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Biogeochemistry of Organotin
and Organolead Compounds
in a Forested Catchment in
NE-Bavaria, Germany

- Doctoral thesis -
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Table of Contents

List of Abbreviation

DBT	Dibutyltin $(C_4H_9)_2Sn^{2+}$
DL	Detection limit
DMT	Dimethyltin $(CH_3)_2Sn^{2+}$
DOT	Dioctyltin $(C_8H_{17})Sn^{2+}$
DPhT	Diphenyltin $(C_6H_5)_2Sn^{2+}$
GC	Gas chromatography
ICP-MS	Inductively coupled plasma – mass spectrometry
LD	Lethal dosis
K_d	Adsorption coefficient
K_p	Gas / particle partition coefficient
MMM	Monomethylmercury CH_3Hg^+
MBT	Monobutyltin $(C_4H_9)Sn^{3+}$
MMT	Monomethyltin CH_3Sn^{3+}
MOT	Monooctyltin $(C_8H_{17})Sn^{3+}$
MPhT	Monophenyltin $(C_6H_5)Sn^{3+}$
NaBEt$_4$	Sodium tetraethylborate $NaB(C_2H_5)_4$
NaBH$_4$	Sodium borohydrate $NaBH_4$
NaBPr$_4$	Sodium tetra(n-propyl)borate $NaB(C_3H_7)_4$
OLC	Organolead compounds
OMC	Organomercury compounds
OTC	Organotin compounds
PVC	Poly(vinyl) chloride
$t_{1/2}$	Half-life
TBT	Tributyltin $(C_4H_9)_2Sn^+$
TEL	Triethyltin $(C_2H_5)_3Pb^+$
TET	Triethyltin $(C_2H_5)_3Sn^+$
TML	Trimethyltin $(CH_3)_3Pb^+$
TMT	Trimethyltin $(CH_3)_3Sn^+$
TOT	Trioctyltin $(C_8H_{17})_3Sn^+$
TPhT	Triphenyltin $(C_6H_5)_3Sn^+$
TTBT	Tetrabutyltin $(C_4H_9)_4Sn$
TTEL	Tetraethyllead $(C_2H_5)_4Pb$
TTML	Tetramethyllead $(CH_3)_4Pb$
TTMT	Tetramethyltin $(CH_3)_4Sn$

Summary

Organotin-compunds (OTC) and Trimethyllead (TML) have a higher toxicity than their corresponding inorganic forms and may affect the functioning of ecosystems. Little is known about their behaviour and fate in the terrestrial environment. The goal of this thesis was to investigate the biogeochemistry of OTC (methyltin, butyltin and octyltin compounds) and TML in a forested catchment, especially their input and output budget. The occurrence of OTC, TML, Sn_{total} and Pb_{total} in the atmosphere, soils, precipitation, and runoff in a forested ecosystem in NE-Bavaria, Germany were investigatedand the inputs and outputs in the solute phase determined. In addition, their ad-desorption and transformation (degradation) in forest soils was studied using batch experiments and long term incubations, respectively.

At the Lehstenbach catchment and in Bayreuth city, OTC and TML concentrations in the gas phase during April to June 2003 was on average 110 pg Sn m^{-3} and 0,34 pg Sn m^{-3}. Tri-, di-substituted and octyl species were the dominant OTC in the gas phase. In aerosols, only butyltin compounds, dimethyltin and monomethyltin (<500 pg Sn m^{-3}) were found and mono-substituted OTC predominated. No significant difference of concentrations in the atmosphere between the two sites was found. For OTC, the washout factors were in the order: mono- $\geq$ di- > tri-substituted OTC, and the gas / particle partition coefficients were mono- >> di- >> tri-substituted OTC. Aerosol particles serve as a sink for OTC in the atmosphere, especially for monomethyltin and monobutyltin. The long-range-transport in the atmosphere seems to be an important source for OTC and TML at both sites.

From August 2001 to August 2002, the concentrations of organic and inorganic tin and lead compounds in precipitation were in the order: fog > throughfall > bulk precipitation. Average concentrations of OTC_{total} ranged from 57 ng Sn l^{-1} in fog to 5.8 ng Sn l^{-1} in bulk precipitation. The concentrations of Sn_{total} were between 490 ng Sn l^{-1} in fog and 140 ng Sn l^{-1} in bulk precipitation, on average. Average concentrations of TML were 1 ng Pb l^{-1} in fog and 0.1 ng Pb l^{-1} in bulk precipitation and 9.6 and 0.76 µg Pb l^{-1} in case of Pb_{total}.

The annual total deposition from the atmosphere, estimated as throughfall + litterfall fluxes, amounted to 3.7 mg Pb ha^{-1} yr^{-1} for TML and 52 g Pb ha^{-1} yr^{-1} for Pb_{total}. The contribution of litterfall was 1.5% and 32%, respectively. The annual total deposition of OTC_{total} was 172 mg Sn ha^{-1} yr^{-1}, with 26% represented by litterfall. The total deposition of Sn_{total} was 4.9 g Sn ha^{-1} yr^{-1}, of which 4.1% was litterfall.

The annual flux with runoff from the catchment was 0.5 mg Pb ha^{-1} yr^{-1} for TML and 2.8 g Pb ha^{-1} yr^{-1} for Pb_{total}. The annual runoff of OTC_{total} and Sn_{total} amounted to 25 mg Sn ha^{-1} yr^{-1} and 2.4 g Sn ha^{-1} yr^{-1}, respectively. All OTC and TML concentrations in runoff were lower than in bulk precipitation, while those of Sn_{total} and Pb_{total} were similar to bulk precipitation. Monobutyltin was the dominating OTC in precipitation and litterfall, but was seldom detected in the runoff. The mass balance showed high retention of tin and lead compounds in the catchment.

The total soil storage of OTC_{total} and Sn_{total} in the catchment were 6.7 g Sn ha^{-1} and 1.9 kg Sn ha^{-1}. Total soil storage in the catchment was 11.6 mg Pb ha^{-1} for TML and 222 kg Pb ha^{-1} for Pb_{total}. The dominance of mono-substituted compounds in precipitation is well reflected in the concentrations and storages of OTC in both upland and wetland soils. 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.

OTC degraded slowly in soils with half-lives (t$_{1/2}$) estimated from 0.5 to 15 years. The first order degradation rate constants of OTC in soils ranged from 0.05 to 1.54 yr^{-1}. The degradation rates in soils were generally in the order mono- $\geq$ di- > tri-substituted OTC. Stepwise dealkylation was observed in all cases of di-substituted OTC, but only in some cases of tri-substituted OTC. Decomposition rates of OTC in the forest floor were higher than in wetland and mineral soils. Slow degradation of OTC in soils might lead to long-term storage of atmospherically deposited OTC in soils. TML degraded rapidly in the forest floor (Oa) with a t$_{1/2}$ of 0.09 years. The degradation of TML in Fen (t$_{1/2}$ = 1.2 years) and in the mineral soil (Bw-C, t$_{1/2}$ = 1.7 years) was much slower. Emission of tetramethyltin and tetramethyllead from wetland soils was not observed, suggesting little Sn and Pb methylation in the wetland soils.

The adsorption and desorption isotherms for all species and soils were linear over the concentration range of 10–100 ng Sn, Pb ml^{-1}. The strength of OTC adsorption correlated well with the carbon content and cation exchange capacity of the soil and was in the order mono- > di- > tri-substituted OTC and butyltin > methyltin compounds. The adsorption and desorption showed a pronounced hysteresis. The desorption of the adsorbed OTC was generally small and was the largest in the case of trimethyltin (desorption 2–12% of the adsorbed amounts). Mono-substituted OTC adsorbed almost irreversibly in all soils (desorption <1% of adsorbed amounts).

The ratio of total soil storages in the catchment to the present annual input was 3.6 years for TML, reflecting the rapid degradation of TML in forest soils. The ratios of OTC soil storages to their present annual deposition ranged from 4.3 to 400 years. These high ratios reflect probably the high stability, low mobility of OTC in soils and the variation of the annual total deposition.

For the first time, the turnover of OTC in the terrestrial environment was quantified. In comparison with aquatic sediments, OTC concentrations in forest soils are considerably lower, and the dominant species are less toxic. Organotin compounds strongly   adsorb to forest soils and degrade slowly, leading to long-term storage in the forest soils. It is concluded that forested soils act as sinks for OTC deposited from the atmosphere. Only little OTC is released from soils into the aquatic environment.

TML and Pb$_{total}$ are still deposited in remote areas even after the use of tetraalkyllead as antiknock-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.

Zusammenfassung

Organozinnverbindungen (OTC) und Trimethyl-Pb (TML) sind toxischer als anorganisches Sn und Pb und können die Funktion von Ökosystemen beeinflussen. Über das Verhalten dieser Stoffe und deren Verbleib in der terrestrischen Umwelt gibt es bisher nur wenig Informationen. Ziel der Arbeit war es die Biogeochemie von OTC (Methyl-Sn, Butyl-Sn, und Octyl-Sn) und von

TML in einem bewaldeten Einzugsgebiet zu untersuchen und insbesondere eine Bilanzierung der Ein- und Austräge vorzunehmen. Dazu wurden die Gehalte von OTC und TML und von gesamt-Sn und gesamt-Pb in der Atmosphäre, im Boden, in den Niederschlägen und im Abfluß eines bewaldetem Ökosystems in NO-Bayern untersucht und die jährlichen Einträge und Austräge in der gelösten Phase bestimmt. Ferner wurde das Absorptionsverhalten und die mikrobielle Stabilität der organischen Spezies im Boden durch Batch-Versuche, bzw. durch Inkubationen untersucht.

Die Konzentrationen von gesamt-OTC und TML in der Gasphase der Atmosphäre im Lehstenbach Einzugsgebiet und in der Stadt Bayreuth lagen im Zeitraum April bis Juni 2003 im Mittel bei 110 pg Sn m^{-3} und 0,34 pg Pb m^{-3}. Bei den OTC dominierten Tri- and Di-substitutierte and Octyl-Verbindungen. Im Aerosol wurden nur Butyl-Sn, Dimethyl-Sn und Monomethyl-Sn gefunden, bei Dominanz von mono-substituierten OTC. TML konnte im Aerosol nicht nachgewiesen werden. Die Konzentrationen in der Atmosphäre unterschieden sich nicht zwischen beiden Standorten. Für OTC waren die Auswaschungssfaktoren in der Reihenfolge: Mono- $\geq$ Di- > Tri-substitutierte OTC, und für die Gas/Partikel-Partitionskoeffizient galt Mono- >> Di- >> Tri-substituierte OTC. Aerosolpartikel sind eine wichtige Senke für OTC in der Atmosphäre, besonders für Monomethyl-Sn und Monobutyl-Sn. Der Ferntransport in der Atmosphäre scheint die wichtigste Quelle für OTC und TML in beiden Untersuchungsgebieten zu sein.

Im Zeitraum von August 2001 bis August 2002 waren die Konzentrationen von OTC, TML und anorganischem Sn und Pb im Niederschlag in der Reihenfolge Nebel > Bestandesniederschlag > Freilandniederschlag. Die mittleren Konzentrationen von gesamt-OTC erreichten 57 ng Sn l^{-1} im Nebel, und 5.8 ng Sn l^{-1} im Freilandniederschlag. Für gesamt-Sn waren die mittleren Konzentrationen zwischen 490 ng Sn l^{-1} im Nebel und 140 ng Sn l^{-1} in Freilandniederschlag. Die mittleren TML Konzentrationen lagen zwischen 1 ng Pb l^{-1} im Nebel und 0.1 ng Pb l^{-1} im Freilandniederschlag, die von gesamt-Pb zwischen 9.6 und 0.76 µg Pb l^{-1}.

Die Depositionsrate berechnet als Summe der Flüsse mit dem Bestandesniederschlag plus Streufall, betrug 3.7 mg Pb ha^{-1} yr^{-1} für TML und 52 g gesamt-Pb ha^{-1} yr^{-1}. Der Streufall machte 1.5 % bzw. 32% der Deposition von TML und von gesamt-Pb aus. Die Depositionrate von gesamt-OTC erreichte 172 mg Sn ha^{-1} yr^{-1}, mit 26% als Streufall, die von gesamt-Sn 4.9 g Sn ha^{-1} yr^{-1}, mit 4.1% als Streufall.

Die jährliche Austrag von TML mit dem Abfluß aus dem Einzugsgebiet betrug 0.5 mg Pb ha^{-1} yr^{-1} und 2.8 g gesamt-Pb ha^{-1} yr^{-1}. Der Austrag von gesamt-OTC und gesamt-Sn erreichte 25 mg Sn ha^{-1} yr^{-1} bzw. 2.4 g Sn ha^{-1} yr^{-1}. Die OTC Konzentrationen im Abfluß waren immer niedriger als im Freilandniederschlag, aber die gesamt-Sn und -Pb Konzentrationen im Abfluß und Freilandniederschlag waren ähnlich. Monobuthyl-Sn dominierte bei den OTC im Niederschlag und Streufall, wurde aber nur selten im Abfluß detektiert. Die Massenbilanz des Einzugsgebietes zeigte die starke Retention aller Sn und Pb Spezies im Einzugsgebiet.

Die Vorräte an gesamt-OTC und gesamt-Sn in den Böden im Einzugsgebiet betrugen 6.7 g Sn ha^{-1} and 1.9 kg Sn ha^{-1}. Die Dominanz von mono-substituierten OTC im Niederschlag spiegelte sich gut in den OTC-Gehalten in Böden und in den Bodenvorräten wieder. Für Pb wurden Bodenvorräte von 11.6 mg Pb ha^{-1} im Falle von TML und 222 kg gesamt-Pb ha^{-1} gemessen. Im

Falle von TML fanden sich mehr als 90% der Bodenvorräte in den Moorböden, die nur 30% der gesamten Fläche einnehmen. Mehr als 90% des Bodenvorräte von gesamt-Pb fanden sich hingegen in den terrestrischen Böden. Dort war TML nur im Auflagehumus nachweisbar..

Der Abbau der OTC im Boden erfolgte nur langsam mit Halbwertzeiten von 0.5 bis 15 Jahren. Die Abbaukonstanten 1. Ordnung lagen zwischen 0.05 und 1.54 Jahr^{-1}. Di-substituierte OTC unterlagen einer schrittweisen Dealkylierung, die bei tri-substituierten Spezies nur teilweise gefunden werden konnte. Die Abbauraten in der Humusauflage waren höher als die im Moorboden bzw. im Mineralboden. Der Abbau war allgemein in der Reihfolge mono- $\geq$ di- > tri-substituierte OTC. Der langsame Abbau von OTC macht einen langfristigen Verbleib der untersuchten OTC in terrestrischen und semiterrestrischen Böden wahrscheinlich. Der Abbau des TML im Auflagehumus war relativ schnell ($t_{1/2}$ = 0.09 Jahre) im Vergleich zum langsamen Abbau im Mineralboden und Moor ($t_{1/2}$ = 1.7 und 1.2 Jahre jeweils). Ausgasung von Tetramethyl-Sn und -Pb aus dem Moorboden wurde nicht beobachtet. Die Methylierung von Sn und Pb in Moorböden ist somit unwahrscheinlich.

Die Adsorptions- und Desorptionsisothermen aller Spezies in Böden waren linear von 10–100 ng Sn, Pb ml^{-1}. Die Adsorptionsstärke von OTC korrelierte gut mit dem C-Gehalt und der Kationenaustauschkapazität des Bodens. Die Adsorptionsstärke war in der Reihenfolge Mono- > Di- > Tri-substituierte OTC und Butyl-Sn > Methyl-Sn. Ad- und Desorption zeigten eine deutliche Hysterese. Die Desorption von adsorbierten OTC war generell gering und am höchsten bei Trimethyl-Sn (2–12 % der adsorbierten Menge). Mono-substitutierte OTC adsorbierten meist irreversibel in allen Böden (Desorption <1 % der adsorbierten Menge).

Das Verhältnis von Bodenvorräten zu aktuellen Depositionsraten war 3.6 Jahre für TML. Dies spiegelt den raschen Abbau von TML in Waldboden wieder. Die Verhältnisse der OTC Bodenvorräte zu den Depositionsraten hatten je nach Spezies eine Spannweite von 4.3 bis 400 Jahren. Die teilweise sehr hohen Verhältnisse reflektieren die hohe Stabilität und niedrige Mobilität von OTC in Böden und gehen möglicherweise auch auf Schwankungen der Depositionsraten in der Zeit zurück.

Das Vorkommen von OTC in der terrestrischen Umwelt wurde hier erstmals untersucht. Im Vergleich zu aquatischen Sedimenten waren die OTC Konzentrationen in Waldböden deutlich niedriger, und die dominanten Spezies weniger toxisch. Die starke Adsorption und der langsame Abbau von OTC führen zu einer langen Verweilzeit in Waldböden. Waldböden repräsentieren eine starke Senke für atmosphärisch eingetragene OTC. OTC werden nur in geringen Mengen an das Grund-und Oberflächenwasser weitergegeben.

TML und gesamt-Pb werden immer noch in beachtlichen Mengen deponiert, obwohl die Anwendung von Tetraalkyl-Pb als Antiklopfmittel seit vielen Jahren eingestellt wurde. Die Depositionsraten sind aber wesentlich niedriger als früher. Waldböden sind eine Senke für deponiertes TML und gesamt-Pb. TML akkumuliert stark in Moorböden und scheint unter anoxischen Bedingungen langfristig stabil. In terrestrischen Böden wird TML hingegen sehr schnell abgebaut. Nur geringe Mengen an TML werden aus Böden in den Abfluß des Einzugsgebietes transportiert.

1. Synthesis

1.1. Introduction

1.1.1. Properties of organolead and organotin compounds

Organotin compounds (OTC) are characterized by a tin atom covalently bound to one or more organic substitutions. The Sn-C bonds are stable in the presence of water, atmospheric oxygen, and heat. They are reported to be stable at temperatures up to 200°C (ZUCKERMAN et al., 1978). However, UV radiation, strong acids and electrophilic agents readily cleave the Sn-C bonds. The chemical and physical properties of OTC depend on the length and number of alkyl groups (Table 1–1).

Because of remarkable various physical and chemical properties, OTC are commercially used in many ways (Table 1–2). The main compounds in commercial use are the R_3SnX, R_2SnX_2, and $RSnX_3$. R_4Sn has no commercial use, but is an important intermediates in the production of less alkylated derivatives.

Table 1-1. Physical properties of selected organotin compounds

Species	Density (g m^{-3})	Melting point (°C)	Boiling point (°C)	Solubility in H_2O (g l^{-1})
TTBT	1.06	−97	145/ 1.3 kPa	−
TBT	1.21	−16	172/ 3.3 kPa	50 (sea water)
DBT	−	39–41	135/ 1.3 kPa	5−17 (water)
MBT	1.69	−	93/ 1.3 kPa	−
TMT	−	37–39	154	−
DMT	−	106−108	188−190	20,000 (sea water)
MMT	−	48−51	171	−

−: no data available

Table 1-2. Industrial use of organotin compounds

Industrial application	Function	Organotin compounds
PVC stablizers	Stabilization against decomposition by heat and light	R_2SnX_2 and $RSnX_3$, R= Me, Bu, Oct
Antiflouling paints	Biocide	R_3SnX, R=Bu, Ph
Agrochemicals	Fungicide, Insecticide, Miticide, Antifeedant	R_3SnX, R=Bu, Ph, Cy
Wood preservation	Insecticide, Fungicide	Bu_3SnX
Glass treatment	Precursor for Sn(IV) oxide films on glass	R_2SnX_2 and $RSnX_3$, R= Me, Bu
Materials protection	Fungicide, Algicide, Bactericide	Bu_3SnX_2
Impregnation of textile	Insecticide, Antifeedant	Ph_3SnX
Poultry farming	Dewormer	Bu_2SnX_2

Peralkylated organolead compounds (OLC) like tetramethyllead (TTML) and tetraethyllead (TTEL) have been used as antiknock additives in gasoline products for several decades (ŁOBÍNSKI, 1995; RHUE et al., 1992). Peralkylated organolead compounds are discharged into the environment from leaded gasoline and can undergo further transformation, such as degradation

(BAENA et al., 2000). The environmental degradation pathway for tetraalkyllead compounds involve ionic di- and tri-alkyllead compounds in addition to inorganic lead. Monoalkyllead are only occasionally present due to their instability (SZPUNAR & ŁOBÍNSKI, 1999; ŁOBÍNSKI, 1995). Ionic OLC are even more mobile than tetraalkyead compounds. They cannot only dissolve in the organic phase, but also in the aqueous phase (CROMPTON, 1998). Some physical properties of lead compounds are listed in the Table 1–3.

Table 1-3. Physical properties of selected lead compounds

Species	Density (g m^{-3})	Melting point (^{o}C)	Boiling point (^{o}C)	Solubility in H$_2$O (g l^{-1})
Pb(NO$_3$)$_2$	4.53	470		376.5
TTEL	1.66	−136.8	200	0.00029
TEL	−	−	−	ca. 200
TTML	2.0	−27.5	110	0.0179

−: no data available

1.1.2. Toxicological relevance of organolead and organotin compounds

Tin in inorganic from is regarded as non-toxic, but the toxicities of OTC are different by several orders of magnitude depending on the organic structures (Table 1–4). Organotin compounds with short alkyl chains or phenyl substations exhibit considerably toxicity and neurotoxicity toward aquatic organisms and mammals. They can also be hazardous to human beings.

Table 1-4. Acute oral toxicity of inorganic tin and organotin compounds to rats

Species	LD$_{50}$, mg kg^{-1}	Species	LD$_{50}$, mg kg^{-1}
SnCl$_2$	700	TTBT	>4,000
TMT-Cl	13	TBT-OAc	380
DMT-Cl$_2$	74	DBT-Cl$_2$	100
MMT-Cl$_3$	1,370	MBT-Cl$_3$	2,140
TET-OAc	4	TPhT-OH	125

Generally speaking, the toxicity of OTC is in the order: R_3Sn^+ > R_2Sn^{2+} > RSn^{3+}, whereas R = alkyl groups. Their action on living organisms is partially due to inhibition of oxidative phosphorylation and partially by mediation of anion exchange across membranes. The nature of the alkyl group determines their toxicity in regard to different species. Compounds of triethyl- and trimethyltin are toxic to mammals, whereas tri-*n*-butyltin salts are known to affect molluscs, bacteria and fungi (DONARD & WEBER, 1985). A comparison of the oral toxicity of different tin compounds to rats is shown in Table 1–4.

Residues of OTC in soils prohibit fungal and bacterial populations (KUTHBUTHEEN et al., 1989a). Natural processes in soils like nitrification and ammonification are affected by OTC (KUTHBUTHEEN et al., 1989b). The bioavailability of OTC in aqueous systems is thought to be higher than that of inorganic tin (RÜDEL, 2003).

The toxicity of the various OLC are determined by the chemical form of the organic component and the structure with tetraalkyllead compounds being the most toxic ones (HEMPEL et al., 2000). In general, OLC are more toxic than inorganic lead compounds, because they are easily

resorbed by skin and more volatile than inorganic lead (CROMPTON, 1998).

Lead compounds destroy the erythrocytes, and can replace the calcium in the bone, being able to result in fatal danger. The toxic effect of lead compounds based on complexation of oxo group of enzymes. It affects all steps process of heme synthesis and porphyrin metabolisms (HIRNER et al., 2000). A comparison of the oral toxicity of different lead compounds to rats is shown in Table 1–5.

Table 1-5. Acute oral toxicity of inorganic lead and organolead compounds to rats

Species	LD_{50}, mg kg^{-1}	Species	LD_{50}, mg kg^{-1}
$Pb(NO_3)_2$	250	TEL	20
TTEL	15	TML	80
TTML	<36		

1.1.3. Organolead and organotin compounds in the environment

Organotin compounds are widely used as fungicides, as stabilizing additives in polymers like polyvinyl chloride, and as antifouling agent in ship paintings (HOCH, 2001). The worldwide production of OTC increased from less than 5,000 tons in 1955 to about 50,000 tons in 1992 (MERCIER et al., 1994). Leaching from soils and landfills (MERSIOWSKY et al., 2001), weathering of plastics (SADIKI & WILLIAMS, 1999; FORSYTH & JAY, 1997; QUEVAUVILLER & DONARD, 1991), and dissolution of ship paintings (BATLEY, 1996) lead to the permanent release of these compounds into aquatic systems. Organotin compounds can be re-emitted from the marine environment to the atmosphere by transformation of ionic OTC into volatile species (TESSIER et al., 2002; AMOUROUX et al., 2000; WEBER, 1999). Furthermore, terrestrial point-sources like landfills also emit volatile OTC (FELDMANN & HIRNER, 1995).

Except anthropogenic sources of OTC, methylated tin species can be formed in the environment by biotic and abiotic methylation. Tin methylation can occur by oxidative addition of methyl groups from reagents occurring in the environment, for example CH_3I, $(CH_3)_3S^+I^-$, $(CH_3)_3N^+CH_2COO^-$, alkylcobalamins (CRAIG & RAPSOMANIKIS, 1985; THAYER et al., 1984; FANCHIANG & WOOD, 1981). Certain microorganisms are able to form methyltin compounds (THAYER, 1989; HALLAS et al., 1982). Tin methylation in the environment was also evident by the presence of some methylbutyltin compounds in the aquatic ecosystems (TESSIER et al., 2002; AMOUROUX et al., 2000). Furthermore, methylated OTC were found in the natural atmosphere of river estuaries (TESSIER et al., 2002; PÉCHEYRAN et al., 1998).

River, estuary and marine ecosystems have been identified as the major environmental sinks of OTC. At the polluted sites, OTC are usually quite enriched in the surface water. Their concentrations can reach to some µg Sn l^{-1} in the water. Sediments are larger reservoirs for OTC than surface waters. The concentrations of OTC in sediments reach often several µg Sn g^{-1} (WILKEN et al., 1994; JANTZEN & WILKEN, 1991; MAGUIRE et al., 1986). In aqueous environment, butyltin compounds were mostly investigated, whereas methyltin, phenyltin and octyltin compounds could be also identified (Table 1–6).

Bioaccumulation seems to be an important sink for OTC in the aquatic ecosystem. The marine bivalves are able to accumulate TBT up to 5 µg g^{-1}. Crustaceans and fish accumulate much lower amounts of TBT because of their ability to degrade TBT in the body (LAUGHLIN, 1996).

Marine mammals and birds also accumulate high level of butyltin compounds in various tissues and organs (KANNAN et al., 1998a, b).

Knowledge about OTC in the atmosphere is scare. BRAMAN & TOMPIKNS (1979) reported concentrations of methyltin compounds in the rainwater up to 22 ng l^{-1}. Volatile OTC, tetramethyltin, detected in the overlying atmosphere of estuaries ranged from 1 to 20 pg m^{-3} (TESSIER et al., 2002).

Generally, the degradation of OTC in the environment may be described as a progressive loss of organic groups from the Sn cation:

$$R_4Sn \rightleftharpoons R_3SnX \rightleftharpoons R_2SnX_2 \rightleftharpoons RSnX_3 \rightleftharpoons SnX_4$$

Degradation of OTC in the environment can be caused biologically and non-biologically. Photolysis provides additionally a fast route for OTC degradation. SKINNER (1964) indicated that cleavage of Sn-C bond occurred under absorption of light. Tributyltin was shown to decompose stepwise in sunlight with half-lives > 89 days, whereas TBT was stable in the dark over two months (MAGUIRE et al., 1983). Photolysis is probably not important at greater depths in water, nor in sediments or soils as a non-biological OTC degradation.

The Sn-C bond can be attacked by both nucleophile and electrophile reagents, for example mineral acid, carboxylic acid and alkalimetal (HOCH, 2001). BARNES et al. (1973) showed the ability of some bacteria, such as *Pseudomonas aeruginosa*, *Pseudomonas putida C*, and *Alicaligenes faecalis*, to degrade phenyltin compounds in the soil. Microalgae, *Skeletonem costatum* and two *Chlorella* species are able to metabolize TBT (TSANG et al., 1999; READER & PELLETIER, 1992) Half-lives of TBT in waters were estimated between 4 to 19 days under different conditions (HUGGETT et al., 1992; SELIGMAN et al., 1986). In contrast, OTC undergo slow decomposition in the sediments. Estimated half-lives of butyltin compounds in sediments range from 0.6 years to 5.2 years (DE MORA & PELLETIER, 1997; DOWSON et al., 1996; SARRADIN et al., 1995).

The alkyl groups on OTC can transfer to other metal ions, like to Hg (HAMASAKI et al., 1995; Thayer, 1995). Studies about the fate and behaviours of OTC in the terrestrial environments are scare.

Adsorption of OTC in sediments and minerals is governed by i) electrostatic interaction between the positive charge on the OTC and the negative charges on the sorbent materials (SUN et al., 1996), ii) complexation of the OTC cation by the negatively charged ligands provided by soil organic matters (ARNOLD et al., 1998), and iii) hydrophobic interaction (ARNOLD et al., 1998; RANDALL & WEBER, 1986).

The pH and salinity influence the adsorption of OTC in sediments. The pH-dependent negative charges on both organic and mineral phases are reduced at low pH (WEIDENHAUPT et al., 1997; ARNOLD et al., 1998), and the maximum adsorption of OTC in sediments was found at pH close to the pK$_a$ of OTC, which is about pH 6–7 for most species (HOCH et al., 2003; 2002; DAI et al., 1993). DONARD & WEBER (1985) and RANDALL & WEBER (1986) found that strongly saline solutions inhibited the adsorption of OTC in sediments because of the competition of other cations to sorbents and anions to OTC, and possible coagulation of sorbents. HOCH & SCHWESIG (2004) demonstrated the adsorption of TBT was largely enhanced with the existence of natural organic matter.

Table 1–6. Concentrations of organotin compounds in the environments

Location				Reference
Water (ng (Sn) l^{-1})	**TBT**	**DBT**	**MBT**	
Sado Estuary, Protugal	18–60	52–160	39–870	QUEVAUVILLER & DONARD 1990
River water, Spain	6.9–41	5.5–68	8.3–488	GOMEZ-ARIZA et al. 1995
Antwerp Harbour, Holland	51–76	217–283	765–1,000	DIRKX et al. 1993
Ganga Plain, India	2–70	2–101	2–20	ANSARI et al. 1998
Marine in Holland	3–310	0.1–810	0.1–3,620	RITSEMA & LAANE 1991
Lake and river water, China	<DL–977	<DL–185	<DL–883	JIANG et al. 2001
Sea water, Japan	0.019	0.017	0.025	HARINO et al. 1992
	TPhT	**DPhT**	**MPhT**	
Sea water, Japan	<DL	0.003	0.027	HARINO et al. 1992
	TMT	**DMT**	**MMT**	
Schwartzbach, Germany	–	0.8	–	RITSEMA & LAANE 1991
Ontario, Canada	<DL–50	20–220	110–530	MAGUIRE et al. 1982
	TOT	**DOT**	**MOT**	
Tuticorin Harbour, India	0.09–0.186	0.02–0.503	0.112–1.93	RAJENDRAN et al. 2001
Sea water, Japan	<DL–0.012	<DL–0.506	0.041–0.795	RAMASWAMY et al. 2004
Sediment (ng (Sn) g^{-1} dry wt)	**TBT**	**DBT**	**MBT**	
River sediment, Spain	1.2–129	1.1–510	0.7–601	GOMEZ-ARIZA et al. 1995
Bay of Arcachon, France	6–151	5–141	16–161	QUEVAUVILLER et al. 1994
San Diego Bay, California	2–185	2–265	2–242	KRAM et al. 1989
Pearl Harbour, Hawaii	5–553	4–367	4–2,830	KRAM et al. 1989
Lake Westeinder, Holland	6–100	6–96	6–520	STÄB et al. 1996
Leman Lake, Switzerland	186	195	627	CARLIER-PINASSEAU et al. 1997
Hamburg, Germany	430	610	5,200	JANTZEN & WILKEN 1991
Toronto, Canada	580	248	539	MAGUIRE 1984
Vancouver, Canada	3,360	8,510	10,780	MAGUIRE et al. 1986
Schwartzbach, Germany	477	547	–	SCHEBEK et al. 1991
Göta älv estuary, Sweden	16.5–366	16.7–98.0	6.5–44.4	BRACK 2002
Antwerpen habor, Belgium	20–141,000	3,000–10,300	1–46,000	CEULEMANS et al. 1998
Seto Inland Sea, Japan	2.2–9.3	0.32–12.8	6.3–18.1	RAJENDRAN et al. 2000
	TPhT	**DPhT**	**MPhT**	
Leman Lake, Switzerland	158	142	319	CARLIER-PINASSEAU et al. 1997
Göta älv estuary, Sweden	<1.5–70.8	<1.2–6.2	<0.8–5.4	BRACK 2002
Antwerpen habor, Belgium	380–5,500	270–1,550	400–6,500	CEULEMANS et al. 1998
Seto Inland Sea, Japan	<DL–0.6	<DL–0.8	<DL–1.8	RAJENDRAN et al. 2000
	TMT	**DMT**	**MMT**	
Schwartzbach, Germany	27	42	69	SCHEBEK et al. 1991
Ontario, Canada	<DL– 750	<DL– 170	<DL–17,190	MAGUIRE et al. 1986
Sado Esturary, South Lisbon	<DL– 120	<DL– 160	<DL–21	QUEVAUVILLER et al. 1989
Rainwater (ng (Sn) l^{-1})	**TMT**	**DMT**	**MMT**	
Florida, USA	<DL–1.1	<DL–4.8	0.65–22	BRAMAN & TOMPIKNS 1979
La Jolla, CA, USA	–	<DL	<DL–10	TUGRUL et al. 1983

–: not determined

The large amount of TTML and TTEL was produced industrially as antiknock additives in gasoline in the past decades (ŁOBÍNSKI et al., 1994). In nature, inorganic lead may undergo abiotic and biotic methylation (THAYER, 2002; CRAIG & RAPSOMANIKIS, 1985; THAYER et al., 1984; AHMAD et al., 1980). Organolead compounds may be present in the environment containing either ethyl and methyl groups, or a mixture of the two (RADOJEVIČ & HARRISON, 1987). Although the use of tetraalkyl lead gasoline has already been banned in most countries, contamination by OLC may be still present in the environment.

After releasing into environment, the OLC undergo the following decomposition:

$$R_4Pb \rightleftharpoons R_3Pb^+ \rightleftharpoons R_2Pb^{2+} \rightleftharpoons Pb^{2+}$$
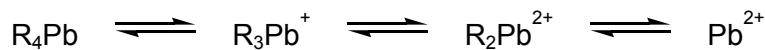
Tetraalkyllead is almost insoluble in water, but di- and trialkyllead are water soluble and quite stable (HEMPEL et al., 2000). Tri- and di-substituted OLC are more stable than tetraalkyllead, but mono-substituted OLC are only occasionally present owing to their instability (BAENA et al., 2000; SZPUNAR & ŁOBÍNSKI, 1999).

Through vehicular emissions, OLC enter the atmosphere and joined the cycle of water, especially ionic OLC. Most of the OLC measured in the air are peralkyllead. The OLC concentrations in the air are usually under hundred ng Pb m^{-3}. They are generally much more concentrated in urban than rural areas (NIELSON et al., 1981; REAMER et al., 1978). Ionic OLC is also detected in the air reaching up to several ng Pb m^{-3}. Both peralkylted and ionic OLC in the atmospheric aerosol particles range around several pg Pb m^{-3} (Table 1–6, HARRISON et al., 1985).

The concentrations of ionic OLC in the atmospheric precipitation are usually in the range of several ten ng Pb l^{-1}, and they can reach over hundred ng Pb l^{-1} in urban areas (Table 1–7, VAN CLEUVENBERGEN et al., 1986; CHAKRABORTI et al., 1984). Organolead compounds accumulate in the snow /ice cores of mountains and in the polar region like Greenland at the level of several fg Pb g^{-1} (HEISTERKAMP et al., 1999; ŁOBÍNSKI et al., 1994). Snow/ ice cores are useful archives of the historical usage of OLC.

Sediments and street dusts are one of the relevant sinks for OLC. The concentrations of OLC were reported to be up to several µg Pb g^{-1} in sediments (JANTZEN & PRANGE, 1995; CHAU et al., 1984), but only at several ng Pb g^{-1} in street dusts (HARRISON & RADOJEVIČ, 1985). Organolead compounds contaminate surface waters through precipitation. Concentrations are usually in the range of ng Pb l^{-1} in seawater and ground water (RADOJEVIČ & HARRISON, 1987). In highway runoff, OLC concentrations can reach up to hundred ng Pb l^{-1} (HARRISON et al., 1986).

Bioaccumulation may be a large sink for OLC in the environment. Peralkylated OLC and their decomposed products accumulated strongly in organisms. Organolead compounds were found up to several µg Pb g^{-1} in the tissues of fishes, shells and algae (MIKAC et al., 1996; CHAU et al., 1984). They also accumulate in terrestrial plants (VAN CLEUVENBERGEN et al., 1990). The OLC concentrations in wines reflect as well the historical usage of OLC as the snow/ ice cores (ŁOBÍNSKI et al., 1997).

Tetraalkyllead degrade very fast in light both in atmosphere and water. In the dark, the degradation proceeds much slower (RADOJEVIČ & HARRISON, 1987). In soils, peralkylated and ionic OLC undergo both biotic and abiotic decomposition. Under different conditions, they decompose in about one or two months (MULROY & OU, 1998; OU et al., 1995a; 1995b; 1994).

The alkyl groups on OLC can transfer to other metal ions, like Hg and Sn (HEMPEL et al., 2000, ROSENKRANZ et al., 1997; HAMASAKI et al., 1995; Tayer, 1995).

Table 1–7. Concentrations of organolead compounds in the environments

Location	TML	DML	TEL	DEL	Reference
Gas (ng (Pb) m^{-3})					
Ireland and U.K.	<DL–19.8	<DL–2.6	<DL–2.6	<DL–5.1	ALLEN et al. 1988
Aerosol (ng (Pb) m^{-3})					
Ireland and U.K.	<DL–2.3	<DL–1.1	<DL–2.6	<DL–23.7	ALLEN et al. 1988
Rainwater (ng (Pb) l^{-1})					
Antwerp, Belgium	17–43	7–10	9–30	18–68	CHAKRABORTI et al. 1984
Ireland and U.K.[a]	0.1–56	0.1–23	<DL–69	0.2–164	ALLEN et al. 1988
Antwerp, Belgium	2.3–90.6	<DL–23.3	<DL–81.3	<DL–73.4	VAN CLEUVENBERGEN et al. 1992
Antwerp, Belgium	18–31	7–8	10–11	19–20	VAN CLEUVENBERGEN et al. 1986
Dortmund, Germany	<DL–62	–	<DL–147	–	BLASZKEWICZ et al. 1987
Snow (pg g^{-1})					
Alpine	<DL–3.4	<DL–3.0	<DL–0.15	<DL–0.57	HEISTERKAMP et al. 1999
Greendland	–	–	0.02–0.16	0.02–0.16	ŁOBIŃSKI et al. 1994
Antwerp, Belgium	11–91	1–14	10–93	2–92	VAN CLEUVENBERGEN et al. 1986
Dortmund, Germany	22–61	–	39–133	–	BLASZKEWICZ et al. 1987
Seawater (ng (Pb) l^{-1})					
Adriatic sea	<DL–3.1	–	<DL–2.3	<DL–2.0	MIKAC et al. 1996
Habour water (ng l^{-1})					
Dortmund, Germany	123	–	40	–	BLASZKEWICZ et al. 1987
Sediment (ng (Pb) g^{-1} dry wt)					
Ontario, Canada	–	–	187	22	CHAU et al. 1984
Colchester, U.K.	0.1	0.2	0.1	<0.1	RADOJEVIČ & HARRISON 1987

–: not determined; a: including dry deposition

1.2. Research objectives and hypotheses

As described in the previous section, OTC were studied in the past only in the aquatic ecosystem. Although OLC in the environment were broadly investigated, little is known about their fate in forest ecosystems. Organotin compounds and OLC were detected in the rainwater (RADOJEVIČ & HARRISON, 1987; TUGRUL et al. 1983), suggesting the potential occurrence of these highly toxic compounds in the forest ecosystem.

Thus, this thesis attempts to contribute to the biogeochemistry of OTC and OLC in forested catchments by investigating the following main topics and hypotheses:

(1). The remote forested catchment is polluted by OTC and OLC from the atmospheric deposition.

(2). The forested catchment serves as a sink for the OTC and OLC either through decomposition or through adsorption in soils.

(3). The mobility of the various OTC and OLC in forest soil is different from species to species.

1.3. Investigation areas

1.3.1. The" Lehstenbach" catchment

The 4.2 km^2 "Lehstenbach" catchment (Figure 3–1), dominated by Norway spruce (*Picea abies* [L.] Karst.) stands of different age, is located in the Fichtelgebirge mountains, NE Bavaria, Germany (11° 52′ 10″ E; 50° 08′ 35″ N). The elevation ranges from 700–880 m a.s.l., and the annual precipitation is approximately 1,100 mm. The mean annual air temperature is about 5 °C. Soils are derived from deeply weathered granite, and form a mosaic of dystric cambisol and podzol (FAQ-classification) with loamy to sandy texture. Approximately 30% of the catchment are covered by wetlands of both bog and fen type.

The Fichtelgebirge region has been strongly affected by acid rain and forest decline during the last decades. Rates of atmospheric deposition of sulfate and protons in the Fichtelgebirge region have decreased significantly during the last decade (KLEMM & LANGE, 1999; ALEWELL et al., 2000), while deposition of nitrogen remains chronically high.

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.
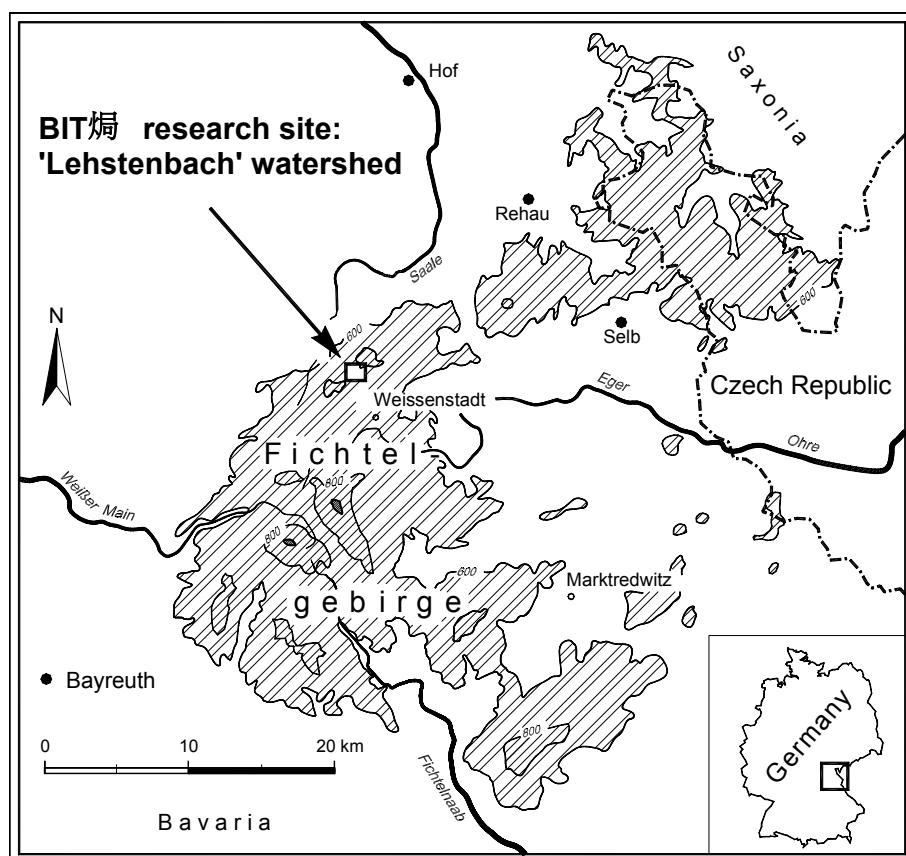

Figure 3–1. The Lehstenbach catchment in the Fichtelgebirge mountains, Bavaria, Germany (by courtesy of P. Gerstberger)

1.3.2. Site description

Upland soils were taken from "Coulissenhieb" and "Weidenbrunnen" site located at the edge of the catchment (Fig. 3−2). The forest floor is a well stratified mor type of approximately 9 cm depth, and consistes of a litter (Oi), a fermented (Oe), and a humified (Oa) organic layer. The pH (H_2O) of the forest floor range from 4.04 in the Oi to 3.39 in the Oa, which represents the lowest pH throughout the whole soil profile. The mineral soil is highly acidic as indicated by low pH and low base saturation of the cation exchange capacity.
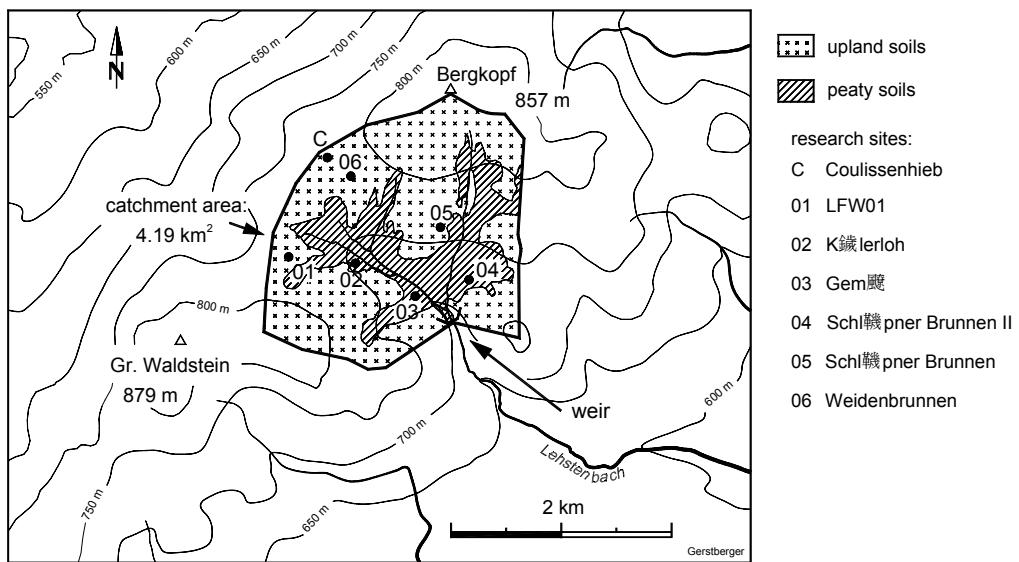

Figure 3−2. Location of the investigated sites at the Lehstenbach catchment (by courtesy of P. Gerstberger)

The wetland soils, Fen and Bog, were sampled at the site "Schlöppner Brunnen" and "Schlöppner Brunnen II" (Fig. 3−2), respectively. The site "Schlöppner Brunnen" is fen covered with *Sphagnum* mosses and classified as Fibric Histosol. Both wetland soils are rich with carbon content up to 44%. The pH(H_2O) of the soils range from 4.37 to 5.20.

1.4. Materials and methods

1.4.1. Reagents

Dibutyltin (DBT), dimethyltin (DMT), dioctyltin (DOT), monobutyltin (MBT), monomethylmercury (MMM), Monomethyltin (MMT), monooctyltin (MOT), tributyltin (TBT), triethyltin (TET), trimethyllead (TML), and trimethyltin (TMT) were purchased commercially with purity 95–99%. Chemical structures of the organometallic compounds studied are shown in Figure. 4–1. Individual stock solutions (10 µg ml^{-1} as Sn, Pb and Hg) of MMM, MMT, MBT, MOT, DMT, DBT, DOT, TML, TMT, TBT were prepared in methanol and stored at -40°C in the dark. A multi-compound working solution with concentration 0.1 µg ml^{-1} as Sn, Pb and Hg was prepared before each use by dilution of the stock solutions with methanol (Merck, p.a. grade). Triethyltin was used as internal standard and prepared in the same way.
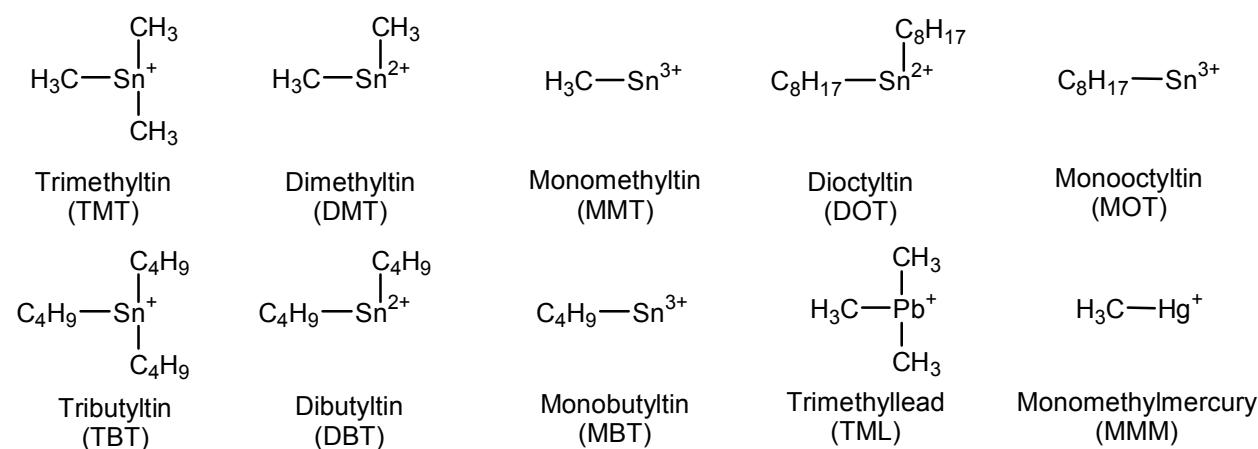

Fig. 4–1. Chemical structures of organotin, organolead, organomercury studied.

De-ionized water was purified in a Milli-Q system (Milli-Q system (Millipore, Milford, MA)). Sodium tetraethylborate (NaBEt$_4$) was from ABCR, sodium borohydride (NaBH$_4$) was from Merck and sodium tetra(n-propyl)borate (NaBPr$_4$) was synthesized by Dümichen, Halle. The derivatization reagent, 2% NaBEt$_4$, NaBH$_4$ or NaBPr$_4$ solution, was prepared before each usage by dissolving reagent in water. The acetate buffer was prepared by dissolving 1 mole sodium acetate in 1 l of water followed by adjusting pH to 4 with glacial acetic acid.

1.4.2. Instrumentation

The GC-ICP-MS coupling consists of two gas chromatographs (HP Model 6890 and 5890) and a ICP-MS (ELAN 5000, Perkin-Elmer SCIEX, Thornhill, ON, Canada). This design allows the analysis of low-volatile and volatile organometallic compounds if combined with different sample introduction methods. Operation parameters of this GC-ICP-MS system are listed in Figure 4–2. More details about the GC (HP 6890)-ICP-MS design for high-boiling analyte speciation and large volume solvent injection were described by GLINDEMANN et al. (2002).

Transfer line

Large volume
Pulsed splitless
injection

Silcosteel tubing, 1.02 mm ID, 1.59 mm OD, 140 ^{o}C

Direct resistance
heating (7 A) →

Carrier gas (He)
2 ml min^{-1}

Injection port
temp.: 250°C

ICP–MS
RF power: 1050 W
Plasma gas flow rate: 15 l min^{-1}
Intermediate gas flow rate: 0.85 l min^{-1}
Nebulizer gas flow rate: 0.70 l min^{-1}
Oxygen flow rate: 15 ml min^{-1}

Ar Ar

Vacuum pump
and Waste →

Oven program
Initial temp.: 50 ^{o}C,
Initial time: 5 min,
Rate: 30 ^{o}C min^{-1},
Final temp.: 320 ^{o}C,
Final time: 1 min.

Retention
gap

GC (HP-6890)

Pressure gauge

← Ar, O$_2$

Gastight syringe

NaOH$_{(s)}$ filter

Column: HP-1, 30 m × 0.25 mm ID, film
thickness 0.25 μm

Carrier gas (He), 2 ml min^{-1} →

6-port-
valve

Oven program
Initial temp.: 35 ^{o}C,
Initial time: 2 min,
Rate: 20 ^{o}C min^{-1},
Final temp.: 200 ^{o}C,
Final time: 2 min.

GC (HP-5890)

Trap 1
Ultimetal tubing, ID 0.53 mm,
uncoated, methyl deactived

Trap 2
Fused silica tubing, ID 0.32 mm,
uncoated, methyl deactived

Trap 2

Trap 1

Column: Chrompack CP-5 Sil CB, 25 m ×
0.32 mm ID, film thickness 0.52 μm

Liquid Ar

Liquid Ar

→ –186°C

Fig. 4–2. Schema of the double GC-ICP-MS coupling for analysing volatile and low volatile organometallic compounds.

1.4.3. General analytical procedures

Water samples or soil- and litter-extracts was adjusted to pH 4 with acetate buffer in the 100 ml glass volumetric flask. Derivatization of organometallic compounds in the solution was done by adding 500 µl 2% aqueous solution of $NaBPr_4$, converting ionic organometallic compounds into peralkylated forms. The derivatization reaction can be described as:

$$R_nM^{(4-n)+} + (4-n)NaBPr_4 \rightleftharpoons R_nPr_{4-n}M + (4-n)BPr_3 + (4-n)Na^+$$

$$MeHg^+ + NaBPr_4 \rightleftharpoons MePrHg + BPr_3 + Na^+$$
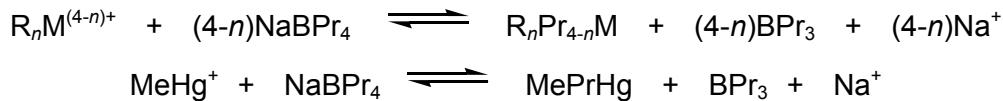
with R=methyl, ethyl, butyl, octyl, phenyl groups; M=Sn, Pb; n=1, 2, 3 (DE SMAELE et al., 1998).
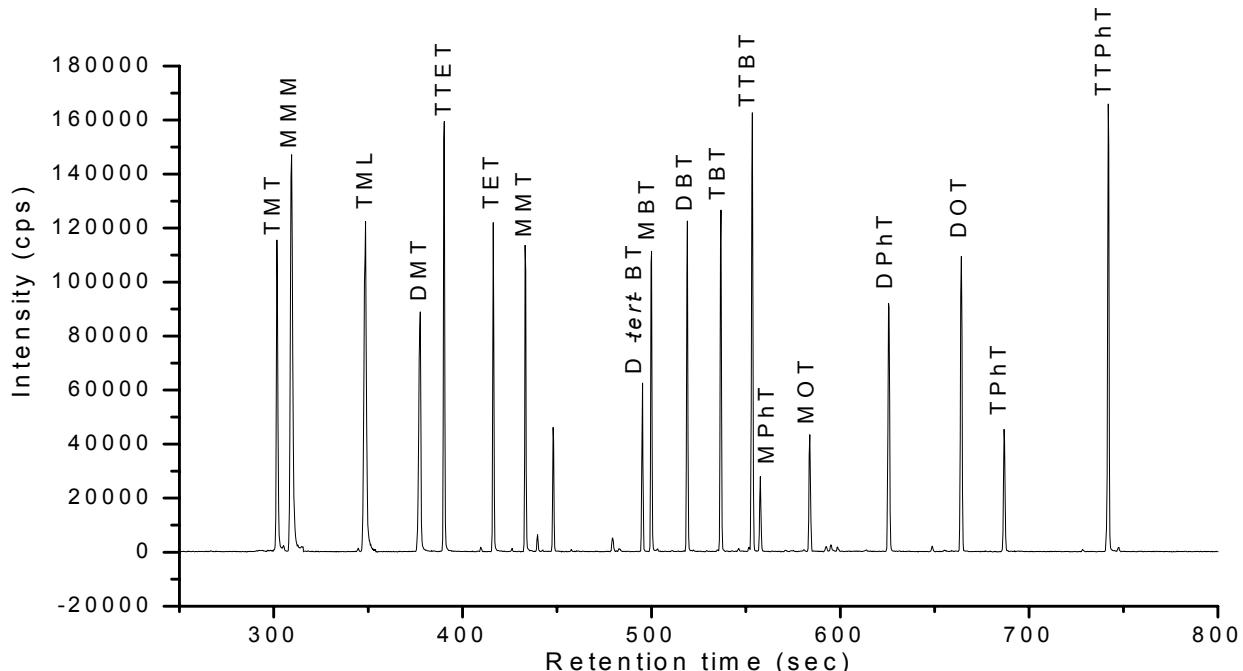
Figure 4–3. Gas chromatogram of organotin, organolead and organomercury compounds. TTET: tetraethyltin, D-*tert*-BT: di-*tert*-butyltin, TTBT: tetrabutyltin, MPhT: monophenyltin, DPhT: diphenyltin, TPhT: triphenyltin, TTPhT: tetraphenyltin.

After extraction with 1 ml cyclopentane by shaking the solution for 10 minutes, the cyclopentane extract was moved to centrifugation (8,800 G) for 10 minutes. The cyclopentane extract was then separated from the aqueous phase and cleaned-up with a glass 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% deactived with water). Organometallic compounds in the cyclopentane extract were then separated by a GC (HP 6890) and detected by ICP-MS, monitoring synchronously [208]Pb, [120]Sn and [202]Hg. A chromatogram of different standards based on this method is shown in Figure 4–3.

Analysis of tetramethyltin (TTMT) and tetramethyllead (TTML) in the gas phase of the incubation experiment was conducted by sampling headspace gas (50 ml) from the incubation bottles with a gastight syringe. The sampled gas was passed through $NaOH_{(s)}$ filled in a pasteur pipette (150 mm length). Samples were then trapped twice (see Fig. 4–2) at approximately –186 °C (cooled in liquid argon) and further measured by GC (HP 5890)-ICP-MS (see **1.4.2.**). The standard deviations were usually 10–15%. The recoveries of TTMT in gas phase and the detection limit

with this method were 80% and 0.4 pg Sn, respectively. The detection limit for TTML was 0.8 pg Pb. The recovery of this method for TTML was about 85%.

Water samples or digested solutions of soils and litter were first filtered with membrane filters. The solutions were then directly measured with ICP–MS (Agilent 7500c Series, Japan), using 5 µg Ge l^{-1} as internal standard.

1.4.4. Sampling in th field and sample preparation

Samplers for throughfall and bulk precipitation had a 200 mm diameter collector and a 5-liter reservoir made of polyethylene (Fig. 4–4). A fine sieve made of polyethylene was used between the collector and reservoir to prevent needles. Samplers were placed in a polyethylene 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 and throughfall were sampled weekly from August 2001 to August 2002.
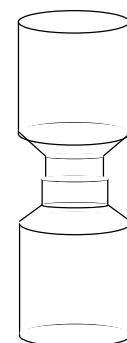
Fig. 4–4.
Precipitation collector

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 & KLEMM (2000). Fog samples were stored in precleaned (double-demineralized water) high density polyethylene bottles at –18°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 (WRZESINSKY, 2004).

Four polyethylene funnels (35 cm diameter) were installed 1 m above ground for litter sampling. Inside each funnel a polytetrafluorethylene net was installed (Fig. 4–5), 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 ^{o}C before analysis.
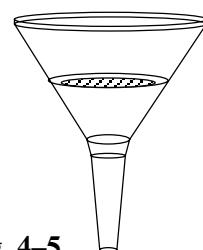

Fig. 4–5.
Litter sampler

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

After sampling, all water samples were filtered by 1 µm glass fiber filters and analysed for OTC and OLC within 48 hours with the method described in **1.4.3.**. For Sn$_{total}$ and Pb$_{total}$ analysis, 50 ml different water samples from each event were first stored in 100 ml polyethylene bottles at 2 ^{o}C in the dark with addition of 100 µl distilled nitric acid after extraction. All samples were measured with ICP–MS at once.

Two upland soil profiles at "Coulissenhieb" and "Weidenbrunnen" as well as a wetland soil "Fen" and "Bog" 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 OTC and TML. The dried samples were ground and stored at 2 °C for long-term

usage.

For analysis of Pb_{total} and Sn_{total} in soils and litter, 0.5 g soils and litter 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 $80^{o}C$, is followed by heating to $170^{o}C$ and finally to $270^{o}C$, lasting for 90 min. The supernatant was then filtered with membrane filter, diluted to 25 ml with Milli-Q water for further analysis (with ICP-MS).

For analysis of OTC and OLC in soils and litter, 0.5 g forest floor or wetland soil 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 tubes. The mixture was shaken horizontally in the dark for 24 hours and subsequently centrifuged for 10 minutes (1,300 G). The solvent was transferred into 100 ml glass volumetric flask and diluted with Milli-Q water to 85 ml. Derivatization and the further analysis was conducted using the method described above.

1.4.5. Degradation experiment

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 $20^{o}C$. 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 $20^{o}C$ in the dark. 10 g of both upland soils (dry weight) with 60% water content of the field capacity was incubated with 50 ng Pb TML and 50 ng Sn OTC under oxic incubation. The air in the headspace was refreshed when CO_2 was over 5%. 25 g wetland soil was incubated with 125 ng Pb TML and 125 ng Sn OTC 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 hours and subsequently centrifuged for 10 minutes (1,200 G). 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 above.

1.4.6. Ad-desorption experiment

Soil samples were taken from the Oa, A and Bw-C horizon of the podzol soil and from a wetland soil (Fen, 10–20 cm depth) were sieved to 5 mm (organic soils) and 2 mm (mineral soils) and air-dried at $20^{o}C$. Soil samples were afterwards grounded, homogenized and stored at $–40^{o}C$ before use.

The batch technique was used to determine the adsorption of OTC and TML. One-gram adsorbent material was suspended in 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 bottles. The suspensions were spiked with OTC and TML solution to yield concentrations ranging from 10 to 100 ng ml^{-1}.as Sn and Pb. The suspensions here were shaken in the dark at 20 ± 1°C for 24 hours to ensure that the adsorption reaction reached equilibrium. After shaking, the samples were centrifuged (at 1,200 G) for 20 minutes; 0.5–40 ml of the supernatant was then analyzed for

OTC and TML with the method described in above.

For the desorption experiments, the supernatant was poured off after centrifuging, and the remaining adsorbent was rinsed once with Milli-Q water for a short time (< 1 minute) before the bottle was refilled to the same volume with artificial rainwater without any OTC and TML. This mixture was also shaken for 24 hours under the same conditions as in the adsorption experiment. Sample preparation and further steps were carried out in the same way as described above.

1.5. Results and discussion

1.5.1. Development of analytical methods

<u>Reducing blank values of organotin compounds</u> (Chapter 2)

The potential OTC contamination from broadly applied PVC in the laboratory (SADIKI & WILLIAMS 1999, 1996) together with the strong OTC adsorption to different laboratory materials (CARTER et al. 1989) led to enormous OTC blank values for OTC trace analysis.

Rinsing bottles with hot distilled water and detergents provided an economical possibility to minimize OTC blank values and was suitable for bottles with all materials. Heating at high temperature (e.g. $300^{\circ}C$) and UV light could decompose OTC into inorganic tin. However, glowing at high temperatures is only suitable for glassware and chemicals with high melting points. UV light treatment is only suitable for solutions. Nitric acid bath was frequently used to reduce OTC blank values (HOCH et al., 2003). Nevertheless, tests of degradation of tri-substituted OTC in 10%, 20%, and 30% nitric acid indicated that the complete degradation of OTC takes more than months.

Methods combining NaBEt$_4$ and organic solvent extraction had the best decontamination effects among all methods, but were not economical. NaBH$_4$ provided another alternative, but was less effective. However, use of NaBEt$_4$ and NaBH$_4$ was restricted to aqueous solution and in certain pH ranges.

<u>Adsorption of organotin compounds to different materials</u> (Chapter 2)

Trimethyltin and DMT showed little adsorption to materials used in the laboratory. TBT adsorbed in negligible amounts to polycarbonate, polyethylene terephthalate G copolymer, aluminium and glass. Strong adsorption (>80%) was observed in both Teflon, both polyethylene, and silanised glass. No apparent adsorption of DBT to aluminum was found. Around 80% of the spiked DBT adsorbed to polycarbonate and polyethylene terephthalate G copolymer and < 50% of the spiked DBT was recovered from the other materials. MMT exhibited little adsorption only to silanised glass, but had >40% adsorption to the other materials. MBT was poorly recovered from most materials and the least adsorption (about 20%) was observed in the low-density polyethylene.

These results reflected the very different adsorption behaviour from OTC with different substitution and alkyl groups. Ignoring the OTC adsorption to container walls may result in underestimate the OTC concentrations in water samples. Using extraction reagents to recover OTC from container walls is suggested to avoid underestimation of OTC concentrations in waters.

<u>Extraction of organotin compounds from soils and litter</u> (Chapter 3)

The available extraction methods for OTC were developed in sediments, but are rarely used for soils (ABALOS et al., 1997). Recovering OTC from the forest soils using classical glacial acetic acid extraction was difficult in some cases. Especially in the case of mono-substituted OTC and DMT, most recoveries in forest floors and wetland soils were less than 10%, indicating strong interaction of these OTC with the natural organic matter. The extraction recoveries of OTC in

soils were in the order: tri- > di- > mono-substituted OTC and octyltin > butyltin > methyltin compounds.

Extraction of OTC from soils using glacial acetic acid was more efficient than Milli-Q water and HCl-methanol solution by providing mild digestion of soil organic matter. Among tested cations (Na, K, Ca, Cu, Al), only addition of Ca^{2+} improved substantially the OTC recovery. The release of the organometallic compounds from soils occur by exchange of organometallic compounds with Ca^{2+}. Tropolone complexed specifically OTC and thereby increased the recovery from soils. The extraction method combining glacial acetic acid, 1 M $CaCl_2$ and 0.1% tropolone can simultaneously recover OTC, OLC and OMC from soils and litter with recoveries at least 40%. This method is simple, highly efficient, and with low contamination. Together with GC-ICP-MS, the method allows the detection of these organometallic compounds in the range of pg g^{-1}.

1.5.2. Biogeochemistry of tin and lead compounds in the forest ecosystem

<u>Organotin and organolead compounds in the atmosphere</u> (Chapter 4)

Methyltin, butyltin, and octyltin compounds and TML were found in the gas phase at Lehstenbach catchment and Bayreuth city with concentrations never exceeding 100 pg m^{-3} as Sn and Pb. Tri- and di-substituted OTC dominated in the gas pahse. In aerosols at both sites, only DMT, MMT, and butyltin compounds were found with the dominance of the mono-substituted OTC. Monobutyltin was the most abundant among all OTC in aerosols with concentrations up to 460 pg Sn m^{-3}, whereas concentrations of most other OTC were usually less than 1 pg Sn m^{-3}. No substantial difference of OTC and TML concentrations in the atmosphere at the two sites was observed, suggesting that urban areas (Bayreuth city) are not specific sources of these compounds.

The gas/ particle partition coefficients (K_p) of OTC in the order mono- >> di- > tri-substituted OTC. K_p of MMT and MBT in the atmosphere were higher than for other OTC. Adsorption to the aerosols might stabilize them against sunlight decomposition in the atmosphere. Therefore, MMT and MBT might be subject to stronger long-range transport than other OTC. Aerosol particles might serve as a sink in the chemical cycles of OTC in the atmosphere, especially for MMT and MBT.

Washout factors (calculated as concentrations of organometallic compounds in rainwater / in air) at both sites ranged from 2 to 3,500 for OTC and from 13 to 400 for TML. DMT, MMT, DBT and MOT had washout factors > 1,000. The washout factors of OTC were in the order: mono- $\geq$ di- > tri-substituted OTC, and methyl- > butyl- > octyltin compounds. The order of the OTC washout factors coincided well with the order of OTC water solubility (mono- > di- > tri-substituted OTC, and methyl- > butyl- > octyltin compounds). Higher substitution and longer-chained alkyl groups led to the lower water solubility. Species with lower washout factors here (especially TMT, and TML) reflected also their higher volatility, suggested by their absence in the aerosol particles.

The large gas/ particle partition coefficients and washout factors of MMT and MBT seemed to lead to the dominance of MBT and MMT in the precipitation and fog in a remote forest ecosystem. The results of the atmospheric speciation suggested that long range transport is an important source of OTC and TML at Lehstenbach catchment and Bayreuth city.

<u>Atmospheric deposition</u> (Chapter 5 & 6)

The concentrations of OTC, TML, Sn_{total} and Pb_{total} in the precipitation were generally in the order: fog > throughfall > bulk precipitation. During the one year monitoring, the concentrations of OTC_{total} in rainwater never exceeded 60 ng Sn l^{-1}, whereas the TML concentrations in rainwater were always < 2.5 ng Pb l^{-1} (Table 5–1). The concentrations of most OTC were usually lower than 1 ng Sn l^{-1}. However, MBT and MOT reached concentrations up to several ten ng Sn l^{-1}. In fog, the OTC and TML concentrations were maximum up to 196 ng Sn l^{-1} and 10 ng Pb l^{-1}, respectively.

The Sn_{total} concentrations in precipitation were usually 10 times higher than those of OTC, whereas the Pb_{total} concentrations 1,000 times higher than those of TML. The stronger OLC degradation by the UV light might cause the extremely low ratios of the TML / Pb_{total} concentration in precipitation (VAN CLEUVENBERGEN et al., 1992). This may be partly explained by the strong accumulation of mono-substituted OTC in aerosol.

The dominance of OTC in precipitation were usually in the order: mono- > di- > tri-substituted OTC and butyltin > octyltin > methyltin compounds. The mono-substituted OTC predominated among OTC in rainwater and fog. In contrast, tri-substituted OTC were the dominant OTC in the aquatic ecosystem in many cases, since direct contamination of OTC is the main source of OTC contamination for the aquatic ecosystem. The OTC in the atmosphere seem to dealkylate during long-term transport, because they are usually unstable in the presence of the sunlight (SELIGMAN et al., 1986, MAGUIRE et al., 1983).

Table 5–1. Median and range of concentrations, adsorption coefficient (K_d), half-life and pools of tin and lead compounds in different environmental compartments at the catchment Lehstenbach

	OTC_{total} ng Sn l^{-1}		Sn_{total} ng Sn l^{-1}		$(CH_3)_3Pb^+$ ng Pb l^{-1}		Pb_{total} µg Pb l^{-1}	
	Ave.	Range	Ave.	Range	Ave.	Range	Ave.	Range
Bulk precip.	5.83	1.29 – 40.7	140	<DL – 680	0.08	<DL – 1.45	0.56	<DL – 5.49
Throughfall	14.7	3.64 – 58.7	390	90.0 – 1,820	0.36	0.06 – 2.17	1.92	0.57 – 4.98
Fog	57.1	24.3 – 196	490	250 – 980	0.32	0.03 – 10.7	9.48	0.48 – 40.0
Runoff	2.19	<DL – 29.0	160	<DL – 1,180	0.05	<DL – 0.29	1.09	0.09 – 4.32
	ng Sn g^{-1}		ng Sn g^{-1}		ng Pb g^{-1}		µg Pb g^{-1}	
Litter	12.9	7.64 – 39.3	38	5.80 – 170	0.02	0.01 – 0.04	6.19	<DL – 19.8
Forest floors	–	<DL – 29.1	–	220 – 1,020	–	<DL – 0.02	–	4.28 – 168
Mineral soils	–	<DL – 0.98	–	170 – 1,050	–	<DL	–	39.5 – 80.2
Wetland sois	–	<DL – 7.60	–	100 – 1,470	–	0.01 – 0.12	–	28.8 – 135
Soil storage	6.7 g Sn ha^{-1}		1.9 kg Sn ha^{-1}		12 mg Pb ha^{-1}		222 kg Pb ha^{-1}	
Soil storage /total actual dep.	46 years		789 years		3.6 years		4,510 years	
K_d	21.4 – 38,400 l kg^{-1}		–		19.7 – 1,630 l kg^{-1}		–	
Half-lives	0.5 – 15 years		–		0.09 – 1.7 years		–	

–: not determined

Trimethyllead concentrations in precipitation at the catchment Lehstenbach were in similar range as in other rural sites in the past (ALLEN et al., 1988, in UK), but much lower than in the past studies in urban areas (BAENA et al., 2000; VAN CLEUVENBERGEN et al., 1992). The effect of

terminated use of OLC as fuel additives in Germany is not easily visible in the data, probably because of the near boarder to the Czech Republic where leaded fuel is still available.

The concentrations of all species in throughfall were all higher than those in bulk precipitation. This indicates dry deposition to the canopy or translocation from soils of these compounds can occur. In case of Sn and Pb compounds, we assumed that the translocation of these compounds is negligible so that the total deposition of these compounds is the sum of the throughfall and litterfall fluxes. Actually, most Sn and Pb compounds showed total deposition less than or equal to the sum of fog and bulk precipitation fluxes, supporting the assumption above.

The concentration of Sn and Pb compounds in the precipitation at the Lehstenbach catchment was in the order OTC >> OLC, and $Pb_{total} > Sn_{total}$ (Table 5–1). The higher OTC concentrations in precipitation pointed out the massive OTC production in industry over OLC. The worldwide production of OLC has been largely reduced. Besides, most OLC emitted into the atmosphere is decomposed by the exposure to sunlight (VAN CLEUVENBERGEN et al., 1992). The accumulation of the mono-substituted OTC in aerosols may reduce such decomposition in the atmosphere. This was reflected by the strong dominance of mono-substituted OTC among OTC in the wet precipitation.

Litterfall (Chapter 5 & 7)

Average concentration of OTC_{total} in litter were 13 ng Sn g^{-1} with MBT and MOT dominating. The proportion of methylated tin in litter was very low, especially TMT and DMT. The abundance of OTC in litter was similar to that in precipitation: mono- > di- > tri-substituted OTC and butyltin > octyltin > methyltin compounds. The average concentration of TML in litter was 0.02 ng Pb g^{-1}. The concentrations of Sn_{total} and Pb_{total} were < 10 times and 10,000 times of their corresponding organic forms.

The low TML concentrations in litter might result from biodegradation in the phyllosphere because of the high microbial activity in this compartment (STADLER et al., 2001). TMT and DMT exhibited extremely low concentrations in the litter. The abundance of methyltin compounds in litter was in the order MMT > DMT >> TMT, suggesting also in situ degradation of methyltin compounds in the phyllosphere. This trend is not very apparent in the case of butyltin compounds.

Similar to MMM, litterfall showed specific importance for Pb_{total} input to the terrestrial ecosystem (Fig. 5–1; SCHWESIG & MATZNER, 2000). Beside atmospheric deposition, large amounts of Pb_{total} might be translocated from soils to leaves (ADRIANO, 2001).

Adsorption in forest soils (Chapter 5 & 8)

The adsorption and desorption isotherms of methyltin and butyltin compounds and TML in the forest soils (Oa, A, Bw-C horizon and Fen) were linear in the concentration range from 10 to 100 ng ml^{-1} as Sn and Pb. For TMT and TML, the adsorption coefficient (K_d) were similar for the Oa and Fen soil ($K_d < 300$) and significantly larger than those for A and Bw-C horizons. DMT, DBT and TBT had K_d in Fen > 10,000, exceeding largely those of the Oa, A and Bw-C horizons. For MMT and MBT, the K_d exceeded 10,000 in Fen and Bw-C horizon. The corresponding adsorption

percentages of MMT and MBT were all close to 100% in all soils, whereas DMT, DBT and TBT had lower adsorption percentages (<90%) in the mineral soils.

The OTC adsorption in soils were generally in agreement with the extraction recovery of OTC from soils: mono- > di- > tri-substituted OTC. The K_d of methyltin compounds and adsorption percentage in the same soil material were generally in the order MMT > DMT > TMT. The K_d and adsorption percentages of butyltin compounds were MBT > DBT > TBT in A and Bw-C horizon and Fen, but MBT > TBT > DBT in Oa horizon. Generally speaking, the K_d and adsorption percentages of butyltin compounds were significantly larger than for methyltin compounds.

Almost all the desorption K_d were much larger than adsorption K_d, indicating the hysteresis of adsorption and desorption. In most cases, the desorption percentages were < 1% of the initial sorbed amount. Only TMT and TML in all soils, TBT in A and Bw-C, and DBT in Bw-C had desorption percentages > 1%.

In general, the adsorption K_d was positively related to the carbon content and cation exchange capacity of the soils. The general order of K_d in all soils (mono- > di- > tri-substituted OTC) pointed out the relevance of electrostatic interaction for the OTC adsorption, especially for mono-substituted OTC. The almost irreversible adsorption of di- and tri-substituted OTC in C-rich soils suggested binding mechanisms other than electrostatic interaction, such as OTC complexation with soil organic matter. This was confirmed by much higher K_d in C-rich soils than those in sediments with low C content (3,000 – 4,000, BERG et al., 2001). The much larger K_d of butyltin than methyltin compounds in Oa and Fen point to hydrophobic interaction between alkyl groups and soil organic matter.

The K_d of OTC and TML in soils were of similar magnitudes to those of other heavy metals in soils (e.g. 270 – 217,000 for Pb, 400 –7,900 for Cd and 200 –13,400 for Zn) (SAUVÉ et al., 2000), but much larger than for some organic pollutants (e.g. 0.13–5.0 for Mesotrione, 1.8–9.3 for 4-Nitrobenzamide) (DYSON et al., 2002; VON OEPEN 1990).

The mobility in forest soils seems to be in the order: mono- > di- > tri-substituted OTC and methyltin > butyltin compounds. The organic matter played an important role in the adsorption of OTC and TML in soils. The results here showed that OTC and TML were scarcely mobile in the forest soil. Adsorption of DMT, DBT and TBT was partly reversible and they seem to be more mobile in the mineral soil than others. TMT and TML had the weakest adsorption and were potentially the most mobile OTC.

Degradation and methylation in forest soils (Chapter 9)

Generally, OTC degraded more rapidly in the Oa soil than in the Bw-C soil and Fen. The half-lives ($t_{1/2}$) of OTC were 0.5–1.5 years in the Oa soil, 1.1–15 years in the Bw-C soil and 1.2–5.6 years in Fen. Degradation of di- and tri-substituted OTC in soils could be stepwise. Trimethyllead degraded much faster in Oa soil ($t_{1/2}$ = 0.09 years) than in the Bw-C soil ($t_{1/2}$ =1.2 years) and Fen ($t_{1/2}$ =1.7 years).

Larger degradation rates of OTC and TML in Oa horizon than in wetland soil and mineral soil coincided well with the higher bioactivity in forest floors under oxic conditions and reflected the relevance of OTC and TML biodegradation in soils (MACASKIE & DEAN, 1990). Only little

information about the groups of microorganisms involved in the OTC degradation is available. For triphenyltin-acetate, degradation was shown by bacteria such as *Pseudomonas aeruginosa*, *Pseudomonas putida C*, and *Alcaligenes faecalis* and decomposition was not observed in sterile soils (BARNES et al., 1973).

The much smaller OTC degradation rates in soil than in water indicated that OTC are stabilized by the adsorption in soil. In the case of, e.g. the herbicide mesotrione its half-live in different soils was positively correlated to its adsorption coefficients (K_d) (DYSON et al., 2002). This indicated that adsorption could be the predominant factor influencing the degradation rate of mesotrione in soil, since the adsorption governs availability of pesticides in the soil solution and to microbes (OGRAM et al., 1985). However, comparing the half-lives of different OTC in our soils with their corresponding K_d, ranging from 21 to 38,400, no relation was found. This seems to be due to the generally high K_d values of OTC.

In some cases, OTC underwent stepwise dealkylation in soils, which is similar to the decay in waters and sediments (DOWSON et al., 1993; MAGUIRE et al., 1983). However, stepwise dealkylation was not evident in the case of tri-substituted OTC in the Fen soil and TMT in the Bw-C horizon. This might result from the larger degradation rates of di- and mono- substituted OTC than tri-substituted OTC in these cases.

Comparing the half-lives of butyltin compounds in different environments shows that the half-lives in soils are similar to those in sediments but much larger than those in waters (HARINO et al., 1997; SARRADIN et al., 1995; DOWSON et al., 1993). The higher bioavailability in water and additional photolytic decomposition may be responsible for the rapid degradation of butyltin compounds in waters (HARINO et al., 1997; MAGUIRE et al., 1983).

No emission of tetramethyltin and tetramethyllead during the incubation of methyltin compounds and TML in Fen was observed. Together with the degradation of methyltin compounds and TML in Fen suggested little tin and lead methylation in the wetland soils. This may based on the nature of the metals, since biomethylation of Hg was reported to be 10,000 times faster than Pb and Sn (THAYER, 2002). However, the methylation of Sn and Pb in wetland soils could not be completely excluded, since the methylated Sn and Pb in soils may transfer rapidly their methyl groups to other receptors, such as Hg (THAYER, 2002; HEMPEL et al., 2000).

Concentrations and pools in forest soils (Chapter 5 & 6)

The OTC concentrations in the upland soils were mostly less than 10 ng Sn g^{-1}. Monobutyltin was by far the dominating species with the highest concentration of about 30 ng Sn g^{-1} in the forest floor. Concentrations of tri-substituted OTC were less than 0.1 ng Sn g^{-1}. Generally speaking, TML had the highest concentration (0.02 ng Pb g^{-1}) in the forest floor. The distribution patterns of OTC and TML were quite similar: they peaked in the forest floor and decreased sharply in the mineral soil. The high concentrations of OTC and TML in the forest floor of upland soils reflected the strong adsorption of OTC and TML onto soil organic matter caused by electrostatic interaction and additional complexation with organometallic compounds (ARNOLD et al., 1998).

Pb$_{total}$ had the highest concentration in the forest floor up to 160 μg Pb g^{-1} in the upland soils, whereas Sn$_{total}$ concentrations peaked in the mineral soil with ca. 1 μg Sn g^{-1}. This vertical

distribution in the mineral soils of Pb_{total} and Sn_{total} indicated the geogenic Pb and Sn compounds in the mineral soils, especially in the case of Sn_{total}.

In the wetland soil, the OTC concentrations were usually less than 1 ng Sn g^{-1}. Concentrations of mono-substituted OTC decreased sharply with increase of the depth. This trend was less apparent for di-substituted OTC, not consistently observed for tri-substituted OTC. Trimethyllead concentrations in Fen peaked at the depth of 10–20 cm and were significantly higher than those in the upland soils. Pb_{total} and Sn_{total} concentrations in wetland soils decreased with depth and had the highest concentration around 140 µg Pb g^{-1} and 1.5 µg Sn g^{-1} in the surface horizon, respectively.

The abundance of OTC in the forest floor and wetland soil was in the order: mono- > di- > tri-substituted OTC and butyltin $\geq$ octyltin > methyltin compounds. The OTC abundance in organic soils corresponded well with that in the atmospheric deposition, suggesting OTC in forest ecosystem originating from atmospheric deposition. In the mineral soil, the OTC concentrations were in the order: tri- > di- > mono-substituted OTC and octyl- > butyl- > methyltin compounds. The same orders were found, comparing the ratios of OTC concentration in deeper and upper horizons in the wetland soil. Therefore, the mobility of the OTC in the upland and wetland soils was suggested here in this order. The results derived from the adsorption experiment demonstrated the OTC mobility in forest soils in the order tri- > di- > mono-substituted OTC with the same alkyl group. However, the adsorption experiments showed the stronger butyltin adsorption than methyltin compounds in forest soils. There seemed to be still many factors affecting the mobility of different OTC in soils in different extents, like dissolved organic carbon complexing OTC, but little such information is available.

At the Lehstenbach catchment, the estimated soils storage of TML was 11.6 mg Pb ha^{-1} with most storage in the wetland soils (>90%). No TML was found in the mineral soils. Even though TML could be mobile in the soil profile, most deposited TML seemes to degrade rapidly in the forest floors. The slow degradation of TML in the wetland soils compared to that in the forest floor contributed to its storage in the wetland soils. In contrast, Pb_{total} and Sn_{total} had the highest storage in the mineral soils (>90%) with the estimated total soil storage of 222 kg Pb ha^{-1} and 1.94 kg Sn ha^{-1}, respectively. The soil storage of OTC_{total} was 6.76 g Sn ha^{-1}. Monobutyltin, MMT and DMT had more than 50% soil storage in forest floor and wetland soil, reflecting their strong adsorption and high stability in the organic soils.

Wetland soils in the forest catchment were identified as a source of MMM (ST. LOUIS et al., 1996). Mercury methylation in the wetland soils might result in the higher MMM concentrations in wetland soils compared to upland soils. At the Lehstenbach catchment, MMM concentrations in wetland soils were up to 20 times higher than in the upland soils (SCHWESIG et al., 1999). In the cases of methyltin compounds and TML, no such enrichment was observed , reflecting little Sn and Pb methylation in the wetland soils.

The soil storage of the organometallic compounds at the Lehstenbach catchment was in the order OTC > OMC > OLC (Table 5–1, SCHWESIG et al., 1999), which did not correspond to the order in the wet precipitation. This was explained by the different internal transformation of these organometallic compounds in the forest soils: Organotin compounds were generally stabile and immobile in the forest soils. Organolead compounds degraded rapidly in the forest soils, especially in the forest floor. Mercury methylation was evident in the wetland soils and served as

an internal source of OMC in the forest ecosystem (SCHWESIG et al., 1999; SCHWESIG, 2001).
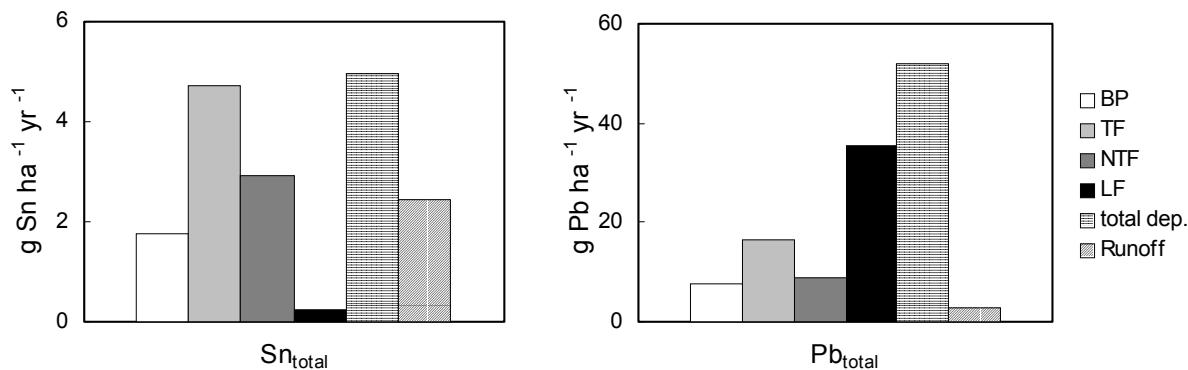

Fig. 5–1 Annual fluxes of total Sn and Pb by bulk precipitation (BP), throughfall (TF), net throughfall (NTF calculated as TF − BP), litterfall (LF), total depostion (LF + TF) and runoff at the catchment Lehstenbach.
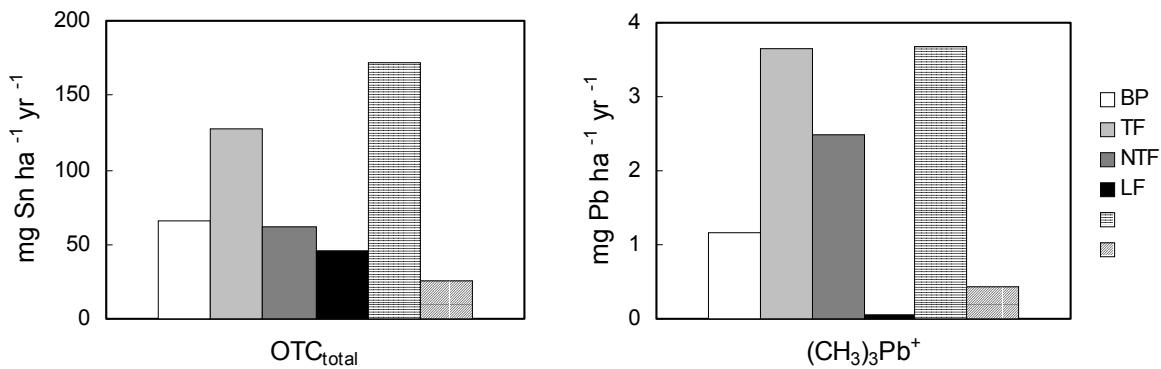

Fig. 5–2 Annual fluxes of total organotin compounds (OTC$_{total}$) and trimethyllead by bulk precipitation (BP), throughfall (TF), net throughfall (NTF calculated as TF − BP), litterfall (LF), total depostion (LF + TF) and runoff at the catchment Lehstenbach.

Runoff (Chapter 5 & 7)

All OTC and TML concentrations in runoff were lower than in the bulk precipitation, reflecting their low mobility or high transformation in the forest soils. Octyltin compounds were the dominant species with average concentrations of less than 1 ng Sn l^{-1}, but with extremes up to 16 ng Sn l^{-1}. The concentrations of methyltin compounds and TML were usually less than 0.1 ng l^{-1} as Sn and Pb. Butlytin compounds were seldom detected in most runoff samples. Sn$_{total}$ and Pb$_{total}$ had concentrations in runoff at similar level of magnitude to those in the bulk precipitation. This might result from leaching of geogenic Sn and Pb from the forest soils.

Elevated MMM, Hg$_{total}$ TML, and Pb$_{total}$ concentrations in runoff, especially during heavy rain and snow smelt (SCHWESIG & MATZNER, 2001), indicating the existence of mobilizable pools on the catchment, during events of high water fluxes which drain mostly surface near soil horizons and leading to higher dissolved organic carbon concentrations in runoff (LISCHEID et al., 2002).

Input-Output-Fluxes (Chapter 5 & 7)

The total annual deposition (calculated as throughfall + litterfall) of OTC_{total} was 172 mg Sn ha^{-1} yr^{-1} with 45 mg Sn ha^{-1} yr^{-1} represented as litterfall (Fig. 5–2). The total annual deposition of TML was 3.7 mg Pb ha^{-1} yr^{-1} with litterfall less than 2 %. The annual runoff fluxes of OTC_{total} and TML (25.3 mg Sn ha^{-1} yr^{-1} and 0.51 mg Pb ha^{-1} yr^{-1}, respectively) were much smaller than the total deposition, indicating that forest soils act as sink for OTC and TML deposited from the atmosphere.

The total annual deposition of Pb_{total} was 52 g Pb ha^{-1} yr^{-1}, to which litterfall contributed about 70%. In contrast, litterfall was only less than 5% of the Sn_{total} total deposition (4.94 g Sn ha^{-1} yr^{-1}) (Fig. 5–1).

The ratios of soil storage to total deposition was 3.6 years for TML, reflecting its high degradation in the forest soils. For OTC, the ratios were generally larger than 20 years. Organotin compounds presented strong accumulation in forest soils. This attributed to the strong adsorption and low degradation in soils. The ratios of soil storage to total deposition for individual OTC ranged from 4.3 to 400 years. Transformation (degradation) of OTC in soils and low deposition rates might explain this variation.

1.6. Conclusion

This study contributes the biogeochemistry of OTC, OLC, Sn_{total} and Pb_{total} in a forest catchment by investigating input and output fluxes, pools, and transformations and the adsorption behaviour in forest soils.

Coming back to the initial hypotheses of this study, the results showed:

(1). <u>The remote forested catchment is polluted by OTC and OLC from the atmospheric deposition.</u>

The total deposition, estimated as throughfall + litterfall, of OTC_{total} (methyltin, butyltin and octyltin compounds) amounted to 172 mg Sn ha^{-1} yr^{-1} at the Lehstenbach catchment. The total depopsition of TML was 3.7 mg Pb ha^{-1} yr^{-1}. Monosubstituted OTC were the dominant species attributing to 82% of OTC_{total} deposition.

In upland soils, OTC and TML could mostly be found in the forest floors. Small amounts of TMT, TBT, DBT, DOT, and MOT were detected in the mineral soils. The vertical distribution of OTC and TML in the wetland soils showed higher concentrations in the upper horizons than in the deeper horizons. Methlylated tin and lead compounds were at the similar concentration level to the other OTC in the wetland soils, suggesting little Sn and Pb methylation in the wetland soils.

The input of OTC and TML through atmospheric deposition and their accumulation in forest soils suggested that Lehstenbach catchment is polluted by OTC and TML. The dominance of monosubstituted OTC in the precipitation and upper soil horizons pointed to that atmospheric deposition act as a sounce of OTC and TML in soils of the forested catchment.

(2). <u>The forested catchment serves as a sink for the OTC and OLC either through deposition or through adsorption in soils.</u>

According to the input and output budget, retention of most investigated species in the catchment were larger than 70%. Monobutyltin was an extreme case with more than 99% of the deposited MBT retained in the catchment. Octyltin compounds, TMT and DMT had more than 30% loss of the deposited species with the runoff. The general high retention of OTC and TML in the forest soils might be attributed to their strong adsorption to forest soils (K_d= 20–38,500). The forest soil acts as sink of the OTC and TML deposited from the atmosphere.

(3). <u>The mobility of the various OTC and OLC in forest soil is different from specie to specie.</u>

The runoff output of OTC and TML were generally <30% of the total deposition at the catchment. The retention of OTC in the catchment is in the general order mono- > di- > tri-substituted OTC, suggesting the mobility of OTC in soils in the reversed order. Monobutyltin seemed to be the most immobile. Octyltin compounds, TMT, TML and DMT were relatively mobile in forest soils.

Mono-substituted OTC predominated in the forest floor and in the upper horizons of the wetland soil. However, tri- and di-substituted OTC had higher concentrations than mono-substituted OTC in the mineral soil and in the deeper horizions of the wetland soil. Octyltin compounds showed more enrichment in the deeper horizons than butyltin and

methyltin compounds. The vertical OTC distribution in the upland and wetland soil profiles suggested the mobility of OTC in soil profiles as tri- > di- > mono-substituted OTC and octyl- > butyl- > methyl-tin compounds.

The adsorption coefficients of OTC were in the order mono- > di- > tri-substituted OTC in all kinds of forest soils. Butyltin compounds had larger adsorption coefficients in soils than methyltin compounds, suggesting the additional hydrophobic interaction provided by the long-chain alkyl groups. The results of ad-desorption experiments showed that the adsorption of most species in C-rich soils were almost irreversible. Trimethyltin and TML adsorption was partly reversible in all soils. In mineral soils, DMT, TBT and DBT exhibited reversible adsorption. The ad-desorption isotherm of OTC and TML showed a pronounced hysteresis.

<u>In summary</u>, the occurrence of OTC in the wet precipitation suggests the entrance of these highly toxic compounds into the terrestrial ecosystem. Organotin compounds were evident to accumulate in the forest soils up to 30 ng Sn g^{-1}, which may potentially influence the microorganisms and the natural process in soils. Generally, OTC in soils degrade slowly and adsorb to soils strongly. They may accumulate in the soils for long time, but the risk of release into the aquatic ecosystem seems small. The OTC contamination is not only threatening the aquatic environment, but also the terrestrial environment.

Even after the terminating the use of OLC, OLC still cycle in the environment. Organolead compounds accumulate little in soils because they degrade rapidly and are slightly mobile related to OTC. The degraded product, inorganic Pb, is less toxic, but may store in soils for longer-term and leach potentially into the aquatic environment. Unlike Hg, methylation in soils is less important source for OTC and OLC.

The abundance of organometallic compounds in the forest soils depends not only on the atmospheric deposition, but also the internal transformation processes in the soils. Forest soils serve generally as sink for deposited organometallic compounds but in different extents, depending strongly on their mobility in soils.

Outlook

On the basis of the results of this study and the literature, the following issues seems to be most important for future research on the biogeochemistry of OTC and OLC in forested ecosystem:

Transalkylation among oranometallic compounds in soils

Methylation of Sn, Pb and Hg was evident in aquatic sediments. Nevertheless, only Hg methylation was observed in wetland soils. There may be Sn and Pb methylation in the wetland soils, but the methyl groups may transalkylate to Hg rapidly. Transalkylation of methyltin and methyllead compounds in soils stands for detoxification, since inorganic Sn and Pb are less toxic. In contrast, transalkylation lead to the enrichment of MMM in soils and enhance the toxicological effects of Hg compounds. Speciation of OMC other than MMM at sites with different degrees of heavy metal contamination may help to estimate the possibility of transalkylation. Using Sn and Pb isotope to study the methylation dynamic in the terrestrial soils may gain more clear sight of Sn and Pb biogeochemical cycle in the terrestrial environment.

Translocation and transformation of OTC in the terrestrial plants

SIMON et al. (2002) demonstrated the transfer of OTC from the spiked nutrient solution to leaves of French beans (*cv. Talisman*). They also observed the TBT in situ degradation in French beans. The occurrence of OTC in the litter may attribute to either translocation to soils or uptake from the atmosphere. Information about the interaction between OTC and terrestrial plants are rare. Therefore, the occurrence of OTC in litter is still spectacular.

The phyllosphere owns high microbial activity (STADLER et al., 2001), suggesting the probable in situ transformation for organometallic compounds such as degradation and methylation. Investigating the transformation of organmetallic compounds in the phyllosphere may help to understand the role of phyllosphere act for biogeochemical cycle of organometallic compounds in the forest ecosystem.

Bioaccumulation and ecotoxicity of OTC in the terrestrial environment

As described in the introduction, most studies about OTC in the environment focused on the aquatic ecosystem. Bioaccumulation may serve as an important sink for OTC in the aquatic ecosystem (KANNAN et al., 1998a, b; LAUGHLIN, 1996). Speciation of OTC in the terrestrial creatures may represent the OTC bioavailability in the terrestrial ecosystem, which may be very different from that in the aquatic ecosystem. Furthermore, information about OTC bioaccumulation in the terrestrial creatures may help understand the fate and behaviour of OTC in the terrestrial food chain.

This study showed that OTC can accumulated in the terrestrial soil up to several ten ng Sg g^{-1} by atmospheric deposition. To evaluate the ecological effect caused by the OTC accumulation in soils is still impossible with the existed knowledge. Residues of OTC in soils prohibit fungal and bacterial populations (KUTHUBUTHEEN et al., 1989a). Natural processes in soils like nitrification and ammonification were evident being affected by OTC (KUTHUBUTHEEN et al., 1989b). However, the test concentrations (>10 μg g^{-1}) are much higher than the values in the natural

soils. More investigation about the influence of OTC accumulation in remote soils on the terrestrial ecosystem is necessary. This will provide the relevant basement for environmental risk assessment and the further strategy for soil remediation.

<u>Leaching and transport of OTC in forest soils</u>

The case of MMM showed enhanced concentrations in runoff during the heavy rain. (LAWSON & MASON 2001; SCHWESIG & MATZNER 2001), suggesting the release of MMM from the forest floor by surficial flow. Release of OTC by surficial flow may be important, since MBT and MMT had their most soil storage in the forest floor. Although the adsorption experiment showed very strong adsorption of mono-substituted OTC in organic soils (K_d > 10,000), many unclear factors may potentially lead to their mobilization, such as decomposition of forest floors, change of chemical conditions and dissolved organic compounds complexation. On the other hand, tri-substituted OTC had more soil storages in the mineral soil. They have smaller K_d, especially in mineral soils (K_d < 2,000). Leaching with ground water seems to be more relevant for OTC with higher substitution.

The high retention of OTC in the forest soil suggests the build-up of OTC in the catchment in the past decades due to anthropogenic input. Thus, even the OTC being regulated, there is still a large insult from the past stored in the catchment. Therefore, OTC will be slowly bled into the streams for decades. Therefore, to gain a more clear sight of OTC mobility in soils is necessary to access the environmental risk caused by OTC releasing from the forested catchment.

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Erklärung

Hiermit erkläre ich, dass ich die vorliegende Arbeit selbständig und keine anderen als die angegebenen Quellen und Hilfsmittel verwendet habe.

Ferner erkläre ich, dass ich anderweitig mit oder ohne Erfolg nicht versucht habe, diese Dissertation einzureichen. Ich habe keine gleichartige Doktorprüfung an einer anderen Hochschule endgültig nicht bestanden.

Bayreuth, ...……………...

Contribution of authors to the publicated articles

2. **Reducing blank values for trace analysis of ionic organotin compounds and their adsorption to different materials** ....……..................by J.-H. Huang

   In <u>International Journal of Environmental Analytical Chemistry</u>, 2004, **84**, 255–265.

3. **Simultaneous extraction of organotin, organolead and organomercury species from soils and litter**...……........by J.-H. Huang, G. Ilgen, E. Matzner

   In <u>Analytica Chimica Acta</u>, 2003, **493**, 23–34.

   <u>J.-H. Huang</u>: conception, sampling, measurements, data analysis, manuscript preparation, correspondence

   <u>G. Ilgen</u>: analytical advice, maintenance of the analytical instruments

   <u>E. Matzner</u>: conception, manuscript preparation, supervisor

4. **Atmospheric speciation of ionic organotin, organolead and organomercury compounds in NE Bavaria (Germany)**...............................……......................................by J.-H. Huang, O. Klemm

   In <u>Atmospheric Environment</u>, 2004, **38**, 5013–5023.

   <u>J.-H. Huang</u>: conception, sampling, sample analysis, data analysis, manuscript preparation, correspondence

   <u>O. Klemm</u>: advice, instrumental support, manuscript preparation

5. **Biogeochemistry of trimethyllead and lead in a forested ecosystem in Germany**…………………….…………..….….…………….………...by J.-H. Huang, E. Matzner

   In <u>Biogeochemistry</u>, in press.

   <u>J.-H. Huang</u>: conception, sampling, measurements, data analysis, manuscript preparation, correspondence

   <u>E. Matzner</u>: conception, manuscript preparation, supervisor

6. **Organotin compounds in precipitation, fog and soils of a forested ecosystem in Germany**…………………..…….…………………...….by J.-H. Huang, D. Schwesig, E. Matzner

   In <u>Environmental Pollution</u>, 2004, **130**, 177–186.

   <u>J.-H. Huang</u>: conception, sampling, measurements, data analysis, manuscript preparation, correspondence

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7. **Biogeochemistry of organotin compounds and tin in a forested catchment in Germany**……………….....…………………………………...……….by J.-H. Huang, E. Matzner

   In the Science of the Total Environment, 2004, **332**, 231−241.

   J.-H. Huang: conception, sampling, measurements, data analysis, manuscript preparation, correspondence

   E. Matzner: conception, manuscript preparation, supervisor

8. **Adsorption and desorption of organotin compounds in organic and mineral soils**…..………………………………………..…………..………..…by J.-H. Huang, E. Matzner

   In European Journal of Soil Science 2004, **55**, 693−698.

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9. **Degradation of organotin compounds in organic and mineral forest soils**........................……………………………………………….……..…….by J.-H. Huang, E. Matzner

   In Journal of Plant Nutrition and Soil Science, 2004, **167**, 33–38.

   J.-H. Huang: conception, sampling, measurements, data analysis, manuscript preparation, correspondence

   E. Matzner: conception, manuscript preparation, supervisor