ELSEVIER

Atmospheric speciation of ionic organotin, organolead and organomercury compounds in NE Bavaria (Germany)

Jen-How Huang[a,*], Otto Klemm[b]

[a]*Department of Soil Ecology, Bayreuth Institute for Terrestrial Ecosystem Research (BITÖK), Dr. Hans-Frisch-Str. 1-3, University of Bayreuth, D-95440 Bayreuth, Germany*
[b]*Institute for Landscape Ecology, Climatology, University of Münster, Robert-Koch-Str. 26, D-48149 Münster, Germany*

Abstract

Organotin (OTC), organolead (OLC) and organomercury (OMC) compounds are highly toxic and exhibit a potential negative effect on terrestrial ecosystems. Individual ionic OTC, OLC and OMC compounds were identified and their concentrations determined in the gas phase, aerosol particles, and bulk precipitation at a rural (Waldstein) and an urban (Bayreuth city) site in NE-Bavaria. At both sites, butyltins, methyltins, octyltins, trimethyllead and monomethylmercury concentrations in the gas phase were $< 100 \, pg \, m^{-3}$ (determined as corresponding Sn, Pb and Hg concentrations, respectively) with the dominance of tri- and di-substituted OTC and octyltins. The same species were found in bulk precipitation with concentrations $< 25 \, ng \, l^{-1}$ (Sn, Pb, Hg) with the dominance of mono-substituted OTC. In aerosols, only butyltins, dimethyltin and monomethyltin ($< 500 \, pg \, Sn \, m^{-3}$) were found and mono-substituted OTC predominated. No significant difference of concentrations of organometallic compounds in the atmosphere at the two sites was found. For OTC, the washout factors was in the order: mono-$\geqslant$di->tri-substituted OTC, and the gas/particle partition coefficients were mono-$\gg$di-$\gg$tri-substituted OTC. The distribution spectrum of OTC in aerosols showed the strong linkage of OTC to the long-lived particles and high accumulation of OTC in the filter at the Waldstein site. The results indicate that long-range-transport of organometallic compounds in the atmosphere is an important source at our both sites. Aerosol particles may serve as a sink in the chemical cycles of OTC in the atmosphere, especially for monomethyltin and monobutyltin.

© 2004 Elsevier Ltd. All rights reserved.

Keywords: Ionic organotin; Trimethyllead; Monomethylmercury; Gas; Aerosol; Bulk precipitation; Waldstein; Bayreuth

1. Introduction

Organotin (OTC), -lead (OLC) and -mercury compounds (OMC) are highly toxic organometallics in the environment. Tin has a larger number of organometallic

derivatives in commercial use than any other element. This gave rise to a dramatic increase in the worldwide production of OTC from less than 5000 tons in 1955 up to 50 000 ton in 1992 (Hoch, 2001). Leaching from soils and landfills (Mersiowsky et al., 2001), weathering of plastics (Quevauviller and Donard, 1991), and dissolution of ship paintings (Batley, 1996) lead to the release of these compounds into aquatic systems. Sediments of rivers, estuaries and marine systems have been identified as the major environmental sinks of OTC. As a

*Corresponding author. Tel.: +49-921-55-57-61; fax: +49-921-55-57-99.

E-mail address: how.huang@bitoek.uni-bayreuth.de (J.-H. Huang).

consequence, there is abundant literature on input, distribution and toxicity of OTC mainly focused on the aquatic environment (Hoch, 2001). Current studies indicated that OTC can be re-emitted from the marine environment to the atmosphere by transformation of ionic OTC into volatile species (Amouroux et al., 2000), and atmospheric transport and deposition was recognized as source of OTC in the terrestrial ecosystems (Huang et al., 2004).

Peralkylated organolead compounds like tetramethyl-lead and tetraethyllead have been used as antiknock additives in gasoline products for several decades (Łobiñski et al., 1994). Lead-containing antiknock additives have been terminated for several years in Central Europe and are still used in many countries of Eastern Europe. In regions of high traffic density like Central Europe, past emissions of OLC during several decades have led to widespread inputs of OLC in urban as well as rural areas (Łobiñski et al., 1994) and even in high altitude alpine regions (Heisterkamp et al., 1999). A recent study demonstrated the occurrence of OLC in the forest ecosystem, even the use of gasoline with lead had been banned for years in Germany (Huang and Matzner, 2004). Long-range atmospheric transport and deposition of OLC were supposed as the main source of OLC in the forest soils.

Mercury is released into the environment by both natural source and human activities. Due to its physicochemical properties, mercury is a widespread element on the global scale and has to be considered as ubiquitous pollutant today. Human activities like combustion of fossil fuels, artisanal gold mining (Nriagu and Wong, 1998) and several industrial, chemical and pharmaceutical application of mercury have significantly increased atmospheric mercury emissions. Consequently, elevated input fluxes and pools of mercury have been found in several environments (Allan, 1999). Especially, high amounts of the highly toxic species monomethylmercury (MMM) in predatory organisms of aquatic food webs have been reported even in remote areas (Wagemann et al., 1998). Research on the biogeochemistry of methylmercury has mainly been focused on the formation and degradation and transport pathway in terrestrial and aquatic ecosystem. Considerable progress has been made in understanding the relevance of mercury cycling and methylation processes in terrestrial and aquatic ecosystems (Gilmour and Henry, 1991). The potential importance of atmospheric deposition of MMM as a source to aquatic ecosystems was confirmed by extensive field measurement and mass balance calculation (Munthe et al., 1995).

Once OTC, OLC and OMC enter the atmosphere, they may join the cycle of water, especially ionic OTC, OLC and OMC. Peralkylated OTC, OLC and OMC in the atmosphere are not likely to be extensively recycled owing to their rapid decomposition and short lifetime in the atmosphere (Lin and Pehkonen, 1999; Radojevic and Harrison, 1987). Besides, peralkylated OTC, OLC and OMC are almost insoluble in the water, but ionic species are water soluble and quite stable (Hempel et al., 2000). Therefore, ionic OTC, OLC and OMC may distribute more widely in the environment than their peralkylated forms and thus exhibit a higher potential to affect vegetation, fauna and humans. Ionic OTC, OLC and OMC in the atmosphere were recognized as an important source of these organometallic compounds in forest soils. However, information about their source, distribution and behavior in the atmosphere is little, particularly in the case of OTC. The goal of this study is to gain insight into the distribution and dynamics of OTC, OLC and OMC in the atmosphere, in particular to understand their gas phase/particle phase distributions at an urban and a remote site, and to assess the potential risk of OTC, OLC and OMC in the atmosphere.

2. Materials and methods

2.1. Site description

The investigation was carried out at the "Waldstein" site in the "Lehstenbach" catchment in the German Fichtelgebirge mountains, located at an elevation of 765 m a.s.l. at 50°09′ N, 11°52′ E (Fig. 1). Mean annual air temperature is 5.3 °C, and mean annual precipitation is 1156 mm (1961–1990 composite, Foken, 2003). The site is dominated by Norway spruce (Picea abies [L.] Karst.) stands of different age. The Fichtelgebirge is
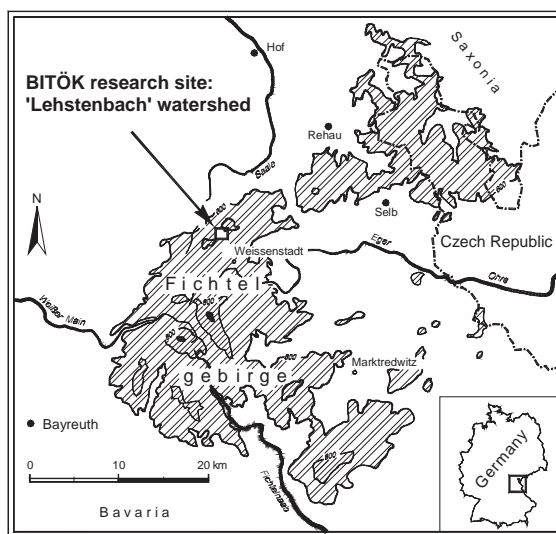

Fig. 1. Location of Lehstenbach catchment and Bayreuth city in NE-Bavaria, Germany.

remote continental site of Central Europe, exhibiting relatively low concentrations of primary air pollutants (Klemm, 2004). Air pollutant concentrations and deposition of pollutants through fog deposition are enhanced when the winds are from the East, i.e. from the more industrialized regions of eastern central Europe (Klemm and Lange, 1999; Thalmann et al., 2002).

Bayreuth is a city with 73 000 inhabitants, about 35 km to the Southwest from the Waldstein site. It is home to a university and small- and medium-sized industries, as well as a local administration center. It lies in the valley of the Red Main River. Road traffic, which is the dominant source of air pollution, is most dense on a traffic circle surrounding the city center. The "Luitpoldplatz" is the intersection with highest traffic intensity in Bayreuth. Samples were collected at an air quality observation station which is operated by the state environmental agency (Bayerisches Landesamt für Umweltschutz, LfU) about 30 m from the Luitpoldplatz intersection.

2.2. Materials

All species analyzed were purchased in the form of chloride with purities between 95% and 99%. Sodium tetra(n-propyl)borate (NaBPr$_4$), 98%, was synthesized by Dümichen, Halle. Individual stock solutions (10 μg ml^{-1} as Sn, Pb, Hg) of monomethyltin (MMT), monobutyltin (MBT), monomethylmercury (MMM), monooctyltin (MOT), dimethyltin (DMT), dibutyltin (DBT), dioctyltin (DOT), trimethyltin (TMT), tributyltin (TBT), and trimethyllead (TML) were prepared in methanol and stored at −40 °C in the dark. Working solutions with a concentration of 0.1 μg ml^{-1} as Sn, Pb and Hg were prepared before each use by dilution of the stock solutions with methanol (Merck, p.a. grade). Triethyltin (TET), which served as internal standard, was prepared in the same way. All glassware used was cleaned with detergents and distilled water at 70 °C.

2.3. Aerosol sampling

We sampled size-segregated aerosol particles with a 5 stages low-pressure impactor (LPI, Berner-type, Hauke KG, Austria). The impaction plates were covered with polyvinyl fluoride foils (Tedlar, DuPont). Glass-fiber filters (GF 9, Schleicher & Schuell, Dassel, Germany) were used as backup filters. The cutoff diameters of the impactor stages were 12.2, 4.05, 1.35, 0.45 and 0.15 μm, respectively. The airflow through the LPI was 75 l min^{-1} (standard conditions). Each aerosol sampling time length was between 2 and 4 days. Aerosol was sampled from end April through mid May 2003 at the Waldstein site (Lehstenbach catchment) and from mid May to mid June 2003 in Bayreuth city.

2.4. Gas sampling

Gas-phase organometallic compounds were sampled by bubbling filtered (0.45 μm) air at 1 l min^{-1} into two bubblers (with 100 glass volumetric flasks) in series. Each bubbler contained 80 ml of double-deionized water and was shielded with aluminum foliage against sunlight. A gas volume meter was installed after each bubbler series to measure the sampled gas volume. After sampling, the concentrations of organometallic compounds in two bubblers were directly analyzed in the volumetric flask with the procedures described in Section 2.7. Each gas sampling time length was between 2 and 4 days. The sampling period was from end April to mid May 2003 at the Waldstein, and from mid May to mid June 2003 in Bayreuth city.

Sampling efficiencies of organometallic compounds in gas phase were tested in Bayreuth city with three days sampling period by bubbling filtered (0.45 μm) air at 1 l min^{-1} into four bubblers in series, each containing 80 ml of double-deionized water. The results showed that >70% of all species were collected in the first two bubblers. This design was demonstrated not to be able to collect peralkylated OLC (recovery <4%, Hewitt et al., 1986). Loss of OLC and OTC was negligible when storing the samples in the dark for at least 72 h at the ambient temperature (Hewitt et al., 1986; Quevauviller and Donard, 1991).

2.5. Bulk precipitation

A polyethylene (PE) funnel (35 cm diameter) was installed 1 m above ground for bulk precipitation sampling. A 2-l PE bottle connected with the funnel was installed in dark PE tube to avoid any impact of sunlight. A fine sieve made of PE was used between funnel and bottle against needles. Bottles and sieves were tested for release of OTC by incubation with artificial rainwater at 5 °C for one week. No release was found. Each sampling time length was between 2 and 4 days. Bulk precipitation was sampled from end April to mid May 2003 at the Waldstein site, and from end April to mid June 2003 in Bayreuth city.

Since organometallic compounds adsorb to container walls to different extent (especially OTC, Huang, 2004), the samples collected in the bottles were directly extracted with extraction solution (glacial acetic acid and 1 M CaCl$_2$ and 0.1% tropolone (Huang et al., 2003)) of volume ratios of about 100:1, by shaking horizontally at 20 °C in the dark for 24 h. The solution (75 ml) was then filtered with glass fiber filter and then adjusted to pH 4 with acetate buffer in the 100 ml glass volumetric flask. Further analysis was done with the procedures described in Section 2.7.

To test recoveries of organometallic compounds f rom PE collectors with our extraction method, 200 ml

Milli-Q water spiked with 20 ng each species was used. After first extraction, the PE collector was consequently twice filled with 200 ml Milli-Q water and extraction solution and extracted. Concentrations of organometallic compounds in three extracts were subsequently determined. The results showed that more than 90% of all organometallic compounds were found in the first extract.

2.6. Extraction of organometallic compounds from aerosols

40 ml Milli-Q water and 1 ml glacial acetic acid with 1 M $CaCl_2$ and 0.1% tropolone was used as the extraction solvent to extract organometallic compounds in aerosol particles. A Tedlar foil and extraction solvent were merged in a 50 ml glass bottle (Scott) and shaken horizontally in the dark overnight. The aliquot was then removed into the 100 ml glass volumetric flask and adjusted to pH 4 with acetate buffer for the further analysis in Section 2.7.

Recoveries of organometallic compounds from aerosol particles were tested by a sample collected with impactor in Bayreuth city for 3 days. After sampling, each foil was extracted with extracts mentioned above consequently three times. The organometallic compounds in the extracts were individually determined. The results showed that more than 90% of all organometallic compounds were found in the first extract.

Filters were spiked with extraction solution in the dark overnight to blank values of organometallic compounds released from filter. The results showed no OLC and OMC but small amounts of DMT, butyltins and octyltins released from filter paper. Thus, the determined concentrations of OTC in the filter stage was calibrated by subtracting the blank values released from filter paper.

2.7. Analysis of organometallic compounds

Derivatization of the liquid sample was done by 10 mg sodium tetra(*n*-propyl)borate ($NaBPr_4$) in the acetate buffer (pH was adjusted to 4), and extracted with 1 ml cyclopentane by vigorous shaking for 10 min. The cyclopentane extract was afterwards centrifuged (8800 g) and cleaned-up with a pasteur pipette (150 mm length) filled with approximately 0.15 g of silica gel (0.063–0.2 μm, glowed at 500 °C overnight, 5% deactived with water) was analyzed with a coupling of a gas chromatograph (HP 6890) to an ELAN 5000 ICP-MS (Perkin-Elmer SCIEX, Thornhill, ON, Canada). More details of the coupling were described by Huang et al. (2003). Detection limits for OTC, TML and MMM in Table 1 were calculated using the 3 times blank signal, and the required sample amount of each matrix.

2.8. Calculation of partition coefficients of organometallic compounds between gas and aerosol particle phases

Calculation of partition coefficients of organometallic compounds between gas and aerosol particle phases was based on the following equation:

$$K_{p,i} = C_{aero,i}/(C_{gas,i} \times TSP),$$

where $C_{aero,i}$ and $C_{gas,i}$ are the concentrations (ng m^{-3} as Sn, Pb, Hg) of the i-compound in the aerosol and gas phase. TSP is the concentration (μg m^{-3}) of the total suspended particles.

TSP was calculated by multiplying average particle number, estimated particle volume and particle density (1.2 g cm^{-3}). Particle size distribution was measured by SMPS (Scanning Mobility Particle Size) each 30 min from 21 to 24 May 2003 and 30 May to 02 June 2003 at the Luitpoldplatz site.

3. Results and discussion

3.1. Organometallic compounds in gas phase at rural and urban sites

Methyltins, butyltins, octyltins, TML and MMM was found in the gas phase at both sites (Tables 2 and 3). However, MMT, DBT, DOT, TML and MMM were not detectable in some events. The OTC concentrations never exceeded 100 pg Sn m^{-3}. Tri- and di-substituted OTC dominated among methyltins and butyltins, whereas MOT is the dominant among octyltins in the

Table 1
Detection limits for ionic OTC, trimethyllead and methylmercury in environmental samples in this study

	TMT	DMT	MMT	TBT	DBT	MBT	MOT	DOT	TML	MMM
Gas (pg Sn m^{-3})[a]	0.28	1.7	0.34	0.52	0.98	3.8	3.1	1.9	0.23	1.5
Aerosol (fg Sn m^{-3})[a]	3.1	18	3.7	5.8	11	42	35	21	2.8	17
Rain water (pg Sn l^{-1})	16	95	19	30	56	220	180	110	15	87

[a] Based on 72 h sample. All units are presented as Pb for TML and as Hg for MMM.

Table 2
Median and range of ionic OTC, trimethyllead, and methylmercury in air (gaseous phase), aerosol and bulk precipitation at the Waldstein site

	Gas[a] (pg Sn m^{-3})			Aerosol[a] (pg Sn m^{-3})			Bulk precipitation[b] (ng Sn l^{-1})		
	Median	Min	Max	Median	Min	Max	Median	Min	Max
TMT	4.67	3.81	6.1	<DL	<DL	<DL	0.13	0.11	0.17
DMT	6.59	2.14	15.6	0.43	0.15	0.62	1.07	0.78	3.63
MMT	<DL	<DL	1.47	0.76	0.39	1.13	1.29	0.40	2.94
TBT	8.63	6.96	23.0	0.20	0.041	0.22	0.12	0.11	0.98
DBT	6.75	<DL	11.9	0.90	0.74	0.92	1.79	1.63	3.43
MBT	12.8	4.41	17.9	71.3	22.0	461	7.71	5.19	22.6
DOT	8.91	<DL	20.7	<DL	<DL	<DL	0.04	<DL	0.5
MOT	87.2	37.0	100.5	<DL	<DL	<DL	1.82	1.15	2.88
TML	0.23	<DL	0.36	<DL	<DL	<DL	0.074	0.034	0.78
MMM	3.70	<DL	4.8	<DL	<DL	<DL	0.22	0.089	0.41

All units are presented as Pb for TML and as Hg for MMM.
[a] Sample size = 5.
[b] Sample size = 3.

Table 3
Median and range of ionic OTC, trimethyllead, and methylmercury in air (gaseous phase), aerosol and bulk precipitation at the Bayreuth city site

	Gas (pg Sn m^{-3})			Aerosol (pg Sn m^{-3})			Bulk precipitation (ng Sn l^{-1})		
	Median	Min	Max	Median	Min	Max	Median	Min	Max
TMT	2.44	1.70	4.50	<DL	<DL	<DL	0.12	0.052	0.24
DMT	4.74	<DL	26.6	1.19	0.22	10.9	0.81	0.58	2.66
MMT	<DL	<DL	1.06	1.13	0.70	1.94	0.52	0.37	1.36
TBT	20.3	7.25	83.0	0.46	0.26	0.77	0.16	0.069	0.88
DBT	17.4	11.7	48.0	4.72	2.85	10.7	2.28	0.37	6.62
MBT	7.11	3.90	23.4	60.0	20.1	116	11.6	5.04	17.6
DOT	2.55	<DL	8.60	<DL	<DL	<DL	0.22	<DL	1.15
MOT	22.0	<DL	61.0	<DL	<DL	<DL	3.17	1.11	4.53
TML	0.32	<DL	1.64	<DL	<DL	<DL	0.045	<DL	0.14
MMM	1.18	<DL	3.10	<DL	<DL	<DL	0.18	<DL	0.79

All units are presented as Pb for TML and as Hg for MMM. Sample size = 9.

gas phase. TMT, TML, MMM and octyltins were never detected in the aerosols. MBT was the highly abundant species with concentrations up to 460 pg Sn m^{-3}, where as concentrations of most other OTC were <1 pg Sn m^{-3}. At both rural and urban sites, concentrations of the organometallic compounds were in a similar level of magnitude in gas and particle phase.

To our knowledge, we have demonstrated the occurrence of ionic OTC in the gas and aerosol particle phases in the atmosphere for the first time. Since the same OTC was identified and natural source of OTC was little in the forest soils (Huang et al., 2004), atmosphere seems to serve as an important source of OTC in the forest ecosystem. However, deposition fluxes can not be calculated from our data set so that the potential risk to the ecosystems cannot be evaluated at this point.

Table 4
Gas/particle partition coefficients (K_p)(m^3 µg^{-1}) and SD of ionic organotin compounds at Bayreuth city site

	K_p(m^3 µg^{-1})	SD
DMT	0.027	0.02
MMT	1.02	0.83
TBT	0.0084	0.0095
DBT	0.079	0.052
MBT	1.35	0.64

Data derived from the event 21–24 May and 30 May–2 June.

TML concentrations in the gas phase were 0.11–38.5 ng Pb m^{-3} at the urban site and 0.2–1.3 ng Pb m^{-3} at the rural site in the past studies (Allen et al., 1988; Harrison and Radojević, 1985). TML

Table 5
Weekly deposition rates of ionic organometallic compounds at the Waldstein and Bayreuth city sites (in $ng\,m^{-2}\,week^{-1}$ as Sn, Pb and Hg)

	TMT	DMT	MMT	TBT	DBT	MBT	MOT	DOT	TML	MMM
Waldstein (rural)	2.28	36.0	30.4	11.6	37.1	231	31.9	2.52	4.11	4.20
Bayreuth city (urban)	2.14	15.3	13.0	3.87	21.7	107	28.3	2.26	0.97	6.55

Average measurement in the period 26 April–15 May 2003.

concentrations in gas phase in our sites were much lower ($<1\,pg\,Pb\,m^{-3}$), reflecting the effect of the terminated use of OLC as fuel additives in Central Europe. The same concentration level of TML in urban and rural site suggests long-term transport as source of OLC in our sites, probably because of the near border to the Czech Republic where leaded fuel is still available.

MMM concentrations in the gas phase were in similar range of the past studies ($0.5–22\,pg\,Hg\,m^{-3}$) (Brosset and Lord, 1995; Lee et al., 2002). MMM concentrations in Waldstein are higher than in Bayreuth city in the gas phase. Since wetland soils were suggested as source of MMM in the forest ecosystem (Schwesig and Matzner, 2000), significant amount of MMM might emit from wetland soils. MMM was not found in the particle phase probably owing to low concentrations in the gas phase.

3.2. Gas/particle partition of organometallic compounds

The gas/particle partition coefficient (K_p) of MBT and MMT were about 1 (Table 4). Comparing to the other organic compounds, MBT and MMT had much higher K_p than organic acid (Kavouras and Stephanou, 2002), reflecting their strong ionic character. K_p of DBT, DMT and TBT were much lower than MBT and MMT. The K_p of DBT and DMT were in similar level to the K_p of organic acid and the K_p of TBT was in similar level to semi-volatile organic compounds (Liang et al., 1997), suggesting the potential long-range transport of OTC to areas never exposed by the corresponding substance.

Our results showed the K_p of OTC in the order mono->di->tri-substituted OTC, reflecting stronger partition of MMT and MBT to particle phases in the atmosphere than other OTC. MBT and MMT seem to be more stabilized by adsorption or absorption by the particles against decomposition by sunlight in the atmosphere. Besides, MMT and MBT seemed subjected to stronger long-range transport according to their very high K_p. These might lead to the dominance of MBT in the precipitation and fog in a remote forest ecosystem (Huang et al., 2004).

To form ultra-fine particle, organic vapors might condense onto inorganic or organic seed particles if at least one compound attains its saturation concentration. Once an organic liquid layer is formed, organic compounds can condense with even at low gas phase

Table 6
Median and ranges of washout factor for ionic organometallic compounds at the Waldstein and Bayreuth city sites

	Median	Min	Max
TMT	54	29	88
DMT	307	27	1605
MMT	403	223	3482
TBT	18	3.7	166
DBT	285	28	1169
MBT	174	96	611
DOT	68	2.4	536
MOT	75	25	1690
TML	157	13	392
MMM	148	49	452

Sample size = 9; $1\,m^3$ of air = 1.226 kg at 15 °C, 1 atm.

concentrations (Kavouras and Stephanou, 2002). Harrison and Laxen (1978) reported an upper limit for the accumulation rate of adsorbed OLC in the atmosphere $0.06\,ng\,Pb\,h^{-1}\,m^{-3}$. Over a 72 h period, this value predicts a concentration $4.32\,mg\,Pb\,m^{-3}$, which is apparently higher than our values in both sites. This seems to result in undetectable TML levels in aerosol particles. Similarly, the absence of TMT, octyltins and MMM in the aerosol particles may reflect their higher saturation concentrations caused by higher fugacity than that of the other species. E.g., in case of butyltins, TBT had the highest concentrations in the gas phase but lowest concentrations in the particle phase. The volatilities of organometallic compounds relate positively to the type and amount of organic substitution. Higher substitution and longer-chained alkyl groups usually lead to the higher volatility.

3.3. Bulk precipitation of organometallic compounds in the atmosphere of rural and urban sites

Similar to in the air, methyltins, butyltins, octyltins, TML and MMM were found in the bulk precipitation (Tables 2 and 3). Mono-substituted OTC were the dominant OTC, and MBT was the most abundant with concentration up to $23\,ng\,Sn\,l^{-1}$. TMT, TBT and DOT exhibited concentrations normally a level of magnitude lower than the other OTC. The concentrations of TML and MMM ($<0.8\,ng\,l^{-1}$ as Pb and Hg) in bulk

precipitation were lower than most OTC. In bulk precipitation, concentrations of the organometallic compounds were in a similar level of magnitude in both rural and urban sites.

All species showed slightly higher estimated deposition rates in rural than in urban site despite MMM. MBT had the maximum deposition rates (231 and 107 ng Sn m^{-2} week^{-1}, Table 5). Weekly fluxes of DMT, MMT TBT, DBT, MBT and TML in Waldstein were at least 2 times of those in Bayreuth city.

3.4. Washout factor for organometallic compounds in rural and urban sites

Washout factors (calculated as organometallic compounds in rainwater/organometallic compounds in air) of OTC in both sites ranged from 2 to 3500 (Table 6). DMT, MMT, DBT and MOT had washout factors >1000. The washout factors of OTC were in the order: mono->=di->tri-substituted OTC, and methyltins>butyltins>octyltins. The washout factors were 13–400 for TML and 50–450 for MMM.

Although many atmospheric parameters and processes have an influence on the measured washout factors, they are indicative of the scavenging efficiencies of individual compounds (Allen et al., 1988). The order of the OTC washout factors coincides well with the order of OTC water solubility (mono->di->tri-substituted OTC, and methyltins>butyltins>octyltins). Higher substitution and longer-chained alkyl groups lead to the lower water solubility. Species with lower washout factors here (especially TMT, TML and MMM) reflect also their higher volatility, suggested by their absence in the

aerosol particles. It should be noted that the washout factors have been calculated from samples collected over several days, and thus represent a composite of different air masses and include periods during which no rain fell but air-sample collection continued. The washout factors presented here provide a rough, time-averaged representation of organometallic compounds behavior.

3.5. Distribution spectrum of organometallic compounds in aerosol particles.

The distribution OTC, including DMT, MMT and butyltins, in the size spectra of aerosol particles (e.g. Fig. 2) shows two clear features: First, this is a (local) maximum in the size range of accumulation range particles (stages 3 and 4 of the impactor). This indicates that OTC is strongly linked to long-lived particles in the atmosphere, indicating that advection of air masses through long-range transport lead to the observed OTC concentration in atmospheric particulate material at both the Waldstein and the Bayreuth city sampling sites. Secondly, a large enrichment in the filter, as compared to the larger particles on the impactor stages, was observed at the Waldstein site. A comparable enrichment of OTC in the filter was observed in Bayreuth city only in a few samples. The enrichment of OTC in the filter indicates that the formation of new particulate material through nucleation from biogenic precursors, which has been shown to be an important process at the Waldstein site (Held et al., 2002) plays an important role in the distribution of OTC between the gas and particle phases. We hypothesize that co-nucleation lead to the incorporation of OTC into ultrafine particles.
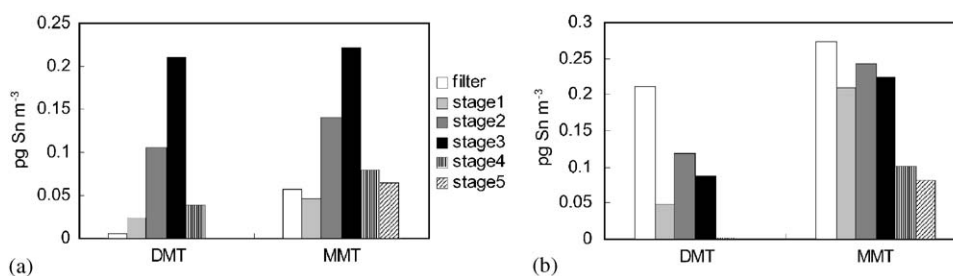

Fig. 2. Distribution of dimethyltin and monomethyltin in the aerosols at the (a) Bayreuth city site and (b) Waldstein site.
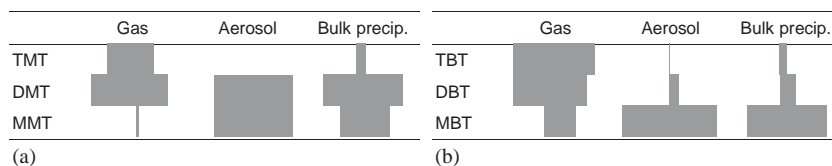

Fig. 3. Relative importance among methyltins (a) and butyltins (b) in gas, aerosol particles and bulk precipitation at the Bayreuth city site.

The OTC were mainly focused on the accumulation-mode aerosols (0.1–2 μm diameter) in Bayreuth city, which penetrate deeply into the human lung. This suggests a potential hazard to human health from the OTC in aerosol particles in the urban environment.

3.6. Relative importance of OTC in the atmosphere

The relative importance of methyltins and butyltins in the aerosol particles and in bulk precipitation were similar (DMT ⩾ MMT > TMT; MBT > DBT > TBT, see Fig. 3). In the gas phase, however, their relative importances were different from each other (DMT > TMT ⩾ MMT and TBT > DBT > MBT, respectively). The results mirror the characters of OTC with different amounts substitution: mono-substituted OTC had highest K_p and washout factors, whereas tri-substituted OTC had lowest K_p and washout factors.

Mono-substituted OTC was demonstrated as the dominant species in forest soils (Huang et al., 2004), indicating OTC in the atmosphere, especially in the aerosols and bulk precipitation, as an important source of OTC in the forest soils. However, the strong depletion of TMT and DMT concentrations

in forest soils suggests their soil storage govern by another factors such as decomposition and mobility in soils.

3.7. Dynamics of organometallic compounds in the rural and urban atmosphere

For the Waldstein site, an analysis of the sources of OTC with help the prevailing wind directions during sample collection is not feasible. Often, the wind direction changed during the sample integration times of three days. However, it is quite striking, that during the only sample period in which easterly wind prevailed during most of the time (around 6 May), the concentrations of MBT (also in gas phase, Fig. 4) and MMT in aerosols were highest (Fig. 5). This indicates that long-distance transport from the east could be a main source for MBT, MMT. In Bayreuth city, OTC concentrations in aerosols showed a quite similar dynamic to the NO_x and PM10 concentrations (Figs. 5 and 6). Locally formation of OTC in aerosols in Bayreuth city seem to be little, indicating that road traffic emissions play a minor role in the formation of aerosol-bound OTC.
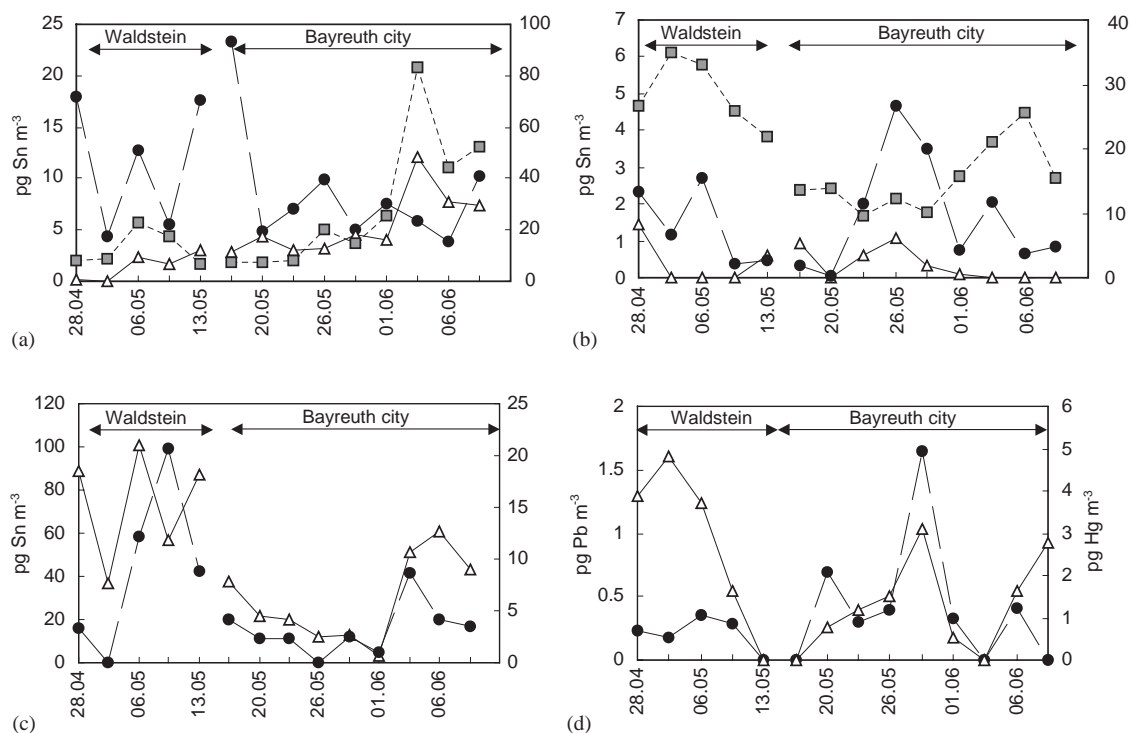

Fig. 4. Dynamic of OTC, MMM and TML concentrations in air (gas phase) at the Waldstein (26 April–14 May 2003) and Bayreuth city site (15 May–09 June 2003). Average of duplicate was shown and all SD < 5%. (a) Left axis: MBT (– • –); right axis: DBT (—△—) and TBT (-- ■ --) (b) left axis: TMT (-- ■ --) and MMT (—△—); right axis: DMT (– • –) (c) left axis: MOT (—△—); right axis: DOT (– • –) (d) left axis: TML (– • –); right axis: MMM (—△—).
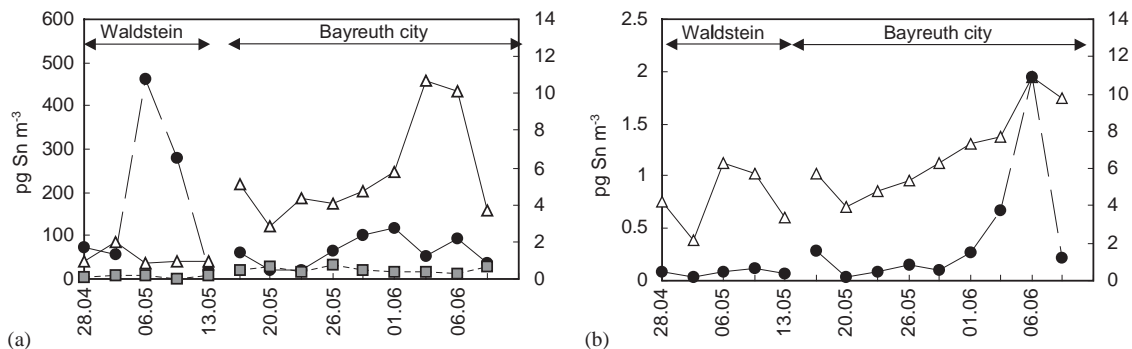
Fig. 5. Dynamic of OTC concentrations in aerosols at the Waldstein site (26 April–14 May 2003) and Bayreuth city site (15 May–09 June 2003) (a) butyltins; left axis: MBT (– • –), right axis: DBT (—△—) and TBT (- - ■ - -) (b) methyltins. Left axis: MMT (—△—); right axis: DMT (– • –).
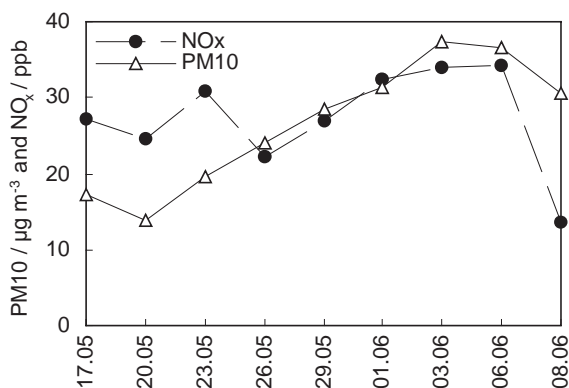

Fig. 6. NO$_x$ (mixing ration in units ppb) and PM10 (concentrations in unit $\mu g\,m^{-3}$) time series at the Bayreuth city site (15 May–09 June 2003); Three-day-averages, synchronous to the sampling intervals of OTC, OLC and OMC are shown.

3.8. Probable sources of organometallic compounds in Waldstein and Bayreuth

The peralkylated OTC, OLC and OMC may serve as the precursor of the ionic species in the atmosphere. In a precursory study at Waldstein, no peralkylated Sn, Pb and Hg species was detected by atmospheric speciation conducted using cryo-trap method. Only DMM was suspected in one sample (Kremer, 2001). The results could not exclude the occurrence of these peralkylated species, but reflect their very low concentrations in the atmosphere ($<0.6\,pg\,m^{-3}$ for Sn, $<0.8\,pg\,m^{-3}$ for Pb, $<16.3\,pg\,m^{-3}$ for Hg).

It is well established that OLC in the atmosphere originate mainly from the anthropogenic emissions in their peralkylated form, although a possible natural source is also suspected (Radojevic and Harrison, 1987). The much lower concentrations of the tetraalkyllead at our sites compared as to those at the urban site (up to $222.6\,ng\,m^{-3}$, Pécheyran et al., 2000) may attribute to

the lack of a source at the remote site, resulting in extremely low TML concentrations. Tetraalkyllead in the atmosphere undergo rapid decomposition involving photolysis, reactions with O(^{3}P), O$_3$ and OH radical and heterogeneous reaction on atmospheric particles (Harrison and Laxen, 1978). Emission of ionic OLC from soils seems little, because of the very low concentrations of ionic OLC in soils (Huang and Matzner, 2004).

Monomethylmercury in the atmosphere may originate from direct emission from the soils and be the product of dimethylmercury (DMM) decomposition (Schroeder and Munthe, 1998). The occurrence of MMM is regarded to be more likely from natural processes (Downs et al., 1998), such as Hg methylation in wetland soils and sediments. Once MMM is formed, it can be further methylated under certain natural conditions to DMM, which may diffuse to the atmosphere (Wallschläger et al., 1995). Reactions of DMM with OH and Cl radicals may lead to the formation of MMM (Schroeder and Munthe, 1998). At Waldstein, 30% of the area is covered with wetland soils enriched with MMM originating mostly from in situ Hg methylation (Schwesig and Matzner, 2000), suggesting the potential occurrence of these two pathways. However, this seems difficult to be proven due to the extreme low DMM concentrations at our sites.

The occurrence of peralkylated OTC in the natural atmosphere (Tessier et al., 2002; Amouroux et al., 2000) suggests that ionic OTC in the atmosphere may result from the decomposition of peralkylated OTC similar to tetraalkyllead and DMM. In addition, ionic OTC may release from environmental medians into atmosphere, e.g. as halides (Saint-Louis and Pelletier, 2004; Mester and Sturgeon, 2002). It is not easy to evaluate the relevance of both pathways for the occurrence of ionic OTC in the atmosphere due to the limited knowledge. However, the very low concentrations of peralkylated OTC point to that the former pathway seems to be less important at our sites.

4. Conclusion

In this study, we have demonstrated the occurrence of ionic OTC, OLC and OMC at fairly low levels of concentrations in the atmosphere at rural and urban sites. No significant difference of concentrations of ionic organometallic compounds in the atmosphere at both sites was found. At these concentrations level, tri- and di-substituted OTC, TML and MMM existed dominantly in the gas phase in the atmosphere. Aerosol particles may serve as a sink in the chemical cycles of OTC in the atmosphere, especially for MMT and MBT. On the contrary, the long-range-transported organometallic compounds in the atmosphere serve as an important source for both rural and urban sites. Furthermore, we demonstrated the advantage of analyzing ionic organometallic compounds in the aerosol particles over analyzing peralkylated species by a cyro-trap technique. For the ionic species much lower detection limits can be achieved. Atmospheric speciation of ionic organometallic compounds with large volume sampling (ca. 400 m^3) is specifically powerful at the remote sites and may provide more precise environmental risk assessment. Further studies should concentrate on a higher time resolution of the sample collection in order to facilitate and improve the analysis of origin and atmospheric dynamics of ionic OTC, OLC and OMC compounds. The deposition to the terrestrial ecosystems should be quantified in order to evaluate the toxic potential of these compounds.

References

Allan, R.J., 1999. Atmospheric mercury contamination of remote aquatic ecosystems in Canada. Water Science Technology 39, 173–177.

Allen, A.G., Radojevic, M., Harrison, R.M., 1988. Atmospheric speciation and wet deposition of alkyllead compounds. Environmental Science & Technology 22, 517–522.

Amouroux, D., Tessier, W., Donard, O.F.X., 2000. Volatization of organotin compounds from estuarine and coastal environments. Environmental Science & Technology 34, 988–995.

Batley, G.E., 1996. In the distribution and fate of tributyltin in the marine environment. In: De Mora (Ed.), Tributyltin: a Case Study of an Environmental Contaminant. Cambridge Environmental Chemistry Series. Cambridge University Press, Cambridge, pp. 139–165.

Brosset, C., Lord, E., 1995. Methylmercury in ambient air. Method of determination and some measurement. Water, Air, and Soil Pollution 82, 739–750.

Downs, S.G., Macleod, C.L., Lester, J.N., 1998. Mercury in precipitation and its relation to bioaccumulation in fish: a literature review. Water, Air, and Soil Pollution 108, 149–187.

Foken, T. (Ed.), 2003. Lufthygienisch-Bioklimatologische Kennzeichnung des oberen Egertales. Bayreuther Forum Ökologie, vol. 100. 70 pp.

Gilmour, C.C., Henry, E.A., 1991. Mercury methylation in aquatic systems affected by acid deposition. Environmental Pollution 71, 131–169.

Harrison, R.M., Laxen, D.P.H., 1978. Sink processes for tetraalkyllead compounds in the atmosphere. Environmental Science & Technology 12, 1384–1392.

Harrison, R.M., Radojević, M., 1985. Measurements of alkyllead compounds in the gas and aerosol phase in urban and rural atmospheres. The Science of the Total Environment 44, 235–244.

Heisterkamp, M., van de Velde, K., Ferrari, C., Boutron, C.F., Adams, F.C., 1999. Present century record of organolead pollution in high altitude alpine snow. Environmental Science & Technology 33, 4416–4421.

Held, A., Nowak, A., Wiedensohler, A., Klemm, O., 2002. Measuring vertical particle fluxes over a coniferous forest using eddy covariance. International Aerosol Conference 2002 (Taipeh).

Hewitt, C.N., Harrison, R.M., Radojevic, M., 1986. The determination of individual gaseous ionic alkyllead species in the atmosphere. Analytica Chimica Acta 188, 229–238.

Hoch, M., 2001. Organotin compounds in the environment—an overview. Applied Geochemistry 16, 719–743.

Huang, J.-H., 2004. Reducing blank values for trace analysis of ionic organotin compounds and their adsorption to different materials. International Journal of Environmental Analytical Chemistry 84, 255–265.

Huang, J.-H., Matzner, E., 2004. Biogeochemistry of trimethyllead and lead in a forested ecosystem in Germany. Biogeochemistry, in press.

Huang, J.-H., Ilgen, G., Matzner, E., 2003. Simultaneous determination of organotin, organolead and organomercury in the soils and litter. Analytica Chimica Acta 493, 23–34.

Huang, J.-H., Schwesig, D., Matzner, E., 2004. Organotin compounds in precipitation, fog and soils of a forested ecosystem in Germany. Environmental Pollution 130, 177–186.

Kavouras, I.G., Stephanou, E.G., 2002. Direct evidence of atmospheric secondary organic aerosol formation in forest

atmosphere through heteromolecular nucleation. Environmental Science & Technology 36, 5083–5091.

Klemm, O., 2004. Trace gases and particles in the atmospheric boundary layer at the Waldstein site: present state and historic trends. In: Matzner, E. (Ed.), Temperate Forest Ecosystem Functioning in a Changing Environment—Watershed Studies in Germany. Springer Ecological Studies, 172, pp. 45–57.

Klemm, O., Lange, H., 1999. Trends of Air Pollution in the Fichtelgebirge Mountains, Bavaria. Environmental Science and Pollution Research 6, 193–199.

Kremer, D., 2001. Nachweis flüchtiger Organometallverbindungen in einer Kläranlage. Diplomarbeit, University Bayreuth, Germany.

Lee, Y.H., Wängberg, I., Munthe, J., 2002. Sampling and analysis of gas phase methylmercury in ambient air. The Science of the Total Environment 304, 107–113.

Liang, C., Pankow, J.F., Odum, J.R., Seinfeld, J.H., 1997. Gas/particle partitioning of semivolatile organic compounds to model inorganic, organic, and ambient smog aerosol. Environmental Science & Technology 31, 3086–3092.

Lin, C.-J., Pehkonen, S.O., 1999. The chemistry of atmospheric mercury: a review. Atmospheric Environment 33, 2067–2079.

Łobiński, R., Boutron, C.F., Candelone, J.P., Hong, S., Szpunar-Łobinska, J., Adams, F.C., 1994. Present century snow core record of organolead pollution in Greenland. Environmental Science & Technology 28, 1467–1471.

Mersiowsky, I., Brandsch, R., Ejlertsson, J., 2001. Screening for organotin compounds in European landfill leachate. Journal Environmental Quality 30, 1604–1611.

Mester, Z., Sturgeon, R.E., 2002. Detection of volatile organometal chloride species in model atmosphere above seawater and sediment. Environmental Science & Technology 36, 1198–1201.

Munthe, J., Hultberg, H., Iverfeldt, Å., 1995. Mechanism of deposition of mercury and methylmercury to coniferous forests. Water, Air, and Soil Pollution 80, 363–371.

Nriagu, J.O., Wong, H.K.T., 1998. Gold rushes and mercury pollution. In: Sigel, A., Sigel, H. (Eds.), Metal Ions in Biological Systems, Mercury and its Effects on Environment and Biology, vol. 34. Deccer, New York, pp. 131–160.

Pécheyran, C., Lalère, B., Donard, O.F.X., 2000. Volatile metal and metalloid species (Pb, Hg, Se) in a European urban atmosphere (Bordeaux, France). Environmental Science & Technology 34, 27–32.

Quevauviller, P., Donard, O.F.X., 1991. Organotin stability during storage of marine waters and sediments. Fresenius Journal of Analytical Chemistry 339, 6–14.

Quevauviller, P., Bruchet, A., Donard, O.F.X., 1991. Leaching of organotin compounds from poly(vinyl chloride) (PVC) material. Applied Organometallic Chemistry 5, 125–129.

Radojevic, M., Harrison, R.M., 1987. Concentrations and pathways of organolead compounds in the environment: a review. The Science of the Total Environment 59, 157–180.

Saint-Louis, R., Pelletier, E., 2004. Sea-to-air flux of contaminants via bubbles bursting. An experimental approach for tributyltin. Marine Chemistry 84, 211–224.

Schroeder, W.H., Munthe, J., 1998. Atmospheric mercury-an overview. Atmospheric Environment 32, 809–822.

Schwesig, D., Matzner, E., 2000. Pools and fluxes of mercury and methylmercury in two forested catchment in Germany. The Science of the Total Environment 260, 213–223.

Tessier, E., Amouroux, D., Donard, O.F.X., 2002. Volatile organotin compounds (butylmethyltin) in three European esturies (Gironde, Rhine, Scheldt). Biogeochemistry 59, 161–181.

Thalmann, E., Burkard, R., Wrzesinsky, T., Eugster, W., Klemm, O., 2002. Ion fluxes from fog and rain to an agricultural and a forest ecosystem in Europe. Atmospheric Research 64, 147–158.

Wagemann, R., Trebacz, E., Boila, G., Lockhart, W.L., 1998. Methylmercury and total mercury in tissues of arctic marine mammals. The Science of the Total Environment 218, 19–31.

Wallschläger, D., Hintelmann, H., Evans, R.D., Wilken, R.-D., 1995. Volatization of dimethylmercury and elemental mercury from river Elbe floodplain soils. Water, Air, and Soil Pollution 80, 1325–1329.