Jen-How Huang

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

- Doctoral thesis -
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<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>DBT</td>
<td>Dibutyltin ((\text{C}_4\text{H}_9)_2\text{Sn}^{2+})</td>
</tr>
<tr>
<td>DL</td>
<td>Detection limit</td>
</tr>
<tr>
<td>DMT</td>
<td>Dimethyltin ((\text{CH}_3)_2\text{Sn}^{2+})</td>
</tr>
<tr>
<td>DOT</td>
<td>Dioctyltin ((\text{C}<em>8\text{H}</em>{17})\text{Sn}^{2+})</td>
</tr>
<tr>
<td>DPhT</td>
<td>Diphenyltin ((\text{C}_6\text{H}_5)_2\text{Sn}^{2+})</td>
</tr>
<tr>
<td>GC</td>
<td>Gas chromatography</td>
</tr>
<tr>
<td>ICP-MS</td>
<td>Inductively coupled plasma – mass spectrometry</td>
</tr>
<tr>
<td>LD</td>
<td>Lethal dose</td>
</tr>
<tr>
<td>(K_d)</td>
<td>Adsorption coefficient</td>
</tr>
<tr>
<td>(K_p)</td>
<td>Gas / particle partition coefficient</td>
</tr>
<tr>
<td>MMM</td>
<td>Monomethylmercury (\text{CH}_3\text{Hg}^+)</td>
</tr>
<tr>
<td>MBT</td>
<td>Monobutyltin ((\text{C}_4\text{H}_9)\text{Sn}^{3+})</td>
</tr>
<tr>
<td>MMT</td>
<td>Monomethyltin (\text{CH}_3\text{Sn}^{3+})</td>
</tr>
<tr>
<td>MOT</td>
<td>Monoctyltin ((\text{C}<em>8\text{H}</em>{17})\text{Sn}^{3+})</td>
</tr>
<tr>
<td>MPhT</td>
<td>Monophenyltin ((\text{C}_6\text{H}_5)\text{Sn}^{3+})</td>
</tr>
<tr>
<td>NaBEt(_4)</td>
<td>Sodium tetaethylborate (\text{NaB(C}_2\text{H}_5)_4)</td>
</tr>
<tr>
<td>NaBH(_4)</td>
<td>Sodium borohydrate (\text{NaBH}_4)</td>
</tr>
<tr>
<td>NaBPPr(_4)</td>
<td>Sodium teta((\text{n-propyl}))borate (\text{NaB(C}_3\text{H}_7)_4)</td>
</tr>
<tr>
<td>OLC</td>
<td>Organolead compounds</td>
</tr>
<tr>
<td>OMC</td>
<td>Organomercury compounds</td>
</tr>
<tr>
<td>OTC</td>
<td>Organotin compounds</td>
</tr>
<tr>
<td>PVC</td>
<td>Poly(vinyl) chloride</td>
</tr>
<tr>
<td>(t_{\frac{1}{2}})</td>
<td>Half-life</td>
</tr>
<tr>
<td>TBT</td>
<td>Tributyltin ((\text{C}_4\text{H}_9)_2\text{Sn}^+)</td>
</tr>
<tr>
<td>TEL</td>
<td>Triethyltin ((\text{C}_2\text{H}_5)_3\text{Pb}^+)</td>
</tr>
<tr>
<td>TET</td>
<td>Triethyltin ((\text{C}_2\text{H}_5)_3\text{Sn}^+)</td>
</tr>
<tr>
<td>TML</td>
<td>Trimethyltin ((\text{CH}_3)_3\text{Pb}^+)</td>
</tr>
<tr>
<td>TMT</td>
<td>Trimethyltin ((\text{CH}_3)_3\text{Sn}^+)</td>
</tr>
<tr>
<td>TOT</td>
<td>Triocetyl tin ((\text{C}<em>8\text{H}</em>{17})_3\text{Sn}^+)</td>
</tr>
<tr>
<td>TPhT</td>
<td>Triphenyltin ((\text{C}_6\text{H}_5)_3\text{Sn}^+)</td>
</tr>
<tr>
<td>TTBT</td>
<td>Tetrabutyltin ((\text{C}_4\text{H}_9)_3\text{Sn})</td>
</tr>
<tr>
<td>TTTEL</td>
<td>Tetraethylead ((\text{C}_2\text{H}_5)_4\text{Pb})</td>
</tr>
<tr>
<td>TTML</td>
<td>Tetramethyllead ((\text{CH}_3)_4\text{Pb})</td>
</tr>
<tr>
<td>TTMT</td>
<td>Tetramethyltin ((\text{CH}_3)_4\text{Sn})</td>
</tr>
</tbody>
</table>
Summary

Organotin-compounds (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 investigated and 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- ≥ 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

Die Konzentrationen von gesamt-OTC und TML in der Gasphase der Atmosphäre im Lehestenbach 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-substituierte und 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 Auswaschungsfaktoren in der Reihenfolge: Mono- ≥ Di- > Tri-substituierte 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 Humusaufklage waren höher als die im Moor- bzw. im Mineralboden. Der Abbau war allgemein in der Reihe mono- ≥ 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 (t½ = 0.09 Jahre) im Vergleich zum langsamen Abbau im Mineralboden und Moor (t½ = 1.7 und 1.2 Jahre jeweils). Ausgasung von Tetramethyl-Sn und -Pb aus dem Moor wurde nicht beobachtet. Die Methylierung von Sn und Pb in Moorböden ist somit unwahrscheinlich.


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.

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.

<p>| Table 1-1. Physical properties of selected organotin compounds |
|------------------|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Species</th>
<th>Density (g m$^{-3}$)</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Solubility in H$_2$O (g l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TTBT</td>
<td>1.06</td>
<td>–97</td>
<td>145/ 1.3 kPa</td>
<td>–</td>
</tr>
<tr>
<td>TBT</td>
<td>1.21</td>
<td>–16</td>
<td>172/ 3.3 kPa</td>
<td>50 (sea water)</td>
</tr>
<tr>
<td>DBT</td>
<td>–</td>
<td>39–41</td>
<td>135/ 1.3 kPa</td>
<td>5–17 (water)</td>
</tr>
<tr>
<td>MBT</td>
<td>1.69</td>
<td>–</td>
<td>93/ 1.3 kPa</td>
<td>–</td>
</tr>
<tr>
<td>TMT</td>
<td>–</td>
<td>37–39</td>
<td>154</td>
<td>–</td>
</tr>
<tr>
<td>DMT</td>
<td>–</td>
<td>106–108</td>
<td>188–190</td>
<td>20,000 (sea water)</td>
</tr>
<tr>
<td>MMT</td>
<td>–</td>
<td>48–51</td>
<td>171</td>
<td>–</td>
</tr>
</tbody>
</table>

$: no data available

<p>| Table 1-2. Industrial use of organotin compounds |
|------------------|------------------|------------------|</p>
<table>
<thead>
<tr>
<th>Industrial application</th>
<th>Function</th>
<th>Organotin compounds</th>
</tr>
</thead>
<tbody>
<tr>
<td>PVC stabilizers</td>
<td>Stabilization against decomposition by heat and light</td>
<td>$R_2SnX_2$ and $RSnX_3$, $R$= Me, Bu, Oct</td>
</tr>
<tr>
<td>Antifouling paints</td>
<td>Biocide</td>
<td>$R_2SnX_2$, $R$=Bu, Ph</td>
</tr>
<tr>
<td>Agrochemicals</td>
<td>Fungicide, Insecticide, Miticide, Antifeedant</td>
<td>$R_3SnX$, $R$=Bu, Ph, Cy</td>
</tr>
<tr>
<td>Wood preservation</td>
<td>Insecticide, Fungicide</td>
<td>$Bu_3SnX$</td>
</tr>
<tr>
<td>Glass treatment</td>
<td>Precursor for Sn(IV) oxide films on glass</td>
<td>$R_2SnX_2$ and $RSnX_3$, $R$= Me, Bu</td>
</tr>
<tr>
<td>Materials protection</td>
<td>Fungicide, Algicide, Bactericide</td>
<td>$Bu_3SnX_2$</td>
</tr>
<tr>
<td>Impregnation of textile</td>
<td>Insecticide, Antifeedant</td>
<td>$Ph_3SnX$</td>
</tr>
<tr>
<td>Poultry farming</td>
<td>Dewormer</td>
<td>$Bu_2SnX_2$</td>
</tr>
</tbody>
</table>

Peralkylated organolead compounds (OLC) like tetramethyllead (TTML) and tetraethyllead (TTEL) have been used as antiknock additives in gasoline products for several decades (ŁOBUNSKI, 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 tetraalkylead compounds involve ionic di- and tri-alkylead compounds in addition to inorganic lead. Monoalkylead are only occasionally present due to their instability (SZPUNAR & ŁOBIŃSKI, 1999; ŁOBIŃSKI, 1995). Ionic OLC are even more mobile than tetraalkylead 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>
<thead>
<tr>
<th>Species</th>
<th>Density (g m$^{-3}$)</th>
<th>Melting point (°C)</th>
<th>Boiling point (°C)</th>
<th>Solubility in H$_2$O (g l$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(NO$_3$)$_2$</td>
<td>4.53</td>
<td>470</td>
<td></td>
<td>376.5</td>
</tr>
<tr>
<td>TTEL</td>
<td>1.66</td>
<td>−136.8</td>
<td>200</td>
<td>0.00029</td>
</tr>
<tr>
<td>TEL</td>
<td>−</td>
<td>−</td>
<td>−</td>
<td>ca. 200</td>
</tr>
<tr>
<td>TTML</td>
<td>2.0</td>
<td>−27.5</td>
<td>110</td>
<td>0.0179</td>
</tr>
</tbody>
</table>

$: no data available

### 1.1.2. Toxicological relevance of organolead and organotin compounds

Tin in inorganic form 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>
<thead>
<tr>
<th>Species</th>
<th>LD$_{50}$, mg kg$^{-1}$</th>
<th>Species</th>
<th>LD$_{50}$, mg kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnCl$_2$</td>
<td>700</td>
<td>TTBT</td>
<td>&gt;4,000</td>
</tr>
<tr>
<td>TMT-Cl</td>
<td>13</td>
<td>TBT-OAc</td>
<td>380</td>
</tr>
<tr>
<td>DMT-Cl$_2$</td>
<td>74</td>
<td>DBT-Cl$_2$</td>
<td>100</td>
</tr>
<tr>
<td>MMT-Cl$_3$</td>
<td>1,370</td>
<td>MBT-Cl$_3$</td>
<td>2,140</td>
</tr>
<tr>
<td>TET-OAc</td>
<td>4</td>
<td>TPhT-OH</td>
<td>125</td>
</tr>
</tbody>
</table>

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-butylin 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 tetraalkylead 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

<table>
<thead>
<tr>
<th>Species</th>
<th>LD$_{50}$, mg kg$^{-1}$</th>
<th>Species</th>
<th>LD$_{50}$, mg kg$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(NO$_3$)$_2$</td>
<td>250</td>
<td>TEL</td>
<td>20</td>
</tr>
<tr>
<td>TTEL</td>
<td>15</td>
<td>TML</td>
<td>80</td>
</tr>
<tr>
<td>TTML</td>
<td>&lt;36</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

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$_3$I, (CH$_3$)$_3$S$^-$, (CH$_3$)$_3$N$^+$CH$_2$COO$^-$, 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 methylbutylin 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:

\[
\begin{align*}
R_4\text{Sn} & \rightarrow R_3\text{SnX} \rightarrow R_2\text{SnX}_2 \rightarrow RSnX_3 \rightarrow \text{SnX}_4
\end{align*}
\]

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

<table>
<thead>
<tr>
<th>Location</th>
<th>Water (ng (Sn) l⁻¹)</th>
<th>Sediment (ng (Sn) g⁻¹ dry wt)</th>
<th>Rainwater (ng (Sn) l⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>TBT</td>
<td>DBT</td>
<td>TBT</td>
</tr>
<tr>
<td>Sado Estuary, Portugal</td>
<td>18–60</td>
<td>52–160</td>
<td>0.7–601</td>
</tr>
<tr>
<td>River water, Spain</td>
<td>6.9–41</td>
<td>5.5–68</td>
<td>16–161</td>
</tr>
<tr>
<td>Antwerp Harbour, Holland</td>
<td>51–76</td>
<td>217–283</td>
<td>16–242</td>
</tr>
<tr>
<td>Ganga Plain, India</td>
<td>2–70</td>
<td>2–101</td>
<td>2–20</td>
</tr>
<tr>
<td>Marine in Holland</td>
<td>3–310</td>
<td>0.1–810</td>
<td>0.1–3,620</td>
</tr>
<tr>
<td>Sea water, Japan</td>
<td>0.019</td>
<td>0.017</td>
<td>0.025</td>
</tr>
<tr>
<td></td>
<td>TPhT</td>
<td>DPhT</td>
<td>MPbT</td>
</tr>
<tr>
<td>Sea water, Japan</td>
<td>&lt;DL</td>
<td>0.003</td>
<td>0.027</td>
</tr>
<tr>
<td></td>
<td>TMT</td>
<td>DMT</td>
<td>MMT</td>
</tr>
<tr>
<td></td>
<td>Schwartzbach, Germany</td>
<td>0.8</td>
<td>–</td>
</tr>
<tr>
<td></td>
<td>Ontario, Canada</td>
<td>&lt;DL–50</td>
<td>20–220</td>
</tr>
<tr>
<td></td>
<td>TOT</td>
<td>DOT</td>
<td>MOT</td>
</tr>
<tr>
<td>Tuticorin Harbour, India</td>
<td>0.09–0.186</td>
<td>0.02–0.503</td>
<td>0.112–1.93</td>
</tr>
<tr>
<td>Sea water, Japan</td>
<td>&lt;DL–0.012</td>
<td>&lt;DL–0.506</td>
<td>0.041–0.795</td>
</tr>
<tr>
<td></td>
<td>TPhT</td>
<td>DPhT</td>
<td>MPhT</td>
</tr>
<tr>
<td></td>
<td>Schwartzbach, Germany</td>
<td>477</td>
<td>547</td>
</tr>
<tr>
<td></td>
<td>Ontario, Canada</td>
<td>&lt;DL–750</td>
<td>270–1,550</td>
</tr>
<tr>
<td></td>
<td>TMT</td>
<td>DMT</td>
<td>MMT</td>
</tr>
<tr>
<td></td>
<td>Schwartzbach, Germany</td>
<td>27</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>Ontario, Canada</td>
<td>&lt;DL–120</td>
<td>&lt;DL–21</td>
</tr>
<tr>
<td></td>
<td>TMT</td>
<td>DMT</td>
<td>MMT</td>
</tr>
<tr>
<td></td>
<td>Schwartzbach, Germany</td>
<td>158</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>Ontario, Canada</td>
<td>&lt;DL–750</td>
<td>&lt;DL–170</td>
</tr>
<tr>
<td></td>
<td>Sado Estuary, South Lisbon</td>
<td>&lt;DL–120</td>
<td>&lt;DL–160</td>
</tr>
<tr>
<td></td>
<td>TMT</td>
<td>DMT</td>
<td>MMT</td>
</tr>
</tbody>
</table>

---: not determined

References:
- Quevauviller & Donard 1990
- Gomez-Ariza et al. 1995
- Dirkx et al. 1993
- Ansari et al. 1998
- Ritsema & Laane 1991
- Jiang et al. 2001
- Harino et al. 1992
- Gomez-Arzia et al. 1994
- Kram et al. 1989
- Kram et al. 1989
- Ståb et al. 1996
- Carlier-Pinasseau et al. 1997
- Jantzen & Wilken 1991
- Maguire 1984
- Maguire et al. 1986
- Maguire et al. 1984
- Schebek et al. 1991
- Brack 2002
- Ceulemans et al. 1998
- Rajendran et al. 2000
- Carlier-Pinasseau et al. 1997
- Rajendran et al. 2000
- Schebek et al. 1991
- Maguire et al. 1986
- Quevauviller et al. 1995
- Braman & Tompkins 1979
- Tugrul et al. 1983
The large amount of TTML and TTEL was produced industrially as antiknock additives in gasoline in the past decades (ŁOBIŃSKI 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 (Radojević & 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:

\[ \text{Tetraalkyllead} \rightarrow \text{Trialkyllead} + \text{Dialkyllead} + \text{Monoalkyllead} + \text{Diatomic lead} \]

Tetraalkyllead is almost insoluble in water, but di- and trialkyllead are water soluble and quite stable (Hempeł 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 & ŁoBiński, 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; ŁoBiński 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 & Radojević, 1985). Organolead compounds contaminate surface waters through precipitation. Concentrations are usually in the range of ng Pb l\(^{-1}\) in seawater and ground water (Radojević & 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 (ŁoBiński et al., 1997).

Tetraalkyllead degrade very fast in light both in atmosphere and water. In the dark, the degradation proceeds much slower (Radojević & 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

<table>
<thead>
<tr>
<th>Location</th>
<th>TML (ng (Pb) m⁻³)</th>
<th>DML (ng (Pb) m⁻³)</th>
<th>TEL (ng (Pb) m⁻³)</th>
<th>DEL (ng (Pb) m⁻³)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas (ng (Pb) m⁻³)</td>
<td>Ireland and U.K.</td>
<td>&lt;DL–19.8</td>
<td>&lt;DL–2.6</td>
<td>&lt;DL–2.6</td>
<td>ALLEN et al. 1988</td>
</tr>
<tr>
<td>Aerosol (ng (Pb) m⁻³)</td>
<td>Ireland and U.K.</td>
<td>&lt;DL–2.3</td>
<td>&lt;DL–1.1</td>
<td>&lt;DL–2.6</td>
<td>ALLEN et al. 1988</td>
</tr>
<tr>
<td>Rainwater (ng (Pb) l⁻¹)</td>
<td>Antwerp, Belgium</td>
<td>17–43</td>
<td>7–10</td>
<td>9–30</td>
<td>CHAKRABORTI et al. 1984</td>
</tr>
<tr>
<td></td>
<td>Ireland and U.K.</td>
<td>0.1–56</td>
<td>0.1–23</td>
<td>&lt;DL–69</td>
<td>ALLEN et al. 1988</td>
</tr>
<tr>
<td></td>
<td>Antwerp, Belgium</td>
<td>2.3–90.6</td>
<td>&lt;DL–23.3</td>
<td>&lt;DL–81.3</td>
<td>VAN CLEUVENBERGEN et al. 1992</td>
</tr>
<tr>
<td></td>
<td>Antwerp, Belgium</td>
<td>18–31</td>
<td>7–8</td>
<td>10–11</td>
<td>VAN CLEUVENBERGEN et al. 1986</td>
</tr>
<tr>
<td>Snow (pg g⁻¹)</td>
<td>Alpine</td>
<td>&lt;DL–3.4</td>
<td>&lt;DL–3.0</td>
<td>&lt;DL–0.15</td>
<td>HEISTERKAMP et al. 1999</td>
</tr>
<tr>
<td></td>
<td>Greeland</td>
<td>–</td>
<td>–</td>
<td>0.02–0.16</td>
<td>ŁOBIŃSKI et al. 1994</td>
</tr>
<tr>
<td></td>
<td>Antwerp, Belgium</td>
<td>11–91</td>
<td>1–14</td>
<td>10–93</td>
<td>VAN CLEUVENBERGEN et al. 1986</td>
</tr>
<tr>
<td></td>
<td>Dortmund, Germany</td>
<td>22–61</td>
<td>–</td>
<td>39–133</td>
<td>BLASZKEWICZ et al. 1987</td>
</tr>
<tr>
<td>Seawater (ng (Pb) l⁻¹)</td>
<td>Adriatic sea</td>
<td>&lt;DL–3.1</td>
<td>–</td>
<td>&lt;DL–2.3</td>
<td>MIKAC et al. 1996</td>
</tr>
<tr>
<td>Habour water (ng l⁻¹)</td>
<td>Dortmund, Germany</td>
<td>123</td>
<td>–</td>
<td>40</td>
<td>BLASZKEWICZ et al. 1987</td>
</tr>
<tr>
<td>Sediment (ng (Pb) g⁻¹ dry wt)</td>
<td>Ontario, Canada</td>
<td>–</td>
<td>–</td>
<td>187</td>
<td>CHAU et al. 1984</td>
</tr>
<tr>
<td></td>
<td>Colchester, U.K.</td>
<td>0.1</td>
<td>0.2</td>
<td>0.1</td>
<td>RADOJEVIĆ &amp; HARRISON 1987</td>
</tr>
</tbody>
</table>

–: 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 (RADOJEVIĆ & 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 km² “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 consists of a litter (Oi), a fermented (Oe), and a humified (Oa) organic layer. The pH (H$_2$O) 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.

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 Fibreric Histosol. Both wetland soils are rich with carbon content up to 44%. The pH(H$_2$O) 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), monoocytlytin (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.

De-ionized water was purified in a Milli-Q system (Milli-Q system (Millipore, Milford, MA)). Sodium tetraethylborate (NaBEt₄) was from ABCR, sodium borohydride (NaBH₄) was from Merck and sodium tetra(etary propyl)borate (NaBPr₄) was synthesized by Dümichen, Halle. The derivatization reagent, 2% NaBEt₄, NaBH₄ or NaBPr₄ 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).
Synthesis and Integration

Liquid Ar

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

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

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

Column: HP-1, 30 m × 0.25 mm ID, film thickness 0.25 \(\mu\)m

Column: Chrompack CP-5 Sil CB, 25 m × 0.32 mm ID, film thickness 0.52 \(\mu\)m

Transfer line
Silcosteel tubing, 1.02 mm ID, 1.59 mm OD, 140 \(^{\circ}\)C

Retention gap

Injector port temp.: 250 \(^{\circ}\)C

Vacuum pump and Waste →

Pressure gauge

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 NaBPr₄, converting ionic organometallic compounds into peralkylated forms. The derivatization reaction can be described as:

\[
\text{R}_n\text{M}^{(4-\text{n})+} + (4-\text{n})\text{NaBPr}_4 \rightarrow \text{R}_n\text{Pr}_{4-\text{n}}\text{M} + (4-\text{n})\text{BPr}_3 + (4-\text{n})\text{Na}^+
\]

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.](image)

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% deactivated with water). Organometallic compounds in the cyclopentane extract were then separated by a GC (HP 6890) and detected by ICP-MS, monitoring synchronously \(^{208}\text{Pb}\), \(^{120}\text{Sn}\) and \(^{202}\text{Hg}\). A chromatogram of different standards based on this method is shown in Figure 4–3.

Analysis of tetramethyltin (TMTT) 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 \(\text{NaOH}_\text{(s)}\) 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 TTTMT 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.

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-deionized 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 °C before analysis.

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 °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$_{\text{total}}$ and Sn$_{\text{total}}$ 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°C, is followed by heating to 170°C and finally to 270°C, lasting for 90 min. The supernatant was then filtered with membrane filter, diluted to 25 ml with Milli-Q water 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°C. Wetland soil was sampled from 10-30 cm depth in the Fen, sieved to 5-mm and directly used for the incubation. All incubations were carried out in amber borosilica bottle (120 ml, Schott), closed gastight at 20°C in the dark. 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°C. Soil samples were afterwards grounded, homogenized and stored at –40°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 ($\text{NH}_4\text{NO}_3$ 11.6 mg l$^{-1}$, $\text{K}_2\text{SO}_4$ 7.85 mg l$^{-1}$, $\text{Na}_2\text{SO}_4$ 1.11 mg l$^{-1}$, $\text{MgSO}_4\cdot7\text{H}_2\text{O}$ 1.31 mg l$^{-1}$, $\text{CaCl}_2$ 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

Reducing blank values of organotin compounds (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°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 NaBEt₄ and organic solvent extraction had the best decontamination effects among all methods, but were not economical. NaBH₄ provided another alternative, but was less effective. However, use of NaBEt₄ and NaBH₄ was restricted to aqueous solution and in certain pH ranges.

Adsorption of organotin compounds to different materials (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.

Extraction of organotin compounds from soils and litter (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

Organotin and organolead compounds in the atmosphere (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 phase. 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- ≥ 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.
Atmospheric deposition (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>
<thead>
<tr>
<th>Compartment</th>
<th>OTC_{total} ng Sn l^{-1}</th>
<th>Sn_{total} ng Sn l^{-1}</th>
<th>(CH_3)_3Pb^+ ng Pb l^{-1}</th>
<th>Pb_{total} µg Pb l^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ave.</td>
<td>Range</td>
<td>Ave.</td>
<td>Range</td>
</tr>
<tr>
<td>Bulk precip.</td>
<td>5.83</td>
<td>1.29 – 40.7</td>
<td>140</td>
<td>&lt;DL – 680</td>
</tr>
<tr>
<td>Throughfall</td>
<td>14.7</td>
<td>3.64 – 58.7</td>
<td>390</td>
<td>90.0 – 1,820</td>
</tr>
<tr>
<td>Fog</td>
<td>57.1</td>
<td>24.3 – 196</td>
<td>490</td>
<td>250 – 980</td>
</tr>
<tr>
<td>Runoff</td>
<td>2.19</td>
<td>&lt;DL – 29.0</td>
<td>160</td>
<td>&lt;DL – 1,180</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Compartment</th>
<th>OTC_{total} ng Sn g^{-1}</th>
<th>Sn_{total} ng Sn g^{-1}</th>
<th>(CH_3)_3Pb^+ ng Pb g^{-1}</th>
<th>Pb_{total} µg Pb g^{-1}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ave.</td>
<td>Range</td>
<td>Ave.</td>
<td>Range</td>
</tr>
<tr>
<td>Litter</td>
<td>12.9</td>
<td>7.64 – 39.3</td>
<td>38</td>
<td>5.80 – 170</td>
</tr>
<tr>
<td>Forest floors</td>
<td>–</td>
<td>&lt;DL – 29.1</td>
<td>–</td>
<td>220 – 1,020</td>
</tr>
<tr>
<td>Wetland soils</td>
<td>–</td>
<td>&lt;DL – 7.60</td>
<td>–</td>
<td>100 – 1,470</td>
</tr>
<tr>
<td>Soil storage</td>
<td>6.7 g Sn ha^{-1}</td>
<td>1.9 kg Sn ha^{-1}</td>
<td>12 mg Pb ha^{-1}</td>
<td>222 kg Pb ha^{-1}</td>
</tr>
<tr>
<td>/total actual dep.</td>
<td>46 years</td>
<td>789 years</td>
<td>3.6 years</td>
<td>4,510 years</td>
</tr>
<tr>
<td>K_d</td>
<td>21.4 – 38,400 l kg^{-1}</td>
<td>–</td>
<td>19.7 – 1,630 l kg^{-1}</td>
<td>–</td>
</tr>
<tr>
<td>Half-lives</td>
<td>0.5 – 15 years</td>
<td>–</td>
<td>0.09 – 1.7 years</td>
<td>–</td>
</tr>
</tbody>
</table>

*: 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 CLEVENBERGEN 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 > methytin 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$_{\text{total}}$ had the highest concentration in the forest floor up to 160 µg Pb g$^{-1}$ in the upland soils, whereas Sn$_{\text{total}}$ 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 ≥ 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 seem 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 stable 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 deposition (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 deposition (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. Butyltin 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).
The total annual deposition (calculated as throughfall + litterfall) of OTC\textsubscript{total} was 172 mg Sn ha\textsuperscript{-1} yr\textsuperscript{-1} with 45 mg Sn ha\textsuperscript{-1} yr\textsuperscript{-1} represented as litterfall (Fig. 5–2). The total annual deposition of TML was 3.7 mg Pb ha\textsuperscript{-1} yr\textsuperscript{-1} with litterfall less than 2 %. The annual runoff fluxes of OTC\textsubscript{total} and TML (25.3 mg Sn ha\textsuperscript{-1} yr\textsuperscript{-1} and 0.51 mg Pb ha\textsuperscript{-1} yr\textsuperscript{-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\textsubscript{total} was 52 g Pb ha\textsuperscript{-1} yr\textsuperscript{-1}, to which litterfall contributed about 70%. In contrast, litterfall was only less than 5% of the Sn\textsubscript{total} total deposition (4.94 g Sn ha\textsuperscript{-1} yr\textsuperscript{-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, $\text{Sn}_{\text{total}}$ and $\text{Pb}_{\text{total}}$ 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). The remote forested catchment is polluted by OTC and OLC from the atmospheric deposition.

The total deposition, estimated as throughfall + litterfall, of OTC$_{\text{total}}$ (methyltin, butyltin and octyltin compounds) amounted to 172 mg Sn ha$^{-1}$ yr$^{-1}$ at the Lehstenbach catchment. The total depoposition of TML was 3.7 mg Pb ha$^{-1}$ yr$^{-1}$. Monosubstituted OTC were the dominant species attributing to 82% of OTC$_{\text{total}}$ 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. Methyolated 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). The forested catchment serves as a sink for the OTC and OLC either through deposition or through adsorption in soils.

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

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 horizons 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.

In summary, 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 seem to be most important for future research on the biogeochemistry of OTC and OLC in forested ecosystem:

Transalkylation among organometallic 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.

**Leaching and transport of OTC in forest soils**

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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1.7. References


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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.

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

3. Simultaneous extraction of organotin, organolead and organomercury species from soils and litter………………………………………………………………………..by J.-H. Huang, G. Ilgen, E. Matzner
J.-H. Huang: conception, sampling, measurements, data analysis, manuscript preparation, correspondence
G. Ilgen: analytical advice, maintenance of the analytical instruments
E. Matzner: conception, manuscript preparation, supervisor

4. Atmospheric speciation of ionic organotin, organolead and organomercury compounds in NE Bavaria (Germany)……………………………………………..by J.-H. Huang, O. Klemm
J.-H. Huang: conception, sampling, sample analysis, data analysis, manuscript preparation, correspondence
O. Klemm: advice, instrumental support, manuscript preparation

5. Biogeochemistry of trimethyllead and lead in a forested ecosystem in Germany…………………………………………………………………………………………….by J.-H. Huang, E. Matzner
In Biogeochemistry, in press.
J.-H. Huang: conception, sampling, measurements, data analysis, manuscript preparation, correspondence
E. Matzner: 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 Environmental Pollution, 2004, 130, 177–186.
J.-H. Huang: conception, sampling, measurements, data analysis, manuscript preparation, correspondence
D. Schwesig: conception, review of manuscript
E. Matzner: conception, manuscript preparation, supervisor
7. Biogeochemistry of organotin compounds and tin in a forested catchment in Germany by J.-H. Huang, E. Matzner
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
J.-H. Huang: conception, sampling, measurements, data analysis, manuscript preparation, correspondence
E. Matzner: conception, manuscript preparation, supervisor

9. Degradation of organotin compounds in organic and mineral forest soils by J.-H. Huang, E. Matzner
J.-H. Huang: conception, sampling, measurements, data analysis, manuscript preparation, correspondence
E. Matzner: conception, manuscript preparation, supervisor