snowmelt and the positive correlation of TML and Pb_{total} concentrations in runoff with throughfall fluxes indicated the existence of mobilizable pools in the catchment, during events of high water fluxes which drain mostly surface near soil horizons and leading to higher DOC concentrations in runoff (Lischeid et al. 2002).

Conclusions

Our data show that TML is still deposited from the atmosphere even after terminated use of tetraalkyllead for years in Germany. TML is strongly adsorbed in organic soils in comparison to mineral soils and the adsorption has a strong hysteresis. In upland soils, TML is rapidly decomposed, but under anoxic conditions the decay is much slower. Forest soils act as sink and filter for atmospherically deposited TML and Pb. Only small amounts of TML are transferred from soils into runoff.

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