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Quantifying the Dynamics of Pesticides in Natural Waters

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Abstract. A variety of trace analytical methods (solid-phase and liquid-liquid extraction, HPLC and GC-MS) for quantitatively assessing the input and behavior of pesticides and their metabolites (*i.e.*, triazines, acetamides, phenoxy acids and organotin compounds) in natural waters and sediments are presented. The results of field studies illustrate the analytical methods performance such as simultaneous determination of compounds with different polarities, low detection limits, and high precision and accuracy.

Introduction

A major goal of environmental research is to quantitatively assess the inputs and behavior of, *e.g.*, pesticides and their important metabolites, in natural waters. This can be achieved by a combination of field measurements and model calculations. Moreover, it makes a tremendous demand of analytical methods because it requires the simultaneous determination of compounds of very different polarities, in various matrices, at low detection limits (ng/l), and with high precision and accuracy. The quality with which the processes in nature can be identified and quantified depends strongly on these latter factors, which makes them even more important. On the one hand these basic conditions call for the development of sophisticated analytical methods, which are highly selective and sensitive, such as solid-phase extraction (SPE), HPLC, CZE, GC/MS, LC/MS-MS, *etc.* On the other hand, such methods have to be easy enough to be applied to a considerable number of samples during the field studies.

With the first example, 'Pesticide Occurrence and Washout Behavior from the Atmosphere by Rain and Their Transport

into Groundwater', I will briefly highlight the challenges of routinely quantifying a broad range of pesticides (neutral and acidic) at low concentrations. The second example, 'Input, Transport and Transformation Processes of Pesticides and their Metabolites in Lakes', stresses the routine, simultaneous quantification of parent compounds and their metabolites. The last issue, 'Resolving the Biocide Tributyltin from Harbor Sediments', will describe extraction of organotin compounds from sediments, and their quantification at low concentrations in small sample volumes.

Simultaneous Quantification of Neutral and Acidic Herbicides

Of the *ca.* 20 different classes of herbicides, the triazines, the acetamides, and the phenoxy acids are among the most widely used compounds worldwide. Prominent compounds include atrazine, metolachlor, and mecoprop, of which several tons are used in Switzerland every year. In recent years, several techniques for multi-pesticide-residue analysis in natural waters have been applied to environmental samples, including SPE-GC/MS, SPE-HPLC, LC/GC, or LC/MS. However, only a few methods allow for the simultaneous determination of both neutral and acidic pesticides. The published methods used liquid-liquid extraction, derivatization of the acidic pesticides with diazomethane, and GC/ECD or GC/FID for separation and detection. More recently, SPE-HPLC and LC/MS were used to achieve the goal of simultaneous detection. However, SPE-

HPLC lacks a reliable, sufficiently sensitive, and highly specific detector, and LC/MS is too sophisticated for routine analysis at trace concentrations. The following example shows the development of a robust and sensitive analytical method for routine analyses. Special emphasis was placed on the simultaneous analysis of a broad range of compounds (*i.e.*, neutral and acidic herbicides), at low concentrations (ng/l level) and with high precision and accuracy.

For the simultaneous enrichment of neutral and acidic pesticides we use graphitized carbon black (GCB) as a solid-phase extraction material, a sequential elution of neutral and acidic compounds from the SPE cartridge, and derivatization of the acidic fraction with diazomethane. The compounds are then quantified by GC/MS. The introduction of isotope labeled internal standards (one for each compound class) enables precise and accurate quantification. This method overcomes the usually cumbersome and tedious sample preparation, particularly for the analysis of acidic substances with GC/MS. In addition, it allows the routine and simultaneous determination of triazines, acetamides, and phenoxy acids in natural waters (for details see [1][2]). An application of this analytical method is illustrated in *Fig. 1*. In close collaboration with bio-geochemists and engineers, the pollution of rain and roof-runoff waters with pesticides (besides other compounds), is currently being investigated at EAWAG. The major goal of this study is to assess whether rain and roof-runoff waters can be considered 'unpolluted' and thus can be infiltrated into groundwater, as enforced by the Swiss legislation. *Fig. 1* shows selected pesticide concentrations during a rain event. The concentrations of all compounds markedly decreased within the first 2 mm of rain. Surprisingly, in this particular study, mecoprop, a herbicide used normally in agricultural applications, was present in some flat roof-runoff water in concentrations up to 30 µg/l, whereas the concentrations in rain water was 10–100 ng/l. Laboratory investigations using an analytical method for enantiomer quantification (GC/MS) confirmed that a roof protection chemical (a bi-ester of mecoprop) added to the bitumen roofing material was the source of the racemic mecoprop in the roof-runoff water [3]. As is discussed in detail elsewhere [4] the occurrence (seasonal and the within event (washout behavior) variation), and the corresponding load of pesticides during rain events from the roofs are important parameters for designing infiltration sites.

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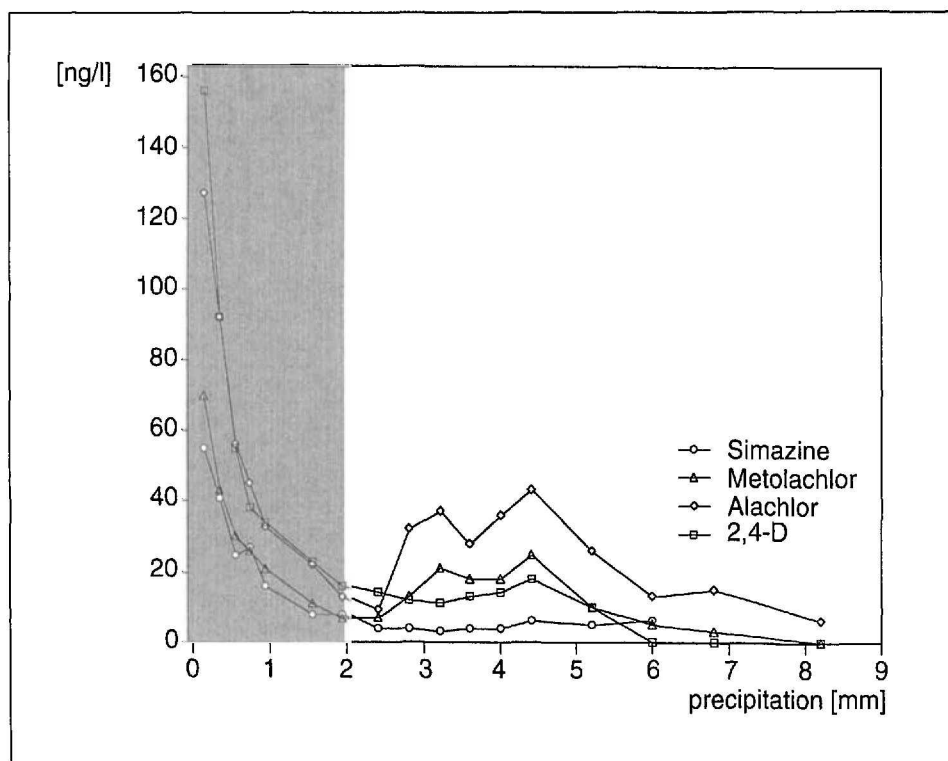


Fig. 1. Variation of the concentrations of some pesticides in rain water during a rain event in April, 1997 in Dübendorf

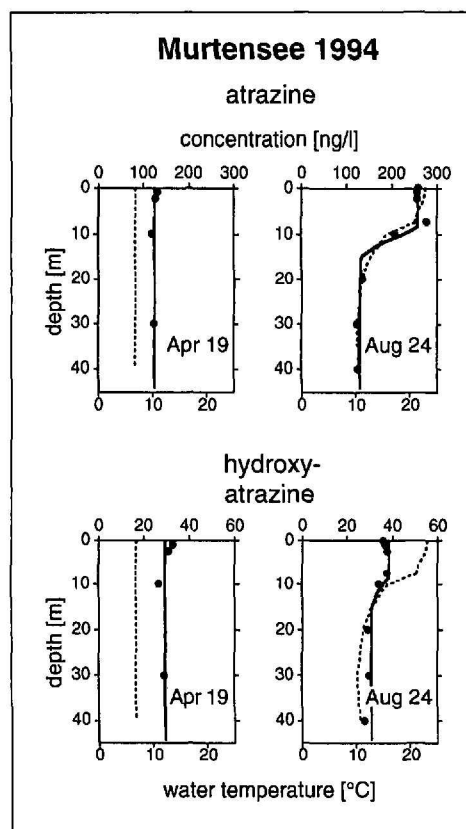


Fig. 2. Selected vertical concentration profiles of atrazine and hydroxyatrazine (dots), and of temperature (dotted lines) measured at the deepest point in Murtensee in 1994. Solid lines: Result of a computer simulation using the input as the sole fitting parameter (for details see [5][7]).

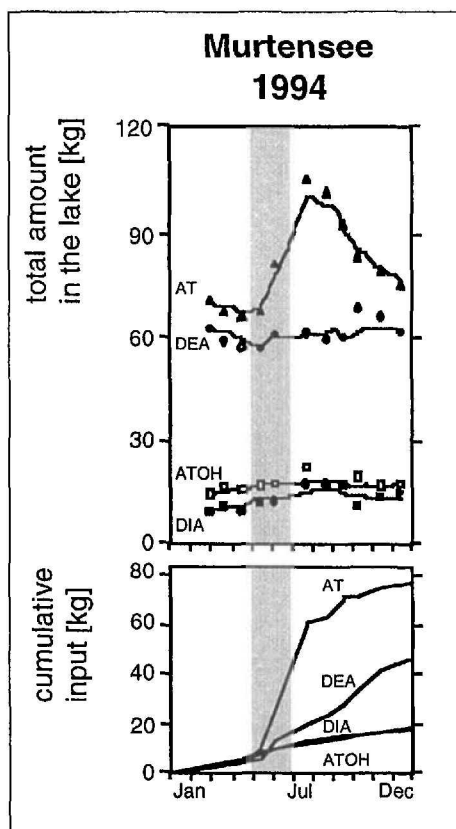


Fig. 3. Top: Time courses of the total amounts of atrazine and its primary metabolites in Murtensee in 1994; dots represent the total measured amount (calculated from the concentration profiles at the deepest point in the lake and of the corresponding water volumes). The solid lines are the results of the computer simulations using the input as the sole fitting parameter (for details see [5][7]). Bottom: Calculated cumulative inputs. The atrazine application period is marked with the shadowed bar.

Atrazine and Its Major Metabolites

Atrazine is still one of the most widely used pesticides worldwide. Until recently, rather little was known, about the occurrence, fate, and behavior of the major metabolites of atrazine in natural waters and in rainwater. For hydroxyatrazine, the major soil metabolite of atrazine, the only methods available were very time consuming and exhibited rather high detection limits. Due to its highly polar character, hydroxyatrazine requires derivatization to make it suitable for GC analysis, but unfortunately, derivatization by silylation or alkylation is not quantitatively reproducible. Clearly there was a need for analytical methods that allow accurate simultaneous determination of atrazine and its primary metabolites (*i.e.*, hydroxyatrazine, desethylatrazine, desisopropylatrazine) at trace levels, especially for the investigation of the input, transport, and transformation processes of these compounds in natural waters. The analytical method developed for this purpose is based on SPE and reversed-phase HPLC with diode-array detection (for details see [5]). Some illustrative results of this method for the investigations of the input and behavior of atrazine and its metabolites in lakes are given in Fig. 2. The selected vertical concentration profiles of atrazine and hydroxyatrazine determined at the deepest point in Murtensee illustrate significant input of both compounds during the atrazine application period in May and June. Fig. 3 shows the total amount of atrazine and its metabolites (top, dots) as well as the calculated inputs into the lake. Based on earlier investigations (see [6]) and in combination with this data set (monthly concentration profiles), it could be shown that the input of atrazine and its metabolites was into the epilimnion of the stratified lake. In addition, the behavior of atrazine and its metabolites in the lake was conservative (no elimination other than flushing), except for July/August where small elimination, most probably due to reaction with $\cdot\text{OH}$ radicals in the epilimnion, was observed (for details see [6][7]).

Tributyltin in Harbor Sediments: Analytical Methods for Sediments and Pore Water

Triorganotin compounds, particularly tributyltin (TBT) and triphenyltin (TPT), are among the most toxic substances ever deliberately released into the environment [8]. They are used as biocides in antifouling paints for boats (mainly TBT), and as

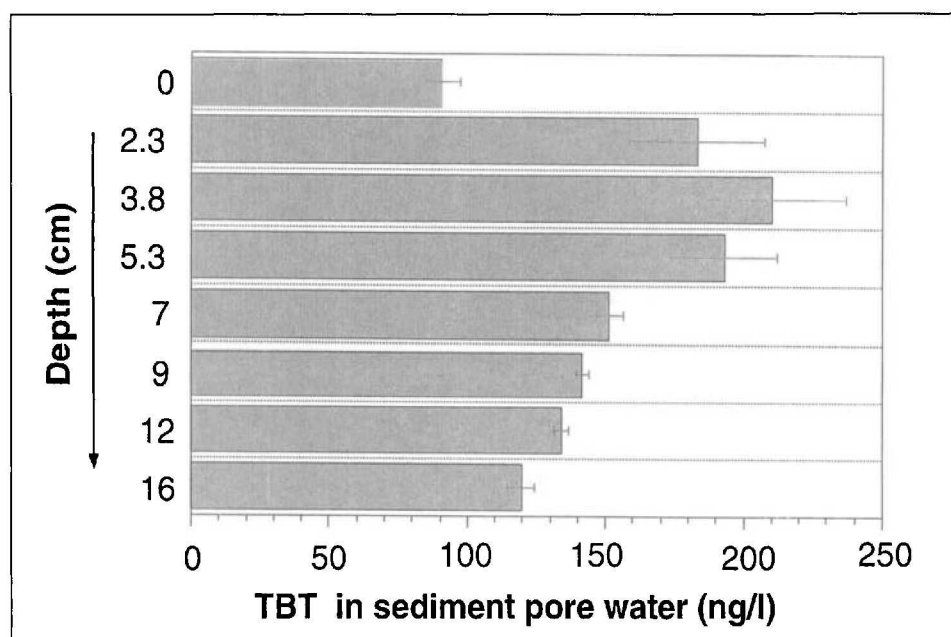


Fig. 4. Measured tributyltin (TBT) concentrations in the pore water of a harbor sediment

fungicides in agricultural applications (mainly TPT). Although the application of organotin compounds as biocides in anti-fouling paints is now restricted in many countries, an important question is whether the sediment bound organotin compounds which have accumulated over decades pose a threat to the aquatic ecosystem. To this end, analytical methods are required that allow to specify and quantify the compounds in sediments, pore waters and in the water column of surface waters. Many procedures, including different derivatization procedures liquid-liquid extraction or SPE, micro wave extraction, and separation and quantification methods (e.g., GC/FPD, HPLC fluorescence, GC-ICP/MS, etc.) have been developed for the determination of tinorganic compounds in environmental samples. However, all these methods have disadvantages such as the lack of specificity, sensitivity, precision, and accuracy. Therefore, we developed an analytical method using isotope-labeled internal standards for mono-, di-, and tri-substituted butyl and phenyl tins. For sediment analysis, accelerated solvent extraction was applied, followed by derivatization with NaBEt_4 , and quantification of the derivatized compounds by GC/MS. For quantification of the very low concentrations in the small sample volumes of sediment pore water (max. 20 ml), we employed aqueous phase derivatization of the compounds with NaBEt_4 followed, by liquid-liquid extraction, and then large volume injection (up to 50 μl). Alternatively we employed on-line coupling of the solid-phase extraction with GC-MS (for details see [9][10]).

Fig. 4 shows the concentration profile of tributyltin in a harbor sediment pore water. The observed concentration profile reflects the history of TBT use. The concentration difference between the pore water of the surface sediments and the overlaying surface water indicates that the sediments currently act probably as a source and not as a sink for organotin compounds in harbor water [9][10].

Future Challenges

The Swiss Federal Agricultural Department has initiated an ambitious project to quantify the effect of the Swiss agricultural policy measures (e.g., direct payments to the farmers) on the input of pesticides into surface waters. Together with the Swiss Federal Research Station in Wädenswil we will try to quantify the yearly input into surface waters of as many relevant pesticides as possible. For this project, new analytical methods quantifying additional types of pesticides including carbamates and urea derivatives will be necessary.

Furthermore, to assess the possible impact of pesticides on aquatic ecosystems, the pesticide metabolites have to be included in such studies. These are, e.g., the recently detected sulfonic and oxanilic metabolites of acetamides herbicides (e.g., of acetochlor for structures see Fig. 5) in surface waters. Since these compounds are optically active, analytical methods for the quantification of the individual enantiomers is required. Therefore, we are currently developing an analytical method

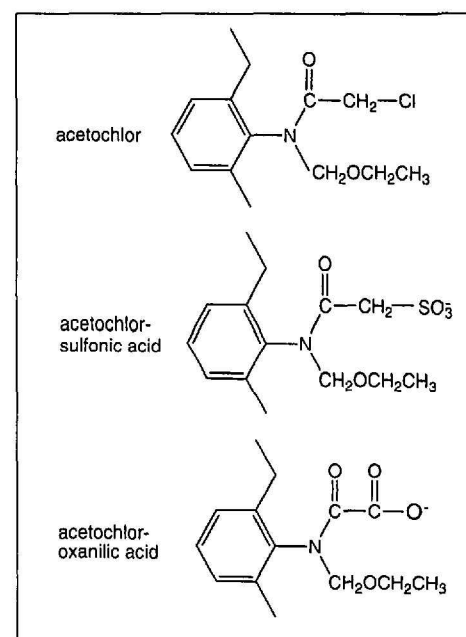


Fig. 5. Structures of acetochlor and its metabolites

for the parent acetamides, their sulfonic and oxanilic metabolites, and enantiomer separation. This includes SPE followed by a sequential elution of the parent compounds and metabolites, and GC/MS, HPLC and CZE as separation and quantification methods. Preliminary work with CZE has shown promising results in separating enantiomers of acetochlor oxanilic acids.

In conclusion, these examples show that quantification of trace organic compounds which cover a broad range of polarities and appear in different matrices presents a real challenge to environmental analytical chemist.

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