



**Pollutants of Priority Concern
in Austrian Rivers**

Mercury and its compounds
Trisphosphates

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CONTENT

FIGURES	5
TABLES	6
SUMMARY AND CONCLUSIONS	8
ZUSAMMENFASSUNG	9
1 INTRODUCTION	11
1.1 Background and significance	11
1.1.1 Mercury	11
1.1.2 Trisphosphates.....	14
1.2 Current state of research	16
1.2.1 Mercury and its compounds	16
1.2.2 Trisphosphates.....	17
1.2.3 Conclusions.....	19
1.3 Research aims	19
2 MATERIALS AND METHODS	20
2.1 Sampling design	20
2.1.1 Rivers and sampling points	20
2.1.2 Sampling periods	24
2.1.3 Samples	25
2.2 Sample collection	25
2.2.1 Water and sediment	25
2.2.2 Suspended particles.....	25
2.2.3 Biota	25
2.3 Laboratory analysis	26
2.3.1 Water.....	26
2.3.2 Sediments and suspended matter	28
2.3.3 Biota	30
2.4 Data treatment	35
2.4.1 Solid – liquid partitioning	35
2.4.2 Bioaccumulation	35
3 RESULTS	36
3.1 Water	36
3.2 Suspended and active bottom sediments	37
3.3 Biota	45
3.3.1 Mercury and methylmercury.....	45
3.3.2 Trisphosphates.....	47
3.4 Partitioning	49
3.4.1 Adsorption to solids	49
3.4.2 Bioaccumulation	51

4	DISCUSSION	54
4.1	Contaminant levels compared among rivers and sampling locations	54
4.1.1	Mercury and methylmercury.....	54
4.1.2	Trisphosphates.....	55
4.2	Contaminant levels among the compartments analysed	57
4.2.1	Mercury and methylmercury.....	57
4.2.2	Trisphosphates.....	58
4.3	Contaminant levels versus critical values/Environmental Quality Standards	61
4.3.1	Environmental quality standards for water.....	61
5	LITERATURE	62
6	ANNEXES	69
Annex 1:	Water, suspended sediment and bottom sediment samples in the river Schwechat at the Brauhaus-Str./Schwechat, Lower Austria	70
Annex 2:	Water, suspended sediment and bottom sediment samples in the river Ager at the Raudaschmühle/Schörfling at Attersee, Upper Austria	71
Annex 3:	Water, suspended sediment and bottom sediment samples in the river Ager at the Scheiblmühle/Timelkam, Upper Austria	72

FIGURES

Figure 1:	Localisation of the two sampling sites at the river Schwechat at Mannswörth and Schwarzmühlbrücke	22
Figure 2:	Characterisation of sampling site Schwechat Mannswörth	22
Figure 3:	Characterisation of sampling site Schwechat Schwarzmühlbrücke	23
Figure 4:	Localisation of the two sampling sites at the river Ager at Unterachmann and Dürnau	23
Figure 5:	Characterisation of sampling site Ager Unterachmann	24
Figure 6:	Characterisation of sampling site Ager Dürnau	24
Figure 7:	Mercury in active bottom sediments (< 40 µm) in the Schwechat River at the GZÜV monitoring sites Mannswörth and Maria Lanzendorf 1993–2006 and mercury in suspended sediment and active bottom sediments in August and November 2007	41
Figure 8:	Distribution pattern of the investigated trisphosphates in the particulate matter samples from the river Schwechat	43
Figure 9:	Distribution pattern of the investigated trisphosphates in the particulate matter samples from the river Schwechat	44
Figure 10:	Calculated log K _{OC} values for suspended matter and sediments	51
Figure 11:	Bioaccumulation Factors (ranges) for total mercury (Hg) and methylmercury (Me-Hg) in fillet and whole body composite samples of fish from the rivers Ager and Schwechat	52
Figure 12:	Proportion (in percent) of methylmercury in total mercury in fillet and whole body composite samples of fish from the rivers Ager and Schwechat during the two sampling periods (P-1, P-2; Table 22)	52
Figure 13:	Bioaccumulation Factors (ranges) for the trisphosphates detected in fillet and whole body composite samples of fish from the rivers Ager and Schwechat	53
Figure 14:	Concentration ranges (minimum-maximum bars) of total mercury (Hg) and methylmercury (Me-Hg) in the rivers Ager and Schwechat over the compartments analysed (measured concentrations are as detailed in Table 13, Table 14, Table 18 to 24; concentrations below the analytical limits were set to zero in this graph, and are as detailed in Table 9, Table 10 and Table 12; mussels were sampled in the Ager river only	58
Figure 15:	Concentration ranges (minimum-maximum bars) of trisphosphates in the Ager River over the compartments analysed (concentrations below the analytical limits are set to zero in this graph; mussels were sampled in the Ager river only but sample volumes were too small for an analysis of the trisphosphates)	59
Figure 16:	Concentration ranges (minimum-maximum bars) of trisphosphates in the Schwechat River over the compartments analysed (concentrations below the analytical limits are set to zero in this graph; mussels were sampled in the Ager River only)	60

TABLES

Table 1:	Identification of the investigated triphosphates	14
Table 2:	physical-chemical properties of the investigated triphosphates obtained from http://www.syrres.com/what-we-do/product.aspx?id=133	15
Table 3:	Location of the river water, suspended and active bottom sediment sampling locations as GPS determined on site (GARMIN Etrex) and verified post-hoc via Geoland air photographs	21
Table 4:	Location of the fish and mussel sampling locations as GPS determined on site (GARMIN Etrex) and verified post-hoc via Google earth satellite images	21
Table 5:	Chromatographic parameters	26
Table 6:	ICPMS parameters	26
Table 7:	Chromatographic parameters	27
Table 8:	MS parameters	27
Table 9:	LOD and LOQ in ng/l for the analysed compounds in river water	28
Table 10:	LOD and LOQ for the analysed compounds in suspended and active bottom sediment samples	29
Table 11:	Morphometric characterisation of the a) fish (chub, <i>Leuciscus cephalus</i>) and b) mussel (zebra mussel, <i>Dreissena polymorpha</i>) samples (sampling points as characterised in Table 4)	31
Table 12:	LOD and LOQ [$\mu\text{g}/\text{kg}$ dry wt] for the various investigated compounds in biota samples	35
Table 13:	Mercury and methylmercury [$\mu\text{g}/\text{l}$] in river water samples	36
Table 14:	Organophosphorus esters [ng/l] in river water samples	37
Table 15:	Chemistry and mineralogy of suspended sediment ($< 40 \mu\text{m}$) and active fine bottom sediment ($< 40 \mu\text{m}$) in the river Schwechat at Brauhausstrasse sampling point	38
Table 16:	Chemistry and mineralogy of suspended sediment ($< 40 \mu\text{m}$) and active fine bottom sediment ($< 40 \mu\text{m}$) in the river Ager at Raudaschlmühle sampling point	39
Table 17:	Chemistry and mineralogy of suspended sediment ($< 40 \mu\text{m}$) and active fine bottom sediment ($< 40 \mu\text{m}$) in the Ager River at Scheiblmühle sampling point	39
Table 18:	Mercury and methylmercury [$\mu\text{g}/\text{kg}$] content in suspended sediments	40
Table 19:	Mercury and methylmercury [$\mu\text{g}/\text{kg}$] content in bottom sediments	40
Table 20:	Triphosphates [$\mu\text{g}/\text{kg}$ dry wt] in suspended sediment and active fine bottom sediments from the river Schwechat at Brauhaus-Str. sampling site	42
Table 21:	Triphosphates [$\mu\text{g}/\text{kg}$ dry wt] in suspended sediment and active fine bottom sediments from the river Ager sampling sites	44

Table 22:	Concentrations of total mercury (Hg) and methylmercury (Me-Hg) ($\mu\text{g}/\text{kg}$; mass base in brackets) in the fish (<i>Leuciscus cephalus</i>) whole body and fillet composite samples collected from two Austrian rivers in two collection periods (samples as detailed in Table 4 and Table 11; whole body concentrations calculated based on the measured fillet and carcass concentrations; for limits of quantification and detection and see Table 12)	46
Table 23:	Concentrations of total mercury (Hg) and methylmercury (Me-Hg) ($\mu\text{g}/\text{kg}$; mass base in brackets) in the mussel (<i>Dreissena polymorpha</i>) whole body samples (soft body, shells excluded) collected from two Austrian rivers in two collection periods (samples as detailed in Table 4 and Table 11)	46
Table 24:	Concentrations of trisphosphates ($\mu\text{g}/\text{kg}$; mass base in brackets) in the whole body and fillet composite samples of fish (<i>Leuciscus cephalus</i>) collected from two Austrian rivers in two collection periods (samples as detailed in Table 4 and Table 11; whole body concentrations calculated on the basis of the measured fillet and carcass concentrations; for limits of quantification and detection see Table 12; TBoEP, TKP, and TEHP levels were below these limits in all fish samples and therefore not included in this table)	47
Table 25:	Apparent solid-liquid distribution coefficient K_d [l/kg] and normalised to the organic carbon content of the adsorbent K_{OC} [l/kg] for suspended matter and sediments	49
Table 26:	Apparent solid-liquid distribution coefficient K_d [l/kg] for suspended matter and sediments	49
Table 27:	Apparent solid-liquid distribution coefficient normalised to the organic carbon content of the adsorbent K_{OC} [l/kg] for suspended matter and sediments	50

SUMMARY AND CONCLUSIONS

The aim of the present study was to generate a basis for an assessment of the occurrence and partitioning of the “priority pollutant” category mercury and its compounds, and the “emerging pollutants” trisphosphates (additives in flame retardants and softeners) in Austrian rivers. In two Austrian rivers (Schwechat and Ager) three abiotic compartments (river water, suspended and bottom sediment) and three biotic compartments (fish, European Chub, *Leuciscus cephalus*, whole body and fillet, and zebra mussel, *Dreissena polymorpha* whole body) were compared for contamination with mercury and methylmercury as well as nine different trisphosphates (organophosphorus esters; TEP, TCEP, TCPP, TPhP, TDCPP, TBP, TBoEP, TKP, TEHP).

The key findings of the present study are as follows:

- Both pollutant categories
 - I. were ubiquitous in the fish samples,
 - II. accumulated in fish and mussels, and
 - III. accumulated on suspended and active bottom sediments.
 - IV. An analysis of the partitioning of the analytes among the different compartments indicated that there was no single compartment suited best for monitoring a broader set of pollutants of priority concern: methylmercury was detected in fish (fillet > whole body) but not in water and sediments; more trisphosphate species were detected in the sediments than in the fish samples (whole body > fillet), and concentrations were highest and all above the detection limits in the suspended sediments fraction.
- The observed mercury levels in water as well as in biota in almost all samples were higher than the respective environmental quality standards. Mercury concentrations in fish reached critical limits for human consumption.
- In order to perform an evaluation, further measurements are required as the EQSs refer to annual average values based on monthly samples. But nevertheless, the described results highlight the necessity of further monitoring as a potential failure to reach the environmental quality target cannot be excluded.
- In order to assess mercury residues in fish with respect to safety for human consumption, further studies with fish species and size classes typically used for human consumption should be conducted.

ZUSAMMENFASSUNG

Das Ziel der vorliegenden Studie war die Schaffung einer Datengrundlage zum Vorkommen und zur Verteilung von Quecksilberverbindungen und Trisphosphaten (Additive in Flammschutzmitteln und Weichmachern) in unterschiedlichen Kompartimenten. In den zwei österreichischen Fließgewässern Ager und Schwechat wurden drei abiotische (Oberflächenwasser, Schwebstoffe und Sedimente) und drei biotische Kompartimente (Fisch: Aitel, *Leuciscus cephalus*, Gesamtfisch und Filet; Muschel: Zebramuschel, *Dreissena polymorpha*, Gesamtmuschel) hinsichtlich ihrer Belastung mit Quecksilber und Methylquecksilber sowie mit neun Trisphosphaten untersucht.

Die wesentlichen Ergebnisse der Studie sind:

- Beide Schadstoffe bzw. Schadstoffgruppen
 - I. waren ubiquitär in den Fischproben vorhanden,
 - II. wurden sowohl in Fischen als auch in Muscheln angereichert (Bioakkumulation) und
 - III. reichern sich in Schwebstoffen und in Sedimenten an (Akkumulation).
 - IV. Die Verteilung in den verschiedenen untersuchten Kompartimenten erlaubt keine einheitliche Ausweisung eines bestimmten Kompartimentes als am besten geeignet für ein Monitoring. Während Methylquecksilber vor allem im Fisch (Filet > Gesamtfisch), nicht aber im Wasser oder in Schwebstoffen bzw. Sedimenten angereichert wurde, wurden Trisphosphate vorwiegend an den Feststoffen und dabei hauptsächlich an den Schwebstoffen angelagert.
- Die beobachteten Quecksilbergehalte im Wasser und vor allem in Biota lagen zumeist im Bereich oder oberhalb der jeweiligen Umweltqualitätsnormen.
- Um eine Bewertung durchführen zu können, sind zusätzliche Messungen erforderlich, da sich die Umweltqualitätsnormen auf Jahresdurchschnittswerte, basierend auf monatlichen Beprobungen, beziehen. Im Zuge der Untersuchungen wurden jedoch weniger Proben gezogen. Nichtsdestotrotz betonen die Ergebnisse die Notwendigkeit weiterer Untersuchungen, da eine potentielle Gütezielverfehlung nicht auszuschließen ist.
- Die Quecksilberkonzentrationen in Fischen überschritten für den menschlichen Konsum kritische Werte. Zur Beurteilung ihres Gefährdungspotentials für den Menschen sollten weitere Studien mit Fischarten durchgeführt werden, die als Lebensmittel konsumiert werden.

1 INTRODUCTION

1.1 Background and significance

1.1.1 Mercury

Mercury has been known since antiquity. It rarely occurs as the free metal in nature. The main ore from which mercury is extracted is cinnabar (mercuric sulphide). Mercury exists in organic (e.g. phenylmercury acetate and methylmercuric chloride) and inorganic (e.g. mercury salt, mercuric II chloride, mercurous I chloride) forms. However, these forms may interconvert over time – organic mercury may slowly decompose to form inorganic mercury while inorganic mercury can be transformed into organic mercury by bacteria in soil and water. Some mercury salts and organic compounds are soluble in water, depending on the chemical species.

Mercury is widely used in the manufacture of thermometers, barometers, diffusion pumps and other instruments. It is also used in making mercury-vapour lamps and advertising signs, and in mercury switches, batteries and other electrical apparatus. Other uses are in the chlor-alkali industry and in dental fillings. Former uses in pesticide, pharmaceutical and paint manufacturing have now been phased out.

Mercury is a silvery-white metal that is liquid at room temperature. It freezes at –39 degrees C and it boils at 357 degrees C at atmospheric pressure. Mercury is appreciably volatile. It is odourless and non-flammable. It forms a number of inorganic and organic compounds, notably mercuric and mercurous chlorides and methyl mercury (UK EA 16.02.2009).

Mercury and its compounds are very toxic to wildlife. As a chemical element mercury that is released into the environment will remain there indefinitely although it may be converted to various forms over time. Organic mercury compounds tend to bioaccumulate in organisms and biomagnify up trophic food chains, and can have a significant effect on aquatic species. Low levels of mercury contamination in water bodies can lead to high concentrations in insects, fish and birds, leading to very toxic contamination in various parts of the ecosystem. Mercury is also toxic to plants and microorganisms, hence its former use as a fungicide and bactericide (UK EA 16.02.2009).

Excessive exposure to mercury and its compounds may affect the brain, digestive system, eye, heart, kidney, lung, reproductive system, skin, and the unborn child (UK EA 16.02.2009).

Mercury is classified as toxic and dangerous to the environment and has to be labelled accordingly (T, N, R23: Toxic by inhalation; R33: Danger of cumulative effects; R50/53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment) (ECB 16.02.2009).

The EU's mercury strategy is a comprehensive plan addressing mercury pollution both in the EU and globally. It contains 20 measures to reduce mercury emissions, cut supply and demand and protect against exposure, especially to methylmercury found in fish (EC 2009). Mercury is the subject of various sub-

stance specific regulations concerning emissions into water, air and soil as well as emissions from products. The main regulations referring to mercury in surface waters and groundwater are (list not complete):

- European Water Framework Directive (2000/60/EC): framework for Community action in the field of water policy and establishing the list of priority substances: mercury is defined as priority hazardous substance
- Environmental quality standards (2008/105/EC): establishing environmental quality standards in the field of water policy
- European Water Protection Directive (2006/11/EC, former Dangerous Substances Directive 76/464/EEC): avoiding pollution caused by certain dangerous substances discharged into the aquatic environment
- Council Directive on mercury discharges (82/176/EEC): establishing limit values and quality objectives for mercury discharges by the chlor-alkali electrolysis industry
- Council Directive on mercury discharges (84/156/EEC): establishing limit values and quality objectives for mercury discharges by sectors other than the chloralkali electrolysis industry
- Groundwater Directive (2006/118/EC): protection of groundwater against pollution and deterioration, member states have to establish threshold values

In January 2009 the European directive establishing environmental quality standards (EQS) in the field of water policy (Directive 2008/105/EC) entered into force and member states are obliged to adopt national legislation to comply with this directive by 13 July 2010.

Directive 2008/105/EC defines a limit value (AA-EQS) for concentrations of mercury and its compounds of 50 ng/l expressed as an annual average value and of 70 ng/l expressed as maximal allowable concentration (MAC-EQS). The EQS refers to the dissolved concentration, i.e. the dissolved phase of a water sample obtained by filtration through a 0.45 µm filter or any equivalent pre-treatment.

Mercury occurs in natural water in several forms including elemental Hg (Hg^0), which is rare in unpolluted waters, ionic Hg (Hg^+ and Hg^{2+}) and methylated Hg (CH_3Hg^+). There is increasing evidence that natural organic materials form strong complexes with mercury, via sulphidic functional groups, which influence the concentration, speciation and subsequent bioaccessibility of mercury in the aquatic environment. Background levels of Hg in surface water are usually very low, typically < 0.1 µg/l. Mercury minerals, such as cinnabar and metacinnabar, are insoluble under normal conditions, and metallic mercury will not react with stream water directly.

The median Hg content in European stream sediment is 40 µg/kg (N=848, < 0.15 mm) with a range from 3 to 13600 µg/kg. Mercury in stream sediment shows only a very weak correlation with antimony Sb (0.25) and zinc Zn (0.22). Mercury in floodplain sediment showed a good correlation (> 0.4) with Copper Cu and Cadmium Cd and a weak correlation with Zinc Zn and Phosphorus pentoxide P_2O_5 . This association points to mineralisation (Cu, Zn, Cd) and possible anthropogenic influence (phosphate fertilisers).

Normal soil (n=1612; < 2 mm) typically contains 20–150 µg/kg Hg, and surface soil values do not tend to exceed 400 µg/kg. The accumulation of Hg is related mainly to the levels of organic carbon C and sulphur S in soil (SALMINEN 2005).

As mercury is known to bioaccumulate and the defined EQS in surface waters requires a sophisticated chemical analysis, directive 2008/105/EC also defines an EQS for biota equal to 20 µg/kg for mercury and its compounds in prey tissue (wet weight). The most appropriate indicator among fish, molluscs, crustaceans and other biota should be chosen.

Mercury emissions are, however, distributed over long distances in the atmosphere and oceans. ... Data on mercury concentrations in fish have been submitted from a number of nations and international organisations. Additionally, many investigations of mercury levels in fish are reported in the literature. Submitted data, giving examples of mercury concentrations in fish from various locations in the world, are summarised in the chapter. The mercury concentrations in various fish species are generally from about 0.05 to 1.4 milligrams of mercury per kilogram of fish tissue (mg/kg) depending on factors such as pH and redox potential of the water, and species, age and size of the fish. Since mercury biomagnifies in the aquatic food web, fish higher on the food chain (or of higher trophic level) tend to have higher levels of mercury. Hence, large predatory fish, such as king mackerel, pike, shark, swordfish, walleye, barracuda, large tuna (as opposed to the small tuna usually used for canned tuna), scabbard and marlin, as well as seals and toothed whales, contain the highest concentrations. The available data indicate that mercury is present all over the globe (especially in fish) in concentrations that adversely affect human beings and wildlife. These levels have led to consumption advisories (for fish, and sometimes marine mammals) in a number of countries, warning people, especially sensitive subgroups (such as pregnant women and young children), to limit or avoid consumption of certain types of fish from various waterbodies. Moderate consumption of fish (with low mercury levels) is not likely to result in exposures of concern. However, people who consume higher amounts of contaminated fish or marine mammals may be highly exposed to mercury and are therefore at risk (UNEP 2002).

With respect to food safety for human consumption, several countries and international organizations have established reference levels for daily or weekly methyl-mercury or mercury intakes which, *based on available data and research, are estimated to be safe (or without appreciable risk to health). The reference intake levels for methylmercury exposures range from 0.7 to 2 µg methylmercury per kilogram body weight (µg/kg body weight) per week (WHO 2008).*

Because fish consumption dominates the pathway for exposure to methylmercury for most human populations, many governments provide recommendations or legal limits for the maximum allowable amount of mercury and/or methylmercury in fish to be sold on the market. For example, Codex Alimentarius guideline levels are 0.5 mg methylmercury/kg in non-predatory fish and 1 mg methylmercury/kg in predatory fish. The US Food and Drug Administration (FDA) has set an action level of 1 mg/kg for methylmercury in finfish and shellfish. The European Community allows 0.5 mg/kg mercury in fishery products (with some exceptions), and Japan allows up to 0.4 mg/kg total mercury (or 0.3 mg/kg methylmercury) in fish (WHO 2008).

As regards mercury, the EFSA adopted on 24 February 2004 an opinion related to mercury and methylmercury in food (1) and endorsed the provisional tolerable weekly intake of 1.6 µg/kg body weight. Methylmercury is the chemical form of most concern and can make up more than 90% of the total mercury in fish and seafood (EC 2006).

According to the Commission Regulation setting maximum levels for certain contaminants in foodstuffs (Ec 2006a, 2006b), maximum levels of mercury in fishery products and muscle meat of fish are 0.50 (mg/kg wet mass), but 1.0 mg/kg wet mass for species listed in chapter 3.3.

The European Food Safety Authority (EFSA) stresses that the main source of human exposure to methylmercury from food is fish and seafood products and provides precautionary advice for vulnerable groups and life phases, in particular pregnancy and early childhood (Ec 2004).

1.1.2 Trisphosphates

Trisphosphates are widely used as additives in flame retardants and softeners and are commonly attributed to the so-called “emerging pollutants”. The term “emerging pollutants” defines chemicals which are emitted to the environment but not yet included in national or international monitoring programmes. In view of their fate and (eco)toxicology they might be subjected to future restrictions, through derivation of quality standards, and be considered in monitoring programmes.

Triphosphates are organophosphate-ester compounds covering a vast group of organic chemical substances. The most important representatives of this group (excepting pesticides) covered by the present study are identified in Table 1. Characteristic physical-chemical properties of the investigated trisphosphates are summarised in Table 2.

Table 1: Identification of the investigated trisphosphates

Name	Abbreviation	CAS	Formulae
Triethyl phosphate	TEP	78-40-0	C ₆ H ₁₂ Cl ₃ O ₄ P
Tri(2-chloroethyl) phosphate	TCEP	115-96-8	C ₆ H ₁₅ O ₄ P
Tri(chloropropyl) phosphate	TCPP	13674-84-5	C ₉ H ₁₈ Cl ₃ O ₄ P
Triphenyl phosphate	TPhP	115-86-6	C ₁₈ H ₁₅ O ₄ P
Tri(dichloropropyl) phosphate	TDCPP	13674-87-8	C ₉ H ₁₅ Cl ₆ O ₄ P
Tributyl phosphate	TBP	126-73-8	C ₁₂ H ₂₇ O ₄ P
Tributoxyethyl phosphate	TBoEP	78-51-3	C ₁₈ H ₃₉ O ₇ P
Trikresyl phosphate	TKP	1330-78-5	C ₂₁ H ₂₁ O ₄ P
Tri(2-ethylhexyl) phosphate	TEHP	78-42-2	C ₂₄ H ₅₁ O ₄ P

Table 2: *physical-chemical properties of the investigated trisphosphates obtained from <http://www.syrres.com/what-we-do/product.aspx?id=133>*

	MW [g/mol]	S _w [g/l]	log P _{ow} [-]	V _p [Pa]
TEP	182.16	500.0	0.8	52
TCEP	285.49	7.0	1.44	8
T CPP	327.57	1.2	2.59	2.69 x 10 ⁻³
TPhP	326.29	0.0019	4.59	8.37 x 10 ⁻⁴
TDCPP	430.91	0.007	3.65	9.81 x 10 ⁻⁶
TBP	266.32	0.28	4.00	1.51 x 10 ⁻¹
TBoEP	398.48	1.1	3.75	3.33 x 10 ⁻⁶
TKP	368.37	0.00036	5.11	8.00 x 10 ⁻⁵
TEHP	434.65	0.0006	9.49	1.10 x 10 ⁻⁵

MW...molecular weight, S_w...water solubility, P_{ow}...octanol-water equilibrium distribution coefficient, V_p...vapour pressure

The draft on the risk assessment of tri(2-chloroethyl) phosphate (TCEP) released in March 2006 concluded that, at present, there is no need for further studies or reduction measures as regards environmental protection, while risk assessment with respect to human health has not yet been completed. Nevertheless, it recognised the carcinogenicity, high toxicity and environmental persistence of this compound. However, TCEP does not meet the PBT criteria (persistence, bioaccumulation and toxicity), as it is not bioaccumulative. Risk assessment for the other two chlorinated compounds has not yet been completed, but tri(chloropropyl) phosphate (T CPP) is also a suspected carcinogen, while the carcinogenicity of tri(dichloropropyl) phosphate (TDCPP) seems to have been proved more clearly. These two compounds with higher log K_{ow} values (Table 2) may therefore eventually meet the PBT criteria and may then require regulatory measures to be taken. In the case of non-chlorinated trisphosphates, neurotoxic effects were found for tributyl phosphate (TBP) and triphenyl phosphate (TPhP), whereas tributoxyethyl phosphate (TBoEP) is also a suspected carcinogenic compound (REEMTSMA et al. 2008).

For TBP, TCEP and TEP harmonised classification exists in Europe:

- TEP is classified as harmful if swallowed (Xn, R22: harmful if swallowed).
- TBP is classified as Carc.Cat. 3, harmful if swallowed and irritating to the skin (Carc.Cat. 3, Xn, Xi; R22: harmful if swallowed; R38: irritating to the skin; R40: limited evidence of a carcinogenic effect).
- TCEP is classified as toxic to reproduction Cat. 2, Carc.Cat. 3, toxic and dangerous to the environment as well as harmful (Repr. Cat. 2 R60: may impair fertility, Carc.Cat. 3 R40: limited evidence of a carcinogenic effect, Xn R22: harmful if swallowed and N R50/53: Very toxic to aquatic organisms, may cause long-term adverse effects in the aquatic environment) and has to be labelled accordingly (T, N) (ECB, 16.02.2009).

In the framework of the authorisation process according to REACH (Regulation (EC) No 1907/2006), Member States Competent Authorities or the European Chemicals Agency (ECHA), upon request of the European Commission, may prepare Annex XV dossiers for the identification of Substances of Very High Concern (SVHC). TCEP, classified as toxic to reproduction (cat. 2), has been identified as a SVHC (ECHA 2009).

Trisphosphates are mostly employed as flame retardants in plastics, textiles and electronic equipment, as well as in furniture and construction, but also for anti-foaming, as additives to lacquers, in hydraulic fluids or floor polish, in hydrometallurgy and as plasticisers. Many trisphosphates are regarded as high-production volume chemicals (HPVC) (REEMTSMA et al. 2008).

1.2 Current state of research

1.2.1 Mercury and its compounds

Metals in general and mercury and its compounds in particular are among the most intensively studied chemical classes in ecotoxicology with the state-of-the-science condensed in textbooks on metal toxicology (e.g., NORDBERG et al. 2007), reproductive toxicology (e.g., GOLUB 2006); ecotoxicology as well as hazard and life-cycle assessment (e.g., PAQUIN et al. 2003; DUBREUIL 2005; ADAMS & CHAPMAN 2007); environmental chemistry and important aspects of the speciation and availability of metals (e.g., SIEGEL 2002).

The ecotoxicology of metals has been reviewed for various biota such as ‘aquatic organisms’ (MANCE 1987), invertebrates (DALLINGER & RAINBOW 1993), fish (SORENSEN 1991), amphibians (LINDER & GRILLITSCH 2000), reptiles (GRILLITSCH & SCHIESARI in press), birds, and mammals, humans in particular (e.g., NORDBERG et al. 2007). Among the mercury targeted reviews, some of the most comprehensive ones were compiled by EISLER (1987, 2006), WOLFE et al. (1998), CHAN et al. (2003), WIENER et al. (2003), and HARRIS et al. (2007). Special issues of journals on mercury ecotoxicity were edited by EVERS & CLAIR (2005) and HARRIS et al. (2008).

Ultimately, the key findings of the Global Mercury Assessment (UNEP 2002) are that

- a. mercury is present throughout the environment;
- b. mercury is persistent and cycles globally;
- c. exposure to mercury has serious effects;
- d. intervention can be successful.

Nowadays, mercury in the environment is recognised as a substance of utmost global concern which has reached a high priority in national and international environmental agencies and commissions such as the

- European Commission DG Environment
<http://ec.europa.eu/environment/chemicals/mercury/>
- European Environment Agency
<http://dataservice.eea.europa.eu/atlas/viewdata/viewpub.asp?id=3204>
<http://dataservice.eea.europa.eu/atlas/available2.asp?type=findkeyword&theme=mercury>
- Environment Canada
<http://www.ec.gc.ca/MERCURY/EN/index.cfm>
http://www.ns.ec.gc.ca/msc/as/chemistry_mercury.html
- United States Environmental Protection Agency (USEPA)
<http://www.epa.gov/mercury/>

- US EPA Framework for Metals Risk Assessment
<http://cfpub.epa.gov/ncea/cfm/recordisplay.cfm?deid=167607>
- United States Geological Survey (USGS)
<http://www.usgs.gov/mercury/>
<http://minerals.usgs.gov/minerals/pubs/commodity/mercury/>
- United Nations Environment Programme (UNEP). Chemicals
<http://ec.europa.eu/environment/chemicals/mercury/>
<http://www.chem.unep.ch/MERCURY/publications/default.htm>
- Environment Agency Austria
<http://www.umweltbundesamt.at/umweltschutz/umweltanalytik/schadstoff/methylhg/>

With regard to “Global Mercury Challenges” the European Council adopted the following conclusions in December 2008:

<http://europa.eu/rapid/pressReleasesAction.do?reference=PRES/08/355&format=HTML&aged=0&language=EN&guiLanguage=en> >

There, the Council of the European Union:

1. *reiterates that mercury is recognised as being persistent, toxic, bioaccumulative and having long-range transport properties.*
2. *affirms its commitment to the overall objective of protecting human health and the environment from the release of mercury and its compounds by minimising and, where feasible, ultimately eliminating global anthropogenic mercury releases to air, water and land.*
3. *recalls that the Council conclusions of 24th June 2005 regarded it as essential to continue and intensify international efforts to reduce mercury emissions and exposure on a global scale with a view to achieving a global phase-out of primary production, preventing surpluses from re-entering the market, as well as phasing out its use and trade, taking into account the availability of alternatives.*
4. *underlines the progress made in implementing the Community Strategy Concerning Mercury since 2005, in particular the adoption of legislative acts exclusively dedicated to mercury: the 2007 Directive relating to restrictions on the marketing of certain measuring devices containing mercury and the Regulation on the banning of exports from the European Union and the safe storage of mercury as from March 2011, which was adopted this year. Under this Regulation, metallic mercury has to be safely stored within the EU in facilities guaranteeing a high level of safety.*

1.2.2 Trisphosphates

Organophosphorus flame retardants and plasticisers belong to the so-called emerging pollutants and have gained interest in the past decade.

Few studies exist on the occurrence and behaviour of trisphosphates in wastewater (MEYER & BESTER 2004; MARKLUND et al. 2005; RODIL et al. 2005; MARTINEZ-CARBALLO et al. 2007). TBoEP, in most cases, showed the highest influent concentrations, but is at least partially removed during wastewater treat-

ment. Whereas TBoEP, TBP and TPhP are moderately removed, the chlorinated trisphosphates TCEP, TCPP and TDCPP usually are not removed during wastewater treatment. Thus, the chlorinated trisphosphates are discharged in nearly undiminished amounts into the aquatic environment. As major removal process for TBP and TPhP in wastewater treatment plants (WWTPs) biodegradation is assumed, since they were completely degraded (but not always mineralised) in laboratory degradation studies (KAWAGOSHI et al. 2002). In such laboratory studies, chlorinated trisphosphates proved to be not biodegradable.

The discharge by wastewater treatment plants is considered the major source of trisphosphates in the aquatic environment. Apparently, especially the recalcitrant chlorinated trisphosphates are also present in surface waters (ANDRESEN et al. 2004; MARTINEZ-CARBALLO et al. 2007). Due to their polarity and poor biodegradability some trisphosphates can also be found in bank filtrates (KNEPPER et al. 1999).

Trisphosphates are used as building materials, in upholstery and in floor polishes and are therefore found in higher concentrations in indoor air samples than in outdoor samples (REEMTSMA et al. 2008). Concentrations in indoor air samples show great variations depending on the usage of e.g. computer or screens, floor polishes or wall coverings. Furthermore they are found in explicitly high concentrations in air samples from hospitals and prisons as a result of their usage as flame retardants in mattresses. TCPP is especially used in the upholstery of cars and public transport vehicles where it is found in 10- to 100-fold higher concentrations compared to private houses (REEMTSMA et al. 2008). Moreover, trisphosphates were also detected in outdoor air samples and environmental samples from remote areas. Thus, air transport also contributes to the distribution of trisphosphates in the environment (REEMTSMA et al. 2008).

Among trisphosphates, organophosphorus (organic phosphate ester) flame retardants include compounds with low to very high hydrophobicity (log Kow 1–9) and therefore, some of these compounds were considered to have a potential for secondary poisoning (VERBRUGGEN et al. 2005). A comprehensive environmental risk assessment and evaluation study has been conducted for TCEP [tris(2-chloroethyl)phosphate], TCPP [tris(1-chloro-2-propyl)phosphate], TDCP [tris(1,3-dichloro-2-propyl)phosphate], TBP [tri-nbutylphosphate], TiBP [tri-iso-butyl phosphate], TEP [triethyl phosphate], TBEP [tris(butoxyethyl) phosphate], TEHP [tris(2-ethylhexyl) phosphate], TPP [triphenylphosphate], and TCP [tricresylphosphate] (VERBRUGGEN et al. 2005). WHO IPCS (World Health Organisation, International Programme on Chemical Safety) has published Environmental Health Criteria Monographs (EHCs) for several flame retardants including TBPP [tris- and bis(2,3-dibromopropyl) phosphate], TBEP [tris(2-butoxyethyl)phosphate], and TCPP among others (<http://www.inchem.org/pages/ehc.html>). Comprehensive field studies on the accumulation of organophosphorus flame retardants in fish are still comparatively scarce, and diverging with regard to the chemical and biological species and compartments analysed as well as to time and space, general environmental conditions, and types and degrees of habitat degradation. Overall, various trisphosphates have been detected in fish from Japan (WHO 1998, 2000), the Netherlands (VERBRUGGEN et al. 2005), the Norwegian Arctic (EVENSET et al. 2009) and Sweden (NATURVARDsverket 2009).

1.2.3 Conclusions

Publications dealing with the fate and effects of mercury and its compounds in abiotic and biotic ecosystem compartments are abundant. Nevertheless, there is still an urgent need

- a. to build a database on the distribution of mercury within food webs in Austria, and
- b. to design the most appropriate monitoring strategies.

Whereas data for mercury and its compounds in abiotic and biotic ecosystems are available, only little information exists on the occurrence, distribution and fate of trisphosphates in the environment.

1.3 Research aims

The aim of the present study was to generate a basis for an assessment of the occurrence and partitioning of the “priority pollutants” mercury and methylmercury, and the “emerging pollutants” trisphosphates in Austrian rivers. For this purpose two Austrian lowland rivers were sampled at various sampling points. The sampled locations represent markedly different types and degrees of anthropogenic modifications. The analysis focused on the distribution of the analytes among the compartments water, particles (suspended and active bottom sediments) and biota (fish and bivalves).

2 MATERIALS AND METHODS

2.1 Sampling design

Mercury and methylmercury as well as organophosphate esters were analysed in biota (fish and mussels), river water, suspended particulate matter (SPM) and sediment samples. Although environmental quality standards usually refer to the water fraction it might be suitable to address other environmental compartments. Especially apolar lipophilic compounds with a low water solubility and high octanol-water distribution coefficient are hardly detectable in water, because they tend to accumulate in biota and/or suspended matter or sediments.

SPM or suspended load in waters is that part of the stream load that is carried in suspension for a considerable period of time, free of contact with the stream bed (BATES & JACKSON 1980). The total amount of any substance in the water is often separated into a particulate phase, the only one subject to gravitational sedimentation, and a dissolved phase. Operationally, the limit between particulate and dissolved phase is generally determined by means of filtration, using a pore size of 0.45 µm. Evidently, this is an operational approach and many colloidal particles will pass through such filters. WHITE (2008) divided suspended particulate matter (SPM) into the wash load which consists of all particles of less than 63 µm and the suspended bed material load consisting of coarser particles intermittently moved from the river bed. The latter typically vary logarithmically with depth toward the stream bed and gain in importance in Mountain Rivers and during storm floods.

The total amount of SPM found in natural waters is generally a complex mixture of substances of different origins with different properties (size, form, density, specific surface, capacity to bind pollutants, etc.). SPM may be divided into an organic (particulate organic material POM) and an inorganic fraction (particulate inorganic material PIM) (HÅKANSON 2007). Both change in composition with decreasing grain size (KRALIK & AUGUSTIN 1993, 1994).

2.1.1 Rivers and sampling points

The two Austrian rivers analysed in this study are part of the Austrian Danube river basin (sub district downstream Jochenstein). They are well characterised with respect to their hydromorphology as well as with regard to abiotic and biotic river quality elements (KRALIK & SAGER 1987a, 1987b; JUNGWIRTH & WOHLSCHLAGER 1995; KRIECHBAUM & MOOG; SCHMEDTJE et al. 2005; MOOG et al. 2006; Wasserinformationssystem Austria <http://wisa.lebensministerium.at>).

- a. The **Schwechat** River (eastern Lower Austria) just east of Vienna is a heavily modified (regulated channel) lowland river impacted by agriculture, industry and urbanization. It is characterised by a low gradient of 0.0031 and a mean flow rate of 7 (2-92) m³/s. The suspended sediment concentration varied according to filtration tests (Annex 1) from 7 to 31 mg/l.
- b. The **Ager** River (pre-alpine Upper Austria) 30 km west of Linz is a lowland river partly impacted by industry and agriculture. It is characterised by a low gradient of 0.0038 as well as mean flow rate of 16 (2-55) m³/s. The suspended sediment concentration (see Annex 1 to Annex 3) is as low as 0.1 to 0.6 mg/l due to no (Raudaschlmühle) – or only a short – distance from the outflow (Scheiblmühle) of Lake Attersee.

Along each river, two sampling locations were selected which are part of the Austrian Water Quality Monitoring System (AWQMS) according to the European Water Framework Directive (WFD) [Water Quality Monitoring Ordinance (*Wassergüte-Erhebungsverordnung WGEV*) Federal Legal Gazette No. 338/1991 until December 2006; Ordinance on the Monitoring of the Status of Water Bodies (*Gewässerzustandsüberwachungsverordnung GZÜV*), Federal Legal Gazette No. 479/2006; *GZÜV-Oberflächengewässer* (Surface Waters); WAGNER & DEUTSCH 2008]. Three to four monitoring sites were selected including contaminated and uncontaminated river sections.

The river water, suspended and active bottom sediment sampling sites are just below a weir not far from the AWQMS monitoring points (Table 3).

Table 3: Location of the river water, suspended and active bottom sediment sampling locations as GPS determined on site (GARMIN Etrex).

River	Sampling point	Position*	Comments
Schwechat	Brauhausstrasse Schwechat	E 16°32'14'' N 48°09'22''	Just before junction with Mitterbach
Ager	Raudaschlmühle Schörfling	E 13°36'29'' N 47°57'07''	at the weir Raudaschlmühle
Ager	Scheiblmühle Timelkam	E 13°37'06'' N 47°59'29''	at the weir Scheiblmühle

* Coordinates of the sampling points (GPS WGS84), midway of sampling stretch;
E...Longitude East, N...Latitude North

The fish and mussel sampling stretches were close to the AWQMS monitoring points as characterised in Table 4 and Figure 1 to Figure 6.

Table 4: Location of the fish and mussel sampling locations as GPS determined on site (GARMIN Etrex) and verified post-hoc via Google earth satellite images.

River	Sampling point	Position*	Length (m) of fish (mussels) sampling stretches
Schwechat	Mannswörth	E 16°29'07,44'' N 48°08'56,21''	1000 (1000)
Schwechat	Schwarzmuhlbrücke Steggasse	E 16°28'24,79'' N 48°08'24,10''	1000 (400)
Ager	Unterachmann	E 13°36'31,42'' N 47°57'49,12''	1000 (400)
Ager	Dürnau	E 13°38'01,74'' N 47°59'43,54''	1000 (400)

* Coordinates of the sampling points (GPS WGS84), midway of sampling stretch;
E...Longitude East, N...Latitude North

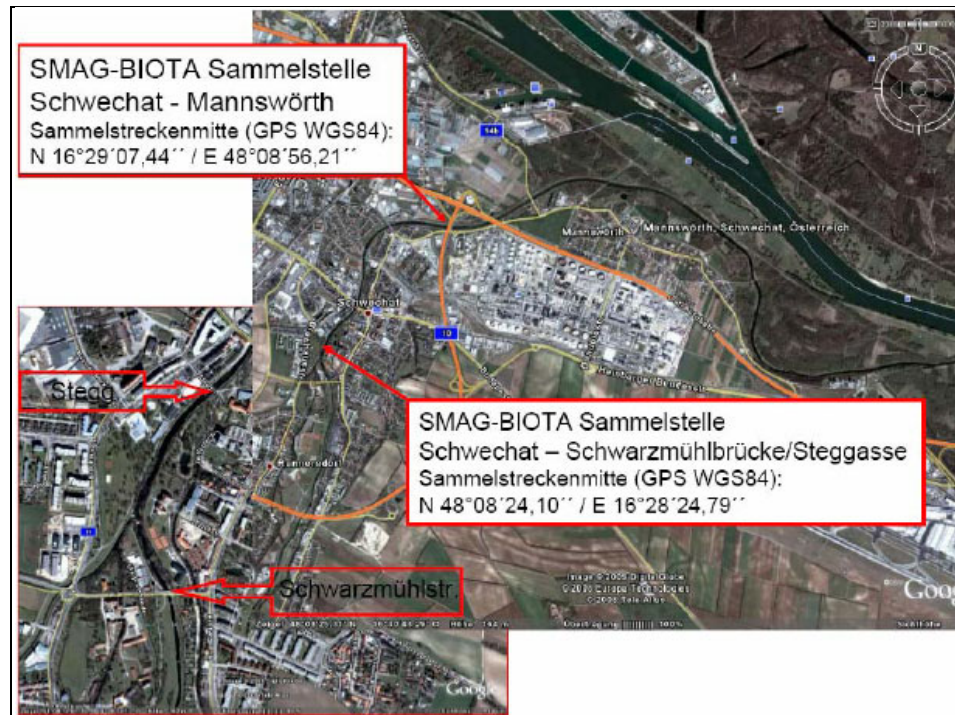


Figure 1: Localisation of the two sampling sites at the river Schwechat at Mannswörth and Schwarzmühlbrücke



Figure 2: Characterisation of sampling site Schwechat Mannswörth (pictures by M. Schabuss)



Figure 3: Characterisation of sampling site Schwechat Schwarzmühlbrücke (pictures by M. Schabuss)

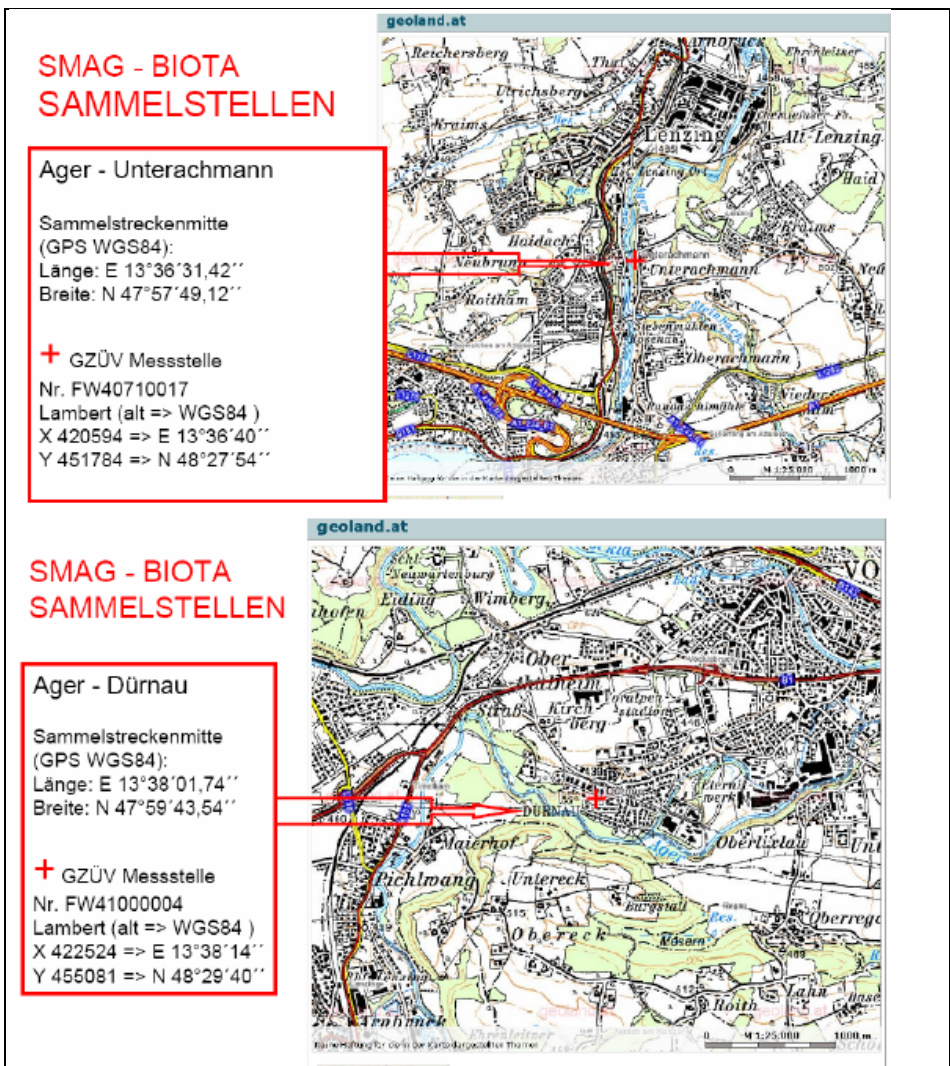


Figure 4: Localisation of the two sampling sites at the river Ager at Unterachmann and Dürnau



Figure 5: Characterisation of sampling site Ager Unterachmann (pictures by M. Schabuss)



Figure 6: Characterisation of sampling site Ager Dürnau (pictures by M. Schabuss)

2.1.2 Sampling periods

All sampling procedures were performed at the four sampling sites during summer (July–September) and late autumn/winter (November–December) 2007.

Fish and mussels were collected during two sampling periods (July and November 2007).

2.1.3 Samples

2.1.3.1 Abiotic compartments

River water and active bottom sediments have been collected as grab sample and as composite samples in summer and late autumn at the same monitoring site. Suspended sediment is trapped in a newly developed continuous sediment sampler (KRALIK et al. in preparation) over variable periods (days – months) according to suspended sediment concentrations.

2.1.3.2 Biotic compartments

Following RÜDEL & WIMMER (2007), two abundant, widely distributed and not endangered freshwater animal species – the chub, *Leuciscus cephalus* (Cyprinidae) and the zebra mussel, *Dreissena polymorpha* (Dreissenidea) – were selected for residue analysis.

Fish sample sizes ranged from 10–30 individuals, whereas 60 mussels per sampling site and period were collected. Fish fillet (axial muscle including skin) and rest of body (carcass including all organs) samples were combined resulting in one fillet and one carcass composite sample per sampling site and period. Similarly, mussel soft tissues (shells excluded) were combined resulting in one composite sample per sampling site and period. Details on sample sizes and morphometry are given in Table 11.

2.2 Sample collection

2.2.1 Water and sediment

All water samples for mercury, methylmercury and trisphosphate analyses were taken in glass containers as grab samples at 20 cm depth. After rinsing the glass containers once, the grab samples were cooled and kept in the dark and transported to the laboratory. Water temperature, electric conductivity and pH of the river water were measured on site (see Annex 1 to Annex 3).

2.2.2 Suspended particles

The suspended sediment samplers were based on the principle of reducing the flow velocity in order to enhance settling and/or coagulation of suspended particles in a sedimentation chamber. The throughput is 2 ml/s. A detailed description of the sample collection procedure is provided in KRALIK et al. (in preparation).

2.2.3 Biota

Sampling for fish was conducted using electric fishing (backpack electro fishing device, type FEG 2000, 150–300 – 600 Volt DC, Motor Honda GXV 140, EFKO-Elektrofischfanggeräte GmbH). Fish were transported to the lab shortly after collection under appropriate, stable and controlled temperature and oxygen conditions in fish transport tanks with liquid oxygen supply.

2.3 Laboratory analysis

2.3.1 Water

2.3.1.1 Mercury and methylmercury

The determination of mercury (Hg) in stabilized water samples ($K_2Cr_2O_7/HNO_3$, pH < 2) was carried out after reduction with sodium borohydride with flow injection cold vapour atomic absorption spectrometry according to ÖNORM (Austrian Standard) EN 1483 (modified).

The determination of methylmercury (Me-Hg) in water samples (stabilised with HNO_3 , pH < 2) was conducted directly after filtration through 0.45 µm membrane filters with high performance liquid chromatography hyphenated to inductively coupled plasma mass spectrometry (HPLC-ICPMS). A detailed description of the analytical method is provided in VALLANT et al. (2007). For further information on chromatographic and ICPMS parameters please refer to Table 5 and Table 6.

Table 5: Chromatographic parameters

HPLC: Perkin Elmer LC 200 System	
Column	Hamilton PRP X-200
Mobile phase	50 mM pyridine, 0.5 % w/w L-cysteine, 5 % v/w methanol, pH 2
Flow rate	0.5 ml/min
Column temperature	50°C
Injection volume	20 µl

Table 6: ICPMS parameters

ICPMS: Perkin Elmer Elan DRC II	
Nebulizer	Sea Spray
Nebulizer gas	~ 1 ml/min
Auxiliary gas	1.6 ml/min
Plasma gas	15 L min ⁻¹
RF Power	1500 W
Autolens	Off
Monitored isotopes	m/z 200, m/z 202

2.3.1.2 Trisphosphates

Trisphosphates were determined by means of liquid chromatography-tandem mass spectrometry (LC-MS/MS) after enrichment of the analytes by liquid extraction (LLE) at pH7.

Briefly, 500 or 1000 g of the sample were adjusted to a pH of 7 and an isotopically marked surrogate standard mixture was added. The samples were extracted thrice by LLE with dichloromethane. The resulting extract was dried with sodium sulphate, evaporated under a nitrogen stream and brought to a final volume of 1 ml.

The extracts were analysed by LC-MS/MS. Details of the chromatographic and MS parameters are summarized in Table 7 and Table 8.

Table 7: Chromatographic parameters

HPLC: Waters Separation Module 2695	
Column	Luna C8(2) 5 μ 150 x 2.0 mm
Mobile phase	A: MeOH, 10 mM ammonium acetate, 0.1% formic acid B: H ₂ O 10 mM ammonium acetate, 0.1% formic acid
Flow rate	0.25 ml/min
Column temperature	20°C
Injection volume	10 μ l

Table 8: MS parameters

MS: Micromass Quattro Micro		
Ionization mode	Electrospray positive	
Capillary Voltage	3.5 kV	
Source Temperature	120 °C	
Desolvation Temperature	250 °C	
Cone Gas Flow	80 l/Hr	
Desolvation Gas Flow	400 l/Hr	
MRM transitions	TEP	183.3>99.3
	TCEP	285.2>99.3
	TCPP	329.2>99.3
	TPhP	327.3>77.2
	TDCPP	431.2>99.3
	TBP	267.5>99.3
	TBoEP	399.4>199.4
	TKP	369.3>91.3
	TEHP	435.5>99.4

2.3.1.3 Limit of detection and limit of quantification

The respective limits of detection (LOD) and quantification (LOQ) in μ g/l are summarised in Table 9 for the various investigated compounds in river water samples.

Table 9: LOD and LOQ in ng/l for the analysed compounds in river water

Substance	River water samples	
	LOQ [ng/l]	LOD [ng/l]
Hg	100	50
Me-Hg	400	100
TEP	9	4.5
TCEP	82	41
T CPP	2.5	0.68
TPhP	2.3	0.61
TDCPP	2.8	0.76
TBP	4.9	1.3
TBoEP	7	1.9
TKP	3	1.5
TEHP	27	7.3

2.3.2 Sediments and suspended matter

2.3.2.1 TIC/TOC

TIC (Total Inorganic Carbon): The determination of the total inorganic carbon was performed according to ÖN EN 13137 by acidifying the samples and measuring the emerging CO₂ gas volume.

TC (Total Carbon): The determination of the total carbon was performed according to ÖN EN 13137 by the combustion of the sample in an oxygen atmosphere. Thereby all carbon is transformed to CO₂ which is detected coulometrically.

TOC (Total Organic Carbon): According to ÖN EN 13137 the TOC is calculated from the difference between TC and TIC.

2.3.2.2 Cations (Al, Ca, Mg) and mercury

Sample preparation – microwave assisted digestion of sediment samples

300 mg portions of the homogenised samples were weighted into quartz digestion vessels. After addition of 6 ml hydrochloric acid and 2 ml nitric acid microwave assisted digestion was performed in an Anton Paar Multiwave system. For quality assurance, digestion of the reference material NBS 2704 River Sediment and ERM-CC580 Estuarine Sediment and digestion blanks were prepared in the same manner.

The determination of the cations (Aluminum, Calcium, and Magnesium) in digests of sediment samples was conducted with ICP-OES according to ÖN EN 11885 (modified).

The determination of Hg in digests of sediment samples was carried out after reduction with sodiumborohydride with flow injection cold vapour atomic absorption spectrometry according to ÖNORM EN 1483 (modified).

2.3.2.3 Methylmercury

Sample preparation – Extraction of sediment samples

300 mg portions of the homogenised samples were weighted into 15 ml polypropylene test tubes. After addition of 5 ml 5 molar hydrochloric acid (sub boiled) the samples were extracted for 15 minutes in ultrasonic bath. The resulting suspensions were centrifuged for 15 minutes at 4500 rpm. The supernatants were decanted and the residues were re-extracted as described above. Afterwards, the two supernatants were combined. An aliquot (1.5 ml) of the supernatant was filtered through 0.45 µm membrane filters. For quality assurance, extraction of the reference material ERM-CC580 Estuarine Sediment and extraction blanks were prepared in the same manner.

The determination of Me-Hg was conducted with high performance liquid chromatography hyphenated to inductively coupled plasma mass spectrometry (HPLC-ICP-MS).

2.3.2.4 Trisphosphates

Five grams of the homogenized sample were weighted in a 50 ml plastic tube and an isotopically marked surrogate standard mixture was added. Samples were extracted for 30 minutes in an ultrasonic bath at room temperature with a mixture of acetonitrile and ethylacetate (70/30 v/v) and centrifuged at 4000 rpm for 10 minutes. The extract was evaporated under a nitrogen stream to a volume of about 4 ml and centrifuged again. The supernatant was evaporated under a nitrogen stream and brought to a final volume of 1 ml.

The extracts were analysed by means of LC-MS/MS as described above.

2.3.2.5 Limits of detection and limits of quantification

The respective limits of detection (LOD) and quantification (LOQ) in µg/kg dry wt are summarised in Table 10 for the various investigated compounds in suspended and active bottom sediment samples.

Table 10: LOD and LOQ for the analysed compounds in suspended and active bottom sediment samples

Substance	Unit	Suspended and active bottom sediment	
		LOQ	LOD
Al	mg/kg dry wt	1700	850
Ca	mg/kg dry wt	20 000	10 000
Mg	mg/kg dry wt	400	200
Hg	µg/kg dry wt	17	9
Me-Hg	µg/kg dry wt	15	4
TEP	µg/kg dry wt	2.2	0.91
TCEP	µg/kg dry wt	14	7.2
TCPP	µg/kg dry wt	2.2	0.92
TPhP	µg/kg dry wt	5.2	2.6
TDCPP	µg/kg dry wt	0.31	0.08

Substance	Unit	Suspended and active bottom sediment	
		LOQ	LOD
TBP	µg/kg dry wt	4.2	2.1
TBoEP	µg/kg dry wt	0.82	0.23
TKP	µg/kg dry wt	0.37	0.18
TEHP	µg/kg dry wt	2.4	0.65

2.3.3 Biota

2.3.3.1 Narcosis, euthanasia, dissection, morphometry, deep freezing

Immediately upon arrival in the Ecotoxicology Laboratory at the University of Veterinary Medicine in Vienna, fish were killed (MS 222, tricaine methane sulphonate followed by brain destruction) according to the European Commission recommendations for the euthanasia of experimental animals (Part 1 and Part 2; CLOSE et al. 1996, 1997). Mussels were deep frozen (−20°C) and subsequently analysed for external morphometry (calliper: Mauser ±0.02 mm measuring error; balance: Sartorius industry, ±1.0 g measuring error) and tissue preparation (Table 11). Definition of body measures followed SCHRECK & MOYLE (1990).

During all stages of sample analysis, particular care was taken in order to avoid any cross contamination of the fish tissues (US EPA 2000).

Immediately after dissection, fish and mussel samples were weighed, packed in labelled plastic bags, stored deep frozen (−20°C), and transported to the Umweltbundesamt in Vienna for further analysis.

Table 11: Morphometric characterisation of the **a**) fish (chub, *Leuciscus cephalus*) and **b**) mussel (zebra mussel, *Dreissena polymorpha*) samples (sampling points as characterised in Table 4).

a - Fish (chub, *Leuciscus cephalus*)

Rivers	Sampling point	Sampling period	Body length		Body height (maximum; mm)	Body mass (fresh total; g)	Statistics
			(total; mm)	(furkal; mm)			
Schwechat	Mannswörth	P-1	166.10	153.53	32.06	49.69	m
			11.81	11.19	3.30	11.91	s
			140.00	130.00	24.40	27.20	min
			187.00	175.00	37.70	77.60	max
			30	30	30	300	n
Schwechat	Mannswörth	P-2	122.50	112.80	21.39	16.32	m
			8.06	7.89	1.57	3.23	s
			110.00	100.00	19.49	11.80	min
			134.00	124.00	24.21	21.60	max
			10	10	10	10	n
Schwechat	Schwarzmühlbrücke	P-2	157.45	145.09	27.97	37.34	m
			22.31	20.53	4.71	15.83	s
			123.00	113.00	20.35	16.40	min
			193.00	177.00	34.68	64.70	max
			11	11	11	11	n
Ager	Unterachmann	P-1	150.09	138.69	26.85	36.18	m
			27.66	25.80	5.55	25.15	s
			120.00	111.00	20.00	16.70	min
			218.00	203.00	41.00	109.90	max
			32	32	32	32	n

Rivers	Sampling point	Sampling period	Body length		Body height (maximum; mm)	Body mass (fresh total; g)	Statistics
			(total; mm)	(furkal; mm)			
Ager	Unterachmann	P-2	171.53	158.60	29.75	46.98	m
			18.15	17.01	3.39	14.78	s
			135.00	125.00	22.70	22.30	min
			204.00	190.00	36.24	76.70	max
			30	30	30	30	n
Ager	Dürnau	P-1	176.43	162.67	31.65	54.93	m
			24.18	22.65	4.28	22.92	s
			140.00	130.00	24.60	26.20	min
			216.00	200.00	38.80	102.00	max
			30	30	30	30	n
Ager	Dürnau	P-2	164.03	150.70	28.33	41.79	m
			29.85	27.35	5.07	22.25	s
			125.00	114.00	21.25	16.10	min
			218.00	197.00	37.60	89.00	max
			30	30	30	30	n

m (arithmetic mean), *s* (standard deviation), *min* (minimum), *max* (maximum), *n* (number of individuals), sampling period P-1 (July 2007), P-2 (November 2007)

b – Mussel (zebra mussel, *Dreissena polymorpha*)

Rivers	Sampling point	Sampling period	Body length		Body mass		Statistics
			(shell, maximum, mm)	(whole body, including shell, g)	(whole body, without shell, g)		
Ager	Unterachmann	P-1	19.89	1.07	0.35	m	
			1.66	0.27	0.13	s	
			15.77	0.67	0.14	min	
			23.40	1.93	0.78	max	
60.00	60.00	60.00	n				
Ager	Unterachmann	P-2	18.35	0.80	0.31	m	
			1.59	0.21	0.08	s	
			14.84	0.48	0.14	min	
			22.93	1.53	0.49	max	
60.00	60.00	60.00	n				
Ager	Dürnau	P-1	21.96	1.50	0.61	m	
			1.97	0.38	0.20	s	
			19.08	0.82	0.32	min	
			27.51	2.38	1.22	max	
60.00	60.00	60.00	n				
Ager	Dürnau	P-2	19.86	1.10	0.42	m	
			2.88	0.48	0.18	s	
			14.46	0.43	0.18	min	
			27.33	2.38	1.04	max	
60.00	60.00	60.00	n				

m (arithmetic mean), *s* (standard deviation), *min* (minimum), *max* (maximum), *n* (number of individuals), sampling period P-1 (July 2007), P-2 (November 2007)

2.3.3.2 Lyphilization, pooling, drying

Fillet (including skin) and rest of body (carcass including all organs) samples were combined resulting in one fillet and one carcass composite sample per sampling site and period. Similarly, mussel soft tissues (shells excluded) were combined resulting in one composite sample per sampling site and period.

2.3.3.3 Chemical analysis

Mercury

Sample preparation – microwave assisted digestion of biota samples

300 mg portions of the homogenised samples were weighted into quartz digestion vessels. After addition of 3 ml nitric acid and 0.5 ml hydrogen peroxide microwave assisted digestion was performed in an Anton Paar Multiwave system. For quality assurance, digestion of the reference material NIST 2976 (Mussel Tissue – Trace Elements and methylmercury) and digestion blanks were prepared in the same manner.

The determination of Hg in digests of fish samples was carried out after reduction with sodium borohydride with flow injection cold vapour atomic absorption spectrometry according to ÖNORM EN 1483 (modified).

Methylmercury

Sample preparation – Extraction of biota samples

250 mg portions of the homogenized samples were weighted into 15 ml polypropylene test tubes. After addition of 5 ml mobile phase (50 mmol pyridine, 0.5% w/w L-cysteine, 5% v/w methanol), the samples were extracted for 15 minutes in an ultrasonic bath. The resulting suspensions were centrifuged for 15 minutes at 4500 rpm. The supernatants were decanted and the residues re-extracted as described above. Afterwards, the two supernatants were combined. An aliquot (1.5 ml) of the supernatant was filtered through 0.45 µm membrane filters. For quality assurance, extraction of the reference material NIST 2976 (Mussel Tissue – Trace Elements and Methylmercury) and extraction blanks were prepared in the same manner.

The determination of Me-Hg was conducted with high performance liquid chromatography hyphenated to inductively coupled plasma mass spectrometry (HPLC-ICPMS).

Trisphosphates

Sample preparation of biota samples was identical to sediment samples.

Limits of detection and limits of quantification

The respective limits of detection (LOD) and quantification (LOQ) in µg/kg dry wt are summarized in Table 12 for the various investigated compounds in biota samples.

Table 12: LOD and LOQ [$\mu\text{g}/\text{kg}$ dry wt] for the various investigated compounds in biota samples

Substance	Fish (whole body)		Fish (fillet)		Mussels	
	LOQ	LOD	LOQ	LOD	LOQ	LOD
Hg	7	4	7	4	7	4
Me-Hg	9	3	9	3	9	3
TEP	0.16	0.081	0.28	0.14	–	–
TCEP	1.5	0.77	2.7	1.3	–	–
TCPP	0.044	0.022	0.17	0.084	–	–
TPhP	0.13	0.063	0.055	0.015	–	–
TDCPP	0.063	0.017	0.072	0.036	–	–
TBP	0.63	0.32	4.4	2.2	–	–
TBoEP	0.18	0.049	0.36	0.18	–	–
TKP	0.08	0.04	0.1	0.051	–	–
TEHP	0.67	0.19	0.7	0.19	–	–

2.4 Data treatment

2.4.1 Solid – liquid partitioning

Specific sorption coefficients were calculated from measured data for the liquid phase, suspended matter and sediments, assuming equilibrium conditions between the different compartments. The apparent distribution coefficient K_d [l/kg] was calculated according to equation 1 (SCHWARZENBACH et al. 1993), where C_s is the adsorbed [$\mu\text{g}/\text{kg}$] and C_w the dissolved [$\mu\text{g}/\text{l}$] concentration.

$$\text{equation 1} \quad K_d = C_s / C_w$$

K_d is constant for linear isotherms, whereas for non-linear isotherms K_d is concentration dependent. The apparent sorption coefficient is normalised to the organic carbon content of the adsorbent according to equation 2, where K_d is the apparent sorption coefficient [l/kg] and f_{oc} is the organic carbon content [%] of the adsorbent.

$$\text{equation 2} \quad K_{oc} = K_d / f_{oc}$$

2.4.2 Bioaccumulation

Bioaccumulation factors (BAF) were calculated following equation 3 (Ec 2003). For values below the limits of detection or quantification, factor 2 replacement values were calculated (LOD/2, LOQ/2: SCHISTERMAN et al. 2003). Because the sampling locations and dates of the fish, water and sediment samples differed within a river, approximated BAF were calculated employing median concentrations of the compounds in the river water.

$$\text{equation 3:} \quad (BAF_{fish} = C_{fish} / C_{water})$$

3 RESULTS

3.1 Water

Whereas mercury was detected in all analysed river water samples, methylmercury was not detectable and all analytical results were below the limit of detection of 0.1 µg/l. With the exception of one sample from the Ager river at Scheiblmühle all measured mercury concentrations were below the limit of quantification of 0.1 µg/l. At the Scheiblmühle sampling point mercury was detected in the water sample, during the sampling campaign in September 2009, at a concentration of 0.3 µg/l. The results are summarised in Table 13.

Table 13: Mercury and methylmercury [µg/l] in river water samples

River	Sampling site	Sampling period	River Water		Analyte
			sample	[µg/l]	
Schwechat	Brauhaus-Str.	30.08.2007	3840	< 0.1	Hg
				n.d.	Me-Hg
		23.11.2007	5610	< 0.1	Hg
				n.d.	Me-Hg
Ager	Raudaschlmühle	26.09.2007	4771	< 0.1	Hg
				n.d.	Me-Hg
		28.11.2007	5641	< 0.1	Hg
				n.d.	Me-Hg
Ager	Scheiblmühle	26.09.2007	4770	0.3	Hg
				n.d.	Me-Hg
		28.11.2007	5646	< 0.1	Hg
				n.d.	Me-Hg

n.d....not detected (LOD 0.1 µg/l); Hg=mercury; Me-Hg=methylmercury

Dissolved as well as total mercury contents also have been measured within the Austrian Water Quality Monitoring System (AWQMS) at various sites along the rivers Schwechat and Ager. Whereas, between 1996 and 1998, total mercury was detectable sporadically at some sampling sites, all measurements since 1999 at all sampled sites along the two rivers have been below the limit of detection (0.06 µg/l or 0.1 µg/l).

Among the trisphosphates, TKP and TEHP were not detected in any of the analysed river water samples. Detection frequencies for the other organophosphorus compounds were as follows: TEP (60%) < TPhP (80%) and TBoEP (80%) < TCEP (100%), TCPP (100%), TDCPP (100%) as well as TBP (100%). The observed concentrations varied notably. Generally, higher concentrations were detected in the river Schwechat than in the river Ager, but it should be noted that only one water sample from the river Schwechat was analysed. In the Ager TEP and TBoEP were detected in concentrations below or in the range of the limit of quantification (9 ng/l for TEP; 7 ng/l for TBoEP). The chlorinated organophosphorus esters TCEP, TCPP and TDCPP as well as TBP and TPhP were the most relevant compounds. The highest concentrations in all river samples

were detected for TCEP and TCPP. The concentrations for TCEP ranged from 93 ng/l up to 190 ng/l (mean 121 ng/l) and the concentrations for TCPP from 10 ng/l up to 76 ng/l (mean 27 ng/l).

When arranging the investigated organophosphorus esters according to their mean concentrations TCEP (121 ng/l) is the most relevant compound followed by TBoEP (36 ng/l), TCPP (27 ng/l), TBP (19 ng/l), TPhP (12 ng/l), TDCPP (10 ng/l), TEP (5.5 ng/l) and TKP as well as TEHP. For the calculation of mean values, analytical results below the limit of detection were set equal to zero and analytical results below the limit of quantification were considered with 75% of the limit of quantification.

The results of the chemical analysis of the investigated triphosphates are documented in Table 14.

Table 14: Organophosphorus esters [ng/l] in river water samples

River	Schwechat		Ager		
	Brauhaus-Str.	Raudaschlmühle	Scheiblmühle		
Sampling site					
Sampling period	11.2007	09.2007	11.2007	09.2007	11.2007
Sample	5610	4771	5641	4770	5646
TEP	14	< 9	n.d.	< 9	n.d.
TCEP	190	93	100	130	93
TCPP	76	12	10	22	15
TPhP	10	15	10	24	n.d.
TDCPP	16	5.5	6.3	17	6.3
TBP	35	12	21	11	14
TBoEP	120	< 7	n.d.	< 7	12
TKP	n.d.	n.d.	n.d.	n.d.	n.d.
TEHP	n.d.	n.d.	n.d.	n.d.	n.d.

*n.d...*not detected

3.2 Suspended and active bottom sediments

The following tables (Table 15 to Table 17) summarise data on chemistry and mineralogy of the analysed suspended sediments and active fine bottom sediments from the various sampling points. The elements aluminium (Al), calcium (Ca) and magnesium (Mg) were analysed to characterise the matrix of the sediments. Total Inorganic Carbon (TIC) and Total Organic Carbon (TOC) indicate the carbonate and the organic matter content. Aluminium represents in these fine sediments (< 40 µm) the clay mineral content. Calcium and Mg as well TIC represent the carbonate content (calcite and dolomite) and TOC the organic matter content in the sediment samples.

The river Schwechat, at the monitoring sites, is a channelised small lowland river with contamination from the southern part of Vienna (Liesing creek) and the industrial area south of Vienna. The contaminants are mainly nutrients and heavy metals. The fine sediments (< 40 µm), consisting of a higher portion of clay minerals and carbonates originating from the Alps, contain an increased organic matter content of about 4–5% compared to 2.7% in Austrian lowland rivers (KRALIK 2005).

The Ager river at the Schlägelmühle is a small lowland river flowing out of the uncontaminated lake Attersee. Most sediments are trapped in the lake and therefore only very small amounts of suspended sediments are transported, but a high calcite content indicates precipitation out of oversaturated river water. The sampling point Scheiblmühle is situated a few kilometres below the outflow of an industrial plant causing mainly zinc contamination. The suspended matter transport is already increased, with a similar high content of organic matter (TOC 5–8.5%), but a considerably lower calcite content. The fine fractions of the Ager sediment are rich in organic matter and even more in carbonates, in particular at the Raudaschlmühle at the outlet of lake Attersee.

The suspended sediment matrix composition compared to the bottom sediment is in all samples enriched in TOC. The matrix of the suspended sediment seems to be extremely influenced by the discharge and suspended load concentration. The Schwechat suspended load in August 2007 varied between 23–32 mg/l whereas in November the load was down to 4–8 mg/l (see Annex 1), with a change in TOC from 3.6 to 10.0% (Table 12). According to a similar pattern the mean suspended sediment load decreased at the Ager-Raudaschlmühle from 0.21 mg/l (August 2007) to 0.04 mg/l (October–December 2007; see Annex 2) with a simultaneous increase in TOC from 5.8 to 7.3% (Table 13).

The suspended load in the Ager about 8 km downstream of the outlet of lake Attersee already had a somewhat higher suspended sediment load of 0.3–0.5 mg/l (see Annex 3).

Table 15: Chemistry and mineralogy of suspended sediment (< 40 µm) and active fine bottom sediment (< 40 µm) in the river Schwechat at Brauhausstrasse sampling point.

Schwechat - Brauhausstrasse					
	Median Sed. [%]	Susp. Sed. [%]		Bottom Sed. [%]	
Sampling period	¹⁾	08.2007	11.2007	08.2007	11.2007
Sample		4011	5614	3844	5609
Al	2.0	1.3	2.3	1.3	2.2
Ca	9.5	9.3	8.3	11	7.3
Mg	2.3	2.3	1.8	2.5	1.9
TIC	-	3.54	2.58	3.66	2.54
TOC	4.4	3.62	9.99	3.02	2.48
Kaolinit	–	4	7	4	3
Illite-mica	–	16	28	16	14
Feldspar	–	3	37	3	2
Quartz	–	41	18	31	59
Calcite	–	16	15	18	10
Dolomite	–	14	10	17	8
Organic Matter	–	6	17	5	4

¹⁾ ...Median of GZÜV (Austrian Quality Monitoring) analyses of active fine bottom sediments of the adjacent monitoring stations (1992–2006)

Table 16: Chemistry and mineralogy of suspended sediment (< 40 µm) and active fine bottom sediment (< 40 µm) in the river Ager at Raudaschlmühle sampling point.

Ager – Raudaschlmühle					
	Median Sed. [%]	Susp. Sed. [%]		Bottom Sed. [%]	
Sampling period	¹⁾	09.2007	11.2007	09.2007	11.2007
Sample		4013	0395	4769	5637
Al	0.99	–	–	0.35	0.35
Ca	20.1	–	–	24.0	28.0
Mg	1.53	–	–	1.1	0.96
TIC	–	7.49	6.89	–	8.91
TOC	3.73	5.75	7.28	–	1.76
Kaolinit	–	0	0	0	0
Illite-mica	–	5	4	4	4
Feldspar	–	0	0	0	0
Quartz	–	22	25	28	21
Calcite	–	67	58	60	71
Dolomite	–	0	0	0	0
Organic Matter	–	10	13	7	3

¹⁾...Median of GZÜV (Austrian Quality Monitoring) analyses of active fine bottom sediments (1992–2006)

Table 17: Chemistry and mineralogy of suspended sediment (< 40 µm) and active fine bottom sediment (< 40 µm) in the Ager River at Scheiblmühle sampling point.

Ager – Scheiblmühle					
	Median Sed. [%]	Susp. Sed. [%]		Bottom Sed. [%]	
Sampling period	¹⁾	09.2007	11.2007	09.2007	11.2007
Sample		4014	0396	4768	5642
Al	1.24	1.5	–	0.25	0.69
Ca	10.21	8.1	–	3.2	13.0
Mg	1.27	0.89	–	0.35	1.7
TIC	–	2.43	4.40	–	4.29
TOC	3.07	4.84	8.64	–	2.50
Kaolinit	–	4	0	1	2
Illite-mica	–	18	9	7	8
Feldspar	–	3	2	2	2
Quartz	–	46	37	67	55
Calcite	–	20	37	13	26
Dolomite	–	0	0	5	12
Organic Matter	–	8	15	2	4

¹⁾...Median of GZÜV (Austrian Quality Monitoring)-analyses of active fine bottom sediments (1992–2006)

Whereas mercury was detected in all analysed particulate matter samples, methylmercury was not detected in any of the sediment samples. All measurements for methylmercury were below the limit of detection of 4 µg/kg dry wt. In the samples from the river Schwechat higher mercury concentrations were detected than in the Ager (see Table 18).

In the river Schechat the mercury concentrations in the suspended sediments amounted to 568 and 423 µg/kg dry wt and in the bottom sediments 337 and 231 µg/kg dry wt were measured. In the Ager notably lower concentrations ranging from 33 to 277 µg/kg dry wt were observed in the bottom sediment. Only one sample from the river Ager's suspended sediments was available resulting in 146 µg mercury per kg dry wt. Whereas in the river Schwechat the concentrations detected in the suspended sediments were 1.7 to 1.8 times higher than the concentrations detected in the bottom sediment, in the river Ager samples comparable values were measured in suspended and bottom sediments. The measured mercury and methylmercury concentrations in sediments are summarised in Table 18 and Table 19.

Table 18: Mercury and methylmercury [µg/kg] content in suspended sediments

River	Site	Period	Size µm	Susp. Sed.		Analyte
				sample	[µg/kg]	
Schwechat	Brauhaus-Str.	08.2007	< 40	4011	568	Hg
					n.d.	Me-Hg
		11.2007	< 40	5614	423	Hg
					n.d.	Me-Hg
Ager	Raudaschlmühle	09.2007	< 40	4011	–	Hg
					–	Me-Hg
		11.2007	< 40	0395	–	Hg
					–	Me-Hg
Ager	Scheiblmühle	09.2007	< 40	4014	146	Hg
					n.d.	Me-Hg
		11.2007	< 40	0396	–	Hg
					–	Me-Hg

n.d...not detected

Table 19: Mercury and methylmercury [$\mu\text{g}/\text{kg}$] content in bottom sediments

River	Site	Period	Size μm	Bottom Sed. sample	Analyte	
					[$\mu\text{g}/\text{kg}$]	
Schwechat	Brauhaus-Str.	08.2007	< 40	3844	337	Hg
					n.d.	Me-Hg
		11.2007	< 40	5609	231	Hg
					n.d.	Me-Hg
Ager	Raudaschmühle	09.2007	< 40	4769	33	Hg
					n.d.	Me-Hg
		11.2007	< 40	5609	37	Hg
					n.d.	Me-Hg
Ager	Scheiblmühle	09.2007	< 40	4768	145	Hg
					n.d.	Me-Hg
		11.2007	< 40	5642	277	Hg
					n.d.	Me-Hg

*n.d...*not detected

Total mercury concentrations in the active bottom sediment in the river Schwechat at two sampling sites a few kilometers above and below the present sampling site are shown over a time period of nearly 15 years in Figure 7 (GZÜV 2009). Strong variations over time are observed in the yearly samples (< 40 μm) compared to the present fine fractions (< 40 μm) of bottom and suspended sediments. In a similar manner the mercury content in the bottom sediments of the river Ager varies between < 50 to 3300 $\mu\text{g}/\text{kg}$. Median values (1992–2004) between 167–286 $\mu\text{g}/\text{kg}$ are comparable to the Hg concentrations found in this study.

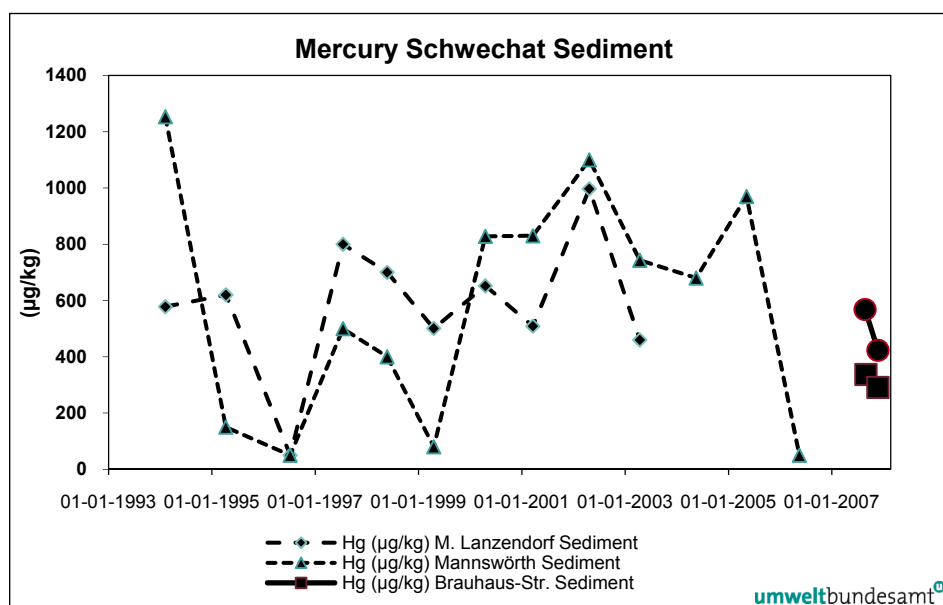


Figure 7: Mercury in active bottom sediments (< 40 μm) in the Schwechat River at the GZÜV monitoring sites Mannswörth and Maria Lanzendorf 1993–2006 and mercury in suspended sediment and active bottom sediments in August and November 2007.

All analysed organophosphorus esters were detected in all particulate matter samples taken from the river Schwechat. The results of the chemical analysis are reported in Table 20.

Table 20: Triphosphates [$\mu\text{g}/\text{kg}$ dry wt] in suspended sediment and active fine bottom sediments from the river Schwechat at Brauhaus-Str. sampling site

Sampling period	Susp. Sed. [$\mu\text{g}/\text{kg}$ dry wt]		Bottom Sed. [$\mu\text{g}/\text{kg}$ dry wt]	
	08.2007	11.2007	08.2007	11.2007
Sample	4011	5614	3847	5609
TEP	8.1	80	15	2.2
TCEP	34	97	76	< 14
T CPP	42	1200	25	6
TPhP	9.9	89	9.6	6.8
TDCPP	11	5.1	11	2.9
TBP	20	16	11	13
TBoEP	18	56	15	11
TKP	9.6	37	7.5	4.3
TEHP	45	88	37	7.4

Very strong variations are observed in the investigated samples. Whereas in the suspended sediment samples the observed concentrations during the 2nd sampling period in November 2007 were notably higher than those observed during the 1st sampling period, the opposite is observed in the bottom sediment samples. During the second sampling period, lower concentrations were detected for most of the investigated triphosphates compared to the first sampling period.

Also, when analysing relative proportions no uniform pattern can be detected and no dominating compound can be identified. With the exception of the bottom sediment sample from November 2007 T CPP, TCEP and TEHP were the compounds showing the highest concentrations in the particulate matter samples from the river Schwechat. TEP, TDCPP and TKP were the organophosphorus esters for which, in all samples, the lowest concentrations were observed. The distribution pattern of the analysed triphosphates is shown in Figure 8.

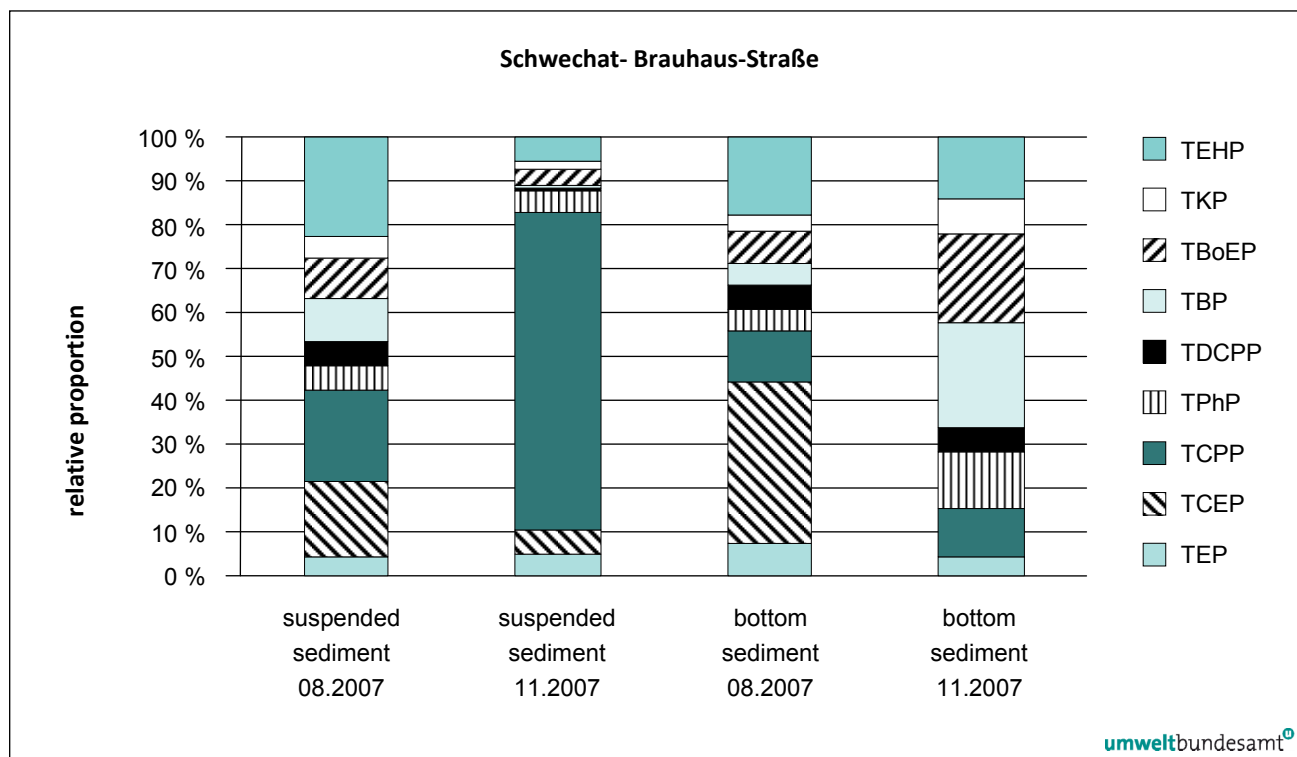


Figure 8: Distribution pattern of the investigated trisphosphates in the particulate matter samples from the river Schwechat

In the particulate matter samples from the river Ager, variations in the trisphosphates concentrations are also observed between the various sampling periods, though not as strong as in the samples from the river Schwechat.

In analogy to the samples from the river Schwechat no uniform pattern can be detected when analysing relative proportions and no dominating compounds can be identified. In three of four bottom sediment samples TCEP is the most abundant compound and also TBP and TCPP are among the substances detected in all samples in relatively high concentrations compared to the other organophosphorus esters. TDCPP, TKP and TEP are of minor relevance in most of the investigated samples and where found in relatively low concentrations. This result corresponds to the observations in the particulate matter samples from the river Schwechat.

The measured concentrations are reported in Table 21 and the relative distribution of the analysed trisphosphates is shown in Figure 9.

Table 21: Triphosphates [$\mu\text{g}/\text{kg}$ dry wt] in suspended sediment and active fine bottom sediments from the river Ager sampling sites

Sampling site	Susp. Sed. [$\mu\text{g}/\text{kg}$ dry wt]		Bottom Sed. [$\mu\text{g}/\text{kg}$ dry wt]		
	Scheiblmühle	Scheiblmühle	Scheiblmühle	Raudaschlmühle	Raudaschlmühle
Sampling period	08.2007	08.2007	11.2007	08.2007	11.2007
Sample	4014	4768	5642	4769	5637
TEP	18	2.9	0.8	n.d.	n.d.
TCEP	21	33	< 14	21	n.d.
T CPP	3.8	6.5	7.1	4	< 2.2
TPhP	48	2.4	< 5.2	< 5.2	< 5.2
TDCPP	4.5	6.4	0.9	0.98	n.d.
TBP	7	5.9	5.4	11	< 4.2
TBoEP	3.8	2.9	2.0	5.2	< 0.82
TKP	26	2.0	1.5	1.6	< 0.37
TEHP	8	3.6	4.0	2.9	n.d.

n.d...not detected

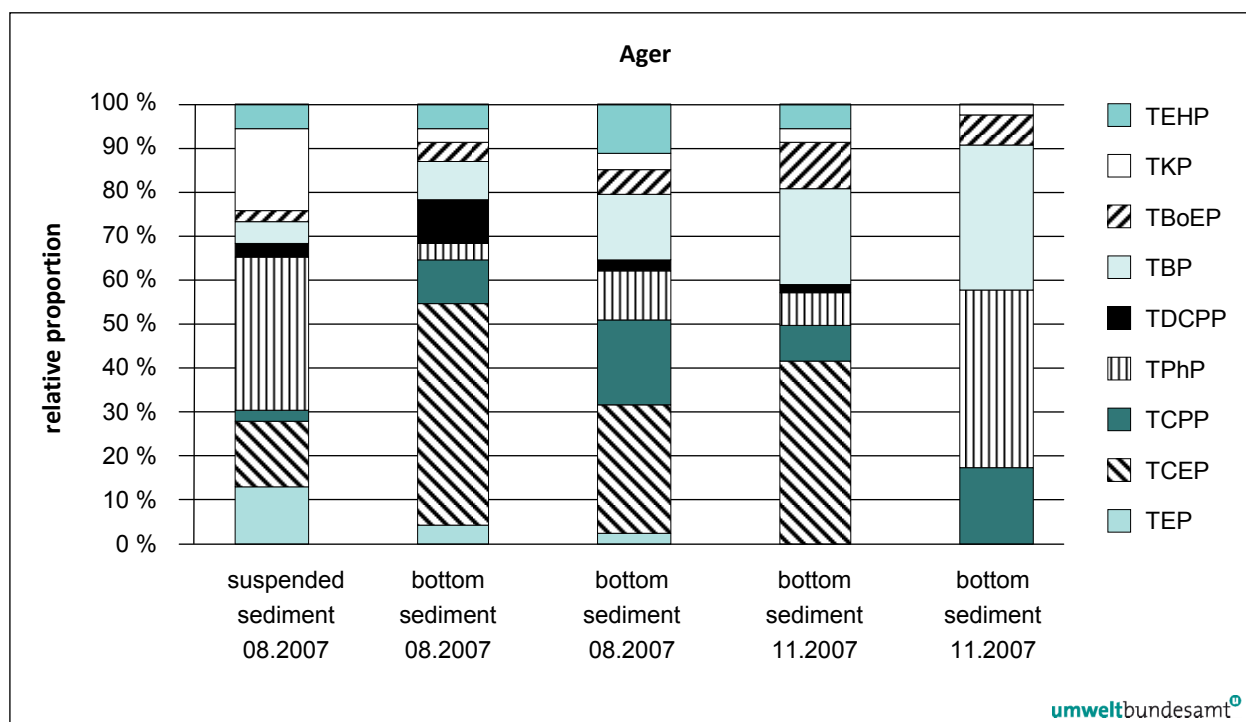


Figure 9: Distribution pattern of the investigated triphosphates in the particulate matter samples from the river Schwechat

3.3 Biota

3.3.1 Mercury and methylmercury

Mercury and methylmercury were detected in all fish composite tissue samples, i.e. from both rivers at all sampling locations for all periods studied (Table 22). Comparing between the two rivers, fish tissue levels were consistently higher in the Schwechat River than in the Ager River.

For the Schwechat River samples, the results did not indicate any differences between the two sampling locations. In contrast to the Ager River samples, dry mass based mercury levels in fish from the sampling location Unterachmann (fillet: 93–131 µg/kg, whole body: 74–275 µg/kg) consistently exceeded those from the Dürnau location (fillet: 78–88 µg/kg, whole body: 65–72 µg/kg); this trend was also evident but less distinct in the wet mass based tissue concentrations, but not evident for methylmercury.

Across all fish samples, the ranges of total mercury levels were: for fillet 78–342 µg/kg (dry mass) and 12–105 µg/kg (wet mass), and for the whole body 65–276 µg/kg (dry mass) and 18–80 µg/kg (wet mass). For the methylmercury levels, concentration ranges were: for fillet 41–226 µg/kg (dry mass) and 5–62 µg/kg (wet mass), and for the whole body 35–202 µg/kg (dry mass), and 8–46 µg/kg (wet mass).

From the dataset, no influence can be derived from the sampling season on the metal tissue concentrations.

In all but one of the fish composite samples, the total mercury residue levels in the fish fillet pools exceeded the whole body levels (proportion whole-body/fillet: 0.79–0.86 based on dry mass, 0.76–0.91 based on wet mass). Only one sample (Ager-Unterachmann, July 2007) showed the reverse relationship (proportion whole-body/fillet: 2.10 based on dry mass, 3.67 based on wet mass). Methylmercury levels showed the same – but less distinct – trend (proportion whole-body/fillet: 0.75–1.04 based on dry mass, 0.74–1.60 based on wet mass).

In all but one of the fish samples, total mercury concentrations exceeded those of methylmercury by factors of around 1.25–2.25 (factors ranges for fillet: 1.51–2.27 dry mass, 1.52–2.20 wet mass based; for the whole body: 1.25–2.11 dry mass, 1.23–2.11 wet mass based). In one sample (Ager-Unterachmann, July 2007) the mercury contents were relatively higher (mercury/methylmercury proportions for fillet 2.18 dry mass, 2.40 wet mass based; whole body: 5.29 dry mass, 5.50 wet mass based).

Mussels were only available from the Ager River. There, total mercury levels ranged from < 7 to 105 and methylmercury from < 9 to 36 µg/kg (wet mass), with the levels being consistently lower in the samples collected in July than in November (see Table 23).

Table 22: Concentrations of total mercury (Hg) and methylmercury (Me-Hg) ($\mu\text{g}/\text{kg}$; mass base in brackets) in the fish (*Leuciscus cephalus*) whole body and fillet composite samples collected from two Austrian rivers in two collection periods (samples as detailed in Table 4 and Table 11; whole body concentrations calculated based on the measured fillet and carcass concentrations; for limits of quantification and detection and see Table 12).

Rivers	Sampling points	SP	Fillet concentrations ($\mu\text{g}/\text{kg}$)		Whole body concentrations ($\mu\text{g}/\text{kg}$)		Analytes
			[dry]	[wet]	[dry]	[wet]	
Schwechat	Mannswörth	P-1	300	105	257	80	Hg
			178	62	148	46	Me-Hg
		P-2	342	82	276	69	Hg
			226	54	170	42	Me-Hg
	Schwarz- mühlbrücke	P-1	n.a.	n.a.	n.a.	n.a.	Hg
			n.a.	n.a.	n.a.	n.a.	Me-Hg
		P-2	317	61	252	49	Hg
			194	37	202	40	Me-Hg
Ager	Unterachmann	P-1	131	12	275	44	Hg
			60	5	52	8	Me-Hg
		P-2	93	24	74	19	Hg
			41	11	35	9	Me-Hg
	Dürnau	P-1	78	20	65	18	Hg
			50	13	38	11	Me-Hg
		P-2	88	22	72	20	Hg
			41	10	42	11	Me-Hg

SP=sampling period: P-1 (July 2007), P-2 (November 2007); n.a. (not analysed)

Table 23: Concentrations of total mercury (Hg) and methylmercury (Me-Hg) ($\mu\text{g}/\text{kg}$; mass base in brackets) in the mussel (*Dreissena polymorpha*) whole body samples (soft body, shells excluded) collected from two Austrian rivers in two collection periods (samples as detailed in Table 4 and Table 11).

Rivers	Sampling points	PS	Whole body concentrations ($\mu\text{g}/\text{kg}$)		Analytes
			[dry]	[wet]	
Ager	Unterachmann	P-1	n.a.	n.a.	Hg
			n.a.	n.a.	Me-Hg
		P-2	105	9	Hg
			36	3	Me-Hg
	Dürnau	P-1	38	n.a.	Hg
			ND	n.a.	Me-Hg
		P-2	56	4	Hg
			17	1	Me-Hg

PS=sampling period: P-1 (July 2007), P-2 (November 2007); n.a. (not analysed); n.d. (not detected); for limits of quantification and detection see Table 12

3.3.2 Trisphosphates

Trisphosphates concentrations measured in fish are summarised in Table 24. Among the trisphosphates analysed in fish, TBoEP, TKP and TEHP levels were below the detection limits in all samples. For the other compounds, TCEP was only detected in the whole body pools but not in the fillet. The frequency of detection and the residue levels were lower in the fillet than in the whole body pools. The frequency of detection in the whole body pools (n=8) decreased from TCEP (n=7), TCEP (n=6), TEP and TPhP (n=5) to TDCPP and TBP (n=3).

Comparing between the two rivers, fish tissue levels were rather similar and ranked at the same orders of magnitude, reaching the following maximum concentrations (Ager/Schwechat River; µg/kg, whole body, dry mass): TEP (5,13/0.96), TCEP (44.6/47.82); TCEP (5.35/6.48), TPhP (6.19/3.05), TDCPP (11.15/5.45), TBP (2.32/8.17),

Among the trisphosphates detected in the whole body fish pools, TCEP always reached the highest residue levels at all sampling sites and tended to be higher in November than in July. But the available data set is not appropriate for detecting temporal trends or site-specific differences within a river.

Mussels were not analysed for trisphosphates in this study.

*Table 24: Concentrations of trisphosphates (µg/kg; mass base in brackets) in the whole body and fillet composite samples of fish (*Leuciscus cephalus*) collected from two Austrian rivers in two collection periods (samples as detailed in Table 4 and Table 11; whole body concentrations calculated on the basis of the measured fillet and carcass concentrations; for limits of quantification and detection see Table 12; TBoEP, TKP, and TEHP levels were below these limits in all fish samples and therefore not included in this table).*

Rivers	Sampling points	SP	Fillet concentrations (µg/kg)		Whole body concentrations (µg/kg)		Analytes
			[dry]	[wet]	[dry]	[wet]	
Schwechat	Mannswörth	P-1	n.d.	n.d.	0.55	0.17	TEP
			n.d.	n.d.	n.d.	n.d.	TCEP
			n.d.	n.d.	5.29	1.66	TCEP
			n.d.	n.d.	3.05	0.95	TPhP
			n.d.	n.d.	5.45	1.71	TDCPP
		P-2	n.d.	n.d.	n.d.	n.d.	TBP
			n.d.	n.d.	0.96	0.24	TEP
			n.d.	n.d.	33.87	8.42	TCEP
			n.d.	n.d.	3.13	0.78	TCEP
			0.46	0.11	2.76	0.69	TPhP
			n.d.	n.d.	n.d.	n.d.	TDCPP
Schwarz- mühlbrücke	P-1	n.d.	n.d.	4.17	1.04	TBP	
		n.a.	n.a.	n.a.	n.a.	TEP	
		n.a.	n.a.	n.a.	n.a.	TCEP	
		n.a.	n.a.	n.a.	n.a.	TCEP	
		n.a.	n.a.	n.a.	n.a.	TPhP	

Rivers	Sampling points	SP	Fillet concentrations (µg/kg)		Whole body concentrations (µg/kg)		Analytes
			[dry]	[wet]	[dry]	[wet]	
			n.a.	n.a.	n.a.	n.a.	TDCPP
			n.a.	n.a.	n.a.	n.a.	TBP
		P-2	n.a.	n.a.	n.a.	n.a.	TEP
			25	4.8	47.82	9.37	TCEP
			n.a.	n.a.	6.48	1.27	TCP
			n.a.	n.a.	n.d.	n.d.	TPhP
			1.3	0.26	3.08	0.60	TDCPP
			8.3	1.6	8.17	1.60	TBP
Ager	Unterachmann	P-1	n.d.	n.d.	n.d.	n.d.	TEP
			n.d.	n.d.	11.77	1.89	TCEP
			n.d.	n.d.	3.72	0.60	TCP
			n.d.	n.d.	6.19	1.00	TPhP
			n.d.	n.d.	11.15	1.79	TDCPP
			n.d.	n.d.	n.d.	n.d.	TBP
		P-2	n.d.	n.d.	1.38	0.36	TEP
			n.d.	n.d.	42.02	10.97	TCEP
			n.d.	n.d.	4.90	1.28	TCP
			0.90	0.23	2.07	0.54	TPhP
			n.d.	n.d.	n.d.	n.d.	TDCPP
			n.d.	n.d.	n.d.	n.d.	TBP
	Dürnau	P-1	n.d.	n.d.	4.28	1.20	TEP
			n.d.	n.d.	28.50	8.00	TCEP
			n.d.	n.d.	2.14	0.60	TCP
			n.d.	n.d.	n.d.	n.d.	TPhP
			n.d.	n.d.	n.d.	n.d.	TDCPP
			n.d.	n.d.	2.32	0.65	TBP
		P-2	n.d.	n.d.	5.13	1.39	TEP
			n.d.	n.d.	44.60	12.12	TCEP
			n.d.	n.d.	5.35	1.45	TCP
			0.59	0.15	2.07	0.56	TPhP
			n.d.	n.d.	n.d.	n.d.	TDCPP
			n.d.	n.d.	n.d.	n.d.	TBP

SP=sampling period: P-1 (July 2007), P-2 (November 2007); n.a. (not analysed); n.d. (not detected); for limits of quantification and detection see Table 12.

3.4 Partitioning

3.4.1 Adsorption to solids

3.4.1.1 Mercury

Calculated K_d [l/kg] and K_{OC} [l/kg] values for mercury on suspended matter and sediments are summarised in Table 25.

Table 25: Apparent solid-liquid distribution coefficient K_d [l/kg] and normalised to the organic carbon content of the adsorbent K_{OC} [l/kg] for suspended matter and sediments

	f _{oc} [%]	K_d [l/kg]	log K_d	K_{OC} [l/kg]	log K_{OC}
suspended matter					
SM 1	3.62	7307	3.86	201842	5.31
SM 2	4.84	487	2.69	10055	4.00
SM 3	9.99	5640	3.75	56456	4.75
sediments					
S 1	3.02	4493	3.65	148786	5.17
S 2	–	1933	3.29	–	–
S 3	2.48	110	2.04	–	–
S 4	1.76	493	2.69	28030	4.45
S 5	2.50	3693	3.57	147733	5.17

Calculated apparent solid-liquid distribution coefficients K_d as well as the organic-carbon normalised solid-liquid partition coefficient K_{OC} vary within a comparable range in suspended sediment and bottom sediment samples. The log K_d values vary from 2.0 l/kg to 3.9 l/kg and the log K_{OC} values vary with 4.0 to 5.3 l/kg. HILLENBRAND et al. (2007) report K_d values for mercury in suspended solids between 124,000 and 164,000 l/kg. Whereas these K_d values are significantly higher than the partitioning coefficients observed in the present study, OKOUCHI & SASAKI (1985) obtained significantly lower K_d values of approx. 400 l/kg.

3.4.1.2 Trisphosphates

The apparent solid-liquid distribution coefficient is calculated according to equation 1 and summarised in Table 26.

Table 26: Apparent solid-liquid distribution coefficient K_d [l/kg] for suspended matter and sediments

	suspended matter		bottom sediments			mean	
TEP	2667	5714	–	430	–	2937	
TCEP	162	511	226	254	–	114	253
TCPP	173	15789	333	295	156	473	2870
TPhP	2000	8900	260	100	390	–	2330
TDCPP	265	319	178	376	–	143	256
TBP	636	457	917	536	150	386	514
TBoEP	854	467	1169	652	–	167	662
TKP	–	–	–	–	–	–	–
TEHP	–	–	–	–	–	–	–

For TCEP, TDCPP, TBP and TBoEP comparable distribution coefficients are calculated for suspended sediments and bottom sediments. The mean calculated apparent K_d values are 253 l/kg for TCEP (114–511 l/kg), 256 l/kg (143–376) for TDCPP, 514 l/kg (150–917) for TBP and 662 l/kg (167–1169) for TBoEP. Those values are in agreement with the respective water solubility and octanol-water distribution coefficients.

For TEP, TCPP and TPhP notably higher solid-liquid distribution coefficients have been calculated for suspended sediments than for bottom sediments. For TEP and TPhP both calculated values are higher than those obtained for the bottom sediment. Whereas the calculated apparent K_d values seem suitable for TPhP due to the low water solubility and high hydrophobic character of the compound, the values obtained for TEP seem to be too high. TEP has a water solubility of 500 g/l and a low octanol-water distribution coefficient of 0.8 indicating that TEP does not tend to adsorb to particles. Hence the calculated solid-liquid distribution coefficient for TEP seems not to be reliable for assessment purposes.

The evaluation of the calculated K_d values for TCPP is difficult as only two strongly diverging values are available for suspended sediments. Whereas one value is comparable to the results obtained for the bottom sediments, the other value is rather high. This high value for TCPP results from the very high concentration measured in the particulate matter sample (see Table 20), representing the highest value measured during the whole measurement campaign.

In order to increase the comparability of the calculated sorption coefficients the apparent K_d values are normalised to the organic fraction of the adsorbents. Considering the respective organic carbon content of the adsorbents the apparent solid-liquid distribution coefficients were transformed into K_{OC} values according to equation 2. The calculated K_{OC} values are documented in Table 27 and the log K_{OC} values are shown in Figure 10.

Table 27: Apparent solid-liquid distribution coefficient normalised to the organic carbon content of the adsorbent K_{OC} [l/kg] for suspended matter and sediments

	suspended matter		sediments			
f_{OC}	4.84	9.99	n.a.	n.a.	1.76	2.5
TEP	55096	57200	–	–		
TCEP	3338	5110	–	–	–	4559
TCPP	3569	158053	–	–	8864	18933
TPhP	41322	89089	–	–	22159	–
TDCPP	5469	3191	–	–	–	5714
TBP	13148	4576	–	–	8523	15429
TBoEP	17643	4671.34	–	–	–	6667
TKP	–	–	–	–	–	–
TEHP	–	–	–	–	–	–

n.a. ... not available

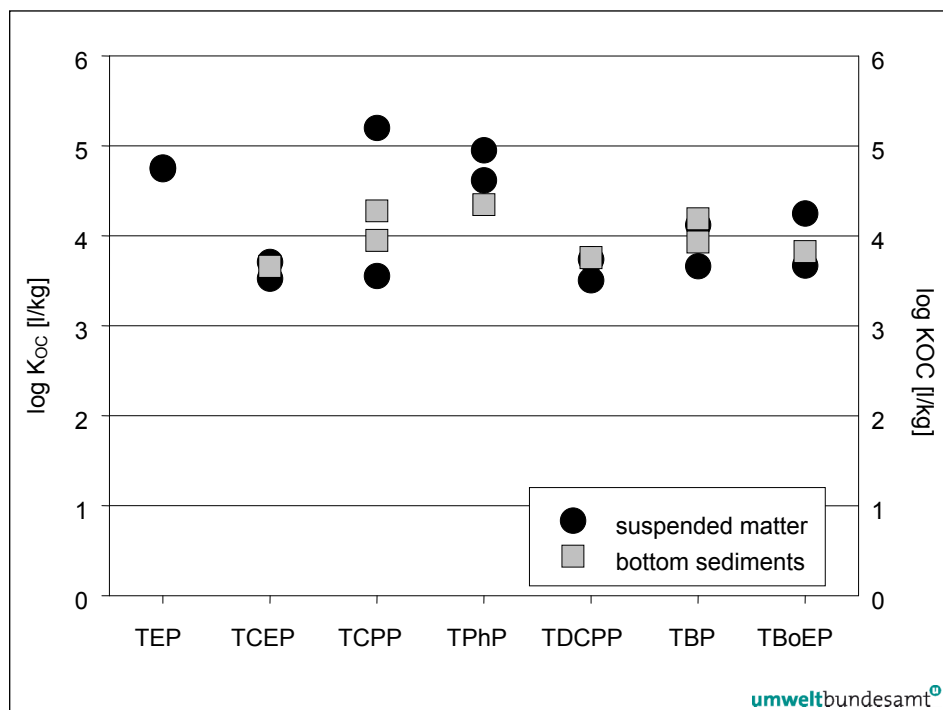


Figure 10: Calculated log K_{OC} values for suspended matter and sediments

Besides TCPP, the calculated K_{OC} values for suspended matter and sediments are comparable. For TCPP one value calculated for suspended matter is notably higher than the other values and is attributed to the very high concentration measured in this particulate matter sample. The value is classified as outlier and not considered for further evaluation.

3.4.2 Bioaccumulation

3.4.2.1 Mercury and methylmercury

Comparing between the rivers and the fish compartments analysed, the Bioaccumulation Factors (relative to river water, equation 3) consistently showed the following ranking (Figure 11): (a) Schwechat > Ager River and (b) total mercury > methylmercury, but (c) fillet > whole body for the Schwechat River only (indicating higher level, longer term exposure in this river). Relative methylmercury contents in the fish composite samples showed no consistent trends (Figure 12).

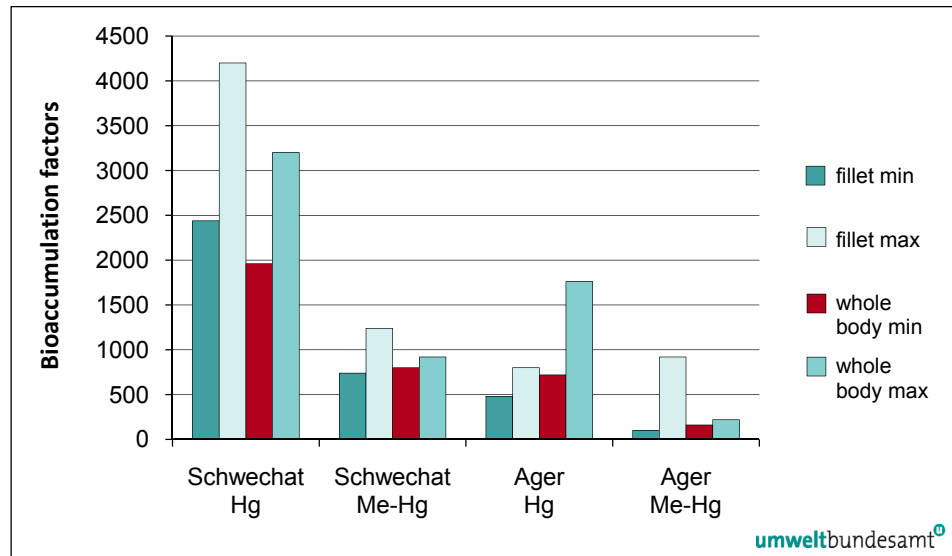


Figure 11: Bioaccumulation Factors (ranges) for total mercury (Hg) and methylmercury (Me-Hg) in fillet and whole body composite samples of fish from the rivers Ager and Schwechat.

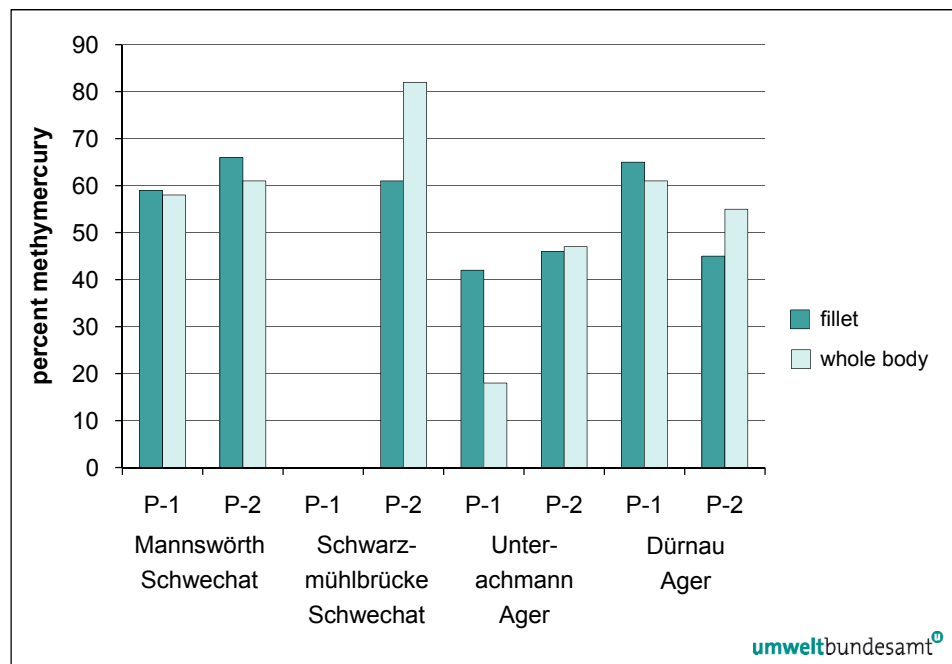


Figure 12: Proportion (in percent) of methylmercury in total mercury in fillet and whole body composite samples of fish from the rivers Ager and Schwechat during the two sampling periods (P-1, P-2; Table 22).

3.4.2.2 Trisphosphates

Comparing between the rivers and the fish compartments analysed, the Bioaccumulation Factors (relative to the river water, equation 3) showed no consistent differences between the Schwechat and Ager River but were consistently higher in the whole body than in the fillet composite samples. In the fillet, bioaccumulation tended to be generally low (with the majority of the residues below

LOD and all below LOD for TEP and TCEP; Table 24) but reached bioaccumulation factors (BAF) values ranging from 50 to 170 (Figure 13). In the whole body samples, BAF values ranged from 50 to 650. Whole body BAF values were highest in TPhP and TDCPP reaching similar maximum levels in both rivers (Figure 13).

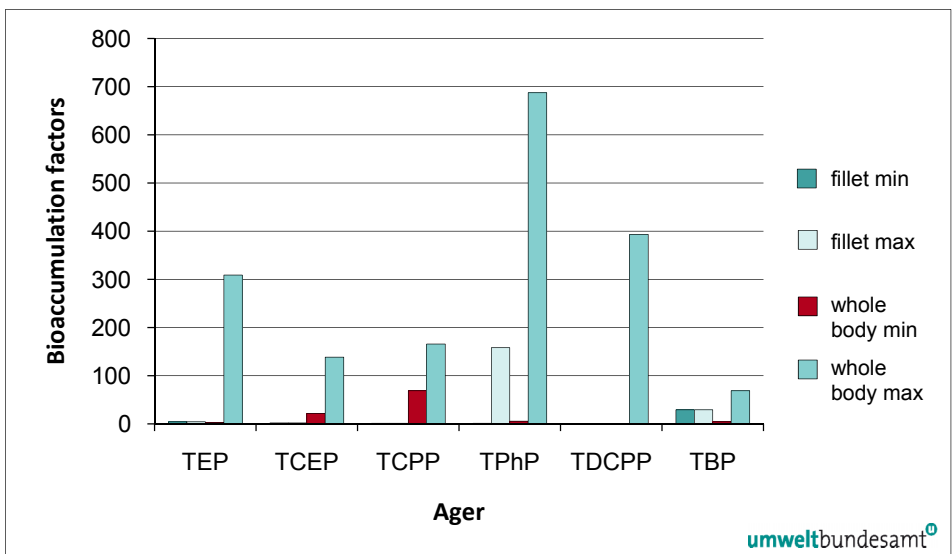
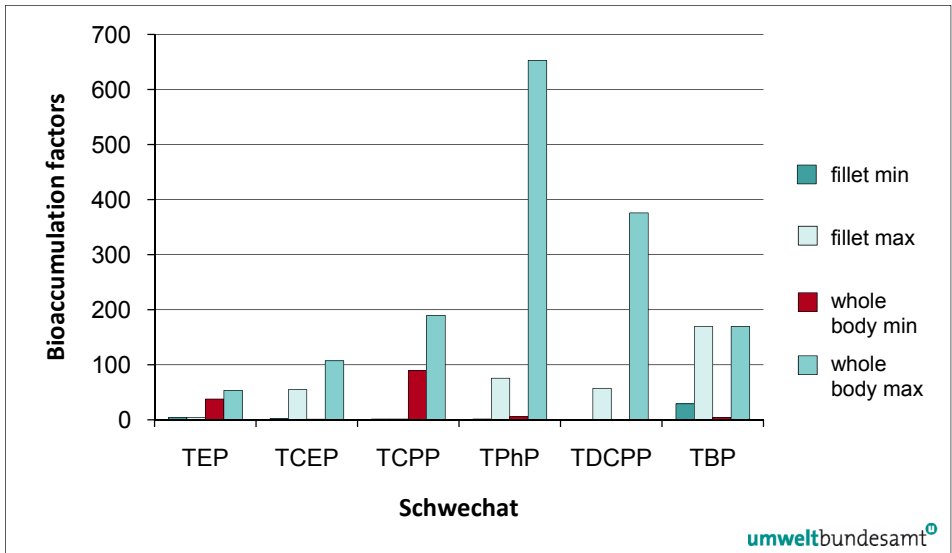


Figure 13: Bioaccumulation Factors (ranges) for the trisphosphates detected in fillet and whole body composite samples of fish from the rivers Ager and Schwechat.

4 DISCUSSION

4.1 Contaminant levels compared among rivers and sampling locations

4.1.1 Mercury and methylmercury

In two Austrian rivers (Schwechat and Ager), three abiotic compartments (river water, suspended and bottom sediment) and three biotic compartments (fish, *L. cephalus*, whole body and fillet, and mussel *D. polymorpha* whole body) were compared for total mercury and methylmercury as well as trisphosphate contamination.

Considering the river water analyses, comparable results were observed in both river systems. Mercury was detected in both rivers at all sampling sites in concentrations below the limit of quantification of 0.1 µg/l. Methylmercury was not detected in the investigated river water samples. These results are in agreement with the results observed within the Austrian Water Quality Monitoring System (AWQMS). Under this monitoring programme all measurements since 1999 have been below the limit of quantification, which was equal to 0.06 µg/l from 1996 to 2001 and equal to 0.1 from 2001–2006, depending on the laboratory performing the analysis.

Total mercury is not easily dissolved in river water. Rather, it is sorbed on particle surfaces, in particular organic complexes but also on clay minerals as well as iron oxides (SALIMINEN 2005). Therefore, mercury concentration away from mineralisations and contamination in natural water ranges from about 0.001 to 0.05 µg/l.

Whereas mercury was detected in all analysed particulate matter samples, methylmercury was not detected. All measurements for methylmercury were below the limit of detection of 4 µg/kg dry wt.

In the samples from the river Schwechat higher mercury concentrations were detected in suspended as well as in bottom sediment samples than in the river Ager sediments.

For mercury data are available from the AWQMS for active bottom sediments (< 40 µm) from the river Schwechat. These concentrations are documented in Figure 7 and the actual measurements fit well into the range of variation observed within the monitoring programme.

Mercury and methylmercury were detected in all fish composite tissue samples, from both rivers studied. Comparing between the two rivers, fish tissue levels were consistently higher in the Schwechat than in the Ager River. In the mussels, mercury and methylmercury were detected in all samples analysed (except methylmercury in one sample). Mussels were only available from the Ager River.

There was no indication that the sampling location influenced the fish metal levels in the Schwechat River. But, in the Ager River, the metal levels in both fish and mussels from the sampling location Unterachmann tended to exceed those from the Dürnau location.

Summarising over all fish (Chub, *Leuciscus cephalus*) analysed in the present study, the ranges of total mercury concentrations were: for fillet 78–342 µg/kg (median: 131, mean: 192.71; dry mass) and 12–105 µg/kg (median: 24, mean: 46.57; wet mass), and for the whole body 65–276 µg/kg (median: 44, mean: 42.71; dry mass) and 18–80 µg/kg (median: 44, mean: 42.71; wet mass). These findings compared well with those reported in the literature from other recent freshwater field surveys in the region (SVOBODOVA et al. 1999; ANDREJI et al. 2005; DUSEK et al. 2005; HOUSEROVA et al. 2006; GRABER et al. 2008; KRUIKOVA et al. 2008): For Austria, the median total mercury concentrations detected in the axial muscle of fish ranged from 42 (carp), 62.7 (perch), 68.2 (trout), to 101.8 (whitefish), and reached 299.4 in a single catfish and 339.2 in a single perch (all values µg/kg wet mass; GRABER et al. 2008). For the Czech Republic, the mean total mercury concentrations in the muscle of chub fish were 83 µg/kg (mean; no mass basis reported; SVOBODOVA et al. 1999), 70–270 µg/kg (median, wet mass; KRUIKOVA et al. 2008), and 135–962 µg/kg (mean, dry mass; HOUSEROVA et al. 2006). Total mercury levels were particularly high (2.85 ± 1.22 mg/kg wet weight) in the muscle of four common Slovak fish species (chub, barbel, roach, and perch) (ANDREJI et al. 2005).

Concentration ranges of methylmercury detected in the present study were: for fillet 41–226 µg/kg (median: 60, mean: 112.86; dry mass) and 5–62 µg/kg (median: 13, mean: 27.43; wet mass), and for the whole body 35–202 µg/kg (median: 52, mean: 98.14; dry mass), and 8–46 µg/kg (median: 11, mean: 23.86; wet mass). For the Czech Republic, mean methylmercury muscle levels ranged from 135–962 (dry mass; HOUSEROVA et al. 2006) and from 60 to 230 (wet mass; KRUIKOVA et al. (2008).

In a comprehensive review, EISLER (2006) concluded that maximum concentrations of total mercury in shark and fish muscle usually did not exceed 2000 µg/kg (fresh mass). To put this into perspective, a large-scale survey conducted in the United States (232 sites in unmined basins, 59 sites in mined basins, overall 34 fish species; SCUDDER et al. 2009) reported total mercury in axial muscle ranging from 14 to 1800 (median: 165, mean: 238, sites in unmined basins), and from 20 to 1950 (median: 235, mean: 351, 59 sites in mined basins) (all values µg/kg, wet mass; SCUDDER et al. 2009).

4.1.2 Trisphosphates

River water from the river Schwechat was analysed once on organophosphorus esters. In the river Ager both sampling sites were sampled and analysed twice. No significant differences are to be observed between the two sampling sites along the river Ager. Notably higher concentrations than in the river Ager have been detected in the one sample from the river Schwechat. The measured concentrations are in line with observations documented in the literature. According to REEMTSMA et al. (2008) most organophosphorus esters occurred at concentrations of 10–200 ng/l in surface waters, with the highest levels being found downstream of wastewater treatment plants (WWTP) discharges.

Also in the current study, the higher trisphosphate concentrations in the river Schwechat compared to the river Ager might be attributed to the relative wastewater proportion due to discharges into the two river systems. Whereas in the river Schwechat, at the sampling point, approx. 10% of the mean daily total

flow is discharged wastewater, this proportion is notably smaller in the river Ager. In the Ager at the estuary into the river Traun approx. less than 2% of the mean daily flow is attributable to wastewater discharges. Treated wastewater is known to be a relevant source for organophosphorus esters in surface waters and concentrations of up to several $\mu\text{g/l}$ (MARTINEZ-CARBALLO et al. 2007; REEMTSMA et al. 2008)

Higher trisphosphate concentrations were detected in river Schwechat suspended as well as bottom sediment samples than in the particulate matter samples from the river Ager. Presuming an equilibrium between solid and liquid phase, this result is attributed to the higher concentrations of organophosphorus esters due to the higher wastewater proportion in the river Schwechat.

In both the Ager and Schwechat River, the observed trisphosphate concentrations were lowest in the river water (and reached the highest values in the suspended solids). While sediment levels in the Schwechat samples tended to exceed those of the Ager samples considerably, contamination of water and whole body fish pools was quite similar in both rivers (Figure 14).

Among the trisphosphates analysed in fish, TBoEP, TKP, and TEHP levels were below detection limits in all samples. Comparing between the two rivers, fish tissue levels appeared lower in the Ager River than in the Schwechat River. Mussels were not analysed for trisphosphates in this study. There was no indication that sampling location influenced the concentrations of trisphosphates in fish.

Maximum trisphosphate concentrations in fish observed in the present study [whole body: TEP (1.39), TCEP (12.12); TCPP (1.45), TPhP (1.00), TDCPP (1.79), TBP (1.60); fillet: TPhP (0.23), TCEP(4.8), TBP(1.6); all values $\mu\text{g/kg}$, wet mass] matched with those reported from Norway (EVENSET et al. 2009) but were exceeded by reports Japan (reviewed in WHO 1998, 2000), and from Sweden (NATURVARDsverket 2009).

Thirteen organophosphorous flame retardants were analysed in samples from the marine environment (seawater, sediment, fish and seabirds) in the Norwegian Arctic. In addition, one freshwater fish species (Arctic char, *Salvelinus alpinus*) from an Arctic lake with high levels of POPs was included in this study. Five of the analytes were not detected in any of the fish samples [DPhBP (< 0.1 – < 0.2), DBPhP (< 0.05 – < 0.1), TBEP (< 0.2 – < 0.6), ToCrP (< 0.08 – < 0.2), TCrP (< 0.08 – < 0.2)]; TEHP was only found in one fish sample (4.6; liver of Atlantic cod); for the Arctic char, the concentrations found in muscle were as follows: TIBP (0.9–4.8), TBP (1.1–3.6), TCEP (0.5–5.0), TCPP (1.4–2.9), TDCP (< 0.3 –6.7), TPhP (0.3–3.2), EHDPP (1.3–16); all values $\mu\text{g/kg}$ wet mass] EVENSET ET AL. 2009).

Fish collected in Japan 1975 and 1978 contained up to 140 $\mu\text{g/kg}$ TCEP and up to 25 $\mu\text{g/kg}$ TDCPP (WHO 1998). Fish (salmon, herring, eel, carp) collected in Sweden were analysed for eleven organophosphorus flame retardants. Particularly high concentrations were reported for TCPP (150 in muscle, 4500 in fat of herring), TPP (800 in muscle, 5000 in fat of carp), and EHDPP (450 in muscle, 13500 in fat of eel) (all values $\mu\text{g/kg}$ wet mass; estimated from graph; NATURVARDsverket 2009).

4.2 Contaminant levels among the compartments analysed

4.2.1 Mercury and methylmercury

Whereas methylmercury was not detectable in the water samples, nearly all measurements for mercury were below the limit of quantification. In all the other compartments, wet mass based levels of the Schwechat River exceeded that of the Ager River.

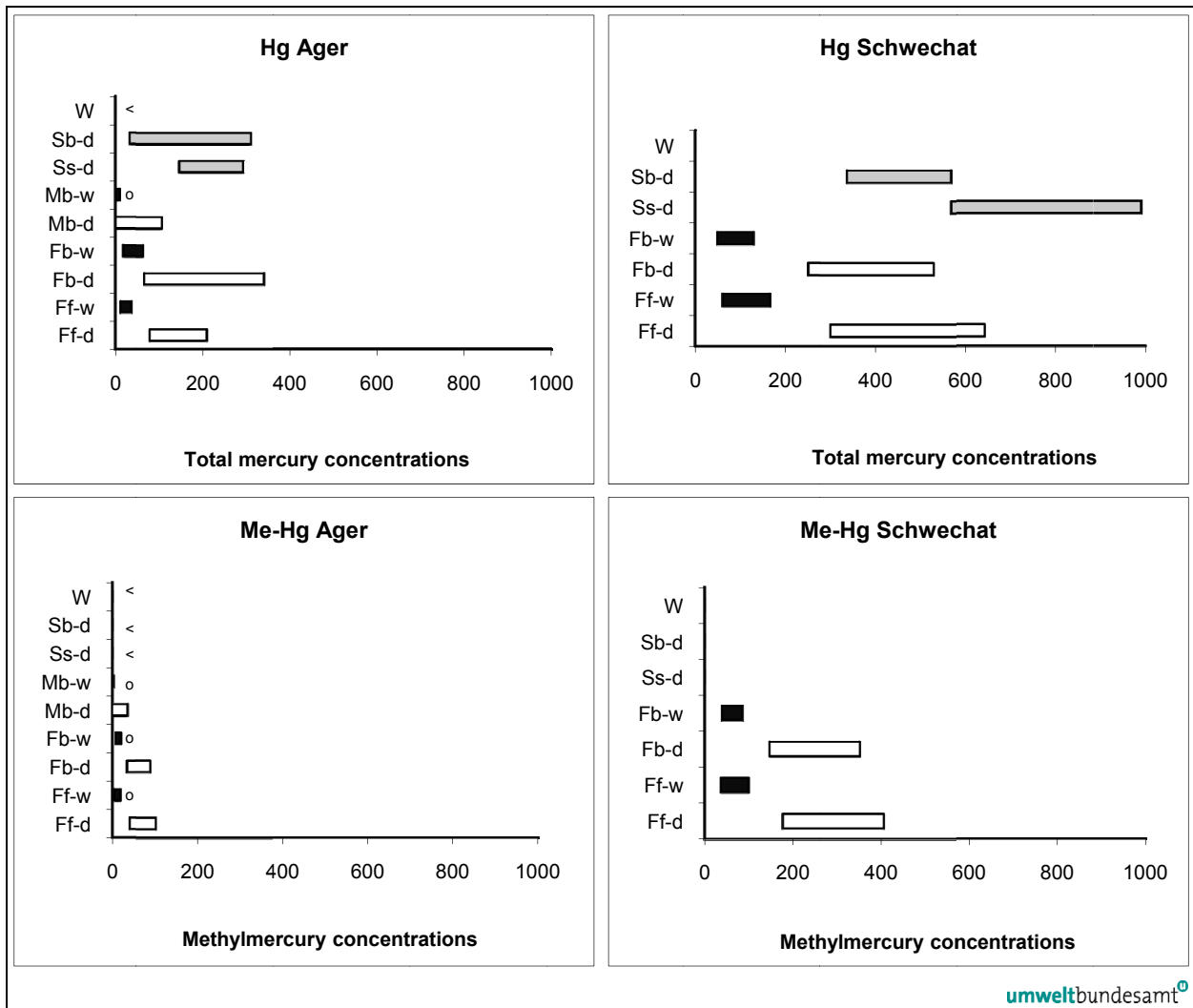
Comparing the ranges of variation over the whole data set as shown in Figure 14, mercury levels were consistently higher in the sediment than in the fish samples. In contrast, methylmercury levels in fish exceeded that of the sediment. Hence, our results conform with the expected, comparatively high potential of the organometallic compound to bioaccumulate in organisms (and to biomagnify in food webs). Mercury and methylmercury concentrations and Bioaccumulation Factors reached higher levels in the fish fillet than in the whole body samples. This trend was more obvious in the overall more contaminated Schwechat river (Figure 14), which again is in accordance with information from the literature indicating that muscle concentrations of metals are particularly high for Hg and especially methylmercury after high-level, long-term exposure (e.g., NORDBERG 2007; WEISBROD et al. 2007; GRILLITSCH & SCHIESARI in press).

The mussel *D. polymorpha* seemed to accumulate mercury to a larger extent than methylmercury, and both metal species to a lower extent than the fish. However, samples sizes in this study were too small for thorough interspecific comparisons.

For mercury, the ranking for observed residue levels was as follows: water < biota and sediments, whereas for methylmercury the level ranking was: water and sediments (all below detection limits) < biota (all fish and all but one mussel pool above the analytical limits) (summarized in Figure 14). Hence, relative to river water, accumulation in fish and mussels was obvious for both metal species at all study sites. Relative to the sediments, accumulation in the biota was obvious for methylmercury only.

Highest mercury concentrations were found in the suspended sediment compartment whereas the methylmercury concentrations were highest in the fish fillet.

In general, 80 to 99% of the mercury in fish was present as methylmercury (HOUSEROVA 2006; SLOOF et al. 1995; EISLER 2006; KRUSE et al. 2008; SCUDDER et al. 2009) but considerable variation in the methylmercury proportion has been reported (KRUSE et al. 2008). In the present study, the methylmercury/total mercury proportion ranges in fish were 42–66% for fillet and 18–82% for the whole body (Figure 12). These results conform with the observations reported by KRUZIKOVA et al. (2008) for the same fish species (*Leuciscus cephalus*) from seven locations in the Czech Republic where in axial muscle samples, the mean methylmercury content tended to increase and variation of the methylmercury content to decrease with increasing size or age of the fish.

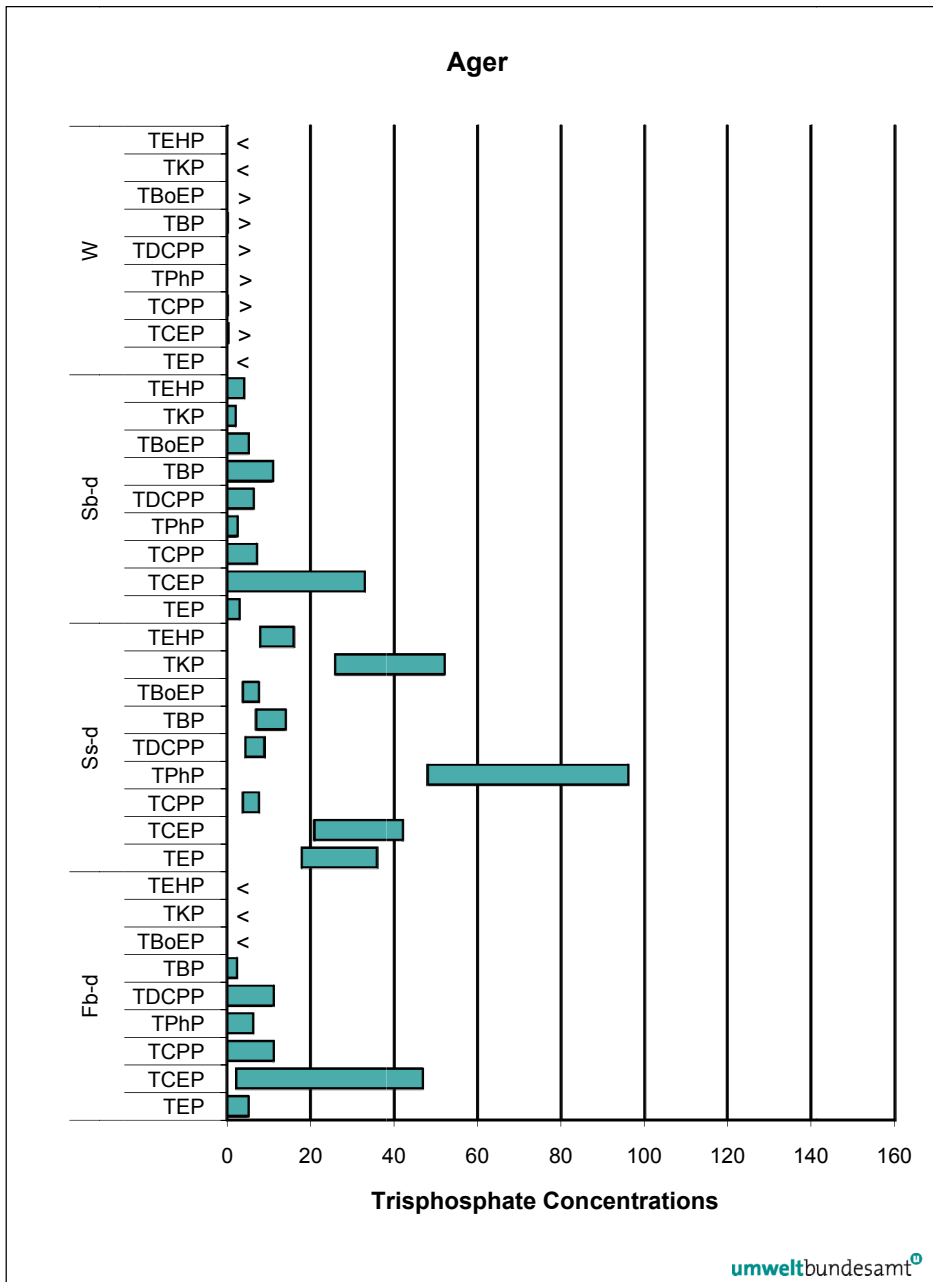


Fb-d (fish whole body, µg/kg, dry mass); Fb-w (fish whole body, µg/kg, wet mass); Ff-d: (fish fillet, µg/kg, dry mass); Ff-w (fish fillet, µg/kg, wet mass), Mb-d (mussel whole soft body, µg/kg, dry mass); Mb-w (mussel whole soft body; µg/kg, wet mass); n.a. (not analysed); Sb-d (bottom sediment, µg/kg, dry mass); Ss-d (suspended sediment, µg/kg, dry mass); W (river water, µg/l); < (residue levels below analytical limits in all samples); o (no data available)

Figure 14: Concentration ranges (minimum-maximum bars) of total mercury (Hg) and methylmercury (Me-Hg) in the rivers Ager and Schwechat over the compartments analysed (measured concentrations are as detailed in Table 13, Table 14, Table 18 to 24; concentrations below the analytical limits were set to zero in this graph, and are as detailed in Table 9, Table 10 and Table 12; mussels were sampled in the Ager river only.

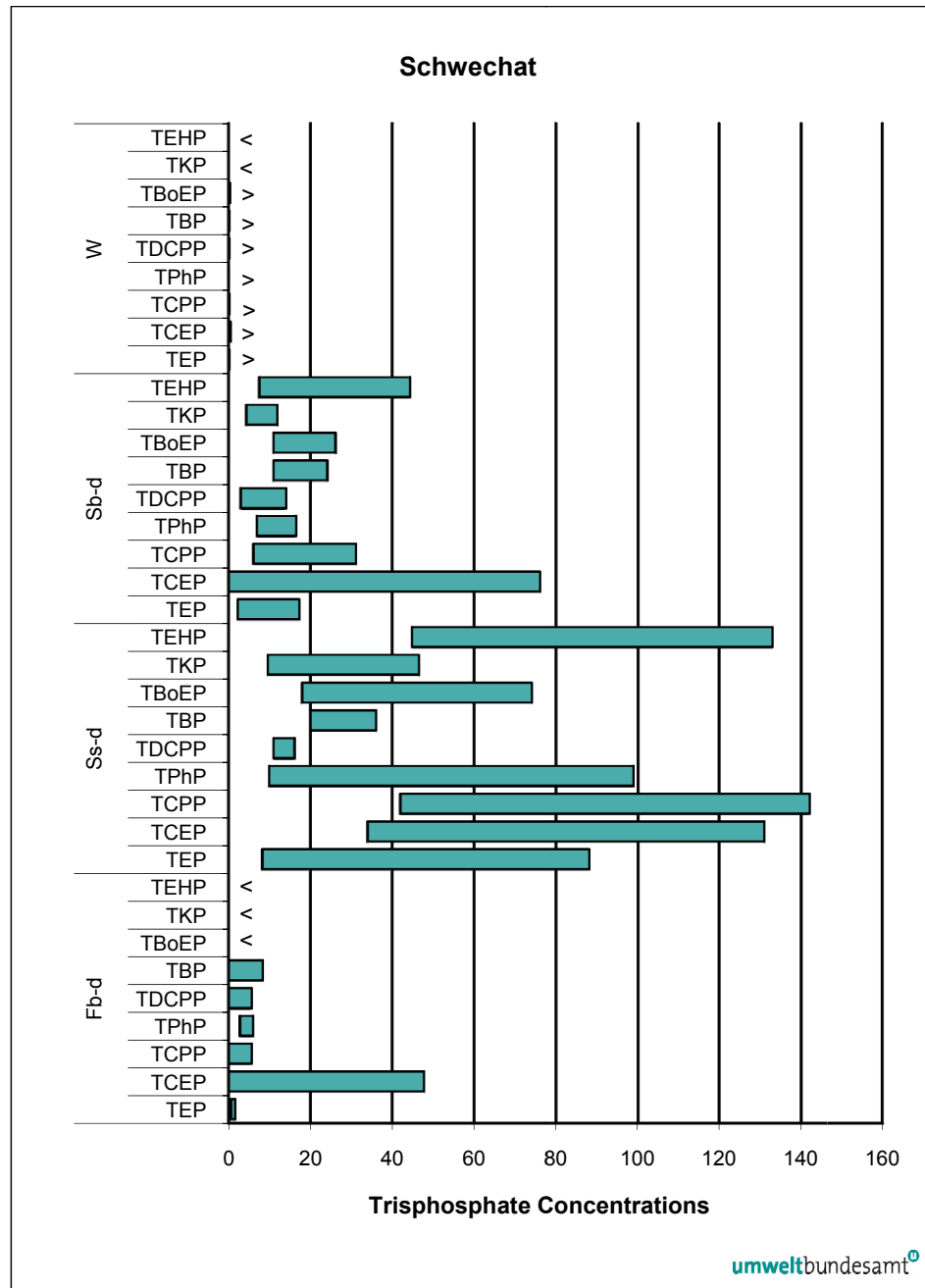
4.2.2 Trisphosphates

Trisphosphates were detected in all environmental compartments analysed (mussels not analysed). Comparing the ranges of variation over the whole data set, trisphosphate levels in fish exceeded that of the river water considerably and seemed rather similar and parallel to those observed in the bottom sediment fraction, but ranked generally below those in the suspended sediment fraction. Distribution between compartments and the respective concentrations are summarised in Figure 15 for the Ager River and in Figure 16 for the Schwechat River.



Fb-d (fish whole body, µg/kg, dry mass); *Fb-w* (fish whole body, µg/kg, wet mass); *Ff-d* (fish fillet, µg/kg, dry mass); *Ff-w* (fish fillet, µg/kg, wet mass), *Mb-d* (mussel whole soft body, µg/kg, dry mass); *Mb-w* (mussel whole soft body, µg/kg, wet mass); *Sb-d* (bottom sediment, µg/kg, dry mass); *Ss-d* (suspended sediment, µg/kg, dry mass); *W* (river water, µg/L); < (residue levels below analytical limits in all samples); o (no data available); > (concentrations in all samples above analytical limits but below 0.2 ng/l)

Figure 15: Concentration ranges (minimum-maximum bars) of trisphosphates in the Ager River over the compartments analysed (concentrations below the analytical limits are set to zero in this graph; mussels were sampled in the Ager river only but sample volumes were too small for an analysis of the trisphosphates).



Fb-d (fish whole body, µg/kg, dry mass); Fb-w (fish whole body, µg/kg, wet mass); Ff-d: (fish fillet, µg/kg, dry mass); Ff-w (fish fillet, µg/kg, wet mass); Mb-d (mussel whole soft body, µg/kg, dry mass); Mb-w (mussel whole soft body; µg/kg, wet mass); Sb-d (bottom sediment, µg/kg, dry mass); Ss-d (suspended sediment, µg/kg, dry mass); W (river water, µg/L); < (residue levels below analytical limits in all samples); o (no data available); > (concentrations in all samples above analytical limits but below 0.2 ng/l)

Figure 16: Concentration ranges (minimum-maximum bars) of trisphosphates in the Schwechat River over the compartments analysed (concentrations below the analytical limits are set to zero in this graph; mussels were sampled in the Ager River only).

4.3 Contaminant levels versus critical values/ Environmental Quality Standards

4.3.1 Environmental quality standards for water

Directive 2008/105/EC defines environmental quality standards (EQS) in the field of water policy. The EQS for mercury and mercury compounds is stabilised for biota and corresponds to 20 µg/kg wet wt. If member states do not apply this biota environmental quality standard, other standards may be defined for water which have to guarantee the same level of protection. The directive proposes 0.05 µg/l to be kept by annual average values (AA-EQS) and 0.07 µg/l as maximum value (MAC-EQS). Both EQS values refer to the dissolved fraction (Ec 2008).

Comparing the measured mercury concentrations in the investigated water samples with the environmental quality standards, no evaluation can be performed. Besides one measurement, all results were below the limit of quantification (LOQ=0.1 µg/l) but above the limit of detection of 0.05 µg/l. The limit of detection corresponds to the AA-EQS and mercury has been detected in all samples even if not quantifiable. Hence, the observed concentrations are higher than the respective environmental quality standard. Nevertheless prior to drawing further conclusions, additional measurements are required as the AA-EQS refers to annual average values based on monthly measurements.

At one sampling site during one sampling campaign mercury was detected at a concentration of 0.3 µg/l. This value is higher than the maximum allowable concentration.

All measured mercury concentrations in fish from the river Schwechat exceeded the respective EQS of 20 µg/kg wet mass (exceedance factors: 3.1–5.3). In the river Ager, out of four measured values one matched, two marginally exceeded, and one fell slightly below this EQS (factors: 0.6–1.2; total mercury, fillet, wet mass). Hence, secondary poisoning of fish predators in the rivers that were examined for this study cannot be excluded.

With respect to food safety for human consumption, the European Community allows 0.5 mg mercury/kg in fishery products (with some exceptions). The total mercury levels observed in the present study were all below this limit value (maximum factor: 0.2; total mercury, fillet, wet mass). But, considering that some of the mercury levels in fish reached this limit approximately, further studies with fish species and size classes typically used for human consumption should be conducted.

No environmental quality standards are available for trisphosphates up to now.

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6 ANNEXES

- Annex 1: Water, suspended sediment and bottom sediment samples in the river Schwechat at the Brauhaus-Str./Schwechat, Lower Austria
- Annex 2: Water, suspended sediment and bottom sediment samples in the river Ager at the Raudaschmühle/Schörfling at Attersee, Upper Austria
- Annex 3: Water, suspended sediment and bottom sediment samples in the river Ager at the Scheiblmühle/Timelkam, Upper Austria

Annex 1: Water, suspended sediment and bottom sediment samples in the river Schwechat at the Brauhaus-Str./ Schwechat, Lower Austria

Sample No.	River	Longitude (° WGS84)	Latitude (° WGS84)	Date (dd.mm.yyyy)	Time (hh:mm)	Air- tempera- ture (° C)	Water- tempera- ture (° C)	Electric con- ductivity (µS/cm 25°C)	pH	Dissolved oxygen (mg/l)	Comments
W 0708 3840	Schwechat	16°31'46"	48°08'38"	30.08.2007	09:45	15.8	17.7	710	7.63	-	Water sample
W 0711 5610	Schwechat	16°31'46"	48°08'38"	23.11.2007				818	9.10	11.5	Water sample
W 0708 3841	Schwechat west	16°31'46"	48°08'38"	20.08.2007	17:00						Suspended sediment 22.8 mg/L
W 0708 3841	Schwechat east	16°31'46"	48°08'38"	30.08.2007	10:30		17.7	710	7.63	-	Suspended sediment 31.8 mg/L
W 0708 3842	Schwechat centre	16°31'46"	48°08'38"	30.08.2007	10:30		17.7	710	7.63	-	Suspended sediment 28.0 mg/L
W 0708 3843	Schwechat west	16°31'46"	48°08'38"	30.08.2007	10:30		17.7	710	7.63	-	Suspended sediment 27.0 mg/L
W 0711 5611	Schwechat east	16°31'46"	48°08'38"	23.11.2007				818	9.1	11.5	Suspended sediment 3.9 mg/L
W 0711 5612	Schwechat centre	16°31'46"	48°08'38"	23.11.2007				818	9.1	11.5	Suspended sediment 8.0 mg/L
W 0711 5613	Schwechat west	16°31'46"	48°08'38"	23.11.2007				818	9.1	11.5	Suspended sediment 7.1 mg/L
S 0709 4011	Schwechat centre	16°31'46"	48°08'38"	20-22.08.2007 24.08.2007							ca. 200 g dry wt. yellowish-brown susp. sediment
S 0711 5614	Schwechat centre	16°31'46"	48°08'38"	14-23.11.2007							ca. 12 g dry wt. susp. sediment
S 0708 3844	Schwechat (W-bank)	16°31'46"	48°08'38"	30.08.2007	12:00						ca. 250 g dry wt. dark-grey to medium brownish silty fine-sediment. Partly covered by alge-mats.
S 0711 5609	Schwechat (W-bank)	16°31'46"	48°08'38"	23.11.2007							ca. 500 g dry wt. sediment

Official gauge (ca. 0.5 km below): Schwechat (Hallenbad; No. 208157) km 10.63km, Altitude: 154.59 m; Recharge area: 1028.9 km²

Annex 2: Water, suspended sediment and bottom sediment samples in the river Ager at the Raudaschlmühle/Schörfling at Attersee, Upper Austria

Sample No.	River	Longitude (° WGS84)	Latitude (° WGS84)	Date (dd.mm.yyyy)	Time (hh:mm)	Air- tempera- ture (° C)	Water- temperature (° C)	Electric con- ductivity (µS/cm 25°C)	pH	Dissolved oxygen (mg/l)	Comments
W 0709 4771	Ager Raudaschlmühle (just above the barrier)	13°36'29"	47°57'07"	26.09.2007	13:30	13.4	15.7	255	8.27	-	Water sample
W 0711 5641	Ager	13°36'29"	47°57'07"	28.11.2007				275	8.15	11.3	Water sample
W 0711 5638	Ager right	13°36'29"	47°57'07"	28.11.2007				275	8.15	11.3	Suspended sediment 0.08 mg/L
W 0711 5639	Ager center	13°36'29"	47°57'07"	28.11.2007				275	8.15	11.3	Suspended sediment 0.06 mg/L
W 0711 5640	Ager left	13°36'29"	47°57'07"	28.11.2007				275	8.15	11.3	Suspended sediment 0.06 mg/L
S 0709 4013	Ager south	13°36'29"	47°57'07"	27.07.- 22.08.2007							ca. 1.2 g dry wt. susp. sediment = ø 0.21 mg/L
S 0802 0395	Ager south	13°36'29"	47°57'07"	26.09.- 21.12.2007							ca. 1.5 g dry wt. susp. sediment= ø 0.04 mg/L
W 0709 4769	Ager Raudaschlmühle (N- bank 50 m above building with electric generators)	13°36'27"	47°57'06"	26.09.2007	14:45						ca. 500 g dry wt. greyish-white silty sedi- ment (calcite precipitation?); partly lower layers dark. 100 m above deposition area for wooden logs
B 0711 5637	Ager(N-bank above Raudaschlmühlemühle)	13°36'27"	47°57'06"	28.11.2007							ca. 200 g dry wt. sediment

Official gauge (ca. 0.3 km below): Ager (Raudaschl Säge No. 205369) km 33.53km, Altitude: 466.31 m; Recharge area: 462.9 km²

Annex 3: Water, suspended sediment and bottom sediment samples in the river Ager at the Scheiblmühle/Timelkam, Upper Austria

Sample No.	River	Longitude (° WGS84)	Latitude (° WGS84)	Date (dd.mm.yyyy)	Time (hh:mm)	Air-temperature (° C)	Water-temperature (° C)	Electric conductivity (µS/cm 25°C)	pH	Dissolved oxygen (mg/l)	Comments
W 0709 4770	Ager (N-bank above Scheiblmühle)	13°37'06"	47°59'29"	26.09.2007	11:45	17.0	17.1	549	8.30	-	Buket sample; flow 6 m ³ / s
W 0711 5646	Ager	13°37'06"	47°59'29"	28.11.2007				466	8.47	11.9	Water sample
W 0711 5643	Ager right	13°37'06"	47°59'29"	28.11.2007				466	8.47	11.9	Suspended sediment 0.38 mg/L
W 0711 5644	Ager center	13°37'06"	47°59'29"	28.11.2007				466	8.47	11.9	Suspended sediment 0.46 mg/L
W 0711 5645	Ager left	13°37'06"	47°59'29"	28.11.2007				466	8.47	11.9	Suspended sediment 0.26 mg/L
S 0709 4014	Ager south	13°37'06"	47°59'29"	27.07.- 22.08.2007							ca. 1.0 g dry wt. brown susp. sediment
S 0802 0396	Ager south	13°37'06"	47°59'29"	14.11.- 21.12.2007							ca. 1.5 g dry wt. susp. sediment
S 0709 4768	Ager(S-bank below Scheiblmühle)	13°37'10"	47°59'30"	26.09.2007	12:10						Medium grey silty-sandy sediment with many leaves and plant remnants
B 0711 5642	Ager(S-bank below Scheiblmühle)	13°37'10"	47°59'30"	28.11.2007							Sediment

Official gouge (ca. 3 km below): Ager (Dürnau No. 206276) km 25.16km, Altitude: 434.32 m; Recharge area: 497.2 km²

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In this report by Umweltbundesamt (Environment Agency Austria) the occurrence of total mercury and methylmercury as well as trisphosphates has been investigated in three different compartments in the aquatic environment: surface waters, sediments, suspended solids and biota. Besides methylmercury, all compounds were detected in all investigated matrices. Methylmercury occurred only in biota. Mercury was found to strongly bioaccumulate in biota and trisphosphates adsorbed predominantly to suspended matter.

Comparing the observed mercury levels in water as well as in biota, almost all measured concentrations were higher than the respective environmental quality standards (EQS). As the evaluation is based on few samples – whereas the EQS refer to annual average values based on monthly sampling – further measurements are required.