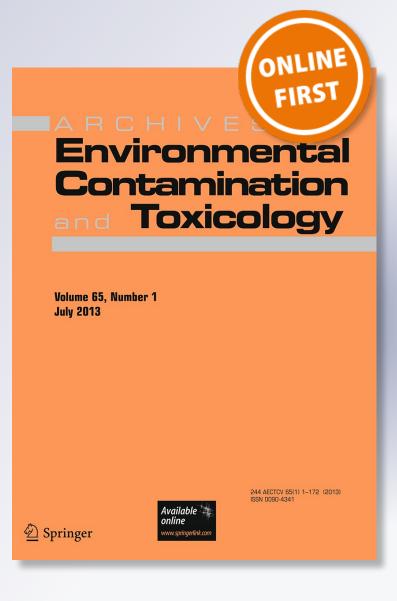
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Dynamics of Organochlorine Contaminants in Surface Water and in *Myriophyllum aquaticum* Plants of the River Xanaes in Central Argentina During the Annual Dry Season

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Abstract The dynamics of organochlorine pesticides (OCPs) and their major metabolites were studied in surface waters and plants of the River Xanaes (province of Córdoba, Argentina) during the annual dry season. The results of the 5-month monitoring study (April to August 2010) showed similar low contamination levels in nonagricultural mountain and agricultural areas in both water and plants. The concentrations of compounds detected in the surface water were <4.5 ng L⁻¹, whereas concentrations of these substances in *Myriophyllum aquaticum* plants were <5 µg kg⁻¹ (dry weight) with the exception of *trans*-permethrin (17.6 µg kg⁻¹, dry weight). Because no notable differences in the contamination level between samples from the mountain and the agricultural area were observed, it was assumed that OCPs may

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Multidisciplinary Institute of Plant Biology, Section Pollution and Bioindicator, Faculty of Physical and Natural Sciences, National University of Córdoba, Av. Vélez Sársfield 1611, 5000 Córdoba, Argentina not play an important role in today's pesticide use in this area. Furthermore, the concentration-time trends for OCPs in the submerged plants showed a generally similar elimination behaviour independent of compound and sampling site, thus indicating an integral rather then a substance-specific process, such as partitioning between the plant and the ambient water. As known, rooted macrophytes can take up contaminants by way of roots, so sediments may be the principal source. To understand the dynamics of these compounds in the river area more deeply, thus further research should include study of the river sediment.

Organochlorine pesticides (OCPs), such as p,p'-DDT, endrin, or lindane, were used intensively for decades, e.g., endosulfan is still used in Argentinean agriculture. Because of the toxicity and/or the persistence of OCPs in the environment, most OCPs were prohibited for commercial production and use. Although many of them have not been used for years, OCPs and their metabolites (e.g., p,p'-DDE, endosulfan sulfate) are commonly found in Argentina in different environmental matrixes at low concentrations (e.g., UNEP report 2002).

OCPs were determined in Argentinean water bodies at concentrations up to μ g L⁻¹ levels (UNEP report 2002). Because of their physicochemical properties, such as lipophilicity, they accumulate in aquatic organisms, e.g., water plants (Doust et al. 1994; Gobas et al. 1991). Because water plants are food and habitat for many water organisms, they play a key role in aquatic ecosystems. During entry of contaminants by, e.g., run-off from agricultural areas, rooted submerged macrophytes with their limited mobility accumulate lipophilic compounds during exposure. Therefore, they can be used as local in situ biomonitors of waterborne contaminants (Gobas et al. 1991).

The occurrence of OCPs in environmental matrixes is not just regional but worldwide due to distributing processes, such as atmospheric transport (Simonich and Hites 1995). Further processes, such as spray-drift or washing-off from plant surfaces during application, must also be considered. Because of their hydrophobic character, these compounds are mainly found associated with organic matter in sediment (Knezovich et al. 1987; Warren et al. 2003). Although OCPs are associated with sediments, they could be remobilised during, e.g., flood events, where they can reach concentrations that are toxic toward exposed wildlife (Grote et al. 2005). This could, e.g., occur annually in areas of intensive agriculture during the first rainfalls after a dry season (Jergentz et al. 2004, 2005; Schulz et al. 2001). After these pesticide pulses, contamination levels decrease over time again to a level similar to background or until further pesticides enter.

The purpose of this study was to characterise and compare the dynamics of selected OCPs and their main metabolites in the submerged *M. aquaticum* plant and surface water between an agricultural and a nonagricultural sampling site of the River Xanaes (province of Córdoba, Argentina) during the annual dry season. It was assumed that contamination levels of OCPs at the nonagricultural sampling site represent the background level and that water is the main contamination source for *M. aquaticum*. Thus, the aims of the study were to determine (1) if a difference of the contamination level with OCPs between the two sampling sites exist, (2) if a decrease of the contamination level with of the contamination level with background level) will be reached during the observation period.

Material and Methods

Chemicals and Standard Solutions

Pesticide-grade hexane (H), methanol, dichloromethane (DCM), and methyl tert-butyl ether (MTBE) were purchased from Sintorgan S. A. (Buenos Aires, Argentina). Silica gel and Na₂SO₄ (both analytical grade) were treated for 12 h at 180 °C before use. Polychlorinated biphenyl congener (PCB) 103 (CAS-RN 60145-21-3) was used as internal standard and was purchased from AccuStandard (New Haven, CT, USA). Mixtures of standards were used for identification and quantification and were purchased from AccuStandard. One mixture of standards (AS-PBR) consisted of α -chlordane, γ -chlordane, chlorobenzilate, chloroneb, chlorothalonil, DCPA, etridiazole, hexachlorobenzene, cis-permethrin, trans-permethrin, propachlor, and trifluralin (AccuStandard). Mixture AS-PA consisted of aldrin, α -BHC, β -BHC, δ -BHC, γ -BHC, p,p'-DDD, p,p'-DDE, p,p'-DDT, dieldrin, endosulfan I, endosulfan II, endosulfan sulfate, endrin, endrin aldehyde, heptachlor, heptachlor epoxide, and methoxychlor (AccuStandard). For details about chemical identities and basic physicochemical properties of the standards, see Supplementary Tables S1 and S2. Chemicals in standard mixtures were delivered dissolved in MTBE.

Investigation Area and Period

The source of the River Xanaes (Rio Segundo) is in the Sierras de Córdoba mountains, which are located in the centre of the province of Córdoba (Argentina), and it flows further through agricultural areas to Lake Mar Chiquita. Thus, one sampling point was in the mountain area (31.7066°S and 64.4892°W), whereas the other was in an area of intensive agriculture (31.8035°S and 64.3063°W) 30 km downstream (Supplementary Fig. S1). The sampling area is sparsely populated such that low contribution from wastewater are assumed. The main crops in the agricultural area are soybean and corn, which are cultivated during the summer. Although most OCPs are prohibited, there are rumours about illegal use. Typically, no fumigations are performed during the winter in this area. The sampling was performed between April and August 2010 directly after the wet season. Average precipitation during this period and in this area is between 9.7 and 52.2 mm (Servicio Meteorológico Nacional, Argentina; http://www.smn.gov. ar/). During the sampling period, light rain occurred occasionally, but there was no obvious run-off. Surface water and M. aquaticum were collected at both sites every 2 weeks during the sampling period. For details about sampling date and the number of samples taken, see Supplementary Table S3.

Sample Treatment for Water Plants

Upper submerged grown M. aquaticum shoots were collected from the river, enclosed in aluminium foil, and transported cooled into the laboratory. The plants were then freeze-dried, ground finely, and stored in amber glass flasks covered with aluminium until extraction. The method described by Miglioranza et al. (1999) was adapted to prepare the samples. Briefly, 2 g of lyophilised plant powder was mixed with 8 g of Na₂SO₄, spiked with 100 μ L of PCB 103 (10 mg L⁻¹ in MTBE), and transferred into a pre-extracted cellulose extraction thimble. Plants were extracted for 8 h using a Soxhlet apparatus with a mixture of H and DCM (1:1 v/v); there were four extraction cycles/hour. Extracts were concentrated to 3 mL under nitrogen. To separate larger plant compounds, such as lipids and chlorophyll, from the extract, gel permeation chromatography (GPC) with Bio Beads S-X3 (200-400 mesh; ≤ 2 kDa) (Bio-Rad Laboratory, Hercules, CA, USA) was performed with a successive elution using a mixture of H and DCM (55:45 v/v). Final clean-up was performed with silica gel chromatography using a mixture of H and DCM (50:50 v/v). The extracts were then concentrated to 0.1 mL under nitrogen, diluted with H to 1 mL, and stored in amber autosampler vials at -20 °C until gas chromatography-electron capture detection (GC-ECD) analysis.

Sample Treatment for Surface Water

One liter of surface water was collected from the river in amber glass flasks covered with aluminium and transported cooled to the laboratory. Each 1-L water sample was then spiked with 100 μ L of PCB 103 (10 mg L⁻¹ in MTBE) and stored for a maximum of 2 days at 3 °C until solid phase extraction (SPE). The proposed SPE disk method for quick-turnaround aqueous phase United States Environmental Protection Agency (USEPA) extraction (3 M, St. Paul, MN, USA) was performed to extract OCPs from the surface water (http://www.sigmaaldrich.com/etc./media lib/docs/Supelco/Instructions/1/t709112.Par.0001.File.tmp/ t709112.pdf). The extraction apparatus with the Empore extraction disk (47 mm, C₁₈; 3M) was cleaned with DCM and conditioned with methanol before sample extraction. After extraction of the 1-L water sample, compounds were re-extracted from the Empore extraction disk using DCM. The sample flask was rinsed with DCM three times and the wash solution was combined with the extract. Finally, the extract was dried with Na₂SO₄, transferred into a tube, and concentrated with nitrogen to 1 mL, diluted with H to 10 mL, and concentrated again to 1 mL. The extract was stored in amber autosampler vials at -20 °C until GC-ECD analysis.

Analytical Method

GC analysis was performed on a GC Agilent 6890 equipped with a ⁶³Ni µ-electron capture detector (ECD; Agilent, Santa Clara, California, USA) split-splitless injector in splitless mode and controlled by ChemStation software (Rev. B. 04.01; Agilent). One microliter of the sample was injected and separated on a dimethyl-polysiloxane capillary (model HP-1; Agilent; 30 m \times 0.25 mm i.d., 25-µm film thickness) with helium as carrier gas using a column head pressure of 20 psi. The injector temperature was 300 °C. The oven temperature was programmed starting at 80 °C and held 1.5 min, followed by increases of 10 °C min⁻¹ up to 150 °C and held for 8 min, then 15 °C min⁻¹ up to 200 °C and held for 6 min, afterward 20 °C min⁻¹ up to 230 °C and held for 5 min, and finally 20 °C min⁻¹ up to 275 °C and held for 5 min. Each sample extract and standard solution was measured twice.

Peak identification was based on retention time and was performed by the injection of single compounds of the standards AS-PBR and -PA. For peak quantification, various concentrations of AS-PBR and -PA were prepared in MTBE and analysed.

For the determination of the extraction performance from water samples, 1 L of distilled water was spiked with either AS-PBR or -PA and treated as a sample e.g., stored for 1 day at 3 °C and followed by SPE extraction. Similarly, the extraction performance from plant samples was determined with the exception that 10 g Na₂SO₄ were spiked with either AS-PBR or -PA. Recoveries from water samples ranged from 69.6 to 135.4 %, whereas recoveries from plant samples ranged from 28.6 to 104.4 % (Supplementary Table S4). Depending on the compound, detection limits in surface water ranged from 0.02 to 0.20 ng L^{-1} and in plants from 0.05 to 1 µg kg⁻¹ (dry weight) (Supplementary Table S4). Contaminations during sample preparation were investigated for water samples by spiking 1 L of distilled water with 100 µL of PCB 103 (10 mg L^{-1} in MTBE) followed by the sample treatment (i.e., stored for 1 day at 3 °C and followed with SPE extraction). Similarly, the contamination of plant samples was determined with the exception that 10 g Na_2SO_4 were spiked with 100 μ L of PCB 103 (10 mg L⁻¹ in MTBE). Depending on the chemical, the concentration of possible laboratory contaminants ranged from ND to 0.13 ng L^{-1} in water, samples whereas in plant samples contamination levels ranged from ND to 1.16 μ g kg⁻¹ (Supplementary Table S4).

The retention time and the likelihood of the pesticide's use were considered when tentatively identifying the chemicals from the water and plant sample extracts. The internal standard PCB 103 and the recovery, as determined during extraction performance analysis, were used for quantification. A compound was considered to occur when its concentration was greater than the concentration of the possible laboratory contamination during sample preparation and it was detected at least three times at one sampling site.

Mathematical Description of the Concentration Decrease

The first order decay function C(t) was used to describe the decrease in concentration of OCPs with time in plant samples (Eq. 1), where parameter $k_{2,pseudo}$ was estimated using the maximum likelihood in the software Origin (OriginLab, Northampton, USA):

$$C(t) = (C_{\max} - C_{ss}) \cdot e^{-k_{2,pseudo} \cdot t}$$
(1)

Here, *t* is time, C_{max} is the highest observed concentration, C_{ss} is the steady-state concentration, and $k_{2,\text{pseudo}}$ may be interpreted as the pseudo-elimination rate. C_{ss} was calculated using the concentrations from the last four samples.

Results and Discussion

Occurrence of OCPs and Metabolites

High concentrations of the OCPs and their major metabolites were expected in the river and submerged plants for the area of intensive agriculture, whereas low pesticide levels were expected in the forested mountain area. Surprisingly, the concentrations detected in the river and plant samples at both sites were comparable (Table 1). Only 10 of the 30 OPCs considered (AS-PBR, -PA) were found. Of these, nine and eight were detected in plants in the agricultural and mountain area, respectively. Seven compounds were found in the agricultural river sample compared with six in the mountain river. The concentration of individual organochlorine compounds in M. aquaticum at both sites was $<5 \ \mu g \ kg^{-1}$ (dry weight) at both sites except for *trans*permethrin, where concentrations $<17.55 \ \mu g \ kg^{-1}$ (dry weight) were found. Concentrations in the surface water were <4.5 ng L⁻¹ at both sampling sites.

Surface Water

No data were found for this river basin in the literature. Although comparison with levels in different region is not optimal, we present a few studies here. During an environmental toxicity assessment of the Paraná River delta (Argentina) in December 1996 by Cataldo et al. (2001), surface water concentrations ≤ 0.62 ng L⁻¹ for γ -chlordane, 0.63 ng L⁻¹ for p,p'-DDE, and 1.62 ng L⁻¹ for heptachlor were found. We observed a similar concentration range in this study. Baudino et al. (2003) monitored OCP levels in surface and groundwater of the two main rivers, San Juan and Jáchal, in the province of San Juan (Argentina) 500 km west of the River Xanaes. Mean concentrations of 6.6 µg L⁻¹ for β -HCH, 1.7 µg L⁻¹ for p,p'-DDE, 0.4 µg L⁻¹ for endosulfan I,

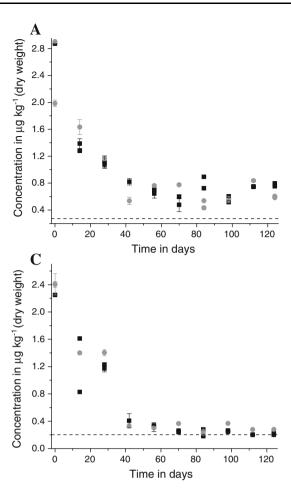
0.48 ug L^{-1} for endrin, and 0.97 ug L^{-1} for heptachlor were found during September 1996 to July 1997. These values are at least 3 orders of magnitude greater (except for heptachlor, which was 300 times greater) than those observed here in the river Xanaes. Di Marzio et al. (2010) measured greater endosulfan (I + II) levels (<25.9 μ g L⁻¹) in water samples collected from narrow and shallow streams flowing through cultivated areas in the province of Córdoba (Argentina). These samples were taken 1 day after application of insecticides; thus, high concentrations of endosulfan were expected (di Marzio et al. 2010). During stream sampling in Pampa Ondulada (Argentina) between October 2002 and March 2004, Marino and Ronco (2005) observed chlorpyrifos concentrations ranging from <0.2 (before application) to 10.8 μ g L⁻¹ (after application). Only low chlorpyrifos concentrations were determined in this study compared with Marino and Ronco (2005) (three orders of magnitude lower). Overall, we conclude that low contamination levels of the nine detected OCPs with their metabolites are present in the surface water of the River Xanaes.

Submerged Plants

Although comparing concentrations in different species is inaccurate due to the different exposure and uptake processes, nonetheless comparison gives an indication of contaminant levels in other areas. Miglioranza et al. (2004) measured the concentration of different organochlorine compounds in the rooted riparian macrophyte *Schoeneoplectus californicus* from a creek running into Los Padres lake (province Buenos Aires, Argentina), in an intensive agricultural area. Dry-weight concentration of 0.8 μ g kg⁻¹ for β -HCH, 1.1 μ g kg⁻¹ for γ -chlordane, 1.3 μ g kg⁻¹ for *p,p'*-DDE, 0.1 μ g kg⁻¹ for endosulfan I, 17.5 μ g kg⁻¹ for endosulfan sulfate, and 0.2 μ g kg⁻¹ for heptachlor were observed in *S. californicus* stems, which is on the same

Compound name	<i>M. aquaticum</i> μ g kg ⁻¹ (dry weight)		Surface water (ng L^{-1})	
	Agricultural area	Mountain area	Agricultural area	Mountain area
β-ВНС	0.59–1.76	0.40-2.43	0.12-0.51	0.10-0.35
γ-Chlordane	0.08-0.27	_	_	-
Chlorpyrifos	1.58-4.91	1.31-4.46	0.22-0.78	0.17-0.48
p,p'-DDE	0.19-0.80	0.10-0.34	_	0.07-0.34
Endosulfan I	0.48-2.87	0.43-2.90	0.03-0.38	0.03-0.35
Endosulfan sulfate	0.11-4.03	0.19-6.31	0.46-4.33	0.56-2.26
Endrin	0.18-2.25	0.22-2.41	0.07-0.20	-
Heptachlor	1.28-4.61	0.74-4.26	0.62-3.34	0.20-1.50
Hexachlorbenzene	_	_	0.08-0.25	-
trans-permethrin	2.93-11.22	5.02-17.55	_	-

Table 1 Concentration ranges
of OCPs and major metabolites
in M. aquaticum and in surface
water



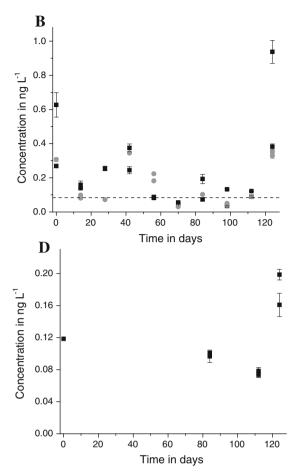


Fig. 1 Concentration-time profiles of endosulfan I (\mathbf{a} , \mathbf{b}) and endrin (\mathbf{c} , \mathbf{d}) in *M. aquaticum* (\mathbf{a} , \mathbf{c}) and surface water (\mathbf{b} , \mathbf{d}) taken from the mountain area (*closed square*) and downstream in an agricultural area (*filled circle*). Every data point represents the mean value of one

order of magnitude as the concentrations observed here. Because of the lack of further data, no conclusion about the contamination level in plants could be made.

Concentration-Time Profiles

The investigated area is characterised by a pronounced dry and wet season. If the major impact of OCPs (and metabolites) in a river is caused through remobilisation and runoff, greater concentrations are expected during and directly after the wet season compared with the dry season. A clear concentration decrease toward a steady concentration was found for plant samples at both sampling sites for β -BHC, chlorpyrifos, endosulfan I, and endrin, whereas relatively constant concentrations were observed in surface water. This concentration–time behaviour is shown for endosulfan I and endrin in Fig. 1. No clear statement about the concentration–time behaviour of γ -chlordane, heptachlor, and *trans*-permethrin could be made because these compounds were only detected sporadically in both plants and water.

sample, whereas the SD represents the difference between technical replicates. The *dotted line* represents the possible laboratory contamination during sample preparation

A concentration increase was observed in plants for the first sampling days for the two metabolites, p.p'-DDE and endosulfan sulfate, followed by a decrease toward a constant concentration (Figs. 2a, c). A similar concentrationtime profile was found for endosulfan sulfate in the water samples taken from the both of the sampling sites (Fig. 2b). Only for p,p'-DDE was a different concentration-time behaviour observed in plant samples taken from either the mountain or the agricultural sampling site (Fig. 2c). The concentration decrease of endrin, endosulfan I, endosulfan sulfate (beginning on day 28), and $p_{,p'}$ -DDE (beginning on day 42) in plant samples could be described using a firstorder decay function (Eq. 1; Supplementary Fig. S2) with the respective parameter values for C_{ss} and $k_{2,pseudo}$ as listed in Table 2. Estimated pseudo-elimination rates $(k_{2,\text{pseudo}})$ for these four compounds from plants were on the same order of magnitude.

The concentration decreases were well described by a first-order decay function. Although estimated $k_{2,pseudo}$ values only result from best fit, these may be interpreted as

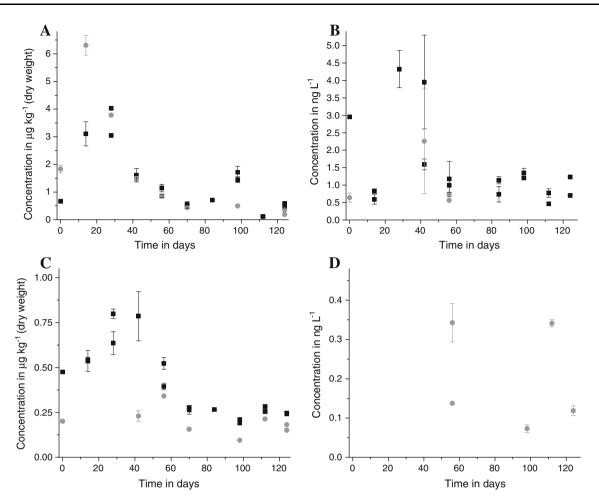


Fig. 2 Concentration-time-profiles of endosulfan sulfate (\mathbf{a} , \mathbf{b}) and p,p'-DDE (\mathbf{c} , \mathbf{d}) in *M. aquaticum* (\mathbf{a} , \mathbf{c}) and surface water (\mathbf{b} and \mathbf{d}) taken from two sampling sites are shown. For further description, see Fig. 1

Compound name	Agricultural area		Mountain area		$\log K_{OW}^{a}$
	$\overline{C_{\rm ss}} \; (\mu {\rm g \; kg^{-1}})$	$k_{2,\text{pseudo}} \text{ (days}^{-1})$	$C_{\rm ss}~(\mu {\rm g~kg}^{-1})$	$k_{2,\text{pseudo}} \text{ (days}^{-1})$	
<i>p</i> , <i>p</i> ′-DDE	0.24	0.076 (±0.009)	0.16	-	6.51
Endosulfan I	0.72	0.081 (±0.009)	0.59	0.048 (±0.006)	3.83
Endosulfan sulfate	0.74	0.087 (±0.030)	0.35	0.076 (±0.004)	3.66
Endrin	0.23	0.042 (±0.004)	0.28	0.042 (±0.006)	5.2

Table 2 $k_{2,pseudo}$, C_{ss} , and $k_{2,pseudo}$ values as calculated using Equation 1

^a PhysProp Database. http://www.syrres.com/esc/physdemo.htm

an overall elimination rate (sum of all uptake and elimination rates) assuming that the uptake and elimination processes follow first-order kinetics. Thus, $k_{2,pseudo}$ may represent elimination dynamics for that compound in plants at the respective sampling site. Because $k_{2,pseudo}$ values determined differ by less than a factor of 2.5 independent of sampling site and compound considered, the elimination may be dominated by an integral process, such as growth dilution. However, growth dilution cannot explain the observed steady-state concentration level (C_{ss}) or the

previous uptake process. Furthermore, Gobas et al. (1991) showed that the elimination rate of lipophilic organochlorine compounds is correlated to the octanol–water partition coefficient (K_{OW}). Assuming that a lipophilic organochlorine compound's elimination rates correlate in *M. aquaticum* with K_{OW} too, differences in $k_{2,pseudo}$ values of detected compounds were expected, but they were not observed, thus indicating that partitioning into water may not dominate the observed elimination dynamic. Thus, further compartments and processes must be considered.

Turgut and Fomin (2002) studied the ability of M. aquaticum for root uptake and translocation of pesticides and showed that all pesticides (trifluralin, triasulfuron, terbutryn, atrazine, and cycloxidim) were taken up by way of the roots and translocated into shoots. Because the contamination level of the river sediment was not studied, thus compound's concentration-time profiles in sediments and plants could not be compared. If we speculate that OCP concentration levels in sediments and plants correlate, the determined $k_{2,pseudo}$ values describes transport processes in the river sediment. This leads to different hypotheses about the sediment contamination as follows: (1) Because sampling was performed directly after the wet season, it may be speculated that the observed concentration decrease is dominated by the decreased entry of water and suspended particles; and (ii) Another explanation for the broadly similar determined $k_{2,pseudo}$ values from plants takes the temperature dependence of desorption kinetics of organic compounds in sediments into account (e.g., Cornelissen et al. 1997; Enell et al. 2005). Cornelissen et al. (1997) showed that slow desorption kinetics are highly dependent on temperature. During the first 40 days of sampling, a decrease in surface waters temperature of ~ 10 K at both sampling sites was observed with temperatures remaining at approximately steady for the remaining campaign (Supplementary Fig. S3). If the first hypothesis is true, then a decrease in the contamination level in the river sediment during sampling may be assumed. In contrast, if the second hypothesis is true, then during the entire sampling a broadly constant contamination level in the sediment may be assumed.

Both hypotheses may explain compounds similar $k_{2,pseudo}$ values but not the previously observed concentration increase only for p,p'-DDE and endosulfan sulfate. Endosulfan sulfate and p,p'-DDE are major metabolites of endosulfan and p,p'-DDT, respectively. Gao et al. (2000) showed that aquatic plants, such as *M. aquaticum*, could metabolise accumulated p,p'-DDT into p,p'-DDE, and it is known that plants (beside other organisms) could metabolise endosulfan into endosulfan sulfate (Gupta and Gupta 1979). Thus, the former determined concentration increase for endosulfan sulfate and p,p'-DDE may be explained by metabolisation of the parent compounds. The partitioning of the synthesised endosulfan sulfate from aquatic organisms into ambient water may explain the observed concentration peak in the river water.

Conclusion

During the entire sampling period, a relatively similar low contamination level of the investigated organochlorine compounds was observed in the mountain and agricultural areas in both surface water and plants taken from the River Xanaes. Assuming that contamination levels in the nonagricultural mountain area represents background levels, then OCPs may not play an important role in "current" pesticide use in the investigated agricultural area; otherwise, a greater OCP concentration would be observed.

Although a similar low contamination level at the two sampling sites was found, a clear concentration decrease over time with a final steady state was observed in the submerged *M. aquaticum*. Because the concentration–time plots of OCPs showed a broadly similar pseudo-elimination rate independent of compound and sampling site, partitioning between the plant and the ambient water may not be the dominant elimination process. The concentration decrease may thus correlate either with decreased entry of the contaminant during the almost dry 5-month sampling regime or the dependence of the compound's desorption rate from sediments on temperature.

In contrast to the observed concentration decrease of the OCPs in plants, a generally constant concentration of these compounds in surface water was found suggesting that river water may not be the main source for plant contamination. Because rooted macrophytes can take up contaminants by way of the roots, sediment may be the principal source. Because the sediment contamination level was not determined here, further research should include the measurement of OCPs in sediment over time.

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References

- Baudino OM, Suero EA, Augusto M, Gimenez ME, Flores N (2003) Monitoring organochlorine pesticides in surface and ground water in San Juan Argentina. J Chil Chem Soc 48:7–12. doi: 10.4067/S0717-97072003000200001
- Cataldo D, Colombo JC, Boltovskoy D, Bilos C, Landoni P (2001) Environmental toxicity assessment in the Paraná River delta (Argentina): simultaneous evaluation of selected pollutants and mortality rates of *Corbicula fluminea* (Bialvia) early juveniles. Environ Pollut 112:379–389
- Cornelissen G, van Noort PCM, Parsons JR, Govers HAJ (1997) Temperature dependence of slow adsorption and desorption kinetics of organic compounds in sediments. Environ Sci Technol 31:454–460
- Di Marzio WD, Sáenz ME, Alberdi JL, Fortunato N, Cappello V, Montivero C et al (2010) Environmental impact of insecticides applied on biotech soybean crops in relation to the distance from aquatic ecosystems. Environ Toxicol Chem 29:1907–1917
- Doust JL, Schmidt M, Doust LV (1994) Biological assessment of aquatic pollution: a review, with emphasis on plants as biomonitors. Biol Rev 2:147–186

- Enell A, Reichenberg F, Ewald G, Warfvinge P (2005) Desorption kinetics studies on PAH-contaminated soil under varying temperatures. Chemosphere 61:1529–1538
- Gao J, Garrison AW, Hoehamer C, Mazur CS, Wolfe NL (2000) Uptake and phytotransformation of o,p'-DDT and p,p'-DDT by axenically cultivated aquatic plants. J Agric Food Chem 48:6121–6127
- Gobas FAPC, McNeil EJ, Lovett-Doust L, Haffner GD (1991) Bioconcentration of chlorinated aromatic hydrocarbons in aquatic macrophytes. Environ Sci Technol 25:924–929
- Grote M, Altenburger R, Brack W, Moschütz S, Mothes S, Michael C, Narten G-B et al (2005) Ecotoxicological profiling of transect River Elbe sediments. Acta Hydrochim Hydrobiol 33:555–569
- Gupta PK, Gupta RC (1979) Pharmacology, toxicology and degradation of endosulfan. A review. Toxicology 13:115–130
- Jergentz S, Pessacq P, Mugni H, Bonetto C, Schulz R (2004) Linking in situ bioassays and population dynamics of macroinvertebrates to assess agricultural contamination in steams of the Argentine Pampa. Ecotoxicol Environ Saf 59:133–141
- Jergentz S, Mugni H, Bonetto C, Schulz R (2005) Assessment of insecticide contamination in runoff and stream water of small agricultural streams in the main soybean area of Argentina. Chemosphere 61:817–826
- Knezovich JP, Harrison FL, Wilhelm RG (1987) The bioavailability of sediment-sorbed organic chemicals: a review. Water Air Soil Pollut 32:233–245
- Marino D, Ronco A (2005) Cypermethrin and chlorpyrifos concentration levels in surface water bodies of the Pampa Ondulada, Argentina. Bull Environ Contam Toxicol 75:820–826

- Miglioranza KSB, Aizpún de Moreno JEA, Moreno VJ, Osterrieth ML, Escalante AH (1999) Fate of organochlorine pesticides in soils and terrestrial biota of "Los Padres" pond watershed, Argentina. Environ Pollut 105:91–99
- Miglioranza KSB, de Moreno JEA, Moreno VJ (2004) Organochlorine pesticides sequestered in the aquatic macrophytes *Schoenoplectus californicus* (C.A. Meyer) Soják from a shallow lake in Argentina. Water Res 38:1765–1772
- Schulz R, Peall SKC, Dabrowski JM, Reinecke AJ (2001) Current-use insecticides, phosphates and suspended solids in the Lourens River, Western Cape, during the first rainfall event of the wet season. Water SA 27:65–70
- Simonich SL, Hites RA (1995) Global distribution of persistent organochlorine compounds. Science 269:1851–1854
- Turgut C, Fomin A (2002) The ability of *Myriophyllum aquaticum* (Vell.) Verdcourt in the uptake and the translocation of pesticides via roots with a view to using the plants in sediment toxicity testing. J Appl Bot 76:62–65
- United Nations Environment Programme Report (2002) Programa de las Naciones Unidas para el Medio Ambiente. Evaluación regional sobre sustancias tóxicas persistentes. Sudamérica oriental y occidental. Informe Regional. Fondo para el medio Ambiente Mundial, Ginebra Suiza
- Warren N, Allan IJ, Carter JE, House WA, Parker A (2003) Pesticides and other micro-organic contaminants in freshwater sedimentary environments—a review. Appl Geochem 18:159–194