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**OCCURRENCE AND BEHAVIOR OF PESTICIDES
DURING STORM WATER INFILTRATION**

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Die eigentliche Erde aber erhebt sich rein in den reinen Himmelsraum, wo die Sterne sind und welchen die meisten, die von diesen Dingen reden, Äther nennen. Wasser, Nebel und Luft aber sind der Niederschlag davon und fließen fortwährend in die Vertiefungen der Erde zusammen. Wir aber wohnen in ihren Vertiefungen, ohne es zu wissen - sondern glauben uns auf der Oberfläche der Erde zu befinden...

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Summary

In recent years, artificial infiltration of storm water (rainwater from impervious areas, such as roads, and roofs) has become increasingly important in urban areas, as it reduces the overloading of sewer systems, and prevents the unwanted dilution of wastewaters. Furthermore, it supports the local natural water cycle in heavily populated regions by recharging the groundwater. Because of these benefits, direct infiltration of unpolluted storm waters is even enforced by Swiss legislation. However, the present uncertainties on the quality of storm waters, and in particular, of roof runoff waters, render the principle of storm water infiltration somewhat ambiguous. The major goal of this work was to contribute to the still rather scarce knowledge on the occurrence and behavior of pesticides and nitrophenols (NPs) in storm water infiltration systems.

For this purpose, an analytical method was developed for the routine simultaneous determination of neutral and acidic pesticides at the low ng/L concentration level in natural waters. It has been validated for, and applied to three important pesticide classes, namely the triazines (e.g., atrazine, and its primary metabolites desethylatrazine, and deisopropylatrazine), the acetamides (e.g., alachlor, metolachlor, and dimethenamid), and the phenoxy acids (e.g., 2,4-D, dichlorprop, and mecoprop). Additionally, a new solid phase extraction material consisting of conglomerated clay minerals (CCMs) was designed that proved to be specifically suited for the selective extraction of nitroaromatic compounds (NACs, and other planar aromatic compounds with electron withdrawing substituents) from aqueous solutions. A fully automated analytical method, using CCMs and online SPE-HPLC, was established for the analysis of selected NPs (e.g., DNOC, and 2,4-DNP), nitrotoluenes (NTs) and nitrobenzenes (NB, e.g., TNT, 4-A-2,6-DNT, and 1,3-DNB) in natural waters.

These analytical tools allowed to trace a set of important pesticides in rainwater, runoff from different types of roofs, and percolating waters during artificial storm water infiltration. From various field studies, the following main results were obtained: the investigated pesticides were mainly present in rainwater during their application period (March to June for most compounds). Atrazine was by far the most important pesticide, and its concentration in rainwater surpassed the Swiss, and EC drinking water standards for single compounds of 100 ng/L several times. Atmospheric deposition mainly occurred in a first flush manner, i.e., with highest concentrations at the begin of a rain event. Pesticide occurrence in roof runoff was found to be heavily influenced by the type of roof. Whereas the pesticide runoff from roofs with little storage capacity usually mirrored the atmospheric washout dynamics, particularly the flat roofs had a strongly equalizing effect on the deposition pattern. The concomitant determination of pesticide

concentrations in roof runoff, and percolating waters of a storm water infiltration site revealed that no significant elimination of these compounds took place on their way into the subsurface.

Annual pesticide loads in rainwater in Switzerland were found to be within the range of a few percent of the applied amount at most. The pesticide load discharged from the atmosphere via roof runoff and artificial storm water infiltration into the subsurface may locally reach a similar order of magnitude as the groundwater pesticide charge in agricultural areas.

NPs were found to occur regularly in rainwaters at concentrations that frequently exceeded the drinking water standards. Also, the annual loads that locally may be transported into the subsurface by storm water infiltration are assumed to be significantly higher for NPs than for pesticides.

Flat roofs equipped with bituminous membranes containing the root protection agent Preventol® B 2 were found to permanently deliver (R,S)-mecoprop. This herbicide was measured in the respective roof runoffs in concentrations of usually 1 to 30 µg/L. Local annual loads in storm water infiltration sites were estimated to reach numbers that equal the amounts used in agriculture, i.e., around 1 kg/ha.

Based on these results, the investigated compounds may be divided into three different categories with regard to their significance for storm water infiltration:

1) Atmospherically delivered pesticides are, even though the respective storm waters do not meet the drinking water standards at times, not likely to cause a significant pollution problem within storm water infiltration sites.

2) Atmospherically delivered NPs, however, may, in terms of occurrence, concentrations, and annual loads, be of significant environmental concern, especially when considering the aggravating characteristics of storm water infiltration sites, such as the concentration of atmospheric loads, and the accelerated passage of the subsurface.

3) Roof delivered (R,S)-mecoprop must be attributed maximal relevance with respect to storm water infiltration and groundwater contamination potential. Concentrations, and annual loads exceed the ones of the atmospherically delivered pesticides by up to 1000 fold.

These findings lead to the conclusion that, when designating contribution areas around drinking water wells or springs, as suggested by experts, storm water infiltration sites should be specifically evaluated.

Zusammenfassung

Während der letzten Jahre hat die künstliche Versickerung von Meteorwasser (auf versiegelte Flächen fallender Niederschlag) insbesondere in dicht besiedelten Gebieten an Bedeutung gewonnen, da sie die Überlastung der Kanalisationsanlagen reduziert und die unerwünschte Verdünnung von Abwässern verhindert. Des weiteren unterstützt sie den natürlichen lokalen Wasserhaushalt durch die Grundwasserneubildung. Aufgrund dieser Vorteile ist die Versickerung von unverschmutztem Meteorwasser in der Schweiz gesetzlich vorgeschrieben. Wegen der bestehenden Ungewissheit über die Qualität von Meteor-, und im speziellen von Dachwasser, bleibt ihre Anwendung jedoch zwiespältig. Das hauptsächliche Ziel der vorliegenden Arbeit war deshalb, einen Beitrag zum Verständnis des Auftretens und Verhaltens von Pestiziden und nitroaromatischen Substanzen (NAS) in Meteorwasserversickerungsanlagen zu leisten.

Zu diesem Zweck wurde eine spurenanalytische Methode zur gemeinsamen Bestimmung von neutralen und sauren Pestiziden in natürlichen Wässern entwickelt. Sie wurde für drei wichtige Pestizidklassen validiert und angewendet, nämlich für die Triazine (z. Bsp. Atrazin, sowie seine wichtigsten Abbauprodukte Desethylatrazin und Desisopropylatrazin), die Acetamide (z. Bsp. Alachlor, Metolachlor und Dimethenamid) und die Phenoxyalkansäuren (z. Bsp. 2,4-D, Dichlorprop und Mecoprop). Des weiteren wurde ein neues Festphasenextraktionsmaterial auf der Basis von Tonmineralien entwickelt, welches sich besonders zur selektiven Extraktion von NAS und anderen planaren aromatischen Verbindungen mit elektronenziehenden Substituenten eignet. Die Verwendung dieses Materials in einer online SPE-HPLC Methode ermöglichte eine vollautomatische Analyse von ausgewählten Nitrotoluolen und Nitrobenzolen (z.Bsp. TNT, 4-A-2,6-DNT und 1,3-DNB), sowie Nitrophenolen (NP, z.Bsp. DNOC und 2,4-DNP).

Diese analytischen Methoden erlaubten, eine Reihe wichtiger Pestizide im Regen, verschiedenen Dachabflüssen, sowie in Sickerwässern während der künstlichen Versickerung von Meteorwasser zu verfolgen. Diverse Feldstudien ergaben folgende Resultate: Die untersuchten Pestizide traten hauptsächlich während ihrer jeweiligen Applikationsperiode (März bis Juni) im Regenwasser auf. Atrazin war bei weitem das wichtigste Pestizid. Seine Konzentration überschritt mehrmals den schweizerischen Trinkwasser-Toleranzwert, sowie den Trinkwasser-Grenzwert der EU von jeweils 100 ng/L. Die atmosphärische Deposition der untersuchten Pestizide erfolgte grösstenteils mit maximalen Konzentrationen zu Beginn eines Regenereignisses, d.h. über einen First Flush. Das Auftreten der Pestizide im Dachabfluss war stark abhängig vom

untersuchten Dachtyp. Während Dächer mit geringer Speicherkapazität die Dynamik der atmosphärischen Deposition der Pestizide in ihrem Abfluss widerspiegeln, bewirkten insbesondere Flachdächer eine Dämpfung des Konzentrationsverlaufes. Die gleichzeitige Analyse von Pestiziden im Dachabfluss und in Sickerwässern einer Meteorwasserversickerungsanlage ergab, dass während der Infiltration keine signifikante Elimination dieser Verbindungen stattgefunden hatte.

Geschätzte jährliche Pestizidfrachten im Regen lagen in der Schweiz im Bereich von wenigen Prozent des landwirtschaftlichen Verbrauchs. Die Fracht, welche aus der Atmosphäre über Dachabflüsse und künstliche Meteorwasserversickerung in den Untergrund gelangt, könnte lokal in derselben Grössenordnung liegen wie die Pestizidfracht einer vergleichbaren landwirtschaftlichen Fläche.

Messungen der NP im Regenwasser ergaben, dass diese regelmässig in Konzentrationen auftraten, welche die Trinkwasser-Toleranzwerte überschritten. Ausserdem waren die abgeschätzten jährlichen Frachten, die lokal über die Meteorwasserversickerung in den Untergrund gelangen können, deutlich höher als diejenigen der untersuchten Pestizide.

Flachdächer, die mit Bitumenbahnen ausgerüstet waren, welche das Wurzelschutzmittel Preventol® B 2 enthielten, setzten permanent (R,S)-Mecoprop frei. Dieses Herbizid wurde in den entsprechenden Dachabflüssen in Konzentrationen zwischen 1 und 30 µg/L gemessen. Die Frachten, welche über die entsprechenden Versickerungsanlagen in den Untergrund gelangten, wurden auf bis zu 100 % der landwirtschaftlich ausgebrachten Menge geschätzt, d.h. ca. 1 kg/ha.

Aufgrund dieser Resultate können die untersuchten Substanzklassen hinsichtlich ihrer Bedeutung für die Meteorwasserversickerung in drei Kategorien unterteilt werden:

1) Atmosphärisch deponierte Pestizide werden, auch wenn sie während der Anwendungsperiode die Trinkwasser-Toleranzwerte im Regenwasser überschreiten können, die Grundwasserqualität im Einzugsgebiet von Meteorwasserversickerungsanlagen kaum beeinträchtigen.

2) Atmosphärisch deponierte NP können hingegen aufgrund ihres ganzjährigen Auftretens in vergleichsweise hohen Konzentrationen und der daraus resultierenden Frachten von einer gewisser Umweltrelevanz sein. Dies insbesondere wegen der spezifischen Eigenheiten von Versickerungsanlagen, wie der Aufkonzentrierung der atmosphärischen Frachten, und der beschleunigten Infiltration.

3) Spezielle Bedeutung kommt dem Herbizid (R,S)-Mecoprop aus Flachdächern zu. Ihm muss von allen untersuchten Substanzen in den entsprechenden Versickerungsanlagen das höchste Grundwasser-Gefährdungspotential zugewiesen

werden. Konzentrationen und jährliche Frachten übertreffen diejenigen der atmosphärisch deponierten Pestizide um einen Faktor von bis zu 1000.

Aufgrund dieser Resultate lässt sich folgern, dass bei der Festlegung von Zuströmbereichen um Trinkwasserfassungen, wie sie von Experten vorgeschlagen wird, auch Meteorwasserversickerungsanlagen berücksichtigt und überprüft werden sollten.

Leer - Vide - Empty

Abbreviations

1,3-DNB	1,3-dinitrobenzene
2-NP	2-nitrophenol
2,4-DNP	2,4-dinitrophenol
2,6-DA-4-NT	2,6-diamino-4-nitrotoluene
4-A-2,6-DNT	4-amino-2,6-dinitrotoluene
ACN	acetonitrile
CCMs	conglomerated clay minerals
CEC	cation exchange capacity
CsCl	caesium chloride
DNOC	2,4-dinitro-6-methylphenol
DOC	dissolved organic carbon
EA	ethyl acetate
EAWAG	Swiss Federal Institute of Environmental Science and Technology
EC	European Community
EC0	zero effective concentration (biomass, or growth rate)
EC50	median effective concentration (biomass, or growth rate)
ECD	electron capture detector
EDA	electron donor-acceptor
FID	flame ionization detector
GC	gas chromatography
GCB	graphitized carbon black
HCl	hydrochloric acid
HO(PEG)OH	polyethylene glycol
HPLC	high performance liquid chromatography
K _{ow}	octanol-water partition coefficient
LC	liquid chromatography
LC50	concentration required to kill 50% of test organisms
LD50	dose required required to kill 50% of test organisms
LiCl	lithium chloride
RSM(PEG)RSM	(R,S)-mecoprop polyethylene glycol diester
RSM(PEG)OH	(R,S)-mecoprop polyethylene glycol monoester
MDL(s)	method detection limit(s)
MeCl ₂	dichloromethane
MeOH	methanol

MS	mass spectrometry
n	number of samples
NaCl	sodium chloride
NACs	nitroaromatic compounds
NAS	Nitroaromatische Substanzen
NaOH	sodium hydroxide
NB	nitrobenzene
NPs	nitrophenols
NTs	nitrotoluenes
PE	polyethylene
pK_a	negative decadic logarithm of the acidity constant
RSM	(R,S)-mecoprop
SD	standard deviation
SIM	single ion monitoring
SPE	solid phase extraction
TFA	trifluoro acetic acid
TNT	2,4,6-trinitrotoluene
WHO	World Health Organisation
λ	wavelength [nm]

1. Introduction

1.1 The Principle of Storm Water Infiltration

Since the end of the last century, urban drainage systems have aimed at a fast and complete transport of both polluted and unpolluted waters from urban areas into the receiving waters. With that strategy, sanitary conditions in residential areas were tremendously improved, and the danger of flooding minimized. Nowadays, both combined and separated sewer systems transport huge amounts of waters over large distances, and the former leads to a mixing of originally less polluted waters with wastewater, which causes unwanted dilution. Moreover, enormous costs will arise during the next decade for renewal, reconstruction, and replacement of the existing installations.

When considering these problems, direct infiltration of storm waters (rainwater runoff from sealed surfaces, such as roads, and roofs) offers an alternative or supplement measure to the conventional sewer systems. The advantages seem to be manifold, including a decrease of hydraulic loads to wastewater treatment plants, a decrease of sewage overflow from combined sewers, a decrease of peak flows in urban drainage systems, and an increase of groundwater recharge (Boller, 1997). It is for these reasons that in Switzerland the infiltration or direct discharge into receiving waters of storm water is even forced by law (Swiss Federal Law on the Protection of Waters, 1993, Article 7, Paragraph 2).

However, the concept of storm water infiltration is somewhat ambiguous, as some considerable drawbacks are inherent, namely the deterioration of soil quality at infiltration sites by adsorption of heavy metals and non-biodegradable organic substances, the increase of the pollutant loading rates by a factor of 5 to 100 by concentrating large runoff areas in small infiltration sites, the decrease of groundwater quality by infiltration of hydrophilic substances and potential leakage of accumulated pollutants, the increased transport of colloidal and dissolved matter to the groundwater by exclusion of humus surface layers at infiltration sites, and the increased potential risk for soil and groundwater by mismanipulation and accidents with chemicals in the catchment of infiltration sites (Boller, 1997).

To date, there is still a lack of data concerning the quality of storm water, especially of roof runoff waters. A few investigations dealt with metals in roof runoff (Quek & Förster, 1993; Yaziz et al., 1989), but much less information is available on organic compounds (Förster, 1993), particularly on pesticides. It is for this reason that a multidisciplinary priority research program on storm water infiltration has been

conducted at EAWAG within the last years. One of the main objectives of this project was to determine the main pollutants in roof runoff, and to elucidate their significance for storm water infiltration systems. This dissertation, placed within the framework of that project, focused on the occurrence and behavior of organic pollutants, namely pesticides and nitroaromatic compounds (NACs), during storm water infiltration.

1.2 Organic Atmospheric Pollutants

Considering the tremendous global consumption of herbicides (around 2.5 million metric tons per year, and 50 % of the total pesticide usage, Albert et al., 1992; WHO, 1990), it is not surprising that many of these compounds have been detected in surface water (Bester & Hühnerfuss, 1993; Buser, 1990), and groundwater (for review, see: Funari et al., 1995). Because of their ubiquitous occurrence in these waters, they have raised considerable concern both from a human health, as well as from an environmental point of view. It is for these reasons, and because of the decision to keep drinking waters free of pesticides, that the Swiss drinking water standard, as well as the EC drinking water limit was set to 0.1 µg/L for individual pesticides, and 0.5 µg/L for the total content.

The introduction of these compounds into the atmosphere mainly occurs during their application by drift, but also by continuous evaporation or wind erosion from soil. Although there are quite a few reports on the occurrence of pesticides in rainwater (Nations & Hallberg, 1992; Richards et al., 1987; Siebers et al., 1994; Trevisan et al., 1993), fog (Glotfelty et al., 1987; Schomburg et al., 1991), roof runoff (Förster, 1993), and percolating waters in agricultural areas (Bergstrom, 1995; Demon et al., 1994; Gish et al., 1995; Kruger et al., 1996), there is a deficiency in integrated studies focusing on the transfer of pesticides from the atmosphere to groundwater during storm water infiltration. Thus, based on the present knowledge, the importance of pesticides with regard to direct infiltration of roof runoff can not be assessed satisfactorily.

Of the about 20 different classes of herbicides, the triazines, the acetamides, and the phenoxy acids are both world-wide, and in Switzerland among the most widely used compounds. Prominent examples include atrazine, metolachlor, alachlor, and 2,4-D of which several tens of metric tons, and several thousands of metric tons are used every year in Switzerland, and the US (Gianessi & Anderson, 1995), respectively. To investigate the most important representatives of this large variety in pesticides, multi-pesticide residue analyses at trace concentrations are required. Routine methods that

offer, on the one hand good sensitivity, and on the other hand, may be used as screening tools, are scarce.

Other organic substances that are of concern with regard to storm water infiltration are the NPs. They are formed in Otto motors and in the atmosphere by photochemical reactions with alkylbenzenes and alkylphenols (Trempe, 1992). Moreover, nitroaromatic pesticides, such as parathion and 2,4-dinitro-6-methylphenol (DNOC), are emitted to the atmosphere by evaporation and drift during application. Even though the fate and behavior of nitrophenols (NPs) in the atmosphere, as well as their occurrence in rainwater, have been extensively studied (e.g., Alber et al., 1989; Herterich, 1991; Leuenberger et al., 1988; Levsen et al., 1990; Lüttke & Levsen, 1997; Lüttke et al., 1997; Richartz et al., 1990; Trempe, 1992), few investigations dealt with NPs in storm water (Förster, 1993). The significance of NPs within storm water infiltration is therefore largely unknown. Also, concomitant studies on NPs together with the main representatives of different pesticide classes are scarce (Geissler & Schöler, 1993). Moreover, the available methods for the detection of NACs in natural waters are rather cumbersome and time-consuming, or lack specificity.

1.3 Biocides as Additives in Construction Materials

Apart from the atmosphere, one can imagine a second major source that may deliver significant amounts of pesticides within storm water infiltration systems, namely the roofs themselves. Biocides are used in considerable amounts as construction material additives, for example in plastics (Swiss annual consumption: 18 - 160 t), or as wood preservatives (40 - 80 t/yr, BUWAL, 1995). Because of the mode of action of biocides, and the prerequisite to be bioavailable in order to serve their purpose, these compounds may have the capacity to enter the environment. The leaching potential, and the influence of such construction chemicals on the quality of wastewaters, and, more specifically on roof runoff water, has not yet been investigated. To address these questions, the roof protection agent Preventol® B 2, which is added to bituminous roofing membranes and belongs to the most widely used organic construction chemicals with biocide activity, served as a model substance for an illustrative case study.

1.4. Objectives of this Work

To contribute to the knowledge on the occurrence and behavior of pesticides and related compounds during storm water infiltration, the present dissertation sought

- 1) To establish a sensitive and specific analytical method that allows the routine simultaneous determination of neutral and acidic pesticides in natural waters at the low ng/L concentration level.
- 2) To develop a fully automated analytical method, using online SPE on conglomerated clay materials (CCMs), and HPLC, for the analysis of selected NACs in natural waters.
- 3) To investigate for a series of important pesticides the occurrence and seasonal variation in concentration, as well as their deposition behavior.
- 4) To provide initial results on the atmospheric occurrence, and washout dynamics of NPs, and to relate them to the respective findings for the pesticides.
- 5) To study the influence of different types of roofs on the runoff loads and dynamics of pesticides.
- 6) To assess the fate of pesticides during percolation into the subsurface within a storm water infiltration site.
- 7) To unravel the processes by which the root protection agent Preventol[®] B 2, being a representative of biocides used as construction chemicals, may enter the aqueous environment, and to elucidate its occurrence in roof runoff.
- 8) To judge the potential of atmospherically, or roof delivered pesticides for groundwater contamination within storm water infiltration systems.

These tasks were pursued as follows:

Chapter 2, and 3 describe the development of the methods for the multi-residue pesticide analysis, and selected NACs, respectively.

Chapter 4 reports on the occurrence and washout dynamics of a series of pesticides in rainwater, the influence of selected roof types on the pesticide roof runoff, as well as the behavior of these substances during infiltration into the subsurface.

Chapter 5 contains initial results on the occurrence and behavior of NPs in rainwater

Chapter 6 investigates the elution of Preventol® B 2 and its hydrolysis product, (R,S)-mecoprop, from bituminous roofing membranes, and the occurrence of (R,S)-mecoprop in roof runoff. The main pathways of (R,S)-mecoprop in the environment are sketched out, and the environmental relevance of this additional source is discussed.

Chapter 7 highlights the major results from the investigations on selected pesticides and NPs in storm water and their interrelationships. Finally, some conclusions on the importance and the pollution potential of these compounds within storm water infiltration systems are drawn.

Leer - Vide - Empty

2. Development of an Analytical Method for the Simultaneous Determination of Neutral and Acidic Pesticides in Natural Waters at the Low Nanogram per Liter Level¹

2.1 Introduction

In order to assess the processes that determine the fate of various pesticides from the atmosphere via roof runoff and infiltration into the subsurface, appropriate analytical methods for the routine simultaneous determination of a large number of such compounds at trace concentrations in water samples are required. To date, the US National Pesticide Survey has developed six different methods for the determination of over 100 pesticides in groundwater with limits of quantification ranging from 0.1 to about 5 µg/L for most compounds (Munch et al., 1990). In addition, several other techniques for multi-residue pesticide analysis in natural waters have recently been applied to environmental samples, including solid phase extraction (SPE)-GC/MS (Benfenati et al., 1990), SPE-HPLC (Schlett, 1991), LC/GC (Noij & Vanderkooi, 1995), or LC/MS (Bagheri et al., 1993; Chiron et al., 1994), but few methods allow the simultaneous determination of both neutral, and acidic pesticides. One of the first methods published by Cessna et al. (1985) used liquid-liquid extraction, derivatization of the acidic pesticides with diazomethane, and GC/ECD and GC/FID for separation and detection. More recently, SPE-HPLC (Di Corcia & Marchetti, 1992; Liska et al., 1992; Nouri et al., 1995), and LC/MS (Cappiello et al., 1994) were used to achieve that goal. However, the former method lacks a reliable, sufficiently sensitive, and highly specific detector, and the latter is too sophisticated for routine analysis at trace concentrations.

In this chapter, a new method that attempts to overcome these drawbacks is described. The method allows the routine simultaneous determination of triazines (Fig. 2.1, a), acetamides (Fig. 2.1, b), and phenoxy acids (Fig. 2.1, c) in natural waters at the low ng/L concentration level. Major emphasis was placed on the simplification of the usually cumbersome and tedious sample preparation, particularly for the analysis of acidic substances with GC/MS.

¹ Bucheli, T.D., F. C. Grüebler, S. R. Müller and R. P. Schwarzenbach. 1997. *Anal. Chem.* 69, 1569-1576.

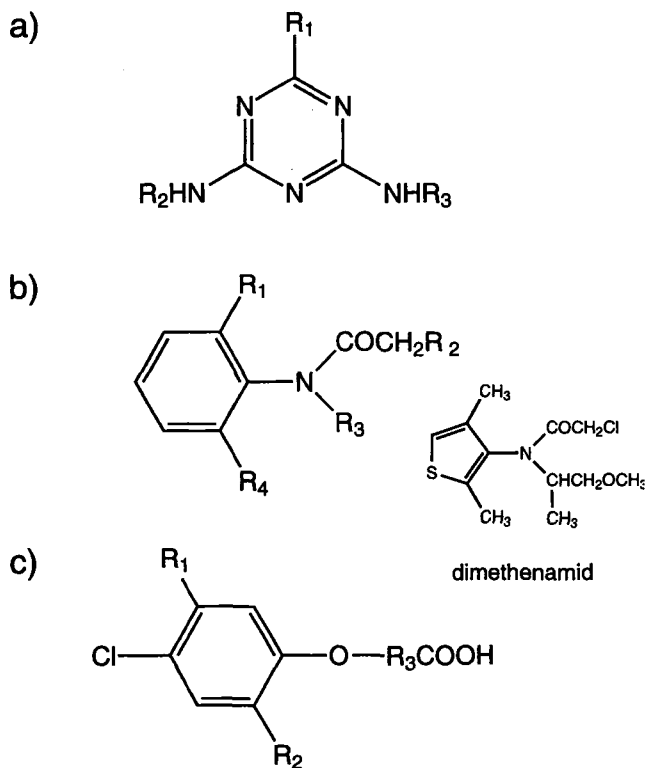


Figure 2.1 Structure of the s-triazines (a), the acetamides (b), and the phenoxy acids (c). The substituents R_1 , R_2 , R_3 , and R_4 for different compounds analyzed are specified in Table 2.1.

2.2 Experimental Section

2.2.1 Materials

The pesticides investigated are listed in Table 2.1. Dimethenamid (99.8 %) was kindly provided by Sandoz Agro LTD (Basle, Switzerland). All other pesticides (purity >97 %) were purchased from Riedel-de Haën (Seelze, Germany). The internal standards pentadeuterioatrazine (ethyl- d_5 , 99 %), ring- $^{13}C_6$ -labelled metolachlor (99 %), and ring- $^{13}C_6$ -labelled dichlorprop (99 %) were obtained from Cambridge Isotope Laboratories (Andover, MA).

Table 2.1 Investigated pesticides and their structures, retention times, and ions monitored

Compound	substituent in position ^a				ret. time [min]	masses [m/z] ^d
	R ₁	R ₂	R ₃	R ₄		
triazines						
atratron	-OCH ₃	-CH ₂ CH ₃	-CH(CH ₃) ₂		11.8	196, <u>211</u>
atrazine	-Cl	-CH ₂ CH ₃	-CH(CH ₃) ₂		13.9	200, <u>215</u>
atrazine-d ₅ ^b	-Cl	-CD ₂ CD ₃	-CH(CH ₃) ₂		13.8	205, <u>220</u>
desethylatrazine	-Cl	-H	-CH(CH ₃) ₂		14.4	172, <u>187</u>
deisopropylatrazine	-Cl	-CH ₂ CH ₃	-H		15.2	<u>173</u> , 158
propazine	-Cl	-CH(CH ₃) ₂	-CH(CH ₃) ₂		13.1	214, <u>229</u>
simazine	-Cl	-CH ₂ CH ₃	-CH ₂ CH ₃		14.7	186, <u>201</u>
terbutylazine	-Cl	-CH ₂ CH ₃	-C(CH ₃) ₃		13.7	214, <u>229</u>
acetamides						
acetochlor	-CH ₃	-Cl	-CH ₂ OCH ₂ CH ₃	-CH ₂ CH ₃	15.1	162, 146
alachlor	-CH ₂ CH ₃	-Cl	-CH ₂ OCH ₃	-CH ₂ CH ₃	15.9	160, 188
dimethenamid	for molecule structure: see Fig. 2.1				15.6	154, 230
metalaxyl	-CH ₃	-OCH ₃	-CHCH ₃ COOCH ₃	-CH ₃	17.9	206, 249
metazachlor	-CH ₃	-Cl	-CH ₂ N ₂ (CH ₃) ₃	-CH ₃	24.4	132, 209
metolachlor	-CH ₂ CH ₃	-Cl	-CHCH ₃ CH ₂ OCH ₃	-CH ₃	17.8	162, 238
metolachlor- ¹³ C ₆ ^c	-CH ₂ CH ₃	-Cl	-CHCH ₃ CH ₂ OCH ₃	-CH ₃	17.8	168, 244
propachlor	-H	-Cl	-CH(CH ₃) ₂	-H	10.1	120, 176
phenoxy acids						
2,4-D	-H	-Cl	-CH ₂ -		9.7	<u>234</u> , 199
dichlorprop	-H	-Cl	-CH(CH ₃)-		8.4	<u>248</u> , 162
dichlorprop- ¹³ C ₆ ^c	-H	-Cl	-CH(CH ₃)-		8.4	<u>254</u> , 168
MCPA	-H	-CH ₃	-CH ₂ -		8.0	<u>214</u> , 141
mecoprop	-H	-CH ₃	-CH(CH ₃)-		7.3	<u>228</u> , 171
2,4,5-T	-Cl	-Cl	-CH ₂ -		12.5	<u>233</u> , <u>268</u>
2,4,5-TP	-Cl	-Cl	-CH(CH ₃)-		10.5	198, <u>282</u>

^a substituents of the structures in Fig. 2.1, a-c. ^b internal standard for GC/MS. ^c internal standards for GC/MS, ring marked isotopes. ^d first number: quantification mass, underlined number: mass of the molecular ion (or the respective methylester for phenoxy acids).

Methanol (MeOH), dichloromethane (MeCl₂), toluene, and ethyl acetate (EA) (all with purity for pesticide residue analysis) were obtained from Burdick & Jackson (Muskegon, MI). Ascorbic acid (> 99.5 %), and trifluoro acetic acid (TFA, > 98 %) were from Fluka AG (Buchs, Switzerland). HCl (37 %) was purchased from Merck (Darmstadt, Germany). Nitrogen (99.995 %) was from Carbagas (Rümlang, Switzerland). Deionized water was further purified with a Nanopure water purification device (NANOpure 4, Skan, Basle, Switzerland).

Diazomethane (ca. 0.4 M in diethyl ether) was freshly produced on the day before use as described in de Boer & Backer (1963) and stored at -20 °C. *Beware: diazomethane is carcinogenic, and, under certain conditions, explosive. All manipulations should be carried out in a hood and with great care!*

2.2.2 Standard Solutions

For all pesticides, stock solutions of 1000 mg/L were prepared by dissolving 25 mg of each compound in 25 mL of MeOH (triazines and acetamides, except dimethenamid) or EA (phenoxy acids, and dimethenamid). All solutions were further diluted with the respective solvents to obtain a final concentration of 20 mg/L per compound. For the triazines, and the acetamides, respectively, standard mixtures (0.4 mg/L, except for atrazine, alachlor, and metolachlor: 1 mg/L) were produced from the single compound solutions. The phenoxy acid standard mixture contained 1 mg/L of each compound. Standard mixtures were used for calibrations and for the preparation of fortified samples. Each internal standard was diluted in toluene to yield a concentration of 7.5 mg/L. All solutions were stored at 4 °C in the dark.

2.2.3 Sampling and Sample Preparation

Roof runoff and rain samples were collected in Tüffenwies, an industrial area in the north-western part of Zurich (for details on the field site, see chapter 4). Lake water was from Murtensee (western part of Switzerland). Ground water samples were taken in the vicinity of the municipal landfill of Winterthur (Riet, Canton Zurich, Switzerland), and the landfill of Kölliken (Canton Aargau, Switzerland). All samples were kept at 4 °C in the dark.

Prior to analysis, water samples were allowed to reach room temperature. Natural water samples were filtered (cellulose nitrate filter, diameter 5 cm, pore size 0.45 µm; Satorius, Goettingen, Germany), and the exact volume of 1 L was spiked with 10 µL (75 ng/L) of each internal standard. For recovery studies, and/or internal calibration, Nanopure water and natural waters were spiked with the standard mixtures of all pesticide classes, and/or internal standards. The samples were shaken vigorously and set aside over night.

2.2.4 Solid Phase Extraction (SPE)

Commercially available 6 mL glass cartridges were filled in the laboratory with 250 mg of GCB (graphitized carbon black, Carbopack B) between two Teflon fritts and mounted on a 12fold-vacuum extraction box (all products from Supelco, Bellafonte, CA). Conditioning of the cartridges and extraction of the samples was carried out as

described in Berg et al. (1995). Briefly, the solid phase was treated with 8 mL MeCl₂/MeOH (80 : 20, v/v), 4 mL MeOH, 20 mL ascorbic acid solution (10g/L, acidified with HCl to pH 2), and 10 mL Nanopure water. 1 L samples were then drawn through the cartridges at a flow rate of 15 mL/min. Thereafter, the solid phase was washed with 5 mL of Nanopure water and 0.5 mL of MeOH, and air dried for 5 minutes.

Sequential elution from the same cartridge was performed by first eluting the neutral fraction with 1 mL of MeOH, and 6 mL of MeCl₂/MeOH (80 : 20, v/v), followed by a second elution of the acidic fraction with 6 mL of MeCl₂/EA (80 : 20, v/v) acidified with TFA (0.2 %, v/v; solution produced immediately before use). After each of the two elution steps, cartridges were air-dried for 5 minutes to allow maximum solvent elution and a minimum of interferences between the two elution solvents. Both fractions were separately collected in conical glass vials (7.5 mL; Supelco, Bellafonte, CA).

Both eluates were concentrated by evaporating the solvent to a final volume of 200 ± 50 µL at ambient temperature using a gentle nitrogen stream for about 30 min. To diminish the remaining MeOH content, 200 µL of EA were then added to the neutral fraction and the volume was again reduced to 200 ± 50 µL. Diazomethane solution (500 µL to 3 mL, varying from sample to sample) was slowly added to the acidic fraction until the solution kept the yellow colour of the derivatization reagent. After 15 minutes, the volume was carefully reduced to 200 ± 50 µL again, whereby the excess derivatization agent was removed. Finally, the solution was passed through a 0.45 µm filter (Spartan 13, Schleicher & Schuell, Dassel, Germany).

2.2.5 GC/MS Analysis

Separation of both the neutral, and acidic analytes was carried out with a Fisons Instruments HRGC 8000 Series on a home made fused silica capillary column (32 m, 0.25 mm i.d., OV240OH (33 % Cyanopropyl, 66 % Methyl), 0.3 µm film thickness), using helium as carrier gas (150 kPa, 2.6 mL/min). 1 µL of the neutral, or the acidic sample, respectively, was injected with split/splitless mode. The injector temperature was 200 °C. The oven temperature was programmed as follows: 1 min at 120 °C, to 195 °C at 20 °C/min, to 225 °C (212 °C for acidic fraction) at 1.5 °C/min, to 260 °C at 5 °C/min (20 °C/min for acidic fraction), 2 min at 260 °C. The interface temperature was 250 °C. Detection was performed with a FI MD 800 mass spectrometer in the electron impact mode (EI⁺, 70 eV) and single ion monitoring (SIM). Identification of a given

analyte was assured by using 2 compound specific ions (see Table 2.1) with identical retention times and a mass ratio similar to the one determined with internal calibration (less than 20 % variation). Undisturbed single ion mass traces exhibiting maximum sensitivity and minimal background noise were used for quantification.

2.2.6 Calibrations, Absolute and Relative Recoveries, and MDLs

Mixtures containing different amounts of standard and internal standard solutions in EA were directly used for external calibrations. For internal calibrations, 1 L of Nanopure water was spiked with standard and internal standard solutions, and the analytes extracted and analysed as described above. Absolute recoveries were determined using external calibrations, and isotope-labelled substances as volumetric standards (Table 2.2). The isotope-labelled substances were added immediately before GC/MS analysis for the neutral fraction, and before derivatization of the acidic fraction. To determine relative recoveries in Nanopure water, samples spiked with both standards, and internal standards before SPE were compared with others samples which were fortified with standards before SPE, but had internal standards added afterwards (Table 2.2). For rainwater, internal standards were added before SPE for all samples, and half of them were spiked with standards. All samples were quantified using internal calibrations.

Table 2.2 Determination procedure for absolute and relative recoveries

	absolute recoveries		relative recoveries	
	Nanopure water	rainwater	Nanopure water	rainwater
calibration:	external (in EA)	external (in EA)	internal	internal
standards added:	before SPE	before SPE	before SPE	before SPE, spiked vs unspiked
internal standards added:	after SPE	after SPE	before vs after SPE	before SPE

The MDLs are defined as three times the standard deviations (SDs) of low spike levels (with reliable corresponding recoveries, Keith, 1991). Note that the SDs of the relative recoveries do not necessarily correspond with the respective MDLs, because they are derived from error propagation calculations (see below, Table 2.3.1-3, ERR).

2.3 Results and Discussion

2.3.1 SPE of Neutral and Acidic Pesticides from Aqueous Samples

Neutral and acidic pesticides were simultaneously extracted from aqueous samples on GCB, and separately eluted therefrom. SPE of the neutral pesticides was carried out according to Di Corcia & Marchetti (1992) and Berg et al. (1995). However, glass rather than plastic cartridges were used because the latter released phthalates which caused interferences in the chromatograms. Such impurities were also found to disturb HPLC chromatograms (Di Corcia & Marchetti, 1992).

A new procedure for sample preparation was developed for the acidic analytes. After the elution of the neutral fraction, MeCl_2/EA (80 : 20 v/v) acidified with TFA (0.2 %, v/v) was used to elute the acidic components which are adsorbed to benzopyrylium ions (Di Corcia et al., 1993). EA was used instead of MeOH, because the alcohol acts as a derivatization reagent for the acid catalysed esterification of the phenoxy acids. This has to be avoided prior to solvent removal, as the more volatile phenoxy esters are prone to evaporation. Also, solvent removal was facilitated, because EA is miscible with MeCl_2 . TFA was used owing to its low pKa and rather high volatility. It evaporates under the nitrogen stream and does not compete with the phenoxy acids for derivatization.

The derivatization of the phenoxy acids with diazomethane was fast and complete (see below), and required, apart from diethyl ether removal and filtration step, no further preparation prior to injection into the GC, as is the case for most other derivatization techniques (Lee et al., 1994). During derivatization, precipitation and coagulation within the eluate was often observed. This phenomenon may be ascribed to polymethylene formation which can take place as a result of dediazonation of diazomethane (Zollinger, 1995). The coagulate had, however, no adverse effect on the analysis and was removed by filtration.

Overall, the concomitant SPE of all analytes from one single sample and the optimized sample preparation of the acidic eluate for the subsequent determination with GC/MS makes the application of the presented method time-efficient and easy to apply. Total sample work-up time is around 12 h for 24 environmental samples.

2.3.2 Separation and Detection of Pesticides with GC/MS

Fig. 2.2 shows the quantification single ion chromatograms of a rainwater sample spiked with 10 ng/L of the investigated pesticides (except for propachlor, acetochlor, and deisopropylatrazine, of which 20 ng/L were added), and 75 ng/L of the internal standards (reduced scale). No pesticides were detected in the respective unspiked samples.

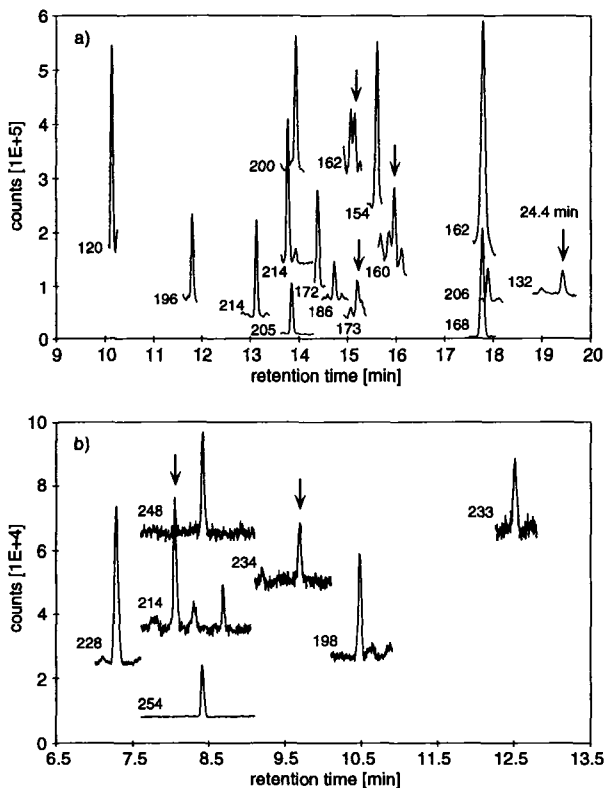


Figure 2.2 Chromatograms (SIM, mass traces of the ions used for quantification) of concentrated neutral (a) and acidic (b) eluates from a 1 L rainwater sample spiked with 10 ng/L of the investigated pesticides (except for propachlor, acetochlor, and deisopropylatrazine: 20 ng/L), and 75 ng/L of the internal standards (scale reduced by a factor of 7.5), respectively. Arrows indicate the analyte peak. Mass traces were vertically arranged for better illustration. For retention times of the analytes: see Table 2.1.

Both the neutral (Fig. 2.2, a), and the acidic analytes (Fig. 2.2, b) could be separated by using the same GC-column with a similar temperature program. Note that a rather polar separation column was used in order to optimize the separation and peak shape of the triazine metabolites (e.g., Fig. 2.2, a; $m/z = 172$, ret. time = 14.4 min.: desethylatrazine). Even at these low concentrations, all substances could be unambiguously identified by applying the above mentioned criteria. For most pesticides, the quantification ions were base line separated from matrix components (e.g., Fig. 2.2, b; $m/z = 214$, ret. time = 8.0 min.: MCPA), and only a few mass traces (in the depicted example namely the ones of acetochlor, deisopropylatrazine, and alachlor) were occasionally disturbed at concentrations close to the MDLs. These disturbances were very much dependent on the environmental matrix (see below), which varied from sample to sample. However, such interferences did not affect the quantification of any of the substances investigated. Hence, the distinct advantage of using a sensitive and specific detector under these analytical conditions is evident.

Note that the retention times of the neutral and acidic pesticides do not overlap (very similar temperature program) and that a concomitant separation of all substances would have been possible. However, qualitatively, a simultaneous elution, concentration, and derivatization of both the neutral, and acidic pesticides by using only the second eluent resulted in markedly reduced recoveries for several of the neutral analytes. Therefore, that technique was not pursued further. Nevertheless, the use of similar GC conditions for the separation and detection of neutral and acidic pesticides renders the presented method efficient and practical.

2.3.3 Linearities, Recoveries, Precision, and MDLs

External calibrations proved to be linear ($0.9942 \leq r^2 \leq 0.9999$) within 10 to 2000 ng/L (5000 ng/L for atrazine, alachlor, metolachlor, and the phenoxy acids) for all substances, except for propachlor, acetochlor, dimethenamid, and metazachlor, which were in a linear range up to 400 ng/L only. Linearity of internal calibrations ($0.975 \leq r^2 \leq 0.9998$) were similar to the external ones, except for desethylatrazine, deisopropylatrazine, and metalaxyl. For these compounds, the linear range was reduced to 400 ng/L. This may be due to competition for sorption sites on the SPE material, and/or exceeding of breakthrough volumes. Note that calibration curves for all the phenoxy acids were linear up to 5000 ng/L. It can be speculated that the acidic compounds exhibit somewhat higher affinity towards the sorption sites on GCB, because of the additional anion exchange mechanism involved (Di Corcia et al., 1993).

Absolute recoveries from Nanopure water fortified with 4 to 50 ng/L were around 90 % for most of the triazines (Table 2.3.1). Simazine, and desethylatrazine showed somewhat reduced values of 66 to 80 %. Acetamides (Table 2.3.2) had recoveries between 84 and 110 %, except for propachlor (around 70 %) and for lower spike levels of acetochlor and metalaxyl (about 60 to 80 %).

Absolute recoveries for the phenoxy acids ranged from about 90 to 110 % (Table 2.3.3). Recoveries in various rainwaters were similar to those in Nanopure water. With decreasing spike levels, however, rather than a decline (for example due to irreversible adsorption on the solid phase), an increase in recoveries was often observed (e.g., for atrazine, terbuthylazine, metazachlor, propachlor, MCPA, and 2,4,5-TP). This may be ascribed to an enhanced background noise in the chromatograms that may cause overestimation of peak areas and, thus, recoveries. Generally, absolute recoveries were similar to those reported by (Di Corcia & Marchetti, 1992) and (Berg et al., 1995), except for simazine, the triazine metabolites, and propachlor. This may be due to the lower spike levels. The comparable numbers also indicate that no losses of the phenoxy acids occurred during the derivatization process.

In Nanopure water spiked with 8 to 50 ng/L, relative recoveries ranged from 88 to 115 % for triazines, 84 to 108 % for acetamides, and 82 to 101 % for phenoxy acids (Table 2.3.1-3). For very low spike levels (2 to 5 ng/L), recoveries of some substances appeared to be reduced (e.g., atrazine, alachlor, and metolachlor, respectively, at 5 ng/L), but remained within the same range as with higher levels for most of the investigated compounds (e.g., simazine, terbuthylazine, and dimethenamid, respectively, at 2-3 ng/L!). Recoveries in spiked rainwaters (8 to 50 ng/L) varied from 81 to 125 % for triazines, 71 to 114 % for acetamides, and 55 to 111 % for phenoxy acids (Table 2.3.1-3). Higher spike levels of 400 to 1000 ng/L revealed similar recoveries (data not shown). Generally, for substances with relatively low absolute recoveries (desethylatrazine, deisopropylatrazine, simazine, acetochlor, metalaxyl, propachlor, and MCPA) their respective relative recoveries were improved because the internal calibrations accounted for analyte losses.

The average precision of the method applied to rainwater fortified with 2 to 50 ng/L of the analytes using internal calibration and internal standard was determined to be 6.0 ± 7.5 % for the triazines, 8.6 ± 7.5 % for the acetamides, and 7.3 ± 3.2 % for the phenoxy acids.

Table 2.3.1 Recoveries and method detection limits (MDLs) of triazines at low concentrations in Nanopure and rainwater

	absolute recovery				relative recovery					
	Nanopure water		rainwater		Nanopure water		rainwater			
	spike level [ng/l]	recovery [%] (SD)	MDL [ng/L]	recovery [%] (SD)	MDL [ng/L]	recovery [%] (ERR) ^b	MDL concentration [ng/l] (SD)	recovery [%] (ERR) ^b		
atraton	20	92 (2)	1.3	90 (4)	2.5	90 (2)	1.0	<i>nd</i>	95 (3)	1.5
	4	95 (3)	0.4	95 (8)	0.9	100 (9)	1.7	<i>nd</i>	85 (6)	1.4
atrazine	50	90 (0)	0.7	89 (2)	3.3	93 (4)	2.4	17 (0.3)	96 (1)	0.8
	25	88 (3)	2.0	102 (2)	1.2	93 (3)	1.9	<i>nd</i>	87 (2)	1.0
desethyl-atrazine	10	91 (4)	1.3	104 (10)	2.9	80 (5)	1.0	75 (1.1)	77 (42)	3.3
	20	80 (5)	3.2	73 (3)	2.0	105 (9)	10.6	4 (0.5)	116 (11)	1.4
deisopropyl-atrazine	10	69 (10)	3.0	80 (3)	1.0	99 (4)	0.9	40 (0.8)	81 (9)	2.4
	4	66 (4)	0.5	83 (7)	0.8	102 (11)	2.6	<i>nd</i>	93 (6)	1.5
deisopropyl-atrazine	20	86 (9)	5.7	89 (14)	8.4	115 (22)	9.8	5.3 (3.7)	125 (56)	11.0
	4	85 (6)	0.7	69 (13)	1.6	88 (12)	3.1	<i>nd</i>	82 (21)	5.0
propazine	20	90 (2)	1.2	96 (2)	1.4	105 (8)	1.6	<i>nd</i>	98 (4)	1.9
	4	91 (3)	0.4	119 (8)	1.0	94 (3)	0.5	<i>nd</i>	90 (3)	0.6
simazine	20	77 (2)	1.0	75 (3)	1.6	86 (13)	0.2	<i>nd</i>	65 (11)	1.0
	4	70 (3)	0.4	64 (4)	0.4	99 (6)	2.3	<i>nd</i>	97 (4)	1.7
terbutylazine	20	92 (2)	1.1	100 (4)	2.3	100 (7)	1.0	<i>nd</i>	112 (16)	2.1
	4	99 (3)	0.3	130 (9)	1.1	83 (18)	0.6	<i>nd</i>	116 (34)	1.2
						93 (4)	0.6	5 (0.2)	104 (11)	0.6
						96 (6)	0.9	<i>nd</i>	91 (6)	1.3
						87 (4)	0.3	7 (0.3)	33 (45)	0.9

^a no pesticides detected in unspiked rainwater. ^b derived from error propagation calculations. *nd* not detectable. **bold numbers**: MDLs considered.

Table 2.3.2 Recoveries and method detection limits (MDLs) of acetamides at low concentrations in Nanopure and rainwater

	absolute recovery				relative recovery						
	Nanopure water		rainwater		Nanopure water		rainwater				
	spike level [ng/l]	recovery [%] (SD)	MDL [ng/L]	recovery [%] (SD)	MDL [ng/L]	spike level [ng/l]	recovery [%] (ERR) ^b	MDL [ng/L]			
acetochlor	20	90 (7)	4.3	88 (12)	7.0	8	95 (5)	1.4	81 (13)	1.8	
	10	67 (10)	3.1	70 (10)	3.0						
alachlor	4	59 (14)	1.7	92 (48)	5.8	50	84 (13)	6.4	7 (0.3)	97 (3)	1.0
	50	95 (3)	4.4	91 (3)	4.2	20	96 (3)	1.1	<i>nd</i>	96 (3)	1.7
	10	85 (6)	1.8	99 (7)	2.2	5	74 (21)	0.9	10 (0.4)	85 (27)	1.2
dimethenamid	20	91 (3)	1.8	99 (0)	0.3	20	91 (9)	0.7	<i>nd</i>	102 (5)	3.0
	4	84 (10)	1.1	99 (7)	0.9	3	101 (19)	1.9	<i>nd</i>	89 (6)	0.8
metalaxy	20	86 (2)	1.1	73 (7)	4.1	20	97 (5)	1.2	<i>nd</i>	107 (20)	11.3
	4	65 (4)	0.4	87 (20)	2.4	8	108 (7)	0.6	<i>nd</i>	92 (8)	1.5
metazachlor	20	110 (8)	4.7	99 (3)	1.8	20	85 (8)	2.9	<i>nd</i>	114 (21)	11.3
	4	101 (8)	1.0	130 (22)	2.7	8	106 (13)	1.9	<i>nd</i>	107 (12)	2.7
metolachlor	50	96 (1)	1.2	102 (2)	3.3	50	89 (7)	1.0	16 (0.0)	93 (2)	0.1
	10	97 (2)	0.5	122 (9)	2.8	20	96 (3)	0.6	<i>nd</i>	90 (1)	0.5
propachlor	20	68 (5)	3.0	64 (1)	0.4	20	98 (22)	6.1	<i>nd</i>	80 (12)	5.9
	4	72 (2)	0.3	92 (7)	0.8	8	106 (14)	2.6	<i>nd</i>	71 (13)	3.0

^a no pesticides detected in unspiked rainwater. ^b derived from error propagation calculations. *nd* not detectable. **bold numbers: MDLs** considered.

Table 2.3.3 Recoveries and method detection limits (MDLs) of phenoxy acids at low concentrations in Nanopure and rainwater

	absolute recovery				relative recovery					
	Nanopure water (n = 3)		rainwater (n = 3) ^a		Nanopure water (n = 4)		rainwater (n = 4)			
	spike level [ng/l]	recovery [%] (SD)	MDL [ng/L]	MDL [ng/L]	spike level [ng/l]	recovery [%] (ERR) ^b	MDL [ng/L]	concentration [ng/l] (SD)	recovery [%] (ERR) ^b	MDL [ng/L]
2,4-D	50	106 (3)	4.3	2.4	50	92 (8)	9.0	21 (2.8)	93 (13)	8.3
	25	98 (5)	4.1	2.8	20	84 (7)	3.5	<i>nd</i>	80 (3)	4.7
dichlorprop	10	108 (7)	2.2	1.2	50	94 (5)	4.3	<i>nd</i>	100 (2)	3.5
	25	92 (5)	6.9	6.5	20	92 (7)	2.7	<i>nd</i>	103 (3)	4.7
MCPA	10	103 (7)	2.1	1.5	50	92 (5)	3.2	<i>nd</i>	96 (7)	10.0
	50	89 (7)	10.9	6.1	20	93 (4)	3.0	<i>nd</i>	94 (2)	3.6
mecoprop	10	96 (68)	20.5	145 (27)	50	99 (6)	5.5	<i>nd</i>	104 (8)	11.6
	25	91 (3)	4.8	16.6	20	101 (7)	3.3	<i>nd</i>	111 (3)	4.2
2,4,5-T	10	91 (7)	4.0	10.5	50	85 (5)	6.7	<i>nd</i>	68 (12)	18.2
	25	101 (10)	7.3	3.2	20	85 (10)	7.5	<i>nd</i>	55 (4)	6.0
2,4,5-TP	10	114 (15)	4.4	3.2	50	82 (8)	10.5	<i>nd</i>	77 (8)	11.9
	25	107 (2)	3.4	10.4	20	90 (9)	3.8	<i>nd</i>	92 (2)	3.2
	10	111 (8)	2.4	0.5						

^a no pesticides detected in unspiked rainwater. ^b derived from error propagation calculations. *nd* not detectable. **bold numbers: MDLs** considered.

For MDLs, the following spike levels were considered: 2 to 5 ng/L for triazines, 3 to 8 ng/L for acetamides, and 10 to 20 ng/L for phenoxy acids. MDLs in Nanopure water were determined to be from 0.2 to 1.0 ng/L for triazines, 0.1 to 1.9 ng/L for acetamides, and 2.1 to 4.4 ng/L for phenoxy acids (Table 2.3.1-3). In rainwater, values ranged from 0.8 to 3.3 ng/L for triazines, 0.5 to 2.7 ng/L for acetamides, and 0.5 to 3.6 ng/L for phenoxy acids (Table 2.3.1-3). Since the MDLs are derived from SDs of several identical samples, which not only depend on matrix effects, but also on the total sample workup variability, they were occasionally found to be slightly lower in rainwater than in Nanopure water. In general, MDLs were within the same range as when determined with a signal to noise ratio of 3, and as the determined instrumental detection limits (data not shown). This is in accordance with the measured absolute recoveries, i.e., no significant amounts of the analytes were lost during SPE. The listed MDLs are generally slightly lower than those reported by Di Corcia & Marchetti (1992) and Berg et al. (1995).

2.3.4 Application of the Method to Natural Water Samples

For further evaluation, the described method was applied to the determination of *neutral and acidic pesticides in lake water, groundwater contaminated with infiltrating water from landfills, rainwater, and roof runoff*. Table 2.4 summarizes the results obtained from analyses of natural waters.

Triazine concentrations measured in spring 1996 in a pooled sample of Murtensee (Table 2.4, lake water) collected from July to December 1994 were between 3 ± 0.2 ng/L and 178 ± 2.5 ng/L. These values were compared with results from measurements of the same samples determined in 1994 with the method described in (Berg et al., 1995) and found to be similar for simazine, and terbuthylazine (less than 3 % variation), but slightly lower for atrazine, desethylatrazine, and deisopropylatrazine (5 %, 17.5 %, and 9 % variation, respectively; Berg, 1996). A moderate degradation of the compounds over the last two years could therefore be suspected. However, no significant degradation of triazine compounds was found to occur when the samples are stored at 4 °C in the dark (unpublished results from our own laboratory), and thus, it is likely that these variations primarily reflect an overall systematic error of the two methods applied.

Table 2.4 Measured concentrations and recoveries of neutral, and acidic pesticides in various natural waters

	lake water ^d (n = 3)		groundwater A ^b (n = 3)		groundwater B ^c (n = 3)		rainwater ^d (n = 1)		roof runoff ^d (n = 1)	
	concentration [ng/L] (SD)	recovery ^e [%] (SD)	concentration [ng/L] (SD)	recovery ^e [%] (SD)	concentration [ng/L] (SD)	recovery ^e [%] (SD)	concentration [ng/L]	recovery ^e [%]	concentration [ng/L]	recovery ^e [%]
triazines										
atrazin	nd	105 (2.0)	nd	93 (9.0)	nd	nd	nd	nd	nd	nd
atrazine	178 (2.5)	112 (10.2)	6 (1.1)	103 (1.6)	nd	nd	609	551	551	551
desethyl- atrazine	92 (1.5)	110 (10.2)	7 (0.8)	70 (6.4)	nd	nd	30	37	37	37
deisopropyl- atrazine	26 (0.6)	92 (3.7)	14 (0.9)	94 (6.0)	nd	nd	18	29	29	29
propazine	3 (0.2)	105 (2.8)	nd	100 (3.7)	nd	nd	41	44	44	44
simazine	24 (0.3)	105 (2.0)	4 (3.3)	98 (8.9)	nd	nd	13	6	6	6
terbutylazine	45 (0.9)	107 (3.8)	nd	106 (3.6)	nd	nd	72	17	17	17
acetamides										
acetochlor	nd	91 (2.5)	nd	291 (85.1)	nd	nd	nd	nd	nd	nd
alachlor	nd	105 (1.5)	nd	97 (4.1)	nd	nd	16	19	19	19
dimethenamid	nd	104 (1.9)	nd	93 (7.3)	nd	nd	nd	nd	nd	nd
metaxyl	nd	96 (2.7)	nd	101 (4.4)	nd	nd	5	4	4	4
metazachlor	8 (0.6)	86 (5.6)	nd	58 (13.0)	nd	nd	7	5	5	5
metolachlor	8 (0.3)	98 (0.8)	nd	98 (1.5)	nd	nd	36	37	37	37
propachlor	nd	103 (2.4)	nd	32 (11.6)	nd	nd	106	69	69	69
phenoxy acids										
2,4-D	nd	100 (1.8)	nd	60 (5.4)	310 (10)	28	10	10	10	10
dichlorprop	nd	99 (1.1)	nd	98 (4.4)	nd	15	9	9	9	9
MCPA	nd	97 (2.5)	nd	31 (5.5)	90 (20)	3	9	9	9	9
mecoprop	43 (2.0)	98 (2.0)	nd	95 (9.2)	2800 (70)	7	12	12	12	12
2,4,5-T	nd	100 (0.9)	nd	97 (4.6)	nd	nd	nd	nd	nd	nd
2,4,5-TP	nd	94 (1.3)	nd	144 (3.4)	nd	nd	nd	nd	nd	nd

^a Murtensee (western part of Switzerland). ^b contaminated groundwater from the Landfill of Riet (Canton Zurich). ^c contaminated groundwater from the Landfill Kölliken (Canton Aargau). ^d onset of a thunderstorm (first 0.2 mm of rain, and first 0.01 mm of roof runoff) from May 29, 1995 in Zurich. ^e relative recoveries; spike levels were 100 ng/L for atrazine, alachlor, metolachlor, and all phenoxy acids, and 40 ng/L for all other pesticides. ^f not detectable.

Moreover, representatives of other pesticide classes were also determined, namely metazachlor, metolachlor, and mecoprop. The derived relative recoveries and method precisions were similar to these obtained with rainwater. This can be explained with the quite similar solution composition of the two aquatic environments. Roughly, measured average DOC contents in rainwater samples were in the low mg/L range, and are typically around 1 mg/L in lake water.

Certain recoveries in contaminated groundwater from the landfill of Riet (Canton Zurich; Table 2.4, groundwater A), however, were markedly altered most probably due to the complex matrix. The samples were completely anaerobic, had a yellowish colour, and a DOC content of 19.8 mg/L. Di Corcia et al. (1993) stated that the presence of 20 mg/L fulvic acids caused a significant decrease in recoveries at least for the acidic pesticides, which under these conditions were partly eluted with the neutral fraction already. Still, the method proved to be rugged enough to provide reliable results even at these adverse conditions for two thirds of the compounds analysed. For example, triazine herbicides with concentrations of less than 20 ng/L could unambiguously be determined. These herbicides probably originated from agricultural applications in the area.

The landfill in K lliken (Canton Aargau) contains unknown amounts of phenoxy acid herbicides, and significant concentrations of these substances were determined in the leachate, which causes a considerable groundwater contamination in the area (Zipper, 1996). A few micrograms of mecoprop and a few hundred nanograms of 2,4-D were found in groundwater streams in 16m depth and about 100m away from the landfill (Table 2.4, groundwater B). This example shows that the presented method can serve as a screening tool in a concentration range from a few ng/L up to a few $\mu\text{g/L}$.

Rain, and roof runoff water from May 1995, i.e., during the application period of various pesticides (Table 2.4, rainwater, and roof runoff, respectively), contained significant amounts of both neutral and acidic analytes. The described method proved to be perfectly suited to assess the large variety of pesticides present in these waters. The most frequently detected substances were atrazine, simazine, terbuthylazine, the triazine metabolites deethyl-, and deisopropylatrazine, alachlor, metolachlor, dichlorprop, and mecoprop. Peak concentrations were determined during the major application period of most herbicides in spring and at the onset of rain events. With values up to 600 ng/L, atrazine concentrations significantly exceeded the Swiss and EC drinking water standards (100 ng/L). Interestingly, the ratio between metabolites of atrazine and their parent compound was much lower in these samples, as compared, for example, with lake water. This indicates that the detected pesticides were applied quite recently, and that their input into the atmosphere probably occurred by drift or fast evaporation, rather

than by wind erosion from soil, where biological degradation could have taken place. Also, in spite of the fact that propazine is not a registered herbicide in Switzerland, it was occasionally detected in both rainwater, and roof runoff. Whereas the ratio of propazine/atrazine was found to be 1 - 4 % in Swiss lakes (Table 2.4, lake water, and Buser, 1990), it appeared to reach 6 - 8 % in rainwater. The fact that propazine is formed as a byproduct in the production of technical atrazine cannot fully explain its occurrence in rainwater at such concentrations. Rather, these findings may give information on the transport scale of pesticides within the atmosphere. The atmospheric transport and deposition of pesticides is further discussed in chapter 4, and, as was demonstrated here, the analytical method on hand is a very apt instrument for that purpose.

2.4 Conclusions

The novelty of the present method consists in the integration and optimization of different analytical tools with specific advantages. The use of isotope-labelled internal standards and internal calibration (compensation of possible analyte losses, high precision and accuracy, and quality control), and a selective solid phase (excellent recoveries for a variety of polar pesticides, reduced matrix effects, sequential elution of different pesticide classes) was combined with a specific detector (unambiguous identification and determination at the low ng/L concentration level). Additionally, emphasis was placed on the optimization of sample preparation and separation. The simultaneous extraction of neutral and acidic pesticides from one single sample, the facilitated sample preparation of the acidic analytes for subsequent analysis with GC/MS, and the separation of both eluates under similar apparatus conditions were measures designed to simplify the application. As a result, the method was able to serve not only as a routine screening tool for the assessment of some of the most widely used herbicides, but also proved rugged and sensitive enough to study their fate and behavior in various kinds of aquatic environments.

Leer - Vide - Empty

3. Conglomerated Clay Minerals (CCMs) as Stationary Phase for SPE and Separation of Aromatic Compounds with Electron Withdrawing Substituents

3.1 Introduction

Recently, it was demonstrated that nitroaromatic compounds (NACs) may adsorb to natural clay minerals in a specific and reversible manner. The dominant adsorption mechanism can be rationalized by electron donor-acceptor (EDA) complex formation with oxygen atoms present at the external siloxane surface(s) of the clay mineral as e^- -donors and the π -system of the NACs as e^- -acceptors. It was shown that the affinity and the adsorption capacity of the clay for NACs were highest for montmorillonite, saturated with weakly hydrated monovalent cations (Haderlein & Schwarzenbach, 1993; Haderlein et al., 1996). These specific features of natural clay minerals are ideal prerequisites for solid phase extraction (SPE) and separation of NACs and other planar aromatic compounds with electron withdrawing substituents from natural waters.

Requirements for SPE materials are manifold, such as sufficiently large porosity, pressure resistance, and the ability for regeneration. These demands are not met by clay minerals in their natural form. Basically, two different techniques for modification of natural clay minerals to serve as a solid phase have been used: the first one can be referred to as the 'clay-coating' technique, where (organo-) clay minerals are attached to a solid phase, such as alumina (Szecsody et al., 1993), or silica gel (Kördel et al., 1995; Nakamura et al., 1990). The second one comprises dry spraying of clay mineral suspensions to produce (quasi-)spherical clay agglomerations (Jinno et al., 1991; Tsvetkov et al., 1994).

Such modifications allowed the use of clay minerals in HPLC for separation of metal complexes (Nakamura et al., 1990) and amino acids (Tsvetkov & Mingelgrin, 1987). Furthermore, their applications in supercritical fluid chromatography (Jinno et al., 1991), and gas chromatography (Baksh & Yang, 1991) were described. Also, clay mineral columns served for studying the pollutant transport in clay-containing groundwater systems (Szecsody et al., 1993), and for determination of adsorption coefficients on soil (Kördel et al., 1995). Although the separation of numerous aromatic compounds, including various NACs, has been conducted with clay mineral columns and organic mobile phases (Tsvetkov et al., 1993; Tsvetkov et al., 1994), the governing processes were different to the one described above and the results were unsatisfactory in terms of plate numbers.

In this work, for the first time, pure clay mineral surfaces have been used as a SPE material, subsequently named conglomerated clay minerals (CCMs). Due to their strong, and quite specific interactions with clay minerals, NACs served as model compounds to assess the performance of this new kind of solid phase. Online SPE-HPLC breakthrough volumes and MDLs of priority pollutants such as DNOC, and 2,4,6-trinitrotoluene (TNT) were determined in Nanopure water, and matrix effects on recoveries from natural waters have been studied. Furthermore, the suitability for offline SPE has been shown, and was compared with commercially available offline SPE materials. Moreover, the applicability to other environmentally relevant aromatic compounds with electron withdrawing substituents (e.g., nitro musks, benzonitriles, and nitrodiazobenzenes) has been evaluated, and the limits of the method for analysis of mononitro-, and aminonitro-compounds are pointed out. Eventually, the potential of spherical clay minerals to serve as a 'reversed' solid phase for analytical separation is discussed.

3.2 Experimental Section

3.2.1 Materials

2-Nitrophenol (2-NP), 2,4-dinitrophenol (2,4-DNP), 1,3-dinitrobenzene (1,3-DNB), thiourea, and alizarin yellow R were from Fluka AG, Buchs, Switzerland. 4-amino-2,6-dinitrotoluene (4-A-2,6-DNT), and 2,6-diamino-4-nitrotoluene (2,6-DA-4-NT) were purchased from Promochem (Wesel, Germany). 2,4-Dinitro-6-methylphenol (DNOC), and 2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile (chlorothalonil) were from Riedl-de Haën (Seelze, Germany). 2,4,6-trinitrotoluene (TNT) was provided from Ems Chemie (Dottikon, Switzerland). Musk ketone, musk tibetene, and musk xylene were a kind donation from Givaudan-Roure Research AG (Dübendorf, Switzerland). The purchased 2,4-DNP was purified by recrystallization in ethyl acetate (EA). All other compounds were used as received.

EA (purity for pesticide residue analysis) was from Burdick & Jackson (Muskegon, MI). Sodium silicate solution (14 % NaOH, 27 % SiO₂), acetonitrile (ACN), HCl (32 %), LiCl, NaCl, NaOH, CsCl, and montmorillonite K10 were purchased from Fluka AG, Buchs, Switzerland. The clay mineral is sold in a protonated form with a cation exchange capacity (CEC) of 30-40 mVal/100g. Nitrogen (99.995 %) was from Carbagas (Rümlang, Switzerland). Deionized water was further purified with a Nanopure water purification device (NANOpure 4, Skan, Basle, Switzerland).

3.2.2 Sampling and Sample Preparation

Rainwater was sampled in Dübendorf (Switzerland) with a 1 m² Teflon rain sampler for bulk samples, and a self-made 5.06 m² funnel coated with a teflon foil for sequential sampling. Roof runoff samples were collected at a stormwater infiltration site in Grütze (Winterthur, Switzerland). For details on these field sites, see chapter 4. Lake water samples were from the epi-, and hypolimnion of Lake Woburn (MA; for details, see Wick & Gschwend, 1997). Groundwater samples were taken in the vicinity of the municipal landfill of Winterthur (Riet, Canton Zurich, Switzerland), and the sewage water was from the sewage treatment plant in Opfikon-Glattbrugg (Canton Zurich, Switzerland). All samples were kept at 4 °C in the dark.

Prior to analysis, water samples were allowed to reach room temperature, and filtered (cellulose nitrate filter, diameter 5 cm, pore size 0.45 µm; Satorius, Goettingen, Germany). For analysis of NPs and alizarin yellow R, the pH of the samples was adjusted to 2.5, using HCl (32 %).

3.2.3 Production of CCMs

20 g/L of montmorillonite K10 were suspended in a 1.6 mM NaOH-solution (to obtain a pH around 6) and set aside for sedimentation of larger particles. After one week, the suspension was transferred to other vessels and NaCl was added (0.01 M). 24 hours later, the supernatant was discharged and the sedimented particles collected. The average size of the resulting fine fraction was found to be < 1 µm, as determined with a Mastersizer X (Malvern Instruments Ltd.), and a screening electron microscopy (type XL-30, Philips). This fraction was put into a dialysis membrane and repeatedly washed (intervals of 24 hours for one week) in 0.1 M aqueous solutions of the chloride salt of the desired cation to produce a homoionic clay. Excess electrolyte was removed by repeated washes (intervals of 12 hours for one week) with Nanopure water.

Prior to dry spraying, the homoionic fine fraction was diluted with Nanopure water to yield a solid content of 13 % (w/w) and sodium silicate was added (2 % of solid content, w/w). Dry spraying was performed with an Anhydro Laboratory Dry Sprayer No. 1 (APV Anhydro AS, Copenhagen, Denmark), using a peristaltic feed pump, and a centrifugal atomizer (45000 rpm) with 63 mm disc diameter. The feed temperature was 18 °C, the inlet air temperature 330 °C, and the outlet air temperature 110 °C. The dry spraying produced CCMs, of which 80 % were found to have a diameter between 2 and 20 µm (determined as above). Finally, the product was then

exposed to 500 °C for 8 h. A Kopecky elutriation apparatus (Fig. 3.1, Möller Glasbläserei, Zurich, for details see, e.g., Walling & Woodward, 1993) was used for further fractionation, i.e., 2-5, 5-10, and 10-20 μm , respectively.

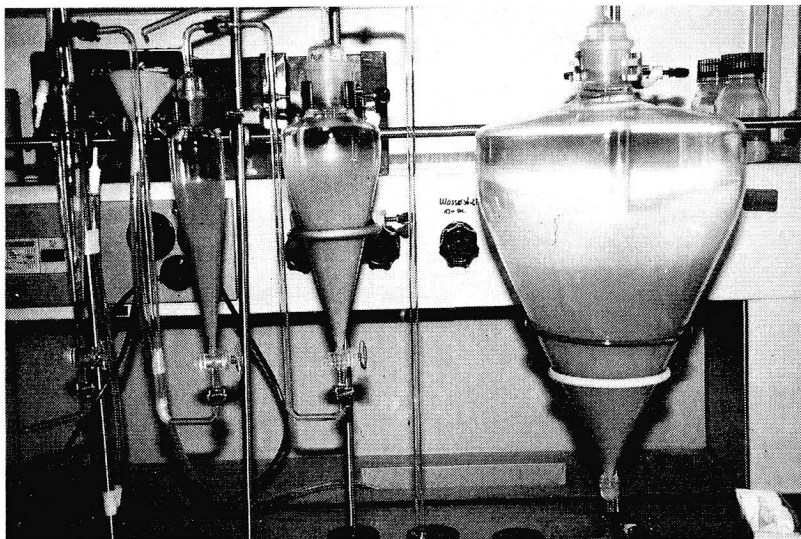


Figure 3.1 Kopecky elutriation apparatus for size separation of CCMs. Nanopure water is pumped at a rate of appr. 11 mL/min through a system of four sedimentation chambers connected in line. The increasing diameters result in decreasing upwards flow velocities within the individual chambers, against which the sedimentation of the CCMs occurs. Particles of similar size range will be trapped in the sedimentation chamber in which the sedimentation velocity equals the one of the opposed flow.

3.2.4 Preparation of Online SPE-HPLC Precolumns, Offline SPE Cartridges, and Separation Columns with CCMs

For online SPE-HPLC, 11mm precolumns (Macherey-Nagel, Oensingen, Switzerland) were dry-packed with CCMs (Li- or Cs-homoionized, 10 to 20 μm size fraction). 6 mL offline SPE plastic cartridges (Supelco, Bellafonte, CA) were filled with 250 mg of CCMs (Li-homoionized, 5 to 10 μm size fraction) between two PE frits. Separation columns (50 mm, 3mm i.d., Macherey-Nagel, Oensingen, Switzerland) with CCMs (Li- or Cs-homoionized, different size fractions) as stationary phase were wet-packed, using the slurry packing technique (Simpson, 1976).

3.2.5 Online SPE-HPLC with CCMs

A HPLC system from Gynkotek (Germering, Germany) was used for enrichment, separation and detection of the analytes. It was equipped with two gradient pumps (M480), an ODS (30) (Ultracarb 5, 150 x 4.6 mm, Phenomenex, Torrance, CA) separation column, a diode array detector (UVD 340S), and up to three valco valves (10(6) port 2 position valve: DC10(6)WK) with electric devices. A valco 12 port 12 position valve (DSD12E) served as an autosampler. These components were controlled by the data acquisition system Gynkosoftware (Gynkotek, Germering, Germany), which allowed a total automatization of the online SPE-HPLC.

Fig. 3.2 schematically shows the experimental setup, and Fig. 3.3 shows its installation in the laboratory. After conditioning of the precolumn filled with CCMs with several pore volumes of CsCl 0.02 M, ACN, and CsCl 0.02 M again, extraction was carried out by pumping the sample through the precolumn (Fig. 3.2) at 4 mL/min. Elution from the precolumn and concomitant separation on the separation column was performed in the 'forward', or 'backflush' mode at 1 mL/min, the latter resulting in slightly better peak shapes.

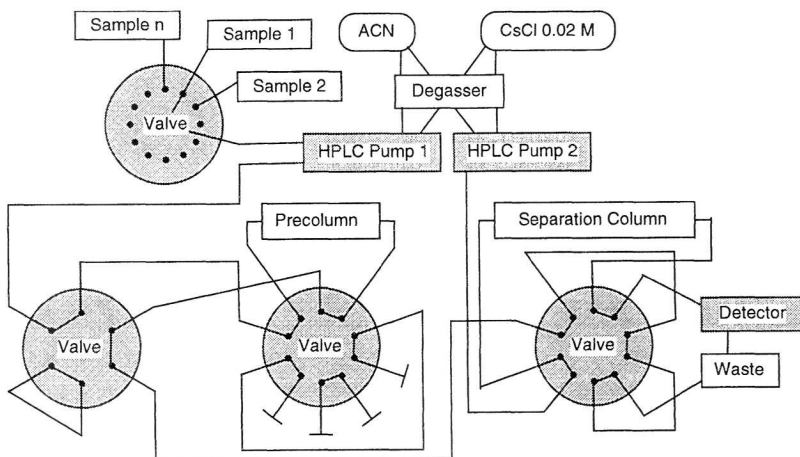


Figure 3.2 Apparative setup for the online SPE-HPLC of the investigated compounds on CCMs. Shaded parts were computer-controlled. Valve positions are as used during the extraction procedure.

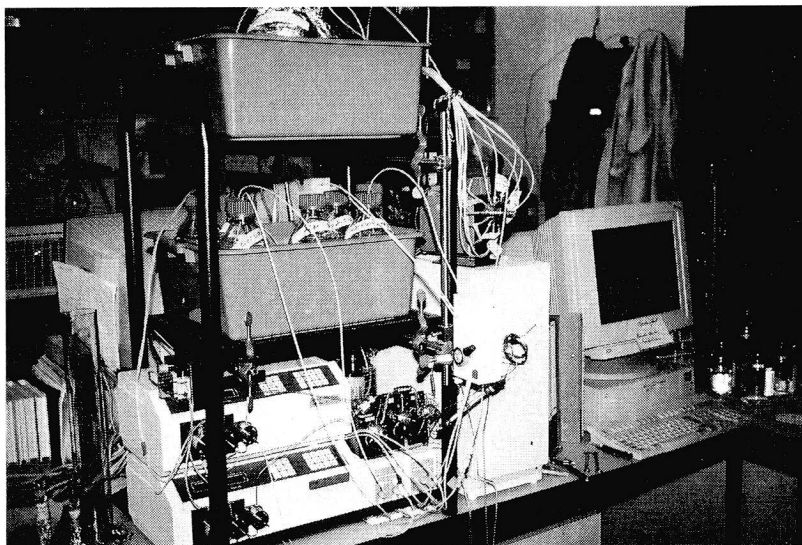


Figure 3.3 Installation of the developed online SPE-HPLC extraction method in the laboratory. The two HPLC pumps, the degassers, and valves, the detector, and the personal computer (from left to right) are placed on a laboratory bench. Samples are put on top of the rack, and mobile phase solutions and solvents underneath.

Two elution gradients were used, the first of which for Nanopure water samples was as follows: 2 min at 100 % CsCl (0.02M), to 20 % ACN in 5 min, to 60 % ACN in 10 min, to 90 % ACN in 2 min, 5 min at 90 % ACN. The second gradient was found to result in a better separation of the environmental matrix and the analytes: to 42 % ACN in 0.5 min, 2.5 min at 42 % ACN, to 30 % ACN in 0.5 min, 3.5 min at 30 % ACN, to 45 % ACN in 5 min, to 60 % ACN in 15 min, to 90 % ACN in 0.5 min, 4.5 min at 90 % ACN. UV-detection of NPs, and NTs and NB, was performed at a wavelength (λ) of 271 nm, and 242 nm, respectively. For analyte confirmation and identification in natural waters, whole spectres were acquired, ranging from 200 to 350 nm wavelength. After regeneration of both columns to 100 % CsCl 0.02 M, and flushing of the capillaries, the next sample was ready for SPE. The overall analysis time for online SPE-HPLC and separation of a 100 mL sample was about 80 min.

3.2.6 Offline SPE with CCMs and Commercial Products

CCM-SPE cartridges were mounted on a 12-fold vacuum extraction box (Supelco, Bellafonte, CA). The material was conditioned with 5 mL CsCl 0.02 M, followed by 5 mL ACN, and 5 mL of CsCl 0.02 M again. Samples of different volumes were drawn through the cartridges at 5 mL/min. Thereafter, the solid phase was washed with 5 mL of CsCl 0.02 M, and air dried for 5 min. Elution was carried out with 5 mL of ACN. The eluate was collected in conical glass vials (7.5 mL; Supelco, Bellafonte, CA) and concentrated to a final volume of 250 to 500 μ L using a gentle nitrogen stream for around 30 min. The solution was diluted with 500 μ L CsCl 0.02 M and the exact volume was measured with a disposable 1 mL syringe and passed through a 0.45 μ m filter (Spartan 13, Schleicher & Schuell, Dassel, Germany).

Offline SPE on Chromabond HR-P (Macherey-Nagel, Düren, Germany), and Porapak RDX (Waters Corp., Milford, MA) was conducted according to the producers' instructions.

3.2.7 HPLC Analysis

Calibrations of all compounds investigated were carried out by injecting standard solutions onto the reversed phase separation column. Injection volumes were 100, or 500 μ L, and injection was carried out by syringe over a Rheodyne valve. Injection volumes of the offline SPE eluates was 100 μ L. Aqueous solutions, solvents, were as with online SPE-HPLC (chapter 3.2.5), and elution gradient 1 was used for separation.

3.3 Results and Discussion

3.3.1 General Characteristics of CCMs, and Implications for Their Use as Stationary Phase

Dry spraying of montmorillonite suspensions (size fraction < 1 μ m) caused the individual particles to form CCMs of almost spherical shape. Fig. 3.4 depicts an electron micrograph of the eventual product after dry spraying of a clay fine fraction, thermal treatment, and size separation.

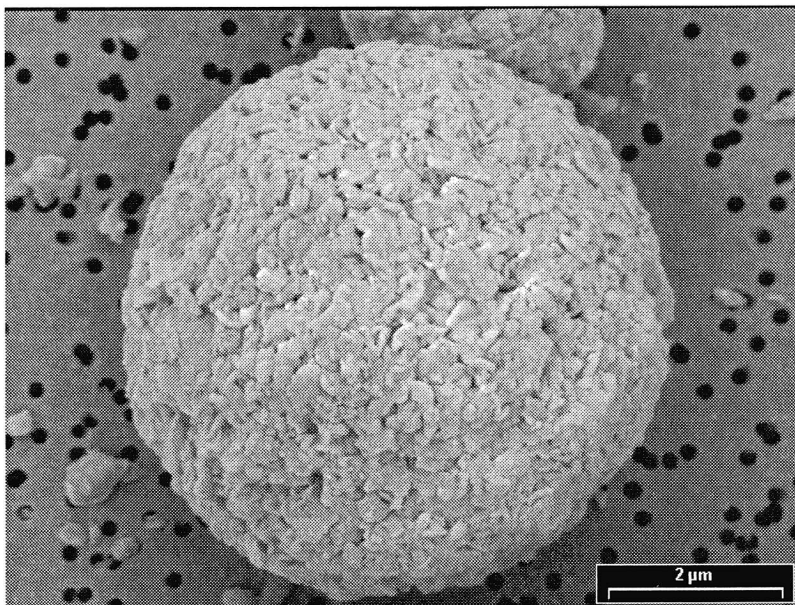


Figure 3.4 Electron micrograph of CCMs after dry spraying, heating, and size separation. Shown are Li-homoionized CCMs of the 5 to 10 μm size fraction. The CCMs consist of an almost spherical agglomeration of individual clay mineral plates.

The CCMs were exposed to 500 °C for 8 hours to prevent their disintegration in aqueous solutions. This thermal treatment caused the interlayers of the clay minerals to collapse and the cations to lose their hydration shells, thus becoming irreversibly bound to the clay surface. Irrespective of the cation adsorbed, the thermal treatment resulted in completely stable material in neutral aqueous solutions. The Li-homoionized material was even able to permanently stand a pH of 2.5, which was important for the enrichment of NPs exhibiting low pKa's.

Because of its small hydration shell, Cs is optimal for the adsorption of NACs and other compounds on clay minerals. To ensure continuous maximum sorption during extraction or separation, 0.02 M CsCl was added to all aqueous solutions, as control experiments without CsCl revealed decreased breakthrough volumes (data not shown). This measure compensated for a possible cation loss from the clay minerals and prevented an exchange with other cations present in environmental samples, as the selectivity of clay minerals is higher for Cs than for most of the other cations (Appelo & Postma, 1993). When working with NPs, and alizarin yellow R, the pH of all aqueous

solutions was adjusted to 2.5 using HCl (32 %). ACN was chosen as the organic eluent, because it may also undergo EDA complex formation with NACs and thus competes with the reactive sites of the clay mineral surfaces (Leggett et al., 1992).

The stability of the CCMs in terms of recoveries when used as online SPE-HPLC material was tested by reanalyzing spiked Nanopure water samples at the beginning and at the end of any sample batch. The recoveries remained consistently high for up to 40 samples, indicating that the solid phase was completely regenerable and suitable for multiple usage. Also, the CCMs proved to be permanently pressure-resistant.

3.3.2 Online SPE-HPLC with CCMs: Breakthrough Curves and MDLs of NACs in Nanopure Water

To assess the potential of the CCMs as a SPE extraction material, breakthrough curves of a set of NPs, nitrotoluenes (NTs), and a nitrobenzene (NB) were determined with online SPE-HPLC. Fig. 3.5 shows a typical chromatogram of a Nanopure water sample spiked with NPs, and Fig. 3.6 depicts the breakthrough curves of NPs (a), and NTs and NB (b), respectively, with 10 nmoles of each compound dissolved in increasing volumes of 20 to 1000 mL.

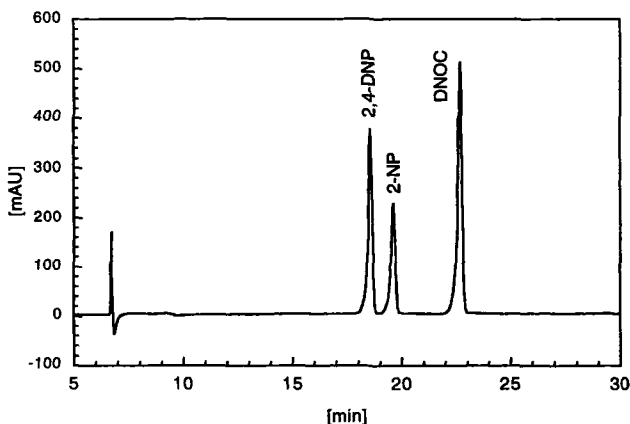


Figure 3.5 Chromatogram of 100 mL Nanopure water sample, spiked with $0.1 \mu\text{M}$ of NPs, after online SPE on Li-homoionized CCMs (10 to $20 \mu\text{m}$), and separation on a reversed phase HPLC column, using gradient 1. $\lambda = 271 \text{ nm}$.

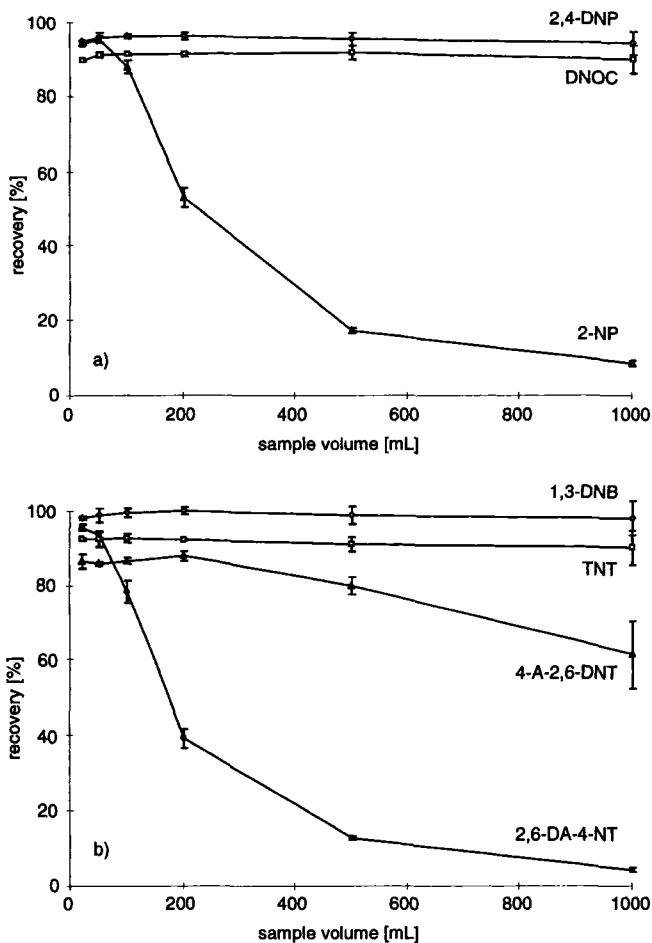


Figure 3.6 Breakthrough curves of NPs (a), and NTs and NB (b) in Nanopure water extracted with CCMs (Li-homoionized, 10 to 20 μm).

Whereas DNOC, 2,4-DNP, TNT, and 1,3-DNB exhibited recoveries > 90 %, irrespective of the sample volume, 4-A-2,6-DNT showed moderately decreasing recoveries at higher volumes (61 ± 9 % at 1000 mL, Fig. 3.6). 2-NP, and 2,6-DA-4-NT revealed a drastic reduction in recovery already at a volume of 200 mL. The presented performance applied to all online setups in use, including Cs-, or Li-homoionized materials, backflush elution, and even sequential elution of first the NPs by deprotonation, and second the NTs and NB with the ACN-gradient (data not shown).

The MDLs of the compounds investigated in Nanopure water are summarized in Table 3.1. These results suggest that the presented method allows to detect primary pollutants such as DNOC, and TNT, as well as certain metabolites and byproducts (e.g., 2,4-DNP, 1,3-DNB, and 4-A-2,6-DNT), in concentrations as low as a few ng/L.

Table 3.1 MDLs of NPs, NTs, and NB in Nanopure water using online SPE-HPLC on CCMs^a

	sample volume [mL]	concentration [nM]	recovery [%]	MDL [nM]	MDL [ng/L]
NPs					
DNOC	1000	0.2	115.5 ± 14.2	0.085	16.8
2,4-DNP	1000	0.2	91.9 ± 5.3	0.032	5.8
2-NP	100	10	108.6 ± 20.1	6.030	839.0
NTs					
TNT	1000	0.05	101.3 ± 5.4	0.008	1.8
4-A-2,6-DNT	100	0.5	92.1 ± 5.3	0.080	16.0
2,6-DA-4-NT	100	10	87.8 ± 1.6	4.800	802.0
NB					
1,3-DNB	1000	0.05	93.3 ± 3.6	0.005	0.9

^a n = 3-4. Method detection limits (MDLs) were calculated using three times the standard deviations of low spike levels (Keith, 1991) at maximum sample volume with reliable corresponding recoveries.

3.3.3 Online SPE-HPLC with CCMs: Matrix Effects, MDLs, and Precision in Natural Waters

Fig. 3.7 depicts a typical chromatogram of an unspiked rainwater sample. For determination of recoveries in various natural waters, all samples were fortified with 0.1 μ M of the analytes, and the sample volume was chosen to be well under the breakthrough volume of all compounds, i.e., 100 mL. Table 3.2 lists the obtained recoveries of the investigated compounds. For most of the investigated model compounds, the environmental matrix did not cause a significant alteration in recoveries compared to the ones found in Nanopure water. Only 2-NP, and 2,6-DA-4-NT, suffered a reduction in recovery in waters with elevated matrix, as represented by DOC content, and ionic strength (Table 3.2). Extremely high DOC concentrations, and high ionic strength, as measured in the hypolimnion of Lake Woburn, MA (Wick & Gschwend, 1997), caused a significant reduction in recovery for 2,4-DNP also. Conclusively, recoveries of most analytes were not negatively affected in natural water samples with low to moderate environmental matrix. Priority pollutants such as DNOC, or TNT

revealed no decrease in recoveries in aqueous samples containing DOC in concentrations as high as 100 mg/L.

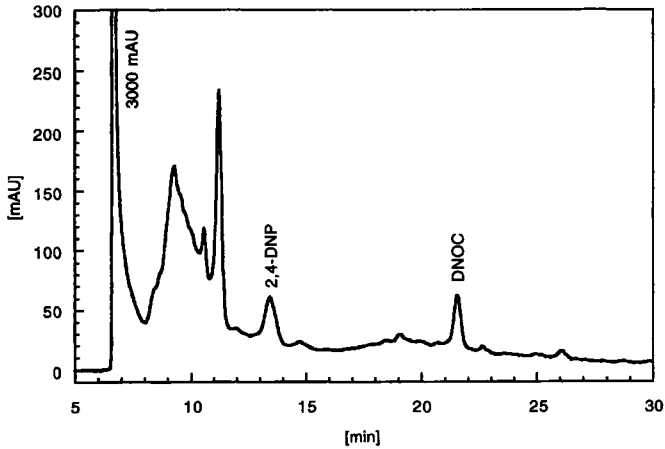


Figure 3.7 Chromatogram of an unspiked rainwater sample, containing $0.707 \mu\text{g/L}$ 2,4-DNP, and $0.476 \mu\text{g/L}$ DNOC, after enrichment on Li-homotonized CCMs (10 to 20 μm), and separation on a reversed phase HPLC column, using gradient 2. $\lambda = 271 \text{ nm}$.

Table 3.2 Recoveries of NPs, NTs, and NB in various natural waters using online SPE-HPLC with CCMs^a

	rainwater	roof runoff water	lake water A ^b	lake water B ^c	waste- water ^d	ground- water ^e
matrix parameters						
DOC [mg/L]			9	100	6	16
conductivity [$\mu\text{S/cm}$]			455	2150		2140
NPs						
DNOC	105.0 \pm 2.9	96.1 \pm 0.5	91.6	91.2 \pm 2.5	98.0 \pm 0.2	99.3 \pm 1.7
2,4-DNP	103.7 \pm 3.3	95.2 \pm 0.6	103.0	68.4 \pm 3.2	96.2 \pm 0.4	89.3 \pm 1.2
2-NP	95.3 \pm 1.0	78.9 \pm 3.5	95.4	38.7 \pm 42.9	94.1 \pm 0.9	9.2 \pm 2.7
NTs						
TNT			101.0 \pm 0.1	96.8 \pm 1.5		
4-A-2,6-DNT			103.8 \pm 0.0	98.8 \pm 3.1		
2,6-DA-4-NT			38.6 \pm 2.4	33.8 \pm 4.8		
NB						
1,3-DNB			101.9 \pm 0.1	101.2 \pm 2.0		

^a no analytes detected in unspiked waters; sample volume was 100 mL, sample concentration 0.1 μM , and $n = 3$. ^b epilimnion of Lake Woburn, MA, $n = 1$ for NPs, and $n = 2$ for NTs and NB. ^c hypolimnion of Lake Woburn, MA, $n = 2$. ^d effluent from the wastewater treatment plant in Opfikon-Glattbrugg (Canton Zurich, Switzerland). ^e contaminated groundwater from the landfill of Riet (Canton Zurich).

MDLs of NPs in rainwater were determined as described in Table 3.1, using sample volumes of 250 mL, spiked to yield concentrations of 0.04 μM . The resulting values were 24 ng/L for DNOC ($n = 3$, 103.3 ± 1.0 % recovery), and 27 ng/L for 2,4-DNP ($n = 3$, 100.3 ± 1.2 % recovery). These numbers are in good agreement with the MDLs determined with Nanopure water (Table 3.1). Note that, if necessary, the MDLs for substances with high breakthrough volumes (> 1 L), e.g., DNOC and TNT, could easily be further reduced by increasing the sample volume. Average precision, as determined with multiple determination of spiked rainwater samples ($n = 3$, 10 nmoles in 250 mL) was 1.2 % for DNOC, and 2.4 % for 2,4-DNP.

3.3.4 Offline SPE with CCMs and Comparison with Commercial SPE Materials

Fig. 3.8 shows typical chromatograms of extracts obtained from offline SPE with CCMs (Fig 3.8. a), and a commercial product (Fig. 3.8. b). Sample volumes were 500 mL, and concentrations were set to 0.5 μM . Chromatograms of environmental samples enriched with the CCMs proved to suffer less disturbance from the matrix present in natural samples as compared to a commercial SPE material. This illustrates the selectivity of the developed material.

Table 3.3 shows the offline performance of CCMs in terms of recoveries from Nanopure, and natural waters, and compares it with the ones obtained with commercially available products.

Table 3.3 Offline SPE of NTs and NB with CCMs, and comparison with commercial SPE materials^a

	CCMs ^b			Porapak RDX			Chromabond HR-P		
	Nanopure water	waste-water ^c	ground-water ^d	Nanopure water	waste-water ^c	ground-water ^d	Nanopure water	waste-water ^c	ground-water ^d
NTs									
TNT	92.2 \pm 6.6	93.3 \pm 3.9	94.3 \pm 5.6	87.7 \pm 1.4	89.7 \pm 1.5	91.7 \pm 2.2	79.6 \pm 7.4	75.8 \pm 2.0	83.3 \pm 1.9
4-A-2,6-DNT	91.2 \pm 6.5	92.0 \pm 4.0	92.4 \pm 5.7	78.6 \pm 0.8	80.4 \pm 2.3	82.6 \pm 1.9	86.3 \pm 4.9	84.2 \pm 0.9	90.2 \pm 0.8
2,6-DA-4-NT	33.7 \pm 7.4	2.7 \pm 0.1	2.0 \pm 0.3	88.1 \pm 1.5	89.7 \pm 3.1	94.1 \pm 1.2	82.4 \pm 3.2	84.3 \pm 1.0	92.6 \pm 1.8
NB									
1,3-DNB	89.6 \pm 6.2	92.6 \pm 3.0	92.5 \pm 5.5	88.7 \pm 1.2	91.7 \pm 1.2	94.2 \pm 2.1	84.7 \pm 5.5	80.3 \pm 4.0	89.1 \pm 1.4

^a no analytes detected in unspiked waters; sample volume was 500 mL, sample concentration 0.5 μM , and $n = 3$. ^b Li-homoionized, 5 to 10 μm . ^c effluent from the wastewater treatment plant in Opfikon-Glattbrugg (Canton Zurich, Switzerland). ^d contaminated groundwater from the Landfill of Riet (Canton Zurich).

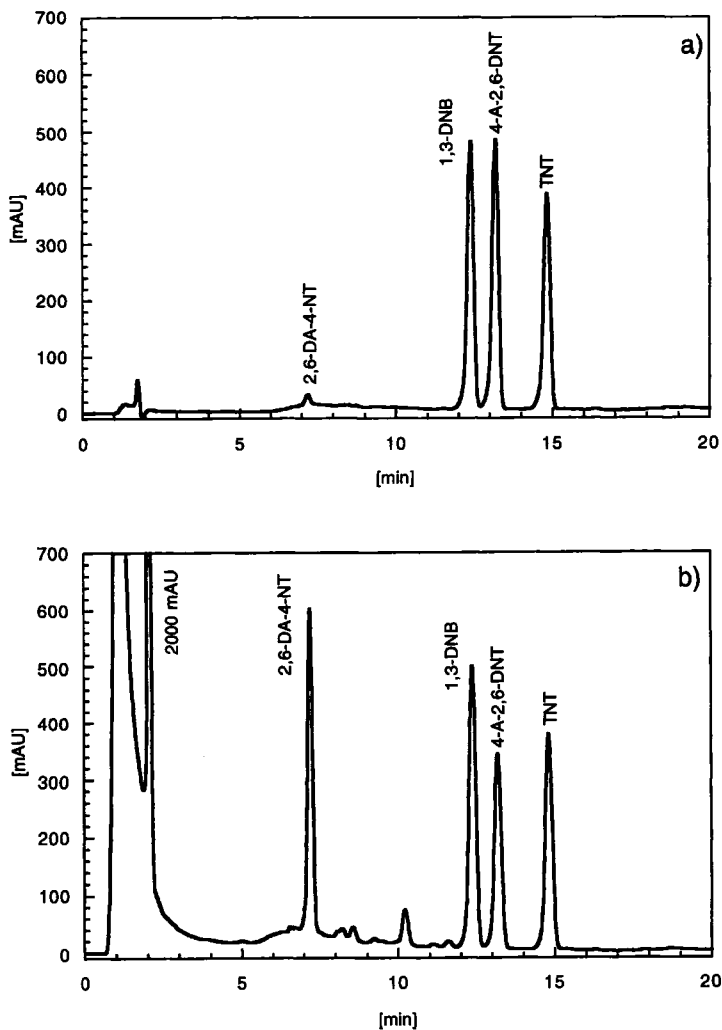


Figure 3.8 Offline SPE of 500 mL contaminated groundwater (Landfill of Riet, Canton Zurich) spiked with 0.5 μM of the investigated NTs and NB on CCMs (a, Li-homoionized, 5 to 10 μm), and on Porapak RDX (b). The DOC content of this sample was around 20 mg/L. The influence of the environmental matrix is clearly enhanced in b, and the peak of 2,6-DA-4-NT reduced in a. $\lambda = 242 \text{ nm}$.

Most of the investigated compounds revealed persistently high recoveries irrespective of the environmental matrix when extracted with CCMs (Table 3.3). The recovery of 2,6-DA-4-NT in Nanopure water, however, was again reduced due to breakthrough, and further diminished in the presence of an environmental matrix. Hence, similar effects as with the above described online SPE-HPLC were observed for the offline SPE of NTs and NB on CCMs. Compared with recoveries obtained with SPE using commercially available products, recoveries with CCMs were similar or even slightly higher for 4-A-2,6-DNT, 1,3-DNB, and TNT. Only for 2,6-DA-4-NT, the commercial products clearly exhibited better recoveries in both Nanopure, and environmental waters.

3.3.5 Applicability of SPE with CCMs for the Enrichment of Other Compounds

In addition to the compounds discussed above, some other NACs and other aromatic compounds with electron withdrawing substituents were used to assess the potential of CCMs as a SPE material. 100 mL with a concentration of 0.1 μM of three nitro musks, a representative of the nitro azocompounds, and one of the benzonitriles were analyzed, using online SPE-HPLC with CCMs. Apart from the nitro groups, all three nitro musks contain a *tert*-butyl substituent. Alizarin yellow R was selected as model compound that represents larger planar aromates, but additionally exhibits π -electron resonance over two aromatic rings due to a connecting azo group. Chlorothalonil only possesses the moderately electron withdrawing substituents chlorine and nitrile. The recoveries obtained from Nanopure, and various natural waters are listed in Table 3.4. High recoveries were achieved in Nanopure water for all three odorants. The recovery of $81 \pm 2 \%$ for alizarin yellow R from Nanopure water reveals the potential of the SPE material for enrichment of such compounds as well. For chlorothalonil a recovery of $100.6 \pm 1.8 \%$ ($n = 3$) was obtained. Moreover, no decrease in the recoveries for any of these compounds was observed in natural waters. This indicates that the application of the presented CCMs is not restricted to NACs, but can serve as a SPE material for a variety of aromatic compounds with electron withdrawing substituents.

Table 3.4 Recoveries of other compounds investigated in Nanopure and various natural waters using online SPE-HPLC with CCMs^a

	Nanopure water	rainwater	waste water ^b	groundwater ^c
nitro musks				
musk ketone	100.3±1.7	96.9±0.7	93.6±2.0	90.2±0.6
musk tibetene	104.8±6.1	103.5±1.4	102.3±1.1	102.9±2.0
musk xylene	106.7±5.4	109.9±1.5	101.4±2.5	108.7±1.0
nitro diazobenzene				
Alizarin yellow R	81.0±2.0 ^d			
benzonitrile				
chlorothalonil	100.6±1.8	100.7±0.3	99.5±0.5	103.0±0.3

^a no analytes detected in unspiked waters; sample volume was 100 mL, and sample concentration 0.1 µM, and n = 3. ^b effluent from the wastewater treatment plant in Opfikon-Glattbrugg (Canton Zurich, Switzerland). ^c contaminated groundwater from the Landfill of Riet (Canton Zurich). ^d n = 2.

3.3.6 CCMs as Stationary Phases in HPLC: Separation of NACs

CCMs revealed a considerable potential to serve as a stationary phase in HPLC columns. Fig. 3.9 shows the separation of three NTs and one NB (20 µl 10 µM injected) on a 5 cm column packed with Cs-homoionized CCMs of 10 to 20 µm. The plate number of this column was around 4500 per meter. With an ACN gradient from 0 % (100 % CsCl 0.02 M) to 50 % (50 % CsCl 0.02 M) within 15 min, baseline separation of the analytes was easily achieved.

Plate numbers, determined with a conservative tracer (thiourea), were up to 6000 per meter for a separation column with Li-homoionized CCMs in the 5 to 10 µm diameter range. For comparison, the plate numbers of commercially available HPLC separation columns are five to ten times higher. To improve the performance of CCM-HPLC columns, uniform particles with a very narrow size distribution would be required, the production of which was beyond the scope of this work. Such columns could be used as an alternative to the conventional reversed phase columns, where separation of certain NACs might pose a problem.

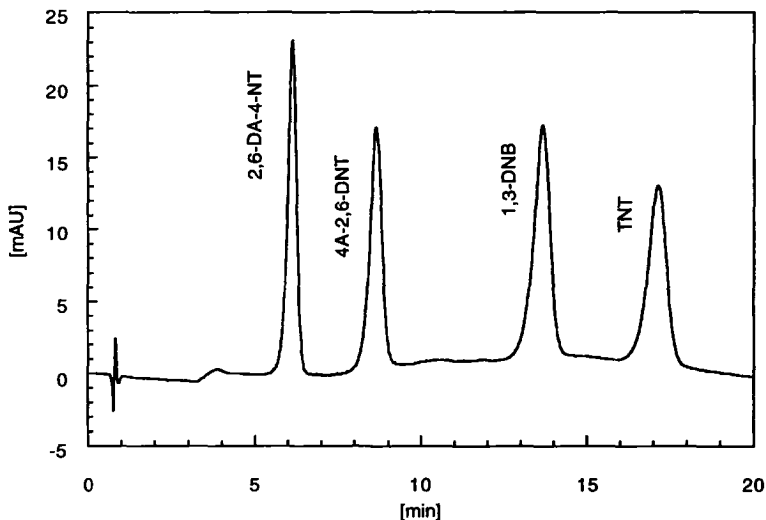


Figure 3.9 Separation of three NTs and one NB on a column wet packed with CCMs (Cs-homoionized, 10 to 20 μm). For HPLC conditions: see text.

3.3.7 Correlation Between K_d of NACs on Natural Clay Minerals and the Analytical Performance of CCMs

Whereas the K_{ow} is a determinant for breakthrough volumes and retention capacity of solid phases in reversed phase chromatography, the K_d of NACs on natural clay minerals, as described by Haderlein & Schwarzenbach (1993) triggers these parameters in the presented case. The treatment during production of the CCMs (e.g., heating) did not have any discernible effect on the specific sorption characteristics. To illustrate this relation, the model NACs used for the assessment of the produced solid phase were chosen to cover a wide range of K_d 's from about 45 for 2-NP to 37'000 for DNOC (K-montmorillonite, data from Haderlein et al., 1996; for physico-chemical properties of the investigated compounds, see appendix A.2). Clearly, breakthrough volumes and MDLs of the compounds in Nanopure water, as well as the influence of the environmental matrix on recoveries from natural waters, corresponded with the respective K_d on homoionized natural clay minerals. Moreover, breakthrough volumes, and MDLs may be anticipated for any substance for which the K_d on natural clay

minerals is known. Roughly, any compound exhibiting a moderate to high K_d on K-montmorillonite (see Haderlein et al., 1996) has the potential to be analyzed with the present method at concentrations below 100 ng/L. Also, the retardation of NACs in clay mineral separation columns correlated with their respective K_d on natural clays.

3.4. Conclusions

It has been demonstrated that CCMs may serve as a solid phase for extraction of planar aromatic compounds with electron withdrawing substituents from aqueous solutions. A set of priority pollutants served as model compounds for the validation of the SPE with the new material in terms of recoveries from Nanopure and various natural waters and MDLs. Breakthrough volumes > 1 L in Nanopure water, and MDLs of a few ng/L in natural waters were obtained for priority pollutants such as DNOC, and TNT, and selected metabolites and byproducts (e.g., 2,4-DNP, 4-A-2,6-DNT, and 1,3-DNB) with an online SPE-HPLC setup. It was also shown that the offline SPE with CCMs successfully competed with commercial products for analysis of, e.g., DNOC, and TNT. Generally, the analytical performance correlated with the strength of the EDA complex formation between analytes and the solid phase. Moreover, the potential of the almost spherical CCMs to be used as a new stationary phase in HPLC was highlighted. The characteristics of the CCMs to be completely regenerable and pressure-resistant, the minimized sample preparation, and the fully automated enrichment, separation and detection of the analytes rendered the online SPE-HPLC method with CCMs perfectly suited for the low-cost routine analysis of NACs and related compounds in various kinds of environmental samples.

4. Occurrence and Behavior of Pesticides During Artificial Roof Runoff Infiltration

4.1 Introduction

Storm water infiltration is becoming increasingly important in urban regions, as it prevents the overloading of sewer systems, and recharges the groundwater underneath sealed areas (Boller, 1997; Mikkelsen et al., 1994). In fact, according to Swiss legislation, unpolluted wastewaters have to be directly percolated into the ground (Federal Law on the Protection of Waters, 1993, Article 7, Paragraph 2). However, when considering that storm water may contain significant levels of pollutants, unrestricted application of this law is somewhat ambiguous, particularly because artificial systems exhibit a deliberately enhanced permeability to achieve accelerated percolation velocity, thus resulting in reduced retention and degradation of both atmospheric, and roof-delivered contaminants in the underground. As pointed out in chapter 1, the importance of pesticides in regard to direct infiltration of storm water has hitherto hardly been assessed.

In this chapter, data from various field studies are presented that aim to evaluate to what extent certain classes of widely used pesticides originating from agricultural applications could pose a problem with respect to groundwater contamination due to the direct infiltration of roof runoff. To this end, several different aspects of roof water infiltration were investigated. First, the occurrence and the seasonal variations in concentration in rainwater were determined for a series of pesticides (i.e., triazines, acetamides, and phenoxy acids). In addition, during selected rain events, the washout dynamics and the resulting temporal development in concentration of these compounds in roof runoff was investigated for three types of roofs, i.e., a clay tile roof, a polyester roof, and a flat gravel roof. Finally, at one field site, a complete analysis of the transport and behavior of selected pesticides from rain via three different roofs into the ground has been performed.

The results presented add some important information to the currently still rather poor knowledge on the transfer of organic pollutants from the atmosphere to groundwater by artificial infiltration of roof runoff during storm water events.

4.2 Experimental Section

4.2.1 Field Sites and Sampling Procedures

4.2.1.1 Rain Samplers

Rainwater was collected at Dübendorf (Canton Zurich), Grüze (an industrial suburb of Winterthur, Canton Zurich), and Tüffenwies (an industrial area in the north-western part of Zurich) with a 1 m² Teflon rain sampler for bulk samples (Fig. 4.1), and a self-made 5.06 m² funnel coated with a teflon foil for sequential rainwater sampling (Fig. 4.2). During dry periods, the latter sampler was covered with a plastic sheet, and washed with Nanopure water and methanol (MeOH) prior to rainwater sampling.



Figure 4.1 Bulk rain sampler (right) as used in Dübendorf, Grüze, and Tüffenwies.

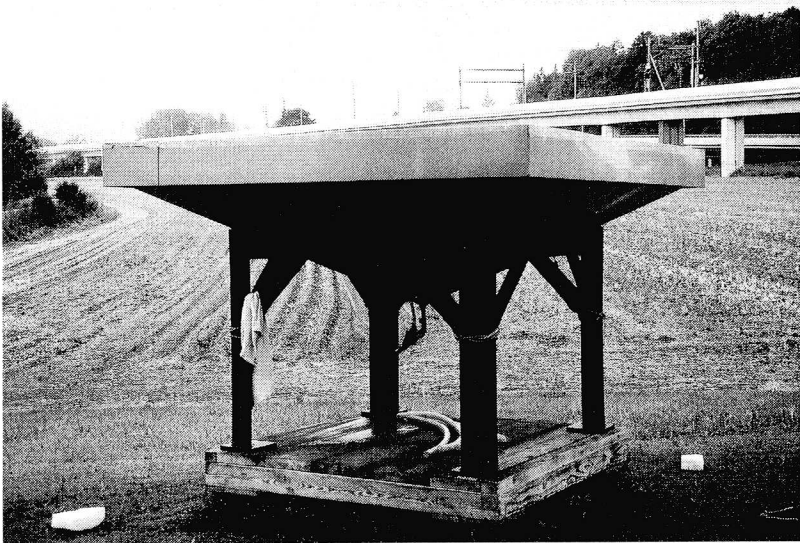


Figure 4.2 Funnel for sequential rainwater sampling.

4.2.1.2 Model Roofs in Tüffenwies

To study the roof runoff dynamics of pesticides during various rain events, a set of three different roofs had been used, namely a polyester roof (Fig. 4.3), a clay tile roof (Fig. 4.4), and a flat gravel roof, that was partly covered with naturally grown vegetation (Fig. 4.5). The polyester, and the flat gravel roof, and the rainwater samplers were located at Tüffenwies, and the clay tile roof was situated on the Werdinsel, a few hundred meters away from the other sampling site. Projected roof areas and inclinations were as follows. Polyester roof: 108.8 m² and 5.6°, clay tile roof: 89.2 m² and 37.96°, and flat gravel roof: 134 m² and 0°. Sampling of sequential roof runoff was automatically performed using an apparatus setup provided by IMETH AG (Wetzikon, Switzerland).



Figure 4.3 Polyester roof in Tüffenwies.



Figure 4.4 Clay tile roof at Werdinsel.

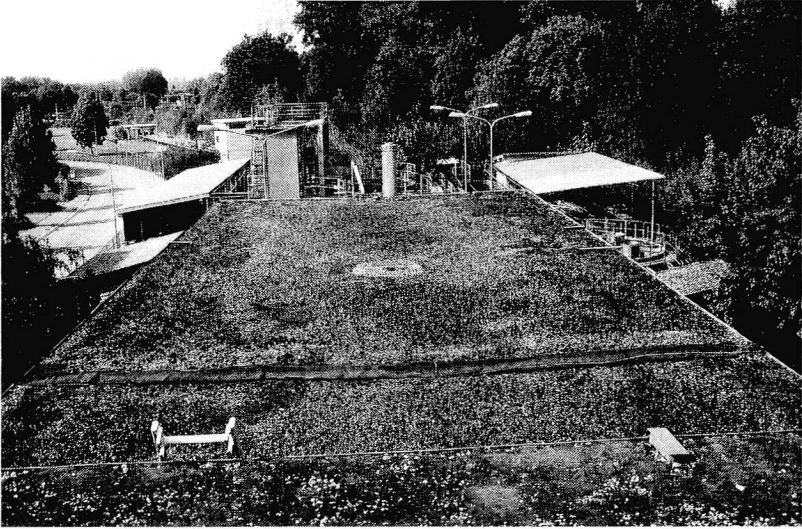


Figure 4.5 Flat gravel roof in Tüffenwies.

4.2.1.3 Storm Water Infiltration Site in Grütze

The storm water infiltration site is situated in Grütze. At this site, the runoff of three different roofs (for overview, see Fig. 4.9), namely a flat gravel roof (3860 m², Fig. 4.6), a flat gravel roof covered with a humic layer (715 m², Fig. 4.7), and, detached, a plastic roof from a nearby gasoline station (485 m², Fig. 4.7) is combined and sampled as described above. The two flat roofs in are equipped with root resistant polymer-modified bituminous roofing membranes from Soprema (Spreitenbach, Switzerland).

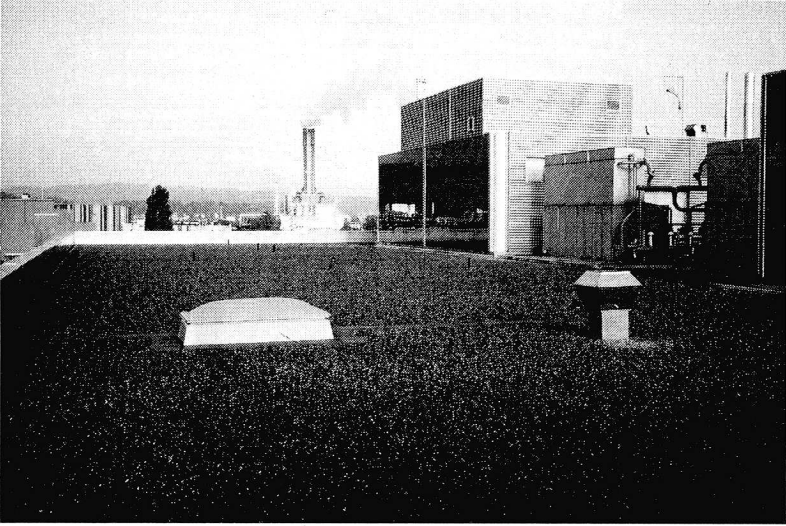


Figure 4.6 Flat gravel roof in Grütze.

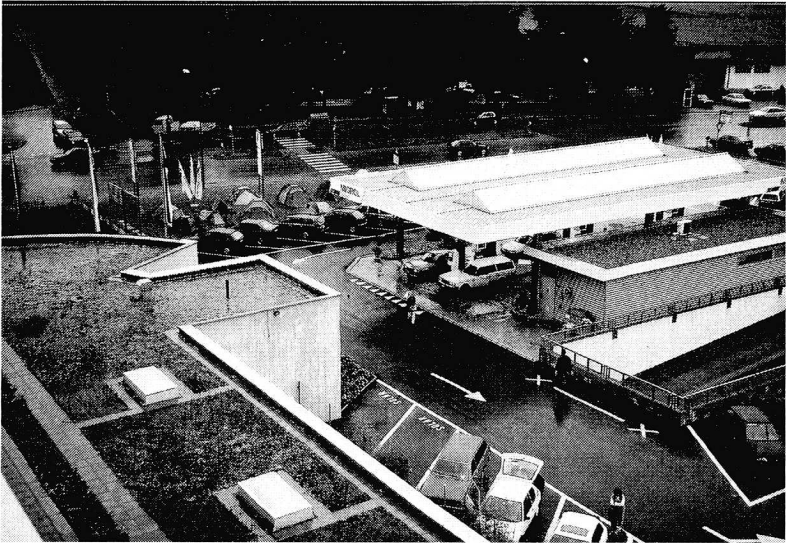


Figure 4.7 Flat roof covered with a humic layer (bottom, left corner) and plastic roof in Grütze (top, right corner), as seen from the top of the flat gravel roof (Fig. 4.6).

The combined roof runoff (Fig. 4.9, 5) is discharged into an infiltration pit (Fig. 4.8 and Fig. 4.9, 6) with an area of 106 m² and 3-4 m depth.



Figure 4.8 Storm water infiltration pit in Grütze with roof runoff inflow (black pipe) and sampling shaft.

Fig. 4.9 schematically depicts the infiltration site, as well as the sampling installations within the subsurface of the pit. At this site, the shallow subsurface sediments consist of a fluvio-glacial gravel. On the top of a 60 cm-drainage gravel layer, some 5-10 cm of humic layer were deposited (Fig. 4.9, 11-13). At the bottom of the infiltration pit, a shaft of 2 m in diameter and depth was inserted into the ground (Fig. 4.9, 7, and Fig. 4.10). From within that shaft, various lysimeters (home made, polyethylene (PE), six half pipes with areas of 3 times 600 cm² each (Fig. 4.9, 8), and three single vessels with 1800 cm² each (Fig. 4.9, 9)) and suction cups (Fig. 4.9, 10, Prenart Super Quarz; PRENART Equipment ApS, Frederiksberg, Denmark) were radial-symmetrically installed. They covered a section of $\pm 100^\circ$ around the direction of the roof runoff inflow and allow the sequential or integrated sampling of percolating water at three different depths (40, 100, and 160 cm, respectively). Sample vessels used were made from either PE or polycarbonate. No significant sorption on lysimeter materials, suction cups, and sample equipment was found for any of the compounds investigated (data not shown). For a more detailed description of the field systems, see (Hoehn & Koch, 1998).

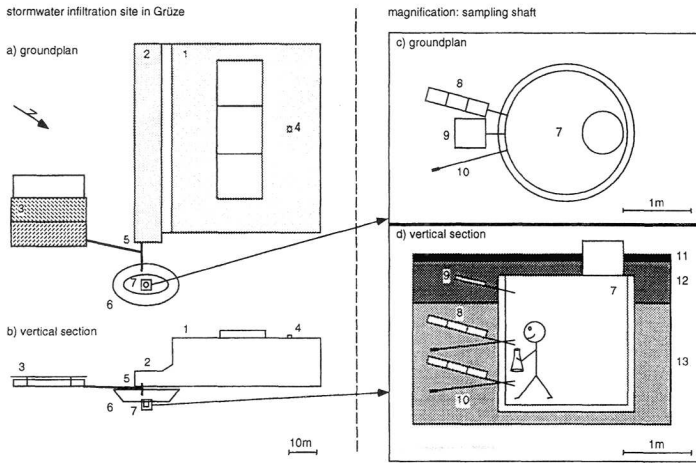


Figure 4.9 Storm water infiltration site in Grütze with groundplan (a), and vertical section (b), and enlarged sections of the sampling shaft within the infiltration pit with groundplan (c), and vertical section (d, simplified). 1 flat gravel roof, 2 flat gravel roof with rooftop planing, 3 plastic roof, 4 Teflon rain sampler, 5 combined roof runoff, discharged through one single pipe into the infiltration pit, 6 infiltration pit, 7 sampling shaft, 8 lysimeters (three in 100 cm, and three in 160 cm depth, each one comprising three compartments with 600 cm² each), 9 lysimeters (three in 40 cm depth with an area of 1800 cm² each), 10 suction cups (three in 100 cm, and three in 160 cm depth), 11 humic layer (10 cm depth), 12 drainage gravel layer (60 cm), 13 natural aquifer sediment of fluvio-glacial gravel.

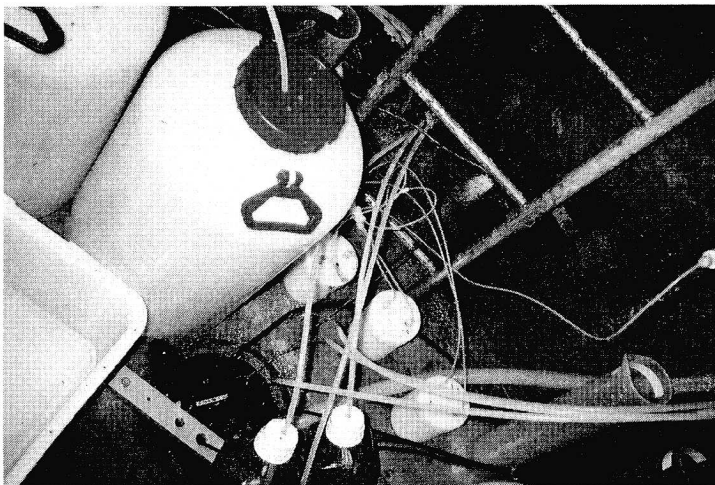


Figure 4.10 Sampling shaft within the subsurface of the storm water infiltration pit. During rain events, the percolating water was caught by various lysimeters and was delivered through tubes inside the shaft.

4.2.2 Pesticide Analysis, and Stability in Natural Waters

Sample treatment, and the analytical method for the determination of selected pesticides is subject to chapter 2. Additionally, chiral separation of the R-, and S-enantiomers of mecoprop and dichlorprop was performed with a fused silica capillary column (FS 71 PS-O86 0.2 % + 20 % Me- β -CD, 0.13 μ m film thickness, 0.25 mm i.d., 15 m). The oven temperature was programmed as follows: 1 min at 60 °C, to 165 °C at 15 °C/min, to 230 °C at 25 °C/min, 3 min at 230 °C. Retention times were 7.74 min, and 7.84 min for R-, and S-mecoprop, and 8.30 min, and 8.38 min for R-, and S-dichlorprop, respectively. Detection limits in rain samples of the chiral compounds were around 1 ng/L (corresponding to a signal to noise ratio of three). Peak areas were used for the determination of the enantiomeric ratios. If only one enantiomer was present, the noise area of the respective missing compound served for calculation of the ratio. In this case, the ratio is a minimum number. All other parameters were as described above.

During earlier investigations, it has been found that triazine pesticides in natural water samples were stable for a few years when stored at 4°C in the dark (see chapter 2). For the main representatives of the acetamides, no significant changes in concentrations were observed within eight months after sampling (metolachlor, recovery: 96 ± 5 %, $n = 4$; alachlor, recovery: 85 ± 14 %, $n = 4$). However, the most important phenoxy acids were significantly degraded within that time period (e.g., (R,S)-mecoprop, recovery: 76 ± 3 %, $n = 3$; and (R,S)-dichlorprop, recovery: 52 ± 40 %, $n = 5$). Note that the degradation of the chiral compounds metolachlor, (R,S)-mecoprop, and (R,S)-dichlorprop may be enantioselective, and that racemization may occur (Garrison et al., 1996; Müller & Buser, 1997; Zipper, 1996). Thus, acetamides and phenoxy acids were only quantified if analysed within the first three months after sampling.

4.3 Results and Discussion

4.3.1 Seasonal Variation in Occurrence and Concentrations of Pesticides in Rainwater

Table 4.1 summarizes the results from 41 subsequent rainwater samples analysed for triazines, acetamides, and phenoxy acids from February to October 1996 in Grütze. In addition, for the most important representatives of each of the compound classes investigated, the specific daily and cumulative loads during this period are

shown in Fig. 4.1.1. From these, and from results obtained at the other sites (Tüffenwies, and Dübendorf, data not shown), some general features are apparent. First, for all three pesticide classes, the compounds most frequently detected are, with a few exceptions (e.g., Propachlor, and (R,S)-dichlorprop, which is of rather marginal importance in Switzerland, and was hardly found in surface waters, Buser & Müller, 1998) also the compounds most frequently used in Switzerland (e.g., atrazine, although its use in Switzerland has been restricted several times within the last years, Müller et al., 1997). Note that the same substances are also important pesticides in many other countries. Within the analyzed compounds, pesticides not registered in Switzerland including atratone, acetochlor, 2,4,5-T, and 2,4,5-TP were never detected in any of the rainwater samples.

Table 4.1 Pesticides in rainwater from February to October 1996 at Grütze

	detected in n samples out of 41	main period of appearance ^a	concentration [ng/L]		total load ^b [ng/m ² /yr]
			median	maximum	
triazines					
atrazine	28	early May - mid July	33	903	13900
desethylatrazine	20	mid May - end of July	29	166	5400
deisopropylatrazine	13	late May - late June	26	137	3000
terbutylazine	13	early April - late June	9	48	1800
simazine	10	late March - begin of July	10	53	700
propazine	1	mid June	7	7	10
acetamides					
alachlor	16	end of April - end of May	19	191	5900
metolachlor	16	begin of May - begin of June	15	124	4400
propachlor	12	mid May - early August	10	48	1300
dimethenamid	4	mid May - mid June	24	78	300
metalaxyl	2	late February - begin of July	14	17	100
metazachlor	1	mid September	12	12	400
phenoxy acids					
R-mecoprop	17	mid April - end of July	10	50	3900
S-mecoprop	11	mid May - late August	10	19	3000
R-dichlorprop	20	end of March - early June	12	106	5100
S-dichlorprop	2	early April - mid May	9	11	300
2,4-D	2	begin of May - early May	16	23	400
MCPA	4	early April - early May	16	27	800

^a the time span in between which 10 %, and 90 %, respectively, of the total load was deposited; begin of: 1st to 6th, early: 7th to 12th, mid of: 13th to 18th, late: 19th to 24th, and end of: 25th to 30th day of the month. ^b assuming no or little application and atmospheric occurrence of the investigated pesticides from November to January.

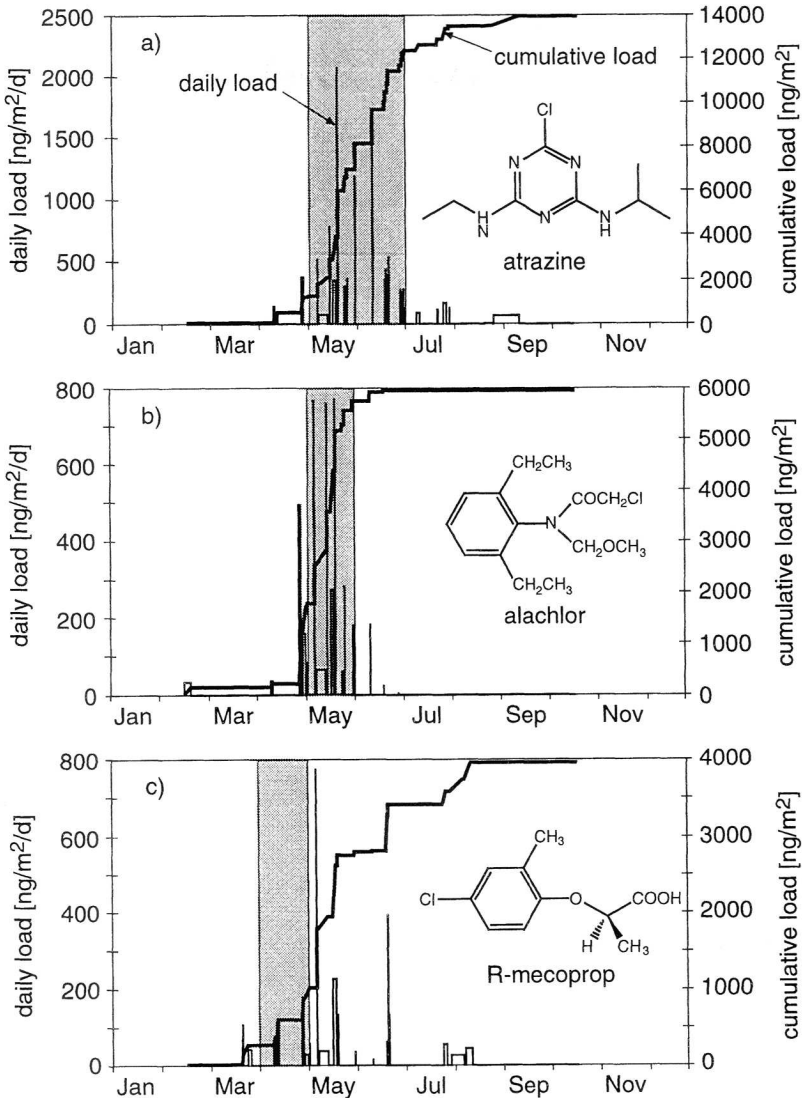


Figure 4.11 Specific daily and cumulative load of atrazine (a), alachlor (b), and R-mecoprop (c) from February to October 1996 in Grütze. Shaded areas indicate the main application period of the individual pesticide.

Most parent compounds were detected at significant concentrations primarily during and/or right after their main application period in spring and early summer (see Fig. 4.11, shaded areas, and Table 4.1, third column). Generally, there was a certain trend in that the more volatile herbicides (e.g., alachlor, and metolachlor) were primarily found during the application period, while the less volatile, and/or ionizable ones (i.e., the phenoxy acids, or atrazine) were still present in rainwater several weeks later. However, further factors, such as the mode of application, and locally different microclimates, may contribute to such observations.

In addition to the parent compounds, some metabolites (i.e., deethyl- and deisopropylatrazine), and enantiomers of optically active herbicides (i.e., S-mecoprop, and S-dichlorprop, which are known to be formed in the environment by racemization of the active R-form, Müller & Buser, 1997) were found quite frequently. Also, maybe not too surprisingly, peak concentrations of the atrazine metabolites, and the S-mecoprop were observed with a delay of between two and six weeks with respect to their parent compounds. Over the season, the desethylatrazine to atrazine, and the R- to S-mecoprop concentration ratios changed markedly from 0.36 ± 0.21 ($n = 12$, average atrazine concentration: 81 ± 109 ng/L) before June 30 to 0.70 ± 0.42 ($n = 8$, average atrazine concentration: 211 ± 299 ng/L) later on, and from 2.05 ± 1.86 ($n = 17$, average R-mecoprop concentration: 14 ± 11 ng/L) to 0.35 ± 0.13 ($n = 8$, average R-mecoprop concentration: 5 ± 1 ng/L, respectively). These findings suggest that after the application period, during several weeks, there was still a significant input of less volatile pesticides and, particularly, of their primary transformation products, into the atmosphere.

For a judgement of the significance of the concentration levels found for the various pesticides in the rainwater, it is useful to compare these values with the Swiss, and EC drinking water standards of 100 ng/L and 500 ng/L for single and total pesticides, respectively. From the data given in Table 4.1, it can be seen that only a few single compounds, and among them, particularly atrazine, significantly exceeded the 100 ng/L limit. Note that a certain dependence of pesticide concentrations on the amount of rain could be observed, with highest numbers for events of a few mm of precipitation only. This is consistent with the observation that these rather polar pesticides are washed out quite efficiently from the atmosphere (see below). Compared to the single compounds, for total pesticides, in spring and early summer, the situation is somewhat more critical, particularly when considering that other important compound classes including, for example, nitrophenols (see Herterich, 1991; Tremp, 1992, and chapter 5) and halogenated acetic acids (Frank et al., 1994; Müller et al., 1996), must be suspected to be concomitantly present in rainwater. Hence, during the main pesticide

application times, rainwater may exhibit total pesticide concentrations that markedly exceed the drinking water standard of 500 ng/L.

4.3.2 Washout Dynamics of Pesticides During Single Rain Events

The knowledge on the deposition characteristics of pesticides is essential for the correct interpretation of the subsequent investigations of roof runoff behavior. As already pointed out above, because of the rather low Henry's law constants of most of the pesticides investigated ($1E-6$ to $1E-9$, dimensionless, for physico-chemical properties of the investigated compounds, see appendix A.1), it can be anticipated that particularly the triazines, and the phenoxy acids should be readily washed out from the atmosphere if mainly present in the gas phase. Thus, a significant drop in concentration of the first few millimeters of rain can be expected for such compounds. This hypothesis was tested by the sequential sampling of rainwater from single rain events during the application period. Fig. 4.12 depicts the concentration dynamics of atrazine for three different rain events in May and June 1995. Concentrations were found to be maximal (up to 3 $\mu\text{g/L}$) at the onset of rain events and rapidly decreased by a factor of 10 - 20 within the first two mm of rain. Thus, the washout of atrazine exhibited a so-called 'first flush' effect, as it also has been observed by Trautner et al. (1992). This was also found to be the case for the other pesticides investigated, and for various other compounds (see, e.g., Tremp, 1992).

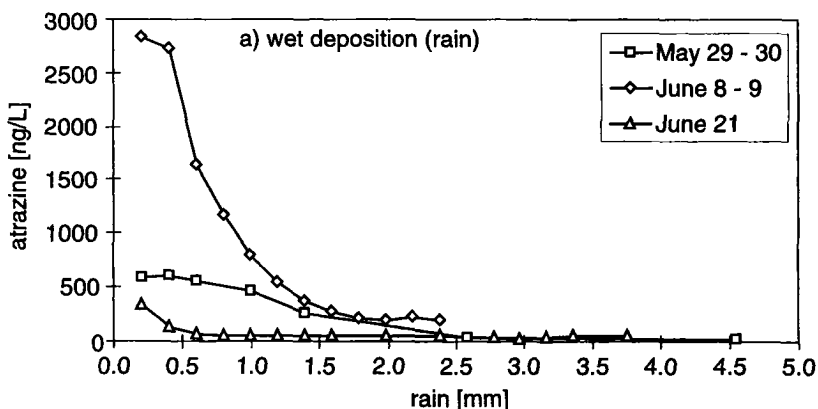


Figure 4.12 Wet deposition dynamics of atrazine during three rain events in Tüffenwies. Rain events were sampled within the application period in 1995.

Fig. 4.13, however, visualizes the possible heterogeneity in the washout dynamics of various substances during certain rain events, using concentration normalized graphs.

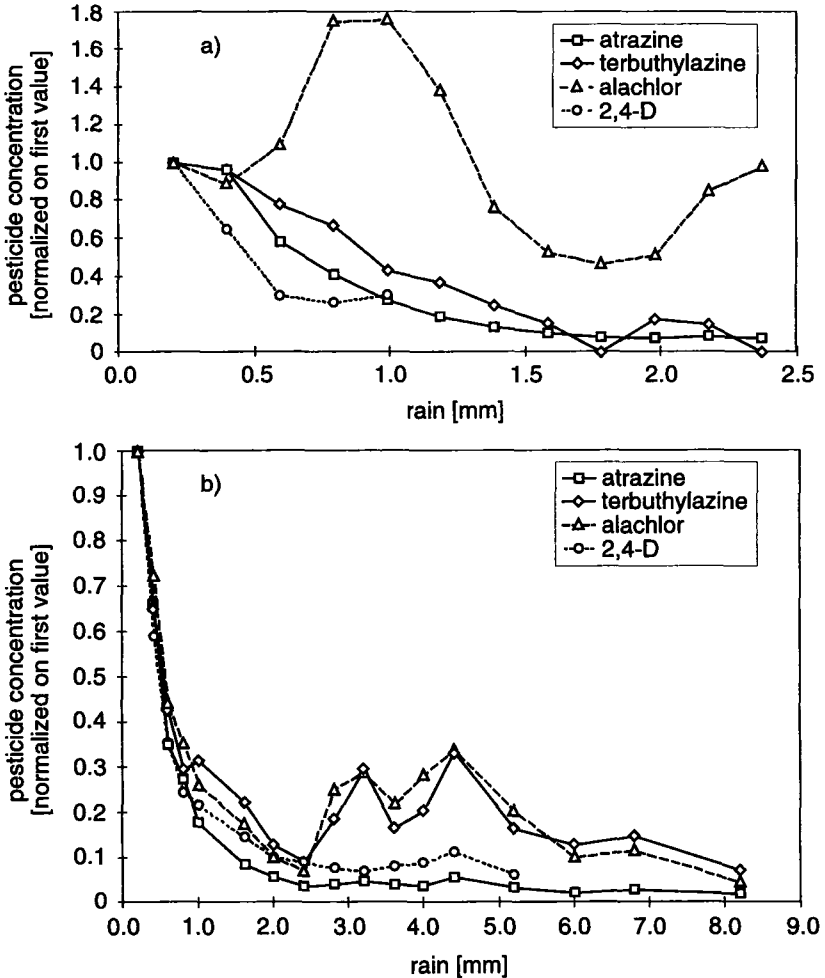


Figure 4.13 Comparison of the wet deposition dynamics of different pesticides: variations to the normally observed first flush washout behavior. a) Rain event from June 8, 1995 in Tüffenwies. Washout of a homogenous, more local air mass. b) Rain event from April 26, 1997 in Dübendorf. Passage of two subsequent air masses of different origin.

On the one hand, Fig. 4.13 a depicts a compound class specific deposition behavior during the washout of a rather homogenous air mass: whereas the triazines (represented by atrazine, and terbuthylazine) and the readily soluble phenoxy acids (e.g., 2,4-D) showed a similar deposition pattern, i.e., a first flush washout effect, the detected more volatile acetamides (alachlor, metolachlor, and dimethenamid) indicated increasing, rather than decreasing concentration in the course of the rain event. On the other hand, subsequent scavenging of air masses with different origin led in an altered deposition pattern that was not compound class specific (Fig. 4.13 b), but depended on the actual pesticide composition of the respective air masses. Nevertheless, in the majority of the rain events investigated, the atmospheric washout of different types of pesticides usually occurred simultaneously and immediately, and with initial concentrations up to a few $\mu\text{g/L}$.

4.3.3 Roof Runoff Dynamics During Single Rain Events

For the runoff from roofs exhibiting a very low water storage capacity and thus a very short water residence time (i.e., the investigated clay tile and polyester roofs), the most important question is whether there is a significant additional input from previous dry deposition of pesticides on the roofs. In Table 4.2, the total loads calculated for various pesticides in runoff from clay tile and polyester roofs are compared to the respective loads in the rainwater. As is evident, in no case, a significant additional input of any of these substances was found for these two types of roofs. Thus, dry deposition of the compounds investigated is of minor importance, which is in accordance with Glotfelty et al. (1990), and Gottschild et al. (1995). Note that for other types of organic compounds, e.g., 4-nitrophenol, which was found to be mainly particle bound (Lüttke & Levsen, 1997), dry exposition has been observed (Hermann et al., 1994). In some cases, even some losses were observed, particularly for minor rain events, which could have been due to sorption of the compounds during initial wetting of the roof surfaces. However, as is illustrated with Fig. 4.14 for atrazine, for clay tile and polyester roofs, in general, the runoff dynamics reflected more or less the washout dynamics of the pesticides from the atmosphere.

Table 4.2 Relative runoff loads of different roof types (normalized to the respective rain load)

	clay tile roof, Tuffenwies	n	polyester roof, Tuffenwies	n	flat gravel roof, Tuffenwies minor rain events (5-15 mm)	n	flat gravel roof, Tuffenwies major rain event (20 mm)	n	combined roof system, Grütze major rain events (> 53 mm)	n
atrazine	0.9 ± 0.3	7	1.2 ± 0.4	4	0.04 ± 0.02	3	0.73	1	0.93	1
desethylarazine	1.0 ± 0.4	7	1.2 ± 0.2	4	0.08 ± 0.03	3	0.82	1		
deisopropylarazine	0.7 ± 0.2	6	0.7 ± 0.1	2	0.10 ± 0.01	2	1.07	1		
terbuthylazine	0.6 ± 0.3	6	1.1 ± 0.3	4	2.28 ± 2.79	4	2.59	1		
simazine	0.7 ± 0.3	5	0.9 ± 0.3	4	0.03	1				
alachlor	1.0 ± 0.2	2								
metolachlor	1.1 ± 0.2	2								
(R,S)-mecoprop	0.6 ± 0.5	2							41.0	1
(R,S)-dichlorprop	0.9	1								
2,4-D	0.8 ± 0.4	2								
MCFA	1.0	1								

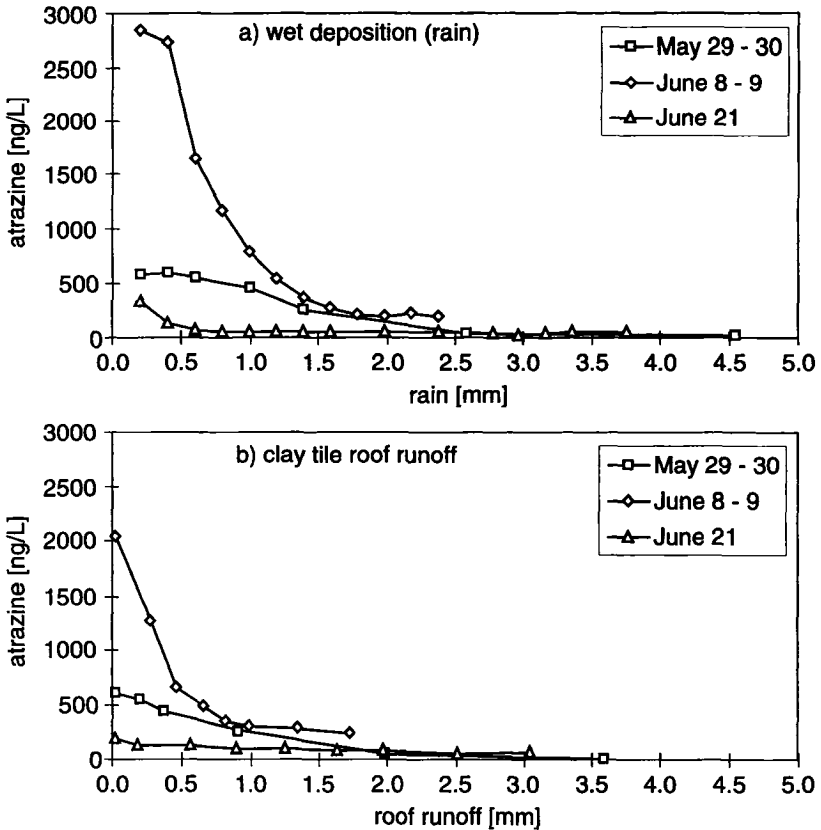


Figure 4.14 Wet deposition (rain, a), and clay tile roof runoff (b) dynamics of atrazine during three rain events in Tüffenwies. Rain events were sampled within the application period in 1995.

A quite different picture was obtained for the flat gravel roofs, owing to their significant water storage capacity. During a rain event, deposited compounds may be retained on the roof which may lead to a significant dampening of concentration fluctuations. This is visualized in Fig. 4.15, which shows the temporal variation in concentration of atrazine in the runoff of the clay tile roof, and of the flat gravel roof, respectively, during the same rain event in Tüffenwies.

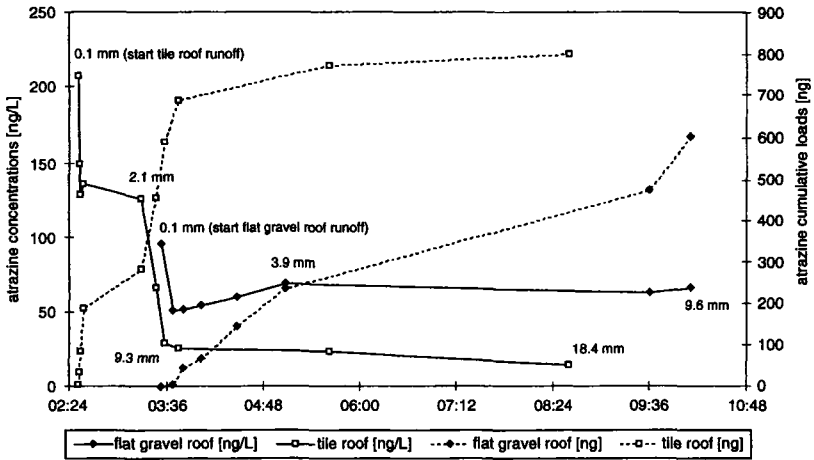


Figure 4.15 Comparison of atrazine in roof runoff from two extremely different roof types during the same rain event (July 3, 1995, Tüffenwies).

The clay tile roof runoff showed a typical first flush behavior with initial atrazine concentrations of about 200 ng/L (Fig. 4.15 open squares, solid line). In contrast, on the flat gravel roof, the first flush was stored and diluted by subsequent rainwater until the water storage capacity was reached, which happened about one hour after the begin of the rain. As is evident from Fig. 4.15 (filled diamonds, solid line), in this case, a much less pronounced first flush behavior and a more or less constant atrazine concentration in the runoff was observed. Note that after the first 10 mm of runoff, the cumulative atrazine loads were quite similar for both roofs (see broken lines in Fig. 4.15), and, when integrating over the whole rain event (> 20 mm), they also corresponded reasonably well to the respective load from the rainwater (Table 4.2, flat gravel roof, Tüffenwies, major rain event). This indicates that no major loss of atrazine (as well as of the other triazines) occurred on the flat roof during this major rain event. Moreover, contrary to roofs with little storage capacity, the flat roof delivered the deposited pesticide loads continuously over the whole rain event (Fig. 4.15, broken lines).

When considering minor rain events, however, the flat gravel roofs may act as a sink, i.e., only minor parts of the total rainwater loads are found in the runoff (see Table 4.2). In such cases, in which the water storage capacity of the roof is only slightly exceeded by the total amount of precipitation, the compounds are retained on the roof. During subsequent dry periods, the compounds may then be (bio)degraded on the roof,

as is indicated by the generally higher desethylatrazine to atrazine ratio in flat roof runoff compared with rainwater (data not shown).

Finally, from the data given in Table 4.2, it can be seen that for some compounds, i.e., terbuthylazine and, particularly (R,S)-mecoprop, the loads in the runoff from certain flat gravel roofs significantly exceeded the loads in the rainfall. These findings demonstrate that flat gravel roofs may also act as sources for pesticides. For terbuthylazine, this additional input could have been due to the application on the roof itself, or in yards nearby. In the case of (R,S)-mecoprop, however, the drastically higher concentrations found in the combined runoff from the roofs in Grütze (i.e., several up to several hundred $\mu\text{g/L}$, see chapter 6) for both enantiomers could not be explained by the direct application of these compounds. It was found that (R,S)-mecoprop stemmed from the hydrolysis of Preventol® B 2, a root protection agent that is added in significant amounts (about 1 % by weight) to polymer modified bituminous roofing membranes used for sealing purposes. Details on the kinetics of the formation of (R,S)-mecoprop from Preventol® B 2, and its elution from bituminous membranes, as well as the results of field studies conducted to assess the significance of this source of pesticides with respect to storm water infiltration are discussed in chapter 6.

4.3.4 Behavior of Pesticides During Artificial Infiltration of Roof Runoff

The knowledge gathered from the above investigations with rain and roof runoff allows an overall understanding of pesticide transport from the atmosphere to groundwater via a combined roof system and the subsequent infiltration into the subsurface. To elucidate the situation within such a field site, data from two succeeding rain events from June 20, 11:00 to 20:00, and June 21, 13:00 to June 23, 24:00, 1996, respectively, are subsequently discussed.

Fig. 4.16 illustrates the flow rate of the combined runoff (lower box) from the three roofs (for details on the field site, see chapter 4.2.1.3), and the temporal development of the atrazine concentration in the roof runoff (upper box) during that period.

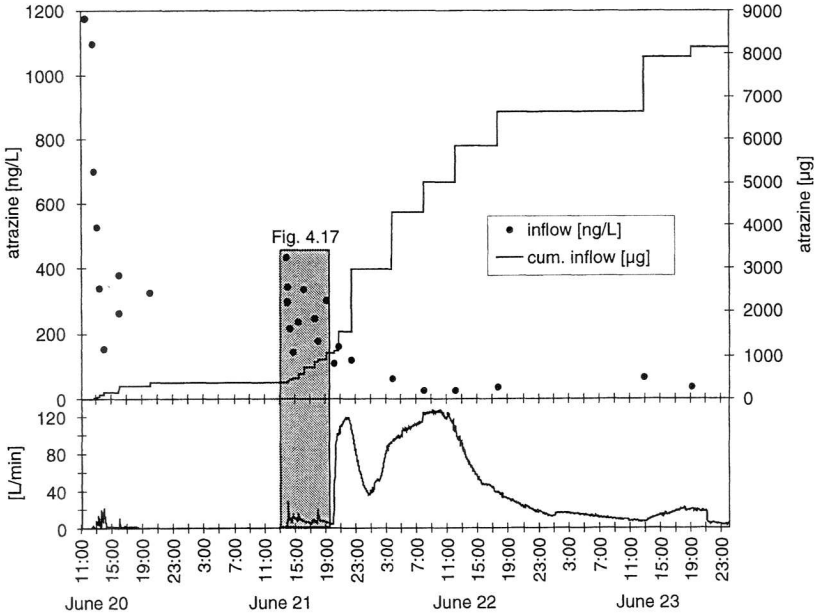


Figure 4.16 Atrazine concentrations and cumulative load in roof runoff (upper box), and runoff flow rate (lower box) into the storm water infiltration site in Grütze during two rain events from June 20, 11:00 to June 23, 24:00, 1996. The shaded area is magnified in Fig. 4.17.

A first flush washout effect from the atmosphere for both events that was still discernible in the roof runoff, which at the onset ultimately originated from the plastic roof (Fig. 4.9, 3). As soon as the two flat roofs (Fig. 4.9, 1, and 2) dominated the total runoff (only during the second rain event, i.e., June 21, 16:00, and thereafter), concentrations appeared to be much more equal. Note that atrazine was permanently present in the roof runoff for several days. All detected substances (i.e., atrazine, desethylatrazine, deisopropylatrazine, terbuthylazine, metolachlor, and dimethenamid) exhibited similar fluctuations in roof runoff concentrations, though at a significantly lower level (for data, see Appendix B). For this reason, atrazine is chosen as a model compound, on which the further discussion will concentrate.

The infiltration of roof runoff water into the subsurface was very fast and complete, i.e., almost no damming up at the soil surface was observed (for details on the hydrological situation, see Hoehn & Koch, 1998). However, the water mainly infiltrated through preferential flow paths, as indicated by the tremendous variability of the water yield from the individual lysimeters (see Fig. 4.17 and explanations below). Tracer

experiments revealed that the residence times of a conservative tracer (fluorescin) and atratone (a triazine pesticide) in first two meters of the subsurface were identical and very short (i.e., between 15 and 50 min. depending on the lysimeter).

Fig. 4.17 (enlarged section from Fig. 4.16) compares the atrazine concentrations in roof runoff samples with such from three lysimeters of different depths and with different water flow from June 21, 13:00 to 19:30.

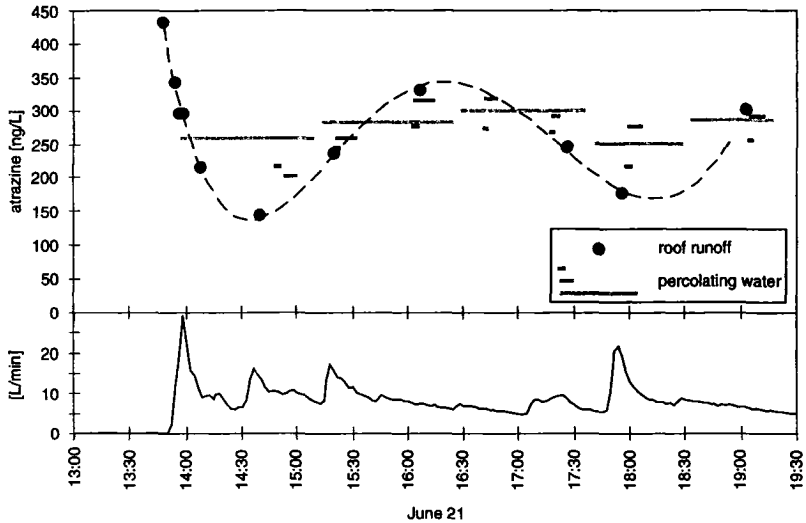


Figure 4.17 Atrazine concentrations in roof runoff and percolating waters (upper box), and runoff flow rate (lower box) into the storm water infiltration site in Grúze at the onset of a rain event from June 21, 13:00 to 19:30, 1996. Black dots indicate roof runoff samples, and the light grey, dark grey, and black bars represent water samples from different lysimeters.

The length of the lines that symbolize atrazine concentrations of the percolating water equals the time needed to provide a sample volume of 2 L, i.e., the water flows were about 0.5 L/min for the fastest, and 0.03 to 0.05 L/min for the slowest flow path. Irrespective of the large difference in the hydrodynamics and the different depth, the alterations in concentrations of roof runoff and percolating water were quite similar, and even minor fluctuations in runoff concentrations were still discernible in the infiltrating water. Moreover, atrazine concentrations in percolating waters were very similar to the one in roof runoff. This provides strong evidence that no degradation of atrazine occurred during the fast infiltration through macropores.

In suction cup water samples, originating from soil fine pores, measured atrazine concentrations were drastically reduced during the first rain event from June 20, as compared with average roof runoff concentrations (79 ng/L, and 254 ng/L, respectively), but reached similar, or even slightly higher concentrations later on (data not shown). Also, the desethylatrazine to atrazine ratio was significantly higher in the first suction cup sample than in roof runoff (0.9, and 0.36, respectively). Again, these numbers became more equal during the second rain event. Both the relatively low initial atrazine concentration and the enhanced desethylatrazine to atrazine ratio in the first suction cup sample indicate that the respective pore water was much older than the one that was currently percolating, but also than the suction cup water sampled later on. The last rain event dated from June 12, and it can be assumed that the atrazine detected in the pore water from June 20 was brought there during the event before. The subsequent approach of both the atrazine concentration and the respective parent to metabolite ratio in suction cup samples towards the values of the actual roof runoff indicates that the water exchange in these fine pores occurred within a few days.

4.3.5 Pesticide Loads from the Atmosphere to Groundwater via Storm Water Infiltration

In order to judge the relevance of atmospherically delivered pesticides with regard to storm water infiltration, and groundwater contamination potential, the transport of these substances from the atmosphere to the subsurface also needs to be discussed in terms of loads.

Table 4.1 contains the cumulative atmospheric pesticide loads from February to October 1996. These amounts deposited within that period are well within the range given in the literature (50 - 1000 mg/ha, Bester et al., 1995; Buser, 1990; Chevreuil et al., 1996; Dankwardt et al., 1997; Gottschild et al., 1995; Helweg, 1995). An estimated annual atmospheric deposition of atrazine in Switzerland would be around 560 kg, which is about 1 to 2 % of the total pesticide amount applied. As the magnitude of atmospheric deposition roughly correlates with the importance of the individual pesticides in terms of usage, it may be supposed that this percentage accounts for a majority of the pesticides investigated.

As already pointed out in chapter 4.3.3, the atmospheric pesticide load surmounted, to a large extent, roofs with low storage capacities, as the investigated clay tile, and polyester roof, and during extensive rain events, a major percentage of the deposited load was also transported over flat gravel roofs. Hence, a considerable part of

the atmospherically deposited pesticides will reach storm water infiltration sites and is there, as highlighted in chapter 4.3.4, likely to be further transported into the subsurface without any considerable reduction in loads.

The annual input from the atmosphere into the investigated infiltration pit can be estimated by multiplying the cumulative rain load from February to October (Table 4.1, and Fig. 4.11) with the total roof area of 5060 m². In the case of atrazine, this results in a total amount of approximately 70 mg. Assuming that 75 % of this may be transported via roof runoff into the infiltration pit with an area of maximal 100 m² (even though the actual area may be much smaller due to the preferential flow observed), the annual charge would be about 50 mg/100 m². This number may be compared with the groundwater charge due to agricultural usage. The maximum annual atrazine dose in Switzerland is 800 g/ha, or 8 g/100 m². Assuming 0.5 % leaching into the groundwater, which is not an unrealistic estimate (for review see Barbash & Resek, 1996), the total load to reach the groundwater in the investigated field site would be comparable to an agricultural area of similar size where these substances are deliberately applied.

Similar orders of magnitudes are obtained when conducting another rough estimation on a nation wide scale. Assuming the total roof area in Switzerland to be about 2 % of the Swiss midland, i.e., 50'000 ha, a total amount of appr. 8 kg is annually deposited thereon. Considering 100 % direct storm water infiltration of the respective roof runoff, and a concentration factor of 50 in area, a charge of 8 g/ha, or 1 % of the amount applied in agriculture, would result.

4.4 Conclusions

In summary, the investigated pesticides were found during their application periods in both rainwater and roof runoff at considerable concentrations, some of which clearly exceeded the directive water standards. Atmospheric deposition of these substances often, but not necessarily, occurred with a first flush, i.e., with maximum initial concentrations. Runoff characteristics strongly depended on the type of roof. Roofs with immediate runoff reflect the respective washout behavior from the atmosphere. Most of the total load deposited was further transported and appeared in roof runoff. Dry deposition is of minor importance for the pesticides investigated. Flat roofs exhibit equal concentrations in their runoff over the time due to their higher storage capacity that leads to dilution of the first flush. The total atmospheric load to reach the runoff of these roofs depended on the meteorology. Whereas minor rain events (rain deposition < storage capacity) with subsequent dry periods may lead to a

significant reduction of the pesticide load in the roof runoff, extensive rain events cause most of the atmospheric load to be further transported. Because of the tendency of flat roofs to equalize runoff concentrations, the runoff load is not concentration, but flux-dependent, and may be delivered more equally over whole rain events. This may have implications on the treatment of such storm waters. Discharge of the first millimetres of roof runoff into wastewater, as carried out for example with an advanced separated sewer system, may be an appropriate measure for roofs with little or no storage capacity, such as inclined clay tile roofs, but will not significantly reduce the load from flat gravel roofs during extensive rain events. Storm water management will, however, have to consider the qualitative aspects of inorganic compounds and heavy metals (see Boller, 1997), for which the situation may be different, and which may be more critical in terms of soil, and groundwater contamination.

The investigated field site revealed that such artificial infiltration pits, which were deliberately designed to allow a fast and efficient percolation of large amounts of storm water, may not be able to significantly reduce the roof runoff pesticide loads. Rough estimations suggest the maximum amounts that locally may reach the groundwater due to storm water infiltration to be in the same range of magnitude as in agricultural areas. Hence, although from a legal point of view, pesticide drinking water standards may occasionally be exceeded by rain, roof runoff, and percolating water, artificial infiltration of storm water is not likely to cause a significant deterioration of groundwater quality in urban areas.

Although it has been shown in this section that pesticides delivered from the atmosphere may not pose a tremendous problem for storm water infiltration, this remains to be shown with NPs, and biocides used as additives construction materials. This task is pursued in the next chapters.

5. Occurrence and Behavior of NPs in Rainwater: Initial Results

5.1 Introduction

The increasing importance of storm water infiltration, its benefits and drawbacks, as well as the existing uncertainty about the significance of organic atmospheric pollutants within that context have already been highlighted in chapter 1. The previous chapter sought to shed some light on the relevance of atmospherically delivered pesticides with regard to storm water infiltration. Although it was found that the investigated pesticides on their own are not likely to pose a problem, e.g., in terms of groundwater contamination, this remains unclear for the total charge of the atmospherically deposited organic compounds.

Other organic compound classes with biocide activity that were stated to be of environmental concern are, e.g., the halogenated acetic acids (Frank et al., 1994; Müller et al., 1996), and the NPs (Herterich, 1991; Tremp, 1992). Due to their widespread occurrence in the atmosphere, and their large wet deposition loads, NPs may be particularly relevant for storm water infiltration.

This chapter presents initial results obtained with the application of the analytical method presented in chapter 3. These results allow to roughly assess the atmospheric occurrence and washout dynamics of some important NPs (i.e., DNOC, and 2,4-DNP).

5.2 Results and Discussion

5.2.1 Seasonal Variation in Occurrence and Concentrations of NPs in Rainwater

Rainwater was continuously sampled from April to July 1997 in Dübendorf and analyzed for DNOC and 2,4-DNP. DNOC was detected in 23 out of 34 single rain events. The median, and maximum concentration was 0.184 µg/L, and 1.690 µg/L, respectively. The concentrations were found to be highest for minor rain events, and long preceding dry periods. Hence, DNOC regularly exceeded the Swiss, and EC drinking water standards of 0.1 µg/L. No seasonal trend in occurrence and concentration could be observed within the period investigated. However, DNOC concentrations were found to be elevated in autumn and winter (Geissler & Schöler, 1993; Herterich, 1991; Tremp, 1992). 2,4-DNP was detected in 4 rain samples with a median, and maximum concentration of 1.394 µg/L, and 2.821 µg/L, respectively.

5.2.2 Washout Dynamics of NPs During Single Rain Events

Further, different rain events were sequentially sampled in Dübendorf, and analyzed for NPs. Fig. 5.1, depicts the dynamic washout behavior of 2,4-DNP during a typical cold front situation (April 26, 1997), and a local summer thunderstorm (July 18, 1997). In the former case, a first flush of the analyte with initial concentrations of almost 4 $\mu\text{g/L}$ was observed, most probably due to an efficient gas phase scavenging mechanism. Note that the deposition dynamics of 2,4-DNP corresponded very well with the one found for a series of other pesticides during the same rain event (see Fig. 7.1). The latter situation revealed for both 2,4-DNP and DNOC (data not shown) more equal concentrations over the whole rain event, which may be explained by intensive advectations of the local air masses. Such a variability in deposition behavior of NPs, and the dependence on the local meteorological conditions was also observed by Tremp (1992).

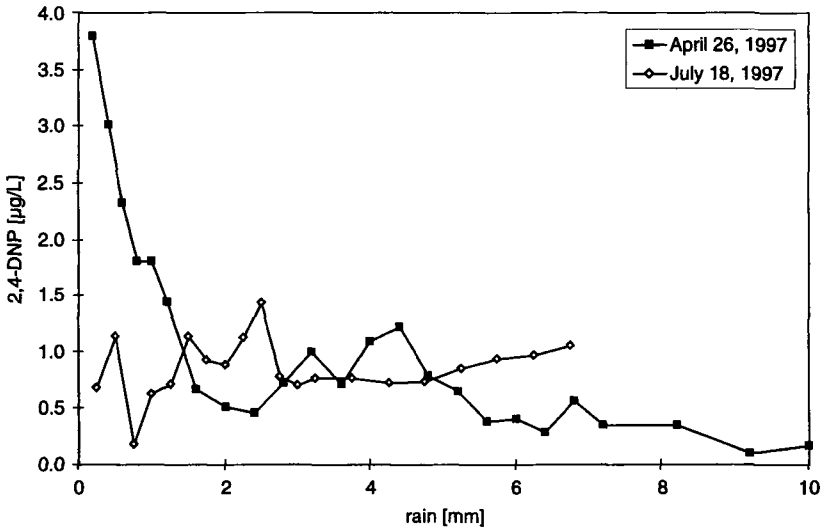


Figure 5.1 Wet deposition dynamics of 2,4-DNP during two rain events under different meteorological conditions: cold front from western direction (April 26, 1997), and local thunderstorm (July 18, 1997).

5.2.3 Atmospheric Loads of NPs

The total load of DNOC deposited within the period studied was $34.7 \mu\text{g}/\text{m}^2$, or $347 \text{ mg}/\text{ha}$. This number corresponds well with the literature (Geissler & Schöler, 1993), although the deposited loads may be elevated in the winter months (Herterich, 1991), leading to estimated annual deposition rates of 0.35 to $8.4 \text{ mg}/\text{m}^2$ (Trempe, 1992). Such annual deposition amounts surpass the numbers reached by other pesticides by a factor of at least 20 (see chapter 4).

As discussed in chapter 4, storm water infiltration sites may not be able to significantly eliminate the atmospherically delivered pesticides, and this is also not likely to occur with NPs.

Leer - Vide - Empty

6. Bituminous Membranes on Flat Roofs as Sources of the Herbicide (R,S)-Mecoprop for Groundwater, Surface Waters, and Waste Water Treatment Plants

6.1 Introduction

In chapter 4, the fate and behavior of atmospherically delivered pesticides during storm water infiltration was discussed. During the investigations at the field site in Grütze, very high concentrations of (R,S)-mecoprop were permanently detected in roof runoff samples which could not be related to atmospheric input (see e.g., Table 4.1). Rather, the roofs themselves were suspected to deliver that compound. Hence, questions about the use of organic construction chemicals with biocide activity arose. Although such substances are used in considerable amounts for example as plastic additives (Swiss annual consumption: 18 - 160 t), or wood preservatives (40 - 80 t/yr, BUWAL, 1995), little is known about their leaching potential, and the capacity to enter the aqueous environment, and thus, their relevance for, e.g., storm water infiltration. This chapter presents an exemplary case study on the occurrence and behavior of a root protection agent in roof runoff.

One of the major problems with flat roofs is to achieve satisfactory sealing properties. Various plastic roofing sheets and polymer modified bituminous roofing membranes were found to exhibit the necessary properties. However, to assure the root resistance of sealing systems, mechanical barriers such as copper or certain plastic sheets are often included. Another technique is to add a root protection agent to the bituminous membranes (about 1 % by weight). Preventol® B 2 is used for that purpose in a quantity of about 30 tons per year in Switzerland (BUWAL, 1995; Riedweg, 1997). The product has been used for at least 10 years (Riedweg, 1997), leading to a total of approximately 300 metric tons of Preventol® B 2 that are currently incorporated in rooftop sealings in Switzerland. Its application comprises bituminous construction materials such as roofing felts, sealants, insulations, and asphalt mixtures, but also the protection of rubber seals against root penetration (Bayer, 1996a). Preventol® B 2 is a polyethylene glycol diester of the selective, systematic, hormone-type herbicide (R,S)-mecoprop, used for post-emergence control of broad-leaved weeds (Tomlin, 1994). The annual consumption of (R,S)-mecoprop is about 30 t in Switzerland, and about 5000 t in the EC (Fielding et al., 1992). The half life of (R,S)-mecoprop in groundwater was found to be up to a few months (Howard et al., 1991; Hughes et al., 1995). Fig. 6.1 shows the structure of Preventol® B 2 and (R,S)-mecoprop, and Table 6.1 summarizes some physico-chemical properties.

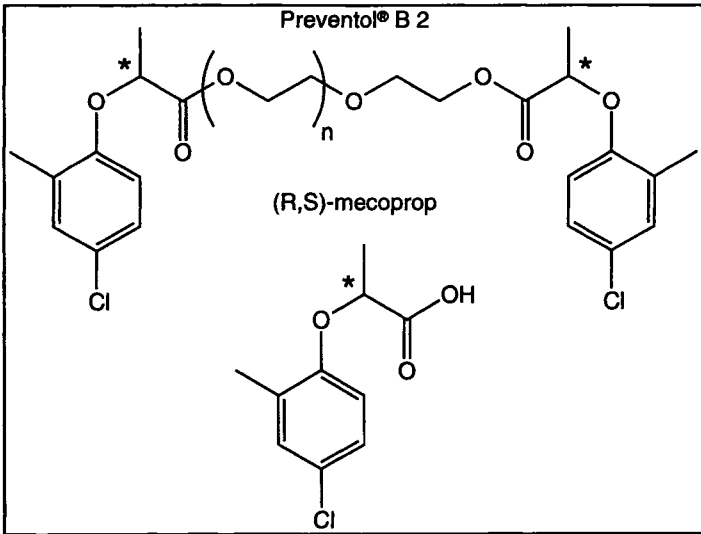


Figure 6.1 Structures of Preventol® B 2, and (R,S)-mecoprop. Stars indicate chiral centres. Note that Preventol® B 2 is a technical product with a polyethylene glycol chain of variable length.

Table 6.1 Physico-chemical and toxicological properties of Preventol® B 2, and (R,S)-mecoprop

	Preventol® B 2 (technical product)	(R,S)-mecoprop
chemical name	bis-(2-(4-chloro-2-methylphenoxy)-propionic acid)-polyethylene glycol ester	(±)-2-(4-chloro-2-methylphenoxy)propanoic acid
CAS-No.	144768-02-5	007085-19-0 (racemate)
molar weight	587.5 g/mol (dimecoprop-tetraethylene glycol ester)	214.6
melting point	- 8 °C	95 °C
boiling point	> 350 °C	
density (20 °C)	1.18 g/cm ³	
viscosity (25 °C)	900 mPas	
vapor pressure (20 °C)	400 Pa	3.1E-4 Pa
solubility (20 °C)	<< 110 mg/L	735 mg/L (20 °C, as acid)
log K _{ow}	7.07	0.1 (pH 7)
pKa (20 °C)	-	3.78
LD50	> 2000 mg/kg (Rat, oral)	930 - 1166 mg/kg (Rat, oral)
EC0	100 mg/L (<i>Scenedemus subspicatus</i>)	
EC0	1000 mg/L (<i>Daphnia magna</i>)	
EC50		420 mg/L (48 h, <i>Daphnia magna</i>)
EC0	25 mg/L (48 h) (<i>Leuciscus idus</i>)	
LC50		150 - 220 (96 h, trout)

data from Bayer (1996a, 1996b) and Tomlin (1994). Note that some of the data given for Preventol® B 2 are suspected to be inaccurate (bold numbers).

The understanding of the dominant mechanisms that lead to an appearance of (R,S)-mecoprop in runoff from roofs equipped with bituminous membranes containing Preventol® B 2 may be useful for the interpretation of field data, and may provide valuable contributions for the design of both future roof sealing products, and flat roof constructions. The hypothesized major processes, namely the hydrolysis of Preventol® B 2, and the elution of Preventol® B 2 and/or (R,S)-mecoprop from bituminous sheets are illustrated with Fig. 6.2.

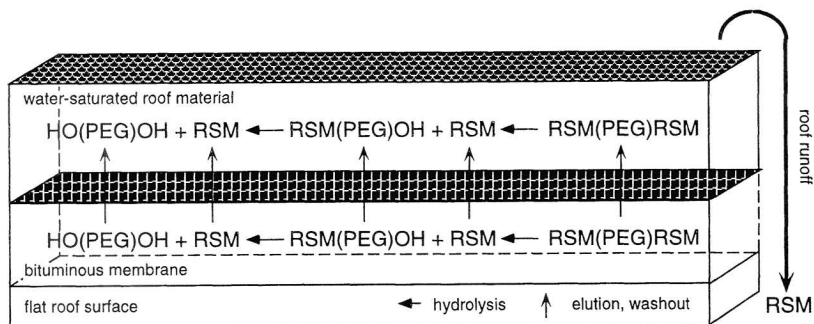


Figure 6.2 Illustration of the hypothesized predominant processes that cause the occurrence of (R,S)-mecoprop (RSM) in roof runoff: Preventol® B 2 ((R,S)-mecoprop polyethylene glycol biester, RSM(PEG)RSM) is suggested to be hydrolyzed either at the water accessible surface of the bituminous membrane (yielding the respective mono-(RSM(PEG)OH) and diester, (HO(PEG)OH)), or in the overlaying water saturated roof material. Furthermore, elution of different PEG-forms, and/or RSM from the bituminous membrane is likely to occur. Note that RSM is subject to racemization and enantioselective degradation (Müller & Buser, 1997).

The roof runoff is at present mainly discharged into waste water treatment plants (WWTP) and its effluent into surface waters. To promote local water cycles and to prevent sewer systems from overloading (for details see Boller, 1997), this runoff pathway, however, has to be deviated into the subsurface by direct infiltration in near future. Considering the substantial amount of Preventol® B 2 used and the forced subsurface infiltration of roof runoff, there is clearly a need to assess the importance of Preventol® B 2 as a (R,S)-mecoprop source for different natural waters, especially for groundwater.

This chapter aims to provide such an assessment by investigations at different levels: First, laboratory experiments were set up to quantify the hydrolysis rate of Preventol® B 2 and to elucidate the relative importance of the different transport and transformation processes affecting the elution of (R,S)-mecoprop from sealing membranes (for illustration see Fig. 6.2). Second, controlled rain events applied on

model roofs were carried out to evaluate the influence of different membranes and rooftop plantings on the concentrations and amounts of (R,S)-mecoprop in roof runoff. Third, runoff measurements on real field systems were used to determine the (R,S)-mecoprop fluxes from roof runoffs under natural conditions. Further, the annual (R,S)-mecoprop fluxes from roofs into groundwater and surface water were estimated and compared with rough flux estimates from agricultural (R,S)-mecoprop applications into these waters. Moreover, a few measurements of (R,S)-mecoprop in WWTP and tributaries are used to discuss the importance of Preventol® B 2 containing sealing membranes as a non-agricultural source of (R,S)-mecoprop in WWTP.

6.2 Experimental Section

6.2.1 Materials

Polymer-modified bituminous roofing membranes (type EP4 WF, SIA-281) were a donation from the three main producers in Switzerland, namely Soprema (Spreitenbach, Switzerland), Paul Bauder AG (Arlenheim, Switzerland), and Vaparoid AG (Dulliken, Switzerland), subsequently named Product 1, 2, and 3, respectively. Preventol® B 2 is a product from Bayer Material Protection (Leverkusen, Germany), and was received from agevogel (Zürich, Switzerland). (R,S)-mecoprop, and 2,4,5-T were purchased from Riedl-de Haën (Seelze, Germany). $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, H_2SO_4 , KOH , NaN_3 , $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, $(\text{NH}_4)_2\text{SO}_4$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ were purchased from Merck (Darmstadt, Germany), and H_3BO_3 , KH_2PO_4 , $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, NaHCO_3 , Na_2CO_3 , $\text{Na}_2\text{HPO}_4 \cdot 2\text{H}_2\text{O}$, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$, and $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were from Fluka AG (Buchs, Switzerland). Deionized water was further purified with a Nanopure water purification device (NANOpure 4, Skan, Basle, Switzerland).

6.2.2 Mineral Medium and Inoculation Solution for Hydrolysis and Elution Experiments

The mineral medium used for non-sterile laboratory experiments consisted of a phosphate buffer (KH_2PO_4 - Na_2PO_4 , pH 7, 0.01 M for hydrolysis, and 0.1 M for elution experiments) containing 0.12 g/L $(\text{NH}_4)_2\text{SO}_4$, 73 mg/L $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, and 1 mg/L $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. The following trace elements were supplied at 0.2 mL/L from an

acidified (H_3BO_3 , 0.1 g/L; H_2SO_4 , 5 mL/L) stock solution containing 2.5 g/L $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$, 0.75 g/L $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 1.3 g/L $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 0.25 g/L $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, 0.3 g/L $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 0.12 g/L $(\text{NH}_4)_6\text{Mo}_7\text{O}_{24} \cdot 4\text{H}_2\text{O}$, and 0.1 g/L $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$.

The inoculum was prepared from soil and roof material (Fig. 6.3) sampled from the flat gravel roof with humic layer in Grüze (see Fig. 4.7, and Fig. 4.9, 2), that was equipped with the Preventol® B 2 containing polymer-modified bituminous roofing membranes. Note that this material was in immediate contact with the bituminous layers. A few hundred grams of the soil material were suspended in the mineral medium for three hours. After one hour of sedimentation, the supernatant was passed through an 8 μm filter (cellulose nitrate filter, diameter 5 cm, Satorius, Goettingen, Germany).

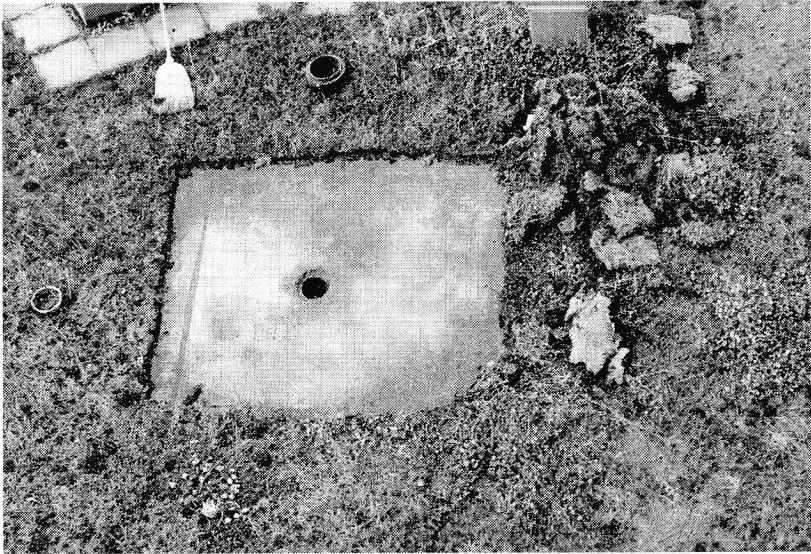


Figure 6.3 Soil and roof material from the flat gravel roof with humic layer in Grüze. The bituminous roofing membrane containing the root protection agent Preventol® B 2 is visible on the exposed roof surface.

6.2.3 Laboratory Experiments

Hydrolysis: a standard solution of Preventol® B 2 in methanol was prepared by adding 1 g of the compound to 100 mL of methanol. 5 L of a 0.01 M K/Na₂-phosphate buffer (pH 7), a 0.01 M K/Na₂-phosphate buffer (pH 7) with the mineral medium and 50 ml of the inoculum, a 0.01 M H_3BO_3 buffer (0.005 M KOH added to yield pH 9),

and a 0.01 M carbonate buffer (pH 10), respectively, were then spiked with 50 μl of the 0.1 g/L standard solution. The resulting Preventol® B 2 concentration was 100 $\mu\text{g/L}$, corresponding to 73 $\mu\text{g/L}$ of the 'bound' (R,S)-mecoprop (assuming a tetraethylene glycol chain). All buffers except the one containing the inoculum were autoclaved prior to the addition of Preventol® B 2, which caused a volume reduction of around 10 % (considered in calculations). Samples were stored at 25 °C. The hydrolysis product (R,S)-mecoprop was determined in each of the samples at different times in duplicate for the sterile setup at pH 7, and in triplicate for all other setups. Sample volumes of 500 to 1000 mL were used for determination of the initial concentration, and 100 mL for the later measurements. Before analysis, the hydrolysis of Preventol® B 2 in samples from experiments at pH 9 and pH 10 was slowed down by decreasing the pH to 7 with the addition of 5 mL of a 1 M phosphate buffer (pH 7).

Elution experiments: circular pieces with a diameter of 4.0 cm were punched out of the polymer-modified bituminous roofing membranes from the three producers, and each was put into a lid of a 100 mL Duran-Schott flask, resulting in an exposable surface area of 7 cm². The flasks were filled with 100 mL of the probe solution, the lids were tightly screwed onto the flasks, and the samples were shaken on a horizontal shaker at 150 min⁻¹. A 0.1 M phosphate buffer (pH 7) with or without mineral medium and 1 mL of the inoculum, as well as a 0.1 M carbonate buffer (pH 10) served as probe solutions. The phosphate buffer without inoculum, and the carbonate buffer were autoclaved prior to usage. Product 1 membranes were exposed to the sterile phosphate and carbonate buffer, and kept both at 4 °C, and 25 °C, respectively. Exposition of product 1 to the non-sterile phosphate buffer was performed at 25 °C only. Product 2, and 3 sheets were exposed to sterile pH 7 solutions at 25 °C. Sterile conditions were assured by addition of 0.6 g/L NaN₃ to all samples, except one (product 1, pH 7, 25 °C, with inoculum). (R,S)-mecoprop content in the 100 mL buffer solutions was measured in duplicate (product 1 at 4 °C, and product 2, and 3), or in triplicate (all other samples) for each sample setup at 4 to 5 different times. Sample volumes were 10 (diluted to 100 mL with Nanopure water) to 50 mL. To assess a possible direct elution of Preventol® B 2 (RSM(PEG)RSM, or the intermediate hydrolysis product, i.e., the monoester with an alcohol moiety, RSM(PEG)OH, see Fig. 6.2), half of the sample volumes from product 1 samples exposed to pH 7 at 25 °C were basified with 250 μL of 10 M KOH to yield a pH of 10, and set aside for at least two hours. This allowed the fast base catalysed hydrolysis of Preventol® B 2 in solution, and then the subsequent analysis of the reaction product (note that there was no direct analysis of Preventol® B 2 available).

6.2.4 Field Sites, Sampling and Sample Preparation

For the investigation of the leaching of mecoprop from flat roofs, model green flat roofs with an area of 25 m² each were used. Both roofs were part of a model roof system set up by the Ingenieurschule Burgdorf (Canton Bern, for details, see Kaufmann, 1996). The first one (roof A, Fig. 6.4, and Fig. 6.5) was designed by Paul Bauder AG (Arlesheim, Switzerland), with a root resistant Plant E bitumin membrane from the constructor. The second one (roof B, Fig. 6.4) was constructed by Optima-Werke (Münchenstein, Switzerland), using a root resistant Sopralen EV3 bitumin sheet from Soprema (Spreitenbach, Switzerland). Sampling of sequential roof runoff was performed manually.

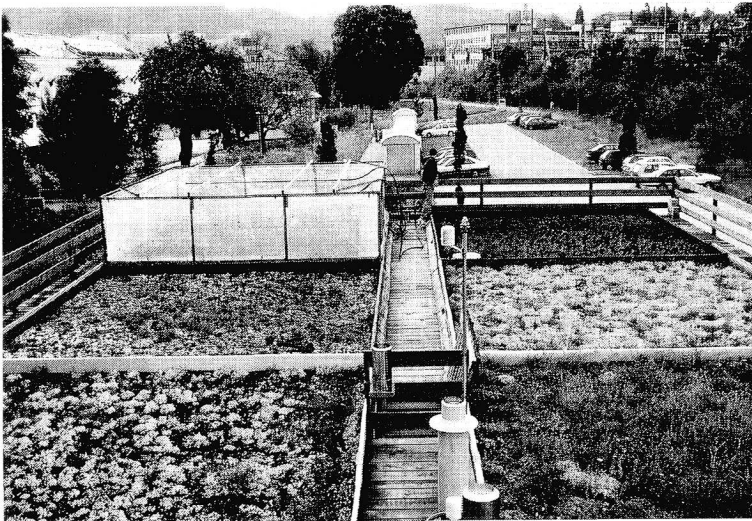


Figure 6.4 Overview of the model roof system in Burgdorf. The artificial rain device is mounted on model roof A (left row, in the rear, see also Fig. 6.5). The model roof B is located in front of the model roof A (left row, in the middle).



Figure 6.5 Model roof A during the conduction of the artificial rain event experiment.

Appearance in roof runoff and elution dynamics of (R,S)-mecoprop from model green flat roofs A, and B in Burgdorf were investigated by exposing the roofs to an artificial rain event: 18 L/m² of tap water were uniformly sprayed with a constant flow onto the model roofs within 30 minutes (for illustration, see Fig. 6.5).

The two flat roofs in Grütze were equipped with polymer-modified bituminous roofing membranes from Soprema (Spreitenbach, Switzerland), containing Preventol® B 2 (EP4 WF). This field site, and the sampling procedure is described in detail in chapter 4.

Greifensee is located 10 km east of Zurich (for details, see Müller et al., 1997). Samples were taken from its major tributaries Aa, and Aabach, and from effluents of three WWTP, namely Maur, Mönchaldorf, and Uster.

All samples were stored at 4 °C in the dark, and analyzed the next day. Prior to analysis, samples were allowed to reach room temperature, and then filtered (cellulose nitrate filter, diameter 5 cm, pore size 0.45 µm; Satorius, Goettingen, Germany).

6.2.5 Analysis

Determination of (R,S)-mecoprop was based on the previously described multiresidue pesticide analysis (chapter 2). To account for the drastically higher concentrations, a second internal standard, namely 2,4,5-T (10 μg) was added to all samples, and the sample volume was adjusted to the expected concentration range (50 to 1000 mL). Separation of R-, and S-mecoprop was performed with a fused silica capillary column (OV-1701-OH 0.2 % + 25 % TBDM- β -CD, 0.13 μm film thickness, 0.25 mm i.d., 15 m). The oven temperature was programmed as follows: 1 min at 60 $^{\circ}\text{C}$, to 120 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$, to 150 $^{\circ}\text{C}$ at 4 $^{\circ}\text{C}/\text{min}$, to 230 $^{\circ}\text{C}$ at 20 $^{\circ}\text{C}/\text{min}$, 5 min at 230 $^{\circ}\text{C}$. Linearity of the analytical method (i.e., SPE, and separation and detection with GC/MS) was confirmed up to 30 μg (R,S)-mecoprop, irrespective of the sample volume. When using 2,4,5-T for quantification, relative recovery in roof runoff samples was 80 %, method precision 14 %, and the method detection limit 40 ng/L. Relative recoveries of (R,S)-mecoprop from 0.1 M buffers were similar at pH 7 and pH 10 (data not shown).

6.3 Results and Discussion

6.3.1 Hydrolysis of Preventol[®] B 2 in Aqueous Solutions

The results from the hydrolysis experiments with the pure chemical Preventol[®] B 2 in aqueous solutions are shown in Fig. 6.6. The rate constants and half lives of Preventol[®] B 2 under different experimental conditions were determined by the respective rates of the product formation of (R,S)-mecoprop. The average (R,S)-mecoprop enantiomeric ratio of all sterile samples was 1.00 ± 0.03 ($n = 71$), indicating that the racemic (R,S)-mecoprop is used for the production of Preventol[®] B 2. Within the pH range from 7 to 10 and under sterile conditions, the initial reaction rate roughly increased with one order of magnitude per pH unit. At pH 7, the rate constant for the abiotic hydrolysis was $4.7\text{E-}4 \text{ h}^{-1}$, corresponding to a half life of 1483 h, or about 60 d. At pH 10, the reaction was accelerated by a factor of 1000, resulting in a rate of $9.6\text{E-}3 \text{ min}^{-1}$, or a half life of 1.2 h. Hence, the hydrolysis is fully base catalyzed at a $\text{pH} \geq 7$.

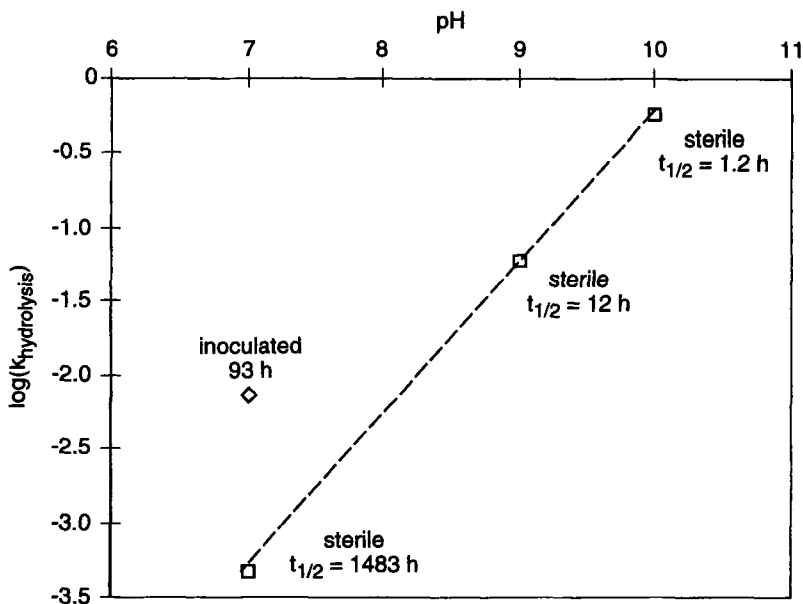


Figure 6.6 Initial hydrolysis reaction rates ($k_{\text{hydrolysis}}$) and half lives ($t_{1/2}$) of Preventol® B 2 in aqueous solutions at 25 °C. The hydrolysis appears to be base-catalyzed at a pH ≥ 7 , and is accelerated by microorganisms. Numbers of samples, and numbers of replicates per sample were as follows: pH 7, sterile: 3, 2; pH 7, inoculated: 2, 3; pH 9, sterile: 1, 1, and 3, 3; pH 10, sterile: 3, 3.

The hydrolysis of Preventol® B 2 was found to be significantly enhanced under non-sterile conditions (at least by a factor of 15, Fig. 6.6). A more accurate determination of the biotic hydrolysis rate is difficult because of the concomitant enantioselective degradation of the product, as is indicated by the (R,S)-mecoprop enantiomeric ratio observed (1.19 ± 0.03 ($n = 3$), (R,S)-mecoprop concentration in solution: $38.2 \pm 2.5 \mu\text{g/L}$) after an incubation time of 100 h at pH 7). An almost complete degradation of both R-, and S-mecoprop occurred within 167 h. The remaining (R,S)-mecoprop concentration then was $1.1 \pm 0.0 \mu\text{g/L}$ ($n = 3$), (R,S)-mecoprop enantiomeric ratio = 1.03 ± 0.03). These findings are in accordance with Müller & Buser (1997), who reported on racemization and enantioselective degradation of (R,S)-mecoprop in soil.

6.3.2 Elution of (R,S)-Mecoprop and its Precursors from Bituminous Roofing Membranes

In a second set of experiments, the elution of (R,S)-mecoprop, and Preventol® B 2 and/or RSM(PEG)OH from bituminous membranes from the three main producers in Switzerland was examined. (R,S)-mecoprop was measured in all samples after an incubation time of 6 hours, indicating the hydrolysis of eluted, or water-accessible Preventol® B 2 incorporated in the bituminous sheet, or the desorption of (R,S)-mecoprop originating from the decomposition of Preventol® B 2 during the production of the bituminous membrane. The latter reason should, however, not play a major role, as the producer stresses the heat-resistance of the product up to 200 - 250 °C (bituminous sheets are produced at a temperature of 180 °C, Bayer, 1996a). Within the time period investigated (270 h), elution rate constants at pH 7 and 25 °C under sterile conditions were 826 mg/m²/yr, or 32.3 %/yr for product 1 (R² of linear correlation: 0.984), 2351 mg/m²/yr, or 92.0 %/yr for product 2 (R²: 0.995), and 391 mg/m²/yr, or 15.3 %/yr for product 3 (R²: 0.936). Hence, a significant difference in elution rates of different products of up to a factor of 6 was observed.

The influence of pH, temperature, and microbiological activity on the elution was more thoroughly investigated with product 1, that exhibited of all three products the medium rate constant. The resulting elution rate constants are compiled in Table 6.2. The average (R,S)-mecoprop enantiomeric ratio of sterile samples (pH 7, and 10, respectively, at 25 °C) was 1.00 ± 0.02 (n = 24). This again confirms that Preventol® B 2 added to bituminous membranes consists of racemic (R,S)-mecoprop, and that no microbiological activity took place during the sterile elution experiments (see below).

The elution rate constant of Preventol® B 2 and/or RSM(PEG)OH (given as (R,S)-mecoprop equivalents) from product 1 at pH 7, 25 °C, and sterile conditions was determined to be 1589 mg/m²/yr (Table 6.2), or 62.6 %/yr of the total Preventol® B 2 content, which is about twice as high as the corresponding rate for (R,S)-mecoprop. This indicates that not only the hydrolyzed Preventol® B 2 (RSM(PEG)OH, see Fig. 6.2) elutes into the aqueous solution (due to an enhanced aqueous solubility as compared with the biester), but that the parent compound (RSM(PEG)RSM) also elutes, and at a similar rate as for (R,S)-mecoprop itself.

Table 6.2 Elution rate constants of (R,S)-mecoprop (RSM), and Preventol® B 2 (RSM(PEG)RSM) and/or the intermediate ester alcohol (RSM(PEG)OH) from a bituminous membrane (product 1)^a

	elution rate constants [mg/m ² /yr]							
	RSM			RSM(PEG)RSM and or RSM(PEG)OH		sum of RSM, and RSM(PEG)RSM and or RSM(PEG)OH		
	sterile 4 °C	sterile 25 °C	non sterile 25 °C	sterile 25 °C	non sterile 25 °C	sterile 4 °C	sterile 25 °C	non sterile 25 °C
pH 7	152	826	3156	1589	2762		2415	5918
pH 10						1035	5602	

^a rate constants were determined from four samples in duplicate (4 °C), or triplicate (all other setups).

At pH 10, the resulting elution rate of (R,S)-mecoprop was 5602 mg/m²/yr (Table 6.2), or 220 %/yr. Assuming similar relative elution rates of (R,S)-mecoprop, and Preventol® B 2, as at pH 7 (i.e., 1:2), the appearance of total (R,S)-mecoprop in solution was enhanced only by a factor of about two. This is in contrast to the influence of such a pH change on the hydrolysis (acceleration of the reaction by three orders of magnitude, see Fig. 6.6, and above). Presuming only a marginal impact of the pH change on diffusive processes, it is obvious that the elution of (R,S)-mecoprop (or Preventol® B 2 itself) from such root protecting bituminous membranes is controlled by diffusion or exposition of Preventol® B 2-containing sites to the aqueous solution, but not by the hydrolysis reaction itself.

Elution rates at 4 °C at both pH 7 and 10 were reduced by a factor of about five as compared to 25 °C (Table 6.2). This reduction can primarily be ascribed to the temperature dependence of the hydrolysis reactions of carboxylic acid esters.

Fig. 6.7 depicts the elution of R-mecoprop, S-mecoprop, and Preventol® B 2 and/or RSM(PEG)OH from polymer-modified bituminous roofing membranes under non sterile conditions. The initial (R,S)-mecoprop elution rate is estimated to be 3156 mg/m²/yr, or 123.5 %/yr, which is about four times higher than in the sterile control (see Table 6.2). In agreement with the biotic hydrolysis experiment (see above), however, enantioselective degradation of (R,S)-mecoprop took place, which prevents the determination of a more accurate biological elution rate. As already indicated above, S-mecoprop seemed to be more readily degradable than the herbicide active form R-mecoprop. Subsequently, however, both enantiomers were degraded almost to depletion, presumably, because a steady state between delivery from the bituminous

sheet and consumption by microorganisms was reached. The initial Preventol® B 2 and/or RSM(PEG)OH release occurred at a rate of 2762 mg/m²/yr (Table 6.2), or 108 %/yr, which is twice as high as with the sterile control. Later on, their content decreased, either because the microbiologically mediated release from the bituminous membrane diminished, or, more probably, because of the growth of the microorganism population feeding on these compounds.

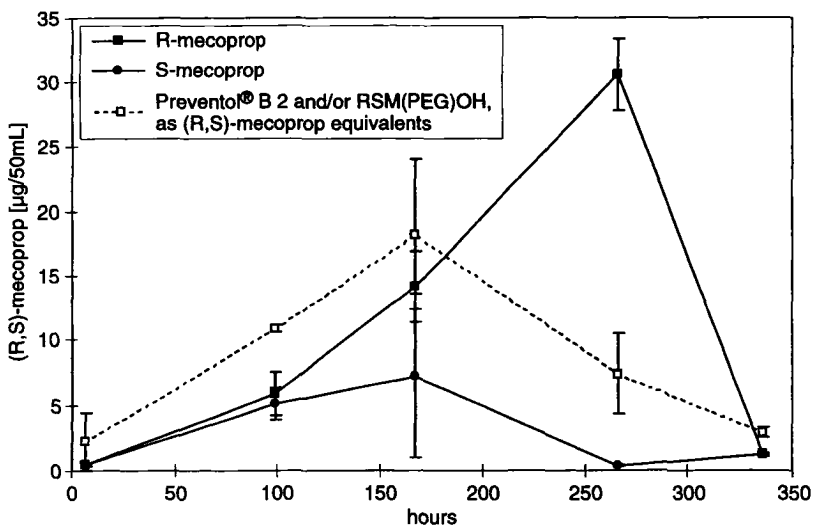


Figure 6.7 Elution of *R*-mecoprop, *S*-mecoprop, and Preventol® B 2 and/or RSM(PEG)OH (given as (R,S)-mecoprop equivalents) from product 1 at pH 7 and 25 °C with inoculum.

In conclusion, the laboratory experiments supported the above suggested hypotheses (Fig. 6.2). Preventol® B 2 was shown to hydrolyse at a considerable rate in aqueous solutions. This hydrolysis also took place when the substance was embedded in a bituminous membrane. Moreover, in spite of its tentatively high K_{ow} of 10^7 (see Table 6.1), Preventol® B 2 itself was released from such sheets into aqueous solutions. The hydrolysis product (R,S)-mecoprop is readily water soluble and may thus easily enter the aqueous environment. Both the hydrolysis of Preventol® B 2, and the elution of the parent compound, and its degradation products was significantly accelerated in the presence of microorganisms, as is the case in the natural environment.

6.3.3 Occurrence and Behavior of (R,S)-Mecoprop in the Runoff from Two Model Roofs

Fig. 6.8 illustrates the appearance of (R,S)-mecoprop in the roof runoff of the two model roofs A and B during an artificial rain event (18 mm/m²/30min). A large difference in the hydrodynamic behavior of the runoff flow was observed between the two systems. Whereas roof A (Fig. 6.8 a) only delivered 235 L of the total applied 450 L within the first 5 1/2 h, 95 % of the total water passed roof B (Fig. 6.8 b) within 3 1/2 h. Also maximum runoff flow was with ca. 16 L/min about eight times larger for roof B (Fig. 6.8 b) as compared to roof A (Fig. 6.8 a). Concentrations determined in the runoff of these roofs were significantly different. The average concentration was about 2 µg/L in roof B runoff (Fig. 6.8 b), but about 35 µg/L for roof A (Fig. 6.8 a). Control measurements with the artificial rainwater revealed (R,S)-mecoprop concentrations < 25 ng/L. Both roofs showed enhanced (R,S)-mecoprop concentrations at the beginning of the artificial rain event. Subsequently, the concentrations remained at a slightly lower level (Fig. 6.8).

The lower concentrations found in roof B runoff cannot be ascribed to the dilution caused by the relatively higher water flow. This becomes obvious when comparing the cumulative (R,S)-mecoprop loads from the two roofs. With ca. 8 mg, the load was about ten times higher in roof A than in roof B (Fig. 6.8). Calculated cumulative loads corresponded well with the ones determined with pooled samples over the whole sampling period (4 % deviation for roof A, and 12 % deviation for roof B, data not shown).

The much higher (R,S)-mecoprop deliverance of roof A may be explained by the different construction of the two roofs. Roof B represents a gravel roof on which, in a later step and with little effort, a rooftop planting had been installed. During the experiment, plant density was very low. On Roof A, however, a thriving vegetation was planted on a substantial substrate with high water retention capacity. As already shown in the laboratory experiments, an enhanced biological activity may lead in an elevated elution of (R,S)-mecoprop. Also, these experiments revealed product specific elution rate constants (see above), and the difference in (R,S)-mecoprop concentrations and loads from the two roofs may partly be ascribed to the application of bituminous sheets from different producers.

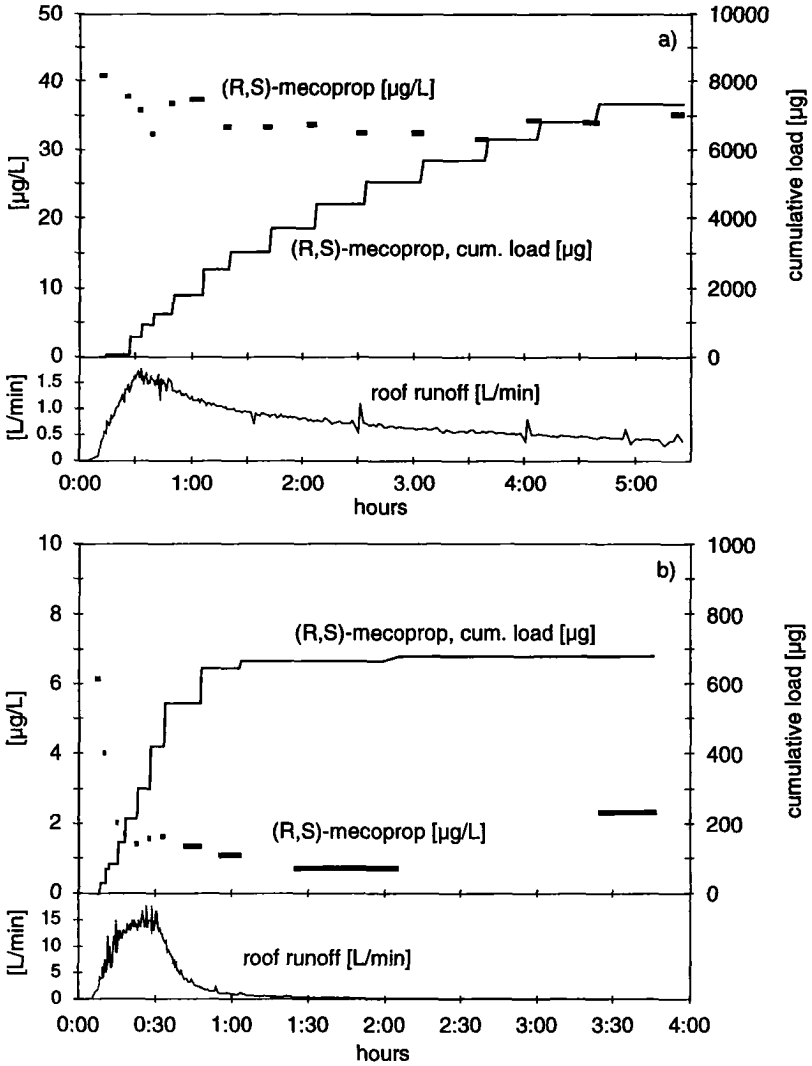


Figure 6.8 (R,S)-mecoprop in model roof A (a), and model roof B (b) runoff. For each roof, the (R,S)-mecoprop concentrations and cumulative loads (upper box), and the respective roof runoff (lower box) are shown.

6.3.4 Occurrence and Behavior of (R,S)-Mecoprop in the Roof Runoff at the Storm Water Infiltration Site in Grütze

Fig. 6.9 shows the combined roof runoff of the three different roofs at Grütze with a total area of 5060 m² (for details, see chapter 4). Two of the three roofs with an area of 4575 m² are equipped with polymer-modified bituminous roofing sheets, containing the roof protecting agent Preventol® B 2.

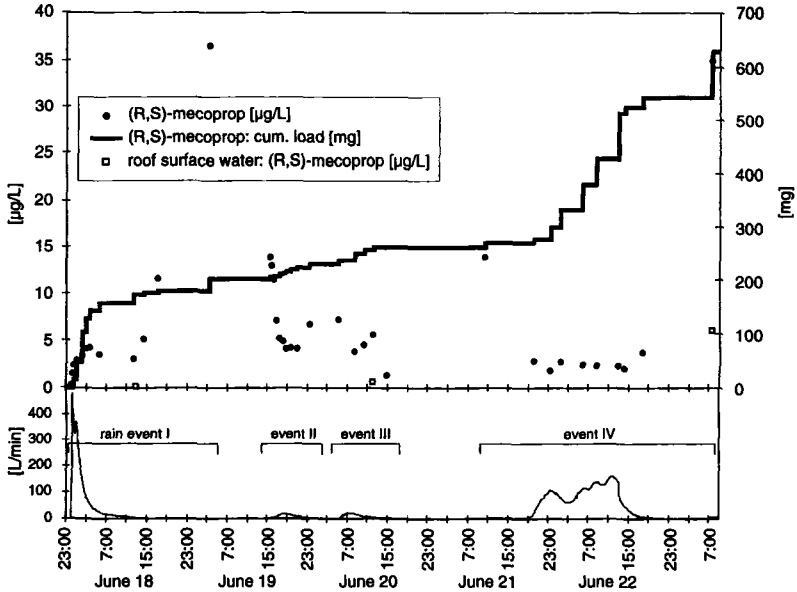


Figure 6.9 (R,S)-mecoprop concentrations and cumulative load in roof runoff (upper box), and runoff flow rate (lower box) into the storm water infiltration site in Grütze (June 17 to 23, 1997). The four rain events indicated in the lower box are referred to in the text.

Roof runoff water was collected over a period of five days and analysed for (R,S)-mecoprop. Within that period, four rain events led to roof runoff with different hydrological characteristics. The first one (Fig. 6.9, June 18, 00:00, 1997) was an intensive thunderstorm that resulted in a maximum roof runoff flow of 500 L/min. Two days later (Fig. 6.9, June 19, 17:00, and June 20, 08:00, 1997), two minor events caused moderate runoff flows of about 30 L/min. Finally, the fourth rain event from June 21, 12:00 until June 22, 18:00, 1997 (Fig. 6.9) provided, after very low initial flow intensities of less than 10 L/min, medium flows up to 150 L/min.

Rainwater collected over that period contained 35 ng/L (R,S)-mecoprop. (R,S)-mecoprop was continuously detected in roof runoff, and the concentrations were heavily influenced by the actual flow, as well as by the foregoing weather situation. For example, the high rain intensity at the start caused a pronounced dilution of (R,S)-mecoprop at the onset of the runoff, where concentrations between 0.1 and 4.2 µg/L were measured (Fig. 6.9). These first samples from June 18, 00:00 until 05:30 exhibited a significantly enhanced (R,S)-mecoprop enantiomeric ratio (1.36 ± 0.12 , $n = 10$), as compared to all the subsequent ones (0.99 ± 0.09 , $n = 29$). This indicates, that an enantioselective biological degradation of (R,S)-mecoprop occurred during the preceding three days with very little precipitation (1.5 mm, which is not enough to cause any roof runoff, but kept the roof sufficiently moist for hydrolysis and degradation). With decreasing flow, concentrations increased, reaching a maximum value up to 35 µg/L. In contrast, a moderate onset of roof runoff (event two, and four) after a dry period flushes the (R,S)-mecoprop that has been produced since the last rain event. Hence, concentrations are elevated at the beginning of such events. Note that the (R,S)-mecoprop concentrations in the overlaying water sampled at the roof surface is generally considerably lower than the one in the roof runoff itself (Fig. 6.9). The average concentration in roof runoff over the period investigated was 3.3 µg/L. A similar study, conducted from November 19 - 22, 1996, revealed an average concentration in roof runoff of 1.5 µg/L, and random samples taken from the surfaces of other roofs equipped with Preventol® B 2 containing bituminous sheets exhibited a similar concentration range (data not shown). The lower concentrations during the winter months may be rationalized with both the reduced hydrolysis rate, and the diminished microbial activity at lower temperatures. However, tentative concentrations up to approximately 500 µg/L (! - not quantifiable with the analytical method applied) were observed in roof runoff after a 18 days dry period with an average temperature of 21.2 ± 4.8 °C in August 1997.

In conclusion, roof runoff (R,S)-mecoprop concentrations of these type of roofs permanently exceeded the Swiss, and EC drinking water standard of 100 ng/L for pesticides by a factor of 10 to 30, and under certain climatic conditions even up to 5000 fold. Note that, in contrast to the findings from laboratory experiments, where Preventol® B 2 was found to be directly eluted from bituminous membranes, no Preventol® B 2 was found in roof runoff. Presumably, the roof protecting agent is retarded in the overlaying roof layers or soil material, where subsequent hydrolysis may take place.

The cumulative load of (R,S)-mecoprop over the five days under investigation was 630 mg (Fig. 6.9), with washout rates from 12 to 54 µg/m²/d. The respective value

for the investigated period in November 1996 was about $4 \mu\text{g}/\text{m}^2/\text{d}$. Maximum washout rates may be as high as $500 \mu\text{g}/\text{m}^2/\text{d}$.

Assuming an annual rain amount of 1200 mm, of which around 80 % pass the roof system of the investigated storm water infiltration site, and an average concentration of $3.3 \mu\text{g}/\text{L}$, an estimated annual load of 12 g is eluted from the roof system. An annual washout rate would then be $2.4 \text{ mg}/\text{m}^2$, or 0.09 ‰ of the total (R,S)-mecoprop. Considering that these 12 g are infiltrated into an area of approximately 100 m^2 , the total charge would be similar to the amounts applied in agricultural areas ($1.2 \text{ kg}/\text{ha}$).

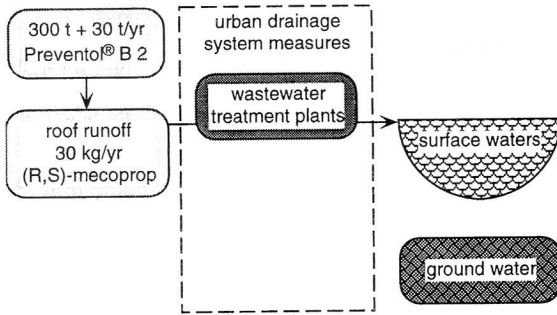
6.3.5 (R,S)-Mecoprop Fluxes from Roofs and Agricultural Applications into Natural Waters

To judge the environmental significance of Preventol® B 2, it is useful to compare the environmental input of (R,S)-mecoprop caused by the leaching from flat roofs equipped with root resistant bituminous sheets with the one by agricultural application. Fig. 6.10 compiles the most important (R,S)-mecoprop flow paths in Switzerland.

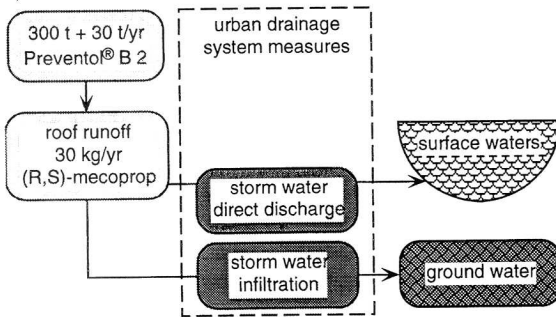
At present, about 300 t of this root protection agent are installed on a flat roof area of about 600 ha. At an average elution rate of about $0.1 \text{ ‰}/\text{yr}$, a total of about 30 kg of (R,S)-mecoprop is eluted from Swiss flat roofs per year. Nowadays, this load is transported by combined sewer systems into the WWTP (Fig. 6.10 a).

Indeed, (R,S)-mecoprop measurements in the major tributaries, and effluents from three WWTP around the Greifensee during October 1997 resulted in considerable (R,S)-mecoprop concentrations of up to $1.5 \mu\text{g}/\text{L}$. With a total input into Greifensee of around 500 g, (R,S)-mecoprop was the most important of about 15 pesticides investigated, including, e.g., the widely used atrazine. Such considerable inputs of (R,S)-mecoprop (and other pesticides) through WWTP into surface waters were also reported by Seel et al. (1996). Further, whereas the river Aa, a tributary to the Greifensee that carries no WWTP water, exhibited an ER of 1.07 ± 0.13 ($n = 9$), the effluents from three WWTP and the Aabach, a tributary with considerable WWTP effluent content, showed an ER of 0.65 ± 0.23 ($n = 21$). This reduced ER may indicate a significant contribution of (R,S)-mecoprop from non-agricultural activities through WWTP, as pointed out by Buser & Müller (1998). The findings of this chapter strongly suggest the application of Preventol® B 2 containing bituminous sealing membranes to be a major non-agricultural source of (R,S)-mecoprop in surface waters.

a) source: root resistant bituminous sheets, actual urban drainage system measures



b) source: root resistant bituminous sheets, future urban drainage system measures



c) source: agricultural usage

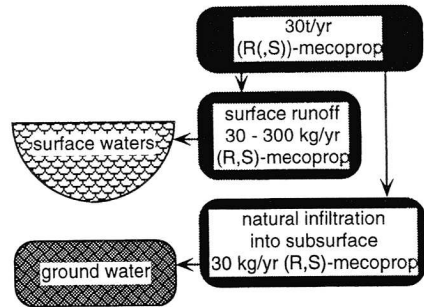


Figure 6.10 Annual (R,S)-mecoprop flow for different sources and urban drainage system measures. Note that the hitherto unknown input into the environment from bituminous membranes via roof runoff (a, and b) is estimated to be in the same order of magnitude as the one caused by agricultural usage (c).

However, due to the propagation of direct infiltration of roof runoff, a substantial part of the eluting (R,S)-mecoprop is prone to contaminate the groundwaters in the near future (Fig. 6.10 b, investigations on transport of pesticides within storm water infiltration sites revealed that a major part may reach the groundwater, see chapter 4). Whereas a certain elimination of (R,S)-mecoprop may be assumed via the WWTP, this is not likely to occur in the future via direct discharge or infiltration of storm water.

For comparison, the agricultural usage of (R,S)-mecoprop in Switzerland is about 30 t/yr, of which up to a few percent (for review see Barbash & Resek, 1996) may reach the groundwater (30 to 300 kg, assuming 1 ‰ to 1 %, Fig. 6.10 c). The input into the groundwater may thus reach similar orders of magnitude from these two sources. Moreover, whereas the input by agricultural usage may be more diffuse, roof runoff infiltration may act more as point sources that permanently and considerably exceed the Swiss, and EC drinking water standard. Hence, on a local scale, groundwater contamination due to infiltration of roof runoff from the roof types under discussion may by far exceed the one caused by agricultural usage. These findings should be considered when designating contribution areas around drinking water wells or springs, as recommended by experts (Hoehn et al., 1994). Additionally, only R-mecoprop is registered as a herbicide, but the racemic mixture is used in the production of Preventol® B 2. Thus, a unregistered herbicide/compound, namely S-mecoprop is continuously brought into the environment.

6.3.6 Need for a New Assessment on the Environmental Benefits of Rooftop Planting and the Use of Preventol® B 2 as a Root Protection Agent

The use of flat roofs, and especially the rooftop planting, offers a valuable tool for ecological urban development. Amongst other advantages, these roofs improve the micro climate in cities, as well as the room climate of the respective houses themselves. They act as a noise barrier and as adsorbers of air pollutants. In Switzerland, the conception of both 'roofgreening', and storm water infiltration, compiles with the ecological objectives of the federal law and, in particular, with the goals of the legislation on: the prevention of water pollution, protection of the natural environment, development planning, as well as the planning and building regulations of some of the cantons (Beins-Franke & Heeb, 1995). However, the presented findings suggest that the environmental benefits due to extended rooftop greening should be newly assessed. Clearly, other solutions than the use of Preventol® B 2 should be pursued to assure the sealing of such roofs. Also, the use of Preventol® B 2 violates the Swiss ordinance

relating to environmentally hazardous substances that prohibits the application of pesticides on roofs.

6.4 Conclusions

Laboratory and field studies revealed that Preventol® B 2 is prone to hydrolyse and elute from bituminous roofing membranes, where it is used as a root protection agent. This study has shown that substantial amounts of its hydrolysis product, the herbicide (R,S)-mecoprop, enter the aqueous environment via roof runoff, which is discharged into the sewer system, but in future more and more directly into surface waters or through direct infiltration into the groundwater. Rough estimates reveal that locally, the groundwater charge with (R,S)-mecoprop due to storm water infiltration may be in the same order of magnitude as the total amount applied on an agricultural area of similar size. On a nation-wide scale, the input of this herbicide into the environment by roof runoff and by agricultural usage is indicated to be similar. Based on these findings, the use of Preventol® B 2 as a root protection agent should be re-evaluated.

Conclusively, Preventol® B 2 stands as a representative of widely used construction chemical biocides, the environmental fate of which up to now remains largely unknown. Such chemicals may enter the environment through paths which may not be suspected or anticipated by producers and consumers.

Leer - Vide - Empty

7. Pesticides and NPs in Storm Water Infiltration: Synopsis and Conclusions

In chapter 4, the occurrence and behavior of selected atmospherically delivered pesticides in rainwater, roof runoff, and during storm water infiltration was elucidated. Chapter 5 provided some initial results on NPs in rainwater, and chapter 6 investigated on the leaching potential of a roof delivered herbicide and its fate in roof runoff. This chapter seeks to relate the results obtained within the individual sections to each other, and draws some general conclusions on the significance of these findings with respect to storm water infiltration.

The concomitant analysis of sequentially sampled rainwater for three classes of pesticides and NPs revealed that these groups of organic atmospheric contaminants exhibited very similar washout dynamics (Fig. 7.1). Most of the investigated substances are, when present in the gas phase, readily washed out during rain events, owing to their low Henry's law constants ($5E-4$ to $3E-9$, for physico-chemical properties of the investigated compounds, see appendix A.1, and A.2).

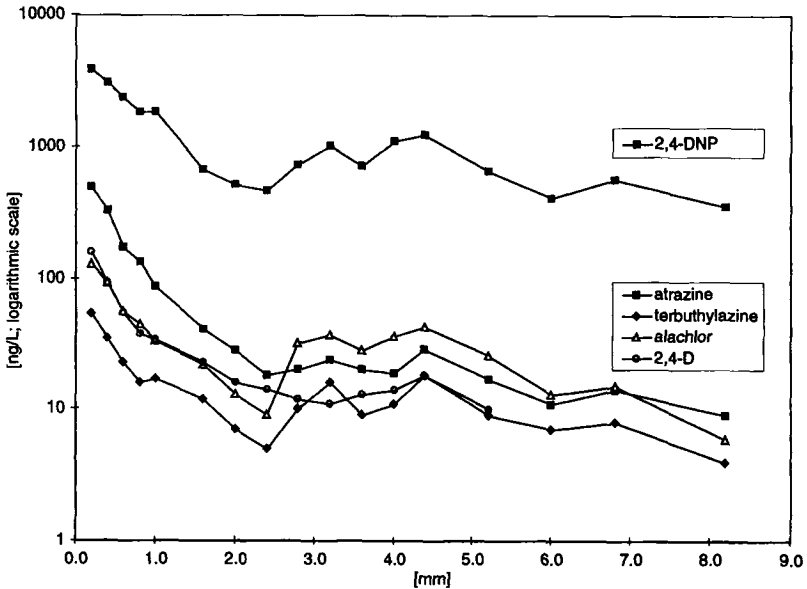


Figure 7.1 Deposition behavior of representatives from three different pesticide classes, and NACs. Rain event from April 26, 1997 in Dübendorf.

From a concentration point of view, however, NPs were much more prominent (Fig. 7.1, and chapter 5.2.1). Moreover, the occurrence of NPs in rain-, and storm waters is not restricted to any season, as was found for most pesticides (chapter 4).

Hence, whereas the atmospherically deposited pesticides may occasionally lead to a temporal infringement of the Swiss, and EC drinking water standards during their application period, certain NPs may regularly and throughout the whole year do so. Also, the annual loads that locally may be transported into the subsurface by storm water infiltration are assumed to be significantly higher for the NPs than for the pesticides.

The second source of pesticides that may be of relevance for storm water infiltration are the roofs themselves, as was pointed out in chapter 6. The use of biocides as construction material additives, as exemplified with the root protection agent Preventol® B 2, was found to permanently deliver the readily soluble (R,S)-mecoprop that was continuously detected in runoff and percolating waters in concentrations that were hardly reached by any atmospheric input.

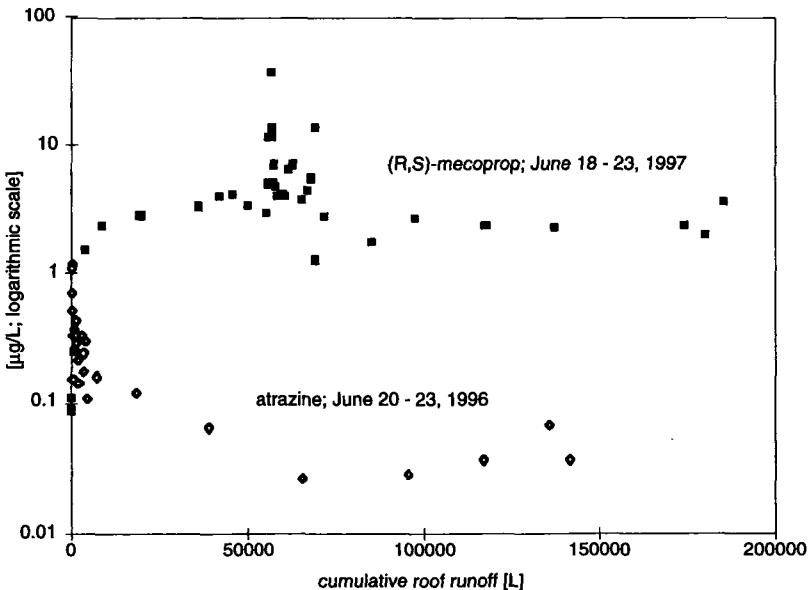


Fig. 7.2 illustrates the differences between pesticides originating from the two different sources. Shown is the atrazine, and (R,S)-mecoprop content in roof runoff during two extensive rain events, dating June 20 - 23, 1996 for atrazine, and June 18 - 23, 1997 for (R,S)-mecoprop.

There is a striking difference in the concentrations of these two herbicides in the combined roof runoff of Grütze, both in regard to absolute numbers, and temporal development. (R,S)-mecoprop concentrations were permanently 10- to 100-fold higher than atrazine numbers. Whereas atrazine exhibited the first flush washout behavior typically found in rainwaters, the concentration dynamics of (R,S)-mecoprop in roof runoff were observed to be more complicated. In the latter case, factors such as dry periods prior to the rain events, micro climatic conditions on the roof surface, and microbiological activity were found to trigger the runoff dynamics of that herbicide.

About 50 mg of atrazine (see chapter 4.3.5), and about 12 g of (R,S)-mecoprop (see chapter 6.3.4) were estimated to be annually discharged into the infiltration site, corresponding to about 1 %, and appr. 100 %, respectively, of the amounts applied on an agricultural area. This clearly indicates that the roof delivered compound is much more important with regard to storm water infiltration than the atmospherically deposited pesticides.

From the presented work, the following general conclusions on the significance of pesticides and NPs for storm water infiltration can be drawn:

1) Atmospherically delivered pesticides are not likely to pose a significant problem for storm water infiltration.

2) NPs, however, are considered to be of significant environmental concern, and the specific characteristics of storm water infiltration, i.e., concentration of loads, and reduced retention capacities of the subsurface, would further increase their adverse potential on a local scale.

3) A significant input of (R,S)-mecoprop occurs in stormwater infiltration sites that receive roof runoff waters from flat roofs containing the root protection agent Preventol® B 2. Although the rooftop greening may have its ecological merits, in such cases, they may be impaired by a likely deterioration of the local ground water quality. Clearly, other solutions to achieve a root, and water resistance of such roofs should be considered.

4) The type of roof largely defines the runoff dynamics of the investigated compounds. In the case of flat roofs, discharge of the first millimetres of roof runoff into waste water, as carried out for example with an advanced separated sewer system, will not significantly reduce the organic pollutant load during extensive rain events.

Generally, because of the environmental concern and the relevance of NPs for storm water infiltration and groundwater quality, and because of the use of bituminous roofing membranes with herbicide activity, storm water infiltration sites should be specifically evaluated when designating contribution areas around drinking water wells or springs.

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Appendix A.1

Table A.1 Physico-chemical properties of the pesticides investigated

	molweight [g/mol]	melting point [°C]	aqueous solubility [mg/L, 20 °C]	vapor pressure [Pa, 20 °C]	log K _{ow} [-]	pKa [-]	Henry constant ^a [-]
triazines							
atratone	211.3	94-96	1650	3.9E-4			4.1E-7
atrazine	215.7	176	33	3.9E-5	2.5		1.1E-7
propazine	229.7	212-214	5	3.9E-6			7.4E-8
simazine	201.7	225-227	6.2	2.9E-6	2.1		3.9E-8
terbutylazine	229.7	177-179	8.5	1.5E-4 ^b	3.04		1.7E-6
acetamides							
alachlor	269.8	40-42	242 ^b	2.9E-3 ^b	3.09		1.3E-6
dimethenamid	275.8		1200 ^b	3.7E-2 ^b	2.15 ^b		3.5E-6
metaxyl	279.3	72	8400	7.5E-4	1.75		1.0E-8
metazachlor	277.8	85	430	4.9E-5	2.13		1.3E-8
metolachlor	283.8		488 ^b	4.2E-3	2.9 ^b		1.0E-6
propachlor	211.7	77	613 ^b	3.1E-2	1.62-2.30		4.3E-6
phenoxy acids							
2,4-D	221.0	141	311 ^{b, c}	1.1E-2	2.58-2.83 ^c	2.64	3.2E-6
dichlorprop	235.1	116-118	350	< 1E-5	1.77	3.0	< 3E-9
MCPA	200.6	119-121	734 ^b	2.3E-5	2.75 ^{b, c}	3.07	2.6E-9
mecoprop	214.6	94-95	734 ^b	3.1E-4	0.46 ^{b, d}		3.7E-8

all data from Tomlin (1994), if not otherwise stated, except for atratone: all data from Anonymous (1991). Note that the aqueous solubilities and vapor pressures are given for solids. ^a calculated from Tomlin (1994), and Anonymous (1991), using data for solids. ^b measured at 25 °C. ^c pH 1. ^d pH 5. ^e pH 7.

Appendix A.2

Table A.2 Physico-chemical properties of the NACs and related compounds investigated

	vapor pressure at 25 °C [atm] ^a		aqueous solubility at 20 °C [mol L ⁻¹] ^a		octanol-water partition coefficient at 25° C ^a		pK _a ^d	Henry constant ^e [-]	K _d ^g [L/kg]
	P ⁰	P ⁰ (L)	c _w ^{sat}	c _w ^{sat} (L)	log K _{ow}	log K _{ow}			
NPs									
2-NP	1.1E-4	1.9E-4	7.8E-3	1.4E-2	1.89	1.89	7.23	5.6E-4	45
2,4-DNP	5.1E-7	6.8E-6	1.8E-3	1.5E-2	1.67	1.67	3.94	1.2E-5	≥ 9000 ^h
DNOC	4.3E-7	2.4E-6	1.0E-3	4.5E-3	2.12	2.12	4.31	1.8E-5	37'000
NTs									
2,6-DA-4-NT					-1.1 ^c				11
4-A-2,6-DNT					0.9 ^c				125
TNT	4.1E-8 ^b		6.6E-4 ^b		1.86 ^b				21500
NB									
1,3-DNB					1.49 ^d				4500
NMs									
musk ketone									
musk xylene									
musk tibetene									
benzotriflile					5.2 ^e				
chlorothalonil									
					2.89 ^f				
nitrodiazobenzene									
alizarin yellow R									

^a Schwarzenbach et al. (1988) ^b Rosenblatt et al. (1991). ^c estimated from K_{ow}(TNT) using π -constants given in Hansch & Leo (1979). ^d Hansch & Leo (1979). ^e Müller (1996). ^f Tomlin (1994). ^g on K-montmorillonite, Haderlein et al. (1996). ^h on Cs-kaolinite, Haderlein & Schwarzenbach (1993).

Appendix B

Appendix B contains the raw data of the investigated pesticides and NPs measured in field studies from 1994 to 1997 at Burgdorf, Dübendorf, Grütze, and Tüffenwies. Data are grouped as follows:

Compounds	Year	Site	page
pesticides	1994	Tüffenwies	1 - 2
pesticides	1995	Tüffenwies	3 - 8
pesticides	1996	Grütze	9 - 17
pesticides	1997	Dübendorf	18 - 19
NPs	1997	Dübendorf	20 - 21
(R,S)-mecoprop	1997	Burgdorf, Grütze	22 - 23

Leer - Vide - Empty

1994, all samples from Tüffenwies,
all concentrations in [ng/L]

	Date	Time	Sample [mm] No.	atrazine	desethyl- atrazine	deisopropyl- atrazine	simazine	terbutyl- azine	propazine	
Rain	25/26.4.			15.0	32	8	n.d.	6	15	n.d.
Flat roof	25/26.4.		1	0.0	19	129	n.d.	5	n.d.	n.d.
Flat roof	25/26.4.		3	0.2	17	123	d.	6	n.d.	n.d.
Flat roof	25/26.4.		5	0.4	22	120	d.	10	n.d.	n.d.
Flat roof	25/26.4.		7	0.6	29	121	6	10	n.d.	n.d.
Flat roof	25/26.4.		9	0.8	28	141	6	9	n.d.	n.d.
Rain	4/5.5.			4.2	99	26	n.d.	26	24	n.d.
Polyester roof	4.5. 06:35		1	0.0	1166	194	n.d.	174	140	11
Polyester roof	4.5. 16:39		3	1.0	54	10	n.d.	12	15	n.d.
Polyester roof	5.5. 00:00		5	1.9	42	15	n.d.	12	13	n.d.
Tile roof	5.5. 07:39		1	0.0	694	152	n.d.	191	96	n.d.
Tile roof	5.5. 17:43		2	1.1	42	9	n.d.	14	15	n.d.
Tile roof	6.5. 03:43		5	2.7	34	10	n.d.	11	15	n.d.
Rain	19/20.6.			8.0	140	57	46	5	7	n.d.
Flat roof	19.6. 23:12		1	0.0	204	89	60	n.d.	166	n.d.
Flat roof	20.6. 08:54		3	0.2	143	122	108	n.d.	401	n.d.
Flat roof	20.6. 10:31		5	0.5	151	133	94	n.d.	250	n.d.
Polyester roof	19.6. 20:56		1	0.0	1620	426	380	72	111	17
Polyester roof	19.6. 21:42		3	0.5	324	104	89	15	21	6
Polyester roof	19.6. 21:53		5	0.8	286	100	44	11	20	n.d.
Polyester roof	19.6. 22:22		7	1.3	215	69	45	9	13	n.d.
Polyester roof	19.6. 22:42		11	2.9	93	32	n.d.	n.d.	5	n.d.
Polyester roof	20.6. 09:13		15	5.8	173	158	58	6	9	3
Tile roof	19.6. 21:47		1	0.0	410	109	93	18	27	n.d.
Tile roof	19.6. 22:23		3	0.5	262	89	40	7	12	n.d.
Tile roof	19.6. 22:30		5	0.9	292	97	55	13	11	d.
Tile roof	19.6. 22:34		7	1.5	205	59	42	15	6	n.d.
Tile roof	19.6. 22:46		11	3.4	91	29	8	n.d.	4	n.d.
Tile roof	20.6. 09:34		15	6.7	171	135	43	n.d.	11	n.d.
Rain	4/5.7.			4.0	128	24	38	10	21	n.d.
Polyester roof	4.7. 23:49		3	0.5	157	20	45	13	34	n.d.
Polyester roof	5.7. 01:43		5	0.9	169	49	53	9	26	n.d.
Polyester roof	5.7. 06:08		7	1.5	94	40	34	8	17	n.d.
Polyester roof	5.7. 08:28		9	2.3	90	57	28	5	12	n.d.
Tile roof	5.7. 00:18		1	0.0	224	62	95	18	34	n.d.
Tile roof	5.7. 03:06		3	0.5	86	39	35	7	14	n.d.
Tile roof	5.7. 08:15		5	0.9	118	80	42	16	21	n.d.
Tile roof	5.7. 08:31		7	1.5	114	78	36	4	20	n.d.
Rain	8.8.			11.3	d.	d.	n.d.	d.	d.	n.d.
Flat roof	8.8. 07:01		1	0.0	18	17	n.d.	n.d.	173	n.d.
Flat roof	8.8. 08:33		3	0.2	15	13	7	n.d.	79	n.d.
Flat roof	8.8. 08:52		5	0.4	15	13	18	n.d.	95	n.d.
Flat roof	8.8. 09:17		7	0.6	15	13	17	n.d.	104	n.d.
Polyester roof	7.8. 20:46		2	0.2	7	4	n.d.	9	22	n.d.
Polyester roof	7.8. 20:54		3	0.4	6	6	n.d.	7	11	n.d.
Polyester roof	7.8. 21:01		5	0.8	d.	4	n.d.	d.	6	n.d.
Polyester roof	7.8. 21:08		7	1.4	d.	d.	n.d.	n.d.	4	n.d.
Polyester roof	7.8. 21:36		9	2.1	d.	d.	n.d.	n.d.	7	n.d.
Polyester roof	7.8. 21:59		11	3.3	d.	d.	n.d.	n.d.	4	n.d.
Polyester roof	8.8. 06:40		13	4.7	d.	d.	n.d.	n.d.	d.	n.d.
Polyester roof	8.8. 07:08		15	6.5	d.	d.	n.d.	n.d.	4	n.d.
Polyester roof	8.8. 07:57		17	9.3	n.d.	n.d.	n.d.	n.d.	d.	n.d.
Tile roof	7.8. 20:58		1	0.0	5	3	n.d.	15	7	n.d.

1994, all samples from Tüffenwies,
all concentrations in [ng/L]

	Date	Time	Sample [mm] No.	atrazine	desethyl- atrazine	deisopropyl- atrazine	simazine	terbutyl- azine	propazine	
Tile roof	7.8.	21:05	3	0.4	d.	d.	n.d.	d.	3	n.d.
Tile roof	7.8.	21:19	5	0.8	d.	d.	n.d.	17	3	n.d.
Tile roof	7.8.	21:44	7	1.4	d.	n.d.	n.d.	5	d.	n.d.
Tile roof	7.8.	22:13	9	2.2	d.	n.d.	n.d.	d.	d.	n.d.
Tile roof	8.8.	06:43	11	3.3	d.	3	n.d.	5	d.	n.d.
Tile roof	8.8.	07:27	13	4.8	d.	n.d.	n.d.	d.	d.	n.d.
Tile roof	8.8.	08:02	15	6.6	n.d.	n.d.	n.d.	d.	n.d.	n.d.

never detected: atratone

n.a.: not analyzed; n.d.: not detected, < MDL; d.: detected, < LOQ

Appendix B raw, pesticide data, 1995, page 3

1995, all samples from Tüffenwies,
all concentrations in [ng/L]

	Date	Time	Sample [mm] No.	atrazine	desethyl- atrazine	deisopropyl- atrazine	simazine	terbutyl- azine	propazine	
Rain	29/30.5.			5.5	148	25	38	7	10	12
Sequential rain	29.5.	18:05	1	0.2	603	32	53	23	109	23
Sequential rain	29.5.		2	0.4	609	30	18	13	72	41
Sequential rain	29.5.		3	0.6	569	35	17	7	50	40
Sequential rain	29.5.		5	1.0	472	79	24	5	26	36
Sequential rain	29.5.		7	1.4	269	65	20	4	17	22
Sequential rain	29.5.		13	2.6	52	15	5	n.d.	5	5
Sequential rain	29.5.	20:23	23	4.5	29	10	d.	d.	7	3
Flat roof	29/30.5.		1	0.2	81	49	24	7	81	4
Tile roof	29.5.	18:33	1	0.0	617	54	58	6	23	52
Tile roof	29.5.	18:58	2	0.2	551	37	29	6	17	44
Tile roof	29.5.	19:04	3	0.4	440	58	19	6	15	39
Tile roof	29.5.	19:13	6	0.9	273	57	19	4	10	20
Tile roof	29.5.	19:45	9	2.0	54	14	6	d.	4	5
Tile roof	29.5.	03:19	12	3.6	17	12	5	d.	5	3
Rain	8/9.6.			18.6	140	29	35	n.d.	n.d.	n.d.
Sequential rain	8.6.	19:05	1	0.2	2838	226	200	34	34	22
Sequential rain	8.6.	19:20	2	0.4	2732	240	221	30	33	23
Sequential rain	8.6.	19:41	3	0.6	1650	222	188	23	27	17
Sequential rain	8.6.	19:45	4	0.8	1182	181	134	25	23	13
Sequential rain	8.6.	19:48	5	1.0	796	127	118	17	15	8
Sequential rain	8.6.	19:55	6	1.2	543	87	82	12	13	6
Sequential rain	8.6.	20:01	7	1.4	379	69	66	13	9	n.d.
Sequential rain	8.6.	20:07	8	1.6	290	57	45	6	5	n.d.
Sequential rain	8.6.	20:12	9	1.8	223	44	38	7	n.d.	n.d.
Sequential rain	8.6.	20:19	10	2.0	210	38	47	8	6	n.d.
Sequential rain	8.6.	20:26	11	2.2	239	53	48	7	5	n.d.
Sequential rain	8.6.	20:29	12	2.4	211	43	42	6	n.d.	n.d.
Tile roof	8.6.	19:17	1	0.0	2041	119	167	27	19	14
Tile roof	8.6.	19:45	2	0.3	1283	161	154	30	21	12
Tile roof	8.6.	19:52	3	0.4	668	79	94	10	10	6
Tile roof	8.6.	20:00	4	0.6	497	27	58	9	9	5
Tile roof	8.6.	20:07	5	0.8	358	25	55	8	5	n.d.
Tile roof	8.6.	20:13	6	1.0	303	31	35	6	5	n.d.
Tile roof	8.6.	20:27	7	1.3	296	30	33	7	6	n.d.
Tile roof	8.6.	20:38	8	1.7	250	30	31	n.d.	5	n.d.
Sequential rain	21.6.	10:58	1	0.2	343	293	184	19	20	7
Sequential rain	21.6.		2	0.4	148	154	99	10	10	n.d.
Sequential rain	21.6.		3	0.6	73	98	63	6	n.d.	n.d.
Sequential rain	21.6.		4	0.8	57	74	50	5	n.d.	n.d.
Sequential rain	21.6.		5	1.0	67	82	50	6	n.d.	n.d.
Sequential rain	21.6.		6	1.2	66	72	42	n.d.	n.d.	n.d.
Sequential rain	21.6.		7	1.4	63	64	33	n.d.	n.d.	n.d.
Sequential rain	21.6.		8	1.6	68	61	38	n.d.	n.d.	n.d.
Sequential rain	21.6.	11:05	10	2.0	60	44	25	5	n.d.	n.d.
Sequential rain	21.6.		12	2.4	62	38	21	n.d.	n.d.	n.d.
Sequential rain	21.6.		14	2.8	46	31	20	n.d.	n.d.	n.d.
Sequential rain	21.6.		15	3.0	39	30	22	n.d.	n.d.	n.d.
Sequential rain	21.6.		16	3.2	47	35	19	n.d.	n.d.	n.d.
Sequential rain	21.6.	11:15	17	3.4	56	40	22	n.d.	n.d.	n.d.
Sequential rain	21.6.	11:20	19	3.8	59	35	17	n.d.	n.d.	n.d.
Tile roof	21.6.	11:00	1	0.0	197	180	137	14	11	n.d.
Tile roof	21.6.	11:02	2	0.2	143	127	87	7	7	n.d.
Tile roof	21.6.	11:02	3	0.6	136	133	92	8	8	n.d.
Tile roof	21.6.	11:04	4	0.9	113	94	64	8	8	n.d.

Appendix B raw, pesticide data, 1995, page 4

1995, all samples from Tüffenwies,
all concentrations in [ng/L]

	Date	Time	Sample [mm] No.	atrazine	desethyl- atrazine	deisopropyl- atrazine	simazine	terbuthyl- azine	propazine	
Tile roof	21.6.	11:05	5	1.3	109	78	58	11	7	n.d.
Tile roof	21.6.	11:08	6	1.6	96	58	35	6	6	n.d.
Tile roof	21.6.	11:11	7	2.0	85	45	26	n.d.	n.d.	n.d.
Tile roof	21.6.	11:14	8	2.5	61	32	16	n.d.	n.d.	n.d.
Tile roof	21.6.	11:17	9	3.0	70	36	29	n.d.	n.d.	n.d.
Rain	3.7.			20.0	42	25	15	n.d.	6	n.d.
Flat roof	3.7.	03:33	1	0.0	96	59	47	6	66	n.d.
Flat roof	3.7.	03:41	2	0.1	51	39	35	n.d.	17	n.d.
Flat roof	3.7.	03:55	4	0.9	52	36	29	n.d.	15	n.d.
Flat roof	3.7.	04:02	5	1.3	55	39	27	n.d.	18	n.d.
Flat roof	3.7.		6	1.9	60	34	27	n.d.	21	n.d.
Flat roof	3.7.	04:28	7	2.6	61	39	29	n.d.	23	n.d.
Flat roof	3.7.		8	3.2	65	38	28	n.d.	26	n.d.
Flat roof	3.7.	05:04	9	3.9	69	51	35	n.d.	31	n.d.
Flat roof	3.7.		10	5.8	78	49	42	n.d.	48	n.d.
Flat roof	3.7.	09:37	11	7.7	63	44	34	n.d.	33	n.d.
Flat roof	3.7.		12	9.6	66	55	37	n.d.	39	n.d.
Tile roof	3.7.	02:30	1	0.0	208	144	121	24	24	n.d.
Tile roof	3.7.	02:31	2	0.2	150	111	70	11	17	n.d.
Tile roof	3.7.	02:32	3	0.6	129	104	73	7	16	n.d.
Tile roof	3.7.	02:35	5	1.4	137	111	76	10	16	n.d.
Tile roof	3.7.	03:18	7	2.1	127	46	22	11	14	n.d.
Tile roof	3.7.	03:28	11	4.7	67	65	25	n.d.	8	n.d.
Tile roof	3.7.	03:35	15	9.3	29	31	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	03:44	17	12.9	26	27	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	05:38	19	16.6	24	26	n.d.	n.d.	6	n.d.
Tile roof	3.7.	08:37	20	18.4	15	17	n.d.	n.d.	n.d.	n.d.

Appendix B raw, pesticide data, 1995, page 5

1995, all samples from Tüffenwies,
all concentrations in [ng/L]

Date	Time	Sample (mm)	alachlor	metolachlor	propachlor	dimethenamid	acetochlor	metaxalof
No.								
Rain	29/30.5.		5.5	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	29.5. 18:05	1	0.2	18	46	58	n.d.	n.d. 8
Sequential rain	29.5.	2	0.4	16	34	106	n.d.	d. 5
Sequential rain	29.5.	3	0.6	14	35	87	n.d.	d. 5
Sequential rain	29.5.	5	1.0	29	50	50	n.d.	d. d.
Sequential rain	29.5.	7	1.4	30	29	37	n.d.	n.d. 5
Sequential rain	29.5.	13	2.6	7	3	10	n.d.	n.d. n.d.
Sequential rain	29.5. 20:23	23	4.5	5	7	6	n.d.	n.d. n.d.
Flat roof	29/30.5.	1	0.2	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Tile roof	29.5. 18:33	1	0.0	35	44	100	n.d.	d. 6
Tile roof	29.5. 18:58	2	0.2	19	37	69	n.d.	d. d.
Tile roof	29.5. 19:04	3	0.4	36	53	84	n.d.	d. 6
Tile roof	29.5. 19:13	6	0.9	28	32	34	n.d.	n.d. 5
Tile roof	29.5. 19:45	9	2.0	8	4	28	n.d.	n.d. n.d.
Tile roof	29.5. 03:19	12	3.6	10	8	3	n.d.	n.d. n.d.
Rain	8/9.6.		18.6	33	n.d.	n.d.	9	37 n.d.
Sequential rain	8.6. 19:05	1	0.2	74	7	n.d.	n.d.	n.d. 36
Sequential rain	8.6. 19:20	2	0.4	66	10	n.d.	n.d.	n.d. 36
Sequential rain	8.6. 19:41	3	0.6	81	7	n.d.	n.d.	n.d. 18
Sequential rain	8.6. 19:45	4	0.8	130	9	n.d.	8	n.d. n.d.
Sequential rain	8.6. 19:48	5	1.0	130	8	n.d.	10	n.d. 10
Sequential rain	8.6. 19:55	6	1.2	102	7	n.d.	8	n.d. n.d.
Sequential rain	8.6. 20:01	7	1.4	56	n.d.	n.d.	5	n.d. n.d.
Sequential rain	8.6. 20:07	8	1.6	39	n.d.	n.d.	5	n.d. n.d.
Sequential rain	8.6. 20:12	9	1.8	35	n.d.	n.d.	6	n.d. n.d.
Sequential rain	8.6. 20:19	10	2.0	38	n.d.	n.d.	8	n.d. n.d.
Sequential rain	8.6. 20:26	11	2.2	63	6	n.d.	21	n.d. n.d.
Sequential rain	8.6. 20:29	12	2.4	72	9	n.d.	28	n.d. n.d.
Tile roof	8.6. 19:17	1	0.0	75	13	n.d.	n.d.	n.d. 41
Tile roof	8.6. 19:45	2	0.3	134	10	n.d.	8	n.d. 6
Tile roof	8.6. 19:52	3	0.4	109	8	n.d.	9	n.d. n.d.
Tile roof	8.6. 20:00	4	0.6	63	6	n.d.	7	n.d. n.d.
Tile roof	8.6. 20:07	5	0.8	50	n.d.	n.d.	n.d.	n.d. n.d.
Tile roof	8.6. 20:13	6	1.0	41	n.d.	n.d.	8	n.d. n.d.
Tile roof	8.6. 20:27	7	1.3	107	13	n.d.	44	n.d. n.d.
Tile roof	8.6. 20:38	8	1.7	152	25	n.d.	81	n.d. n.d.
Sequential rain	21.6. 10:58	1	0.2	24	10	10	n.d.	8 6
Sequential rain	21.6.	2	0.4	6	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	3	0.6	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	4	0.8	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	5	1.0	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	6	1.2	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	7	1.4	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	8	1.6	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6. 11:05	10	2.0	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	12	2.4	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	14	2.8	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	15	3.0	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6.	16	3.2	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6. 11:15	17	3.4	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Sequential rain	21.6. 11:20	19	3.8	n.d.	n.d.	n.d.	n.d.	n.d. n.d.
Tile roof	21.6. 11:00	1	0.0	11	n.d.	n.d.	n.d.	n.d. n.d.
Tile roof	21.6. 11:02	2	0.2	6	n.d.	n.d.	n.d.	n.d. n.d.
Tile roof	21.6. 11:02	3	0.6	5	n.d.	n.d.	n.d.	n.d. n.d.
Tile roof	21.6. 11:04	4	0.9	n.d.	n.d.	n.d.	n.d.	n.d. n.d.

1995, all samples from Töffenwies,
all concentrations in [ng/L]

	Date	Time	Sample [mm] No.	metazachlor	(R,S)- mecoprop	(R,S) dichlorprop	2,4-D	MCPA	2,4,5-T	2,4,5-TP
Rain	29/30.5.		5.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	29.5.	18:05	1	0.2	d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	29.5.		2	0.4	d.	15	28	n.d.	n.d.	n.d.
Sequential rain	29.5.		3	0.8	12	11	10	16	n.d.	n.d.
Sequential rain	29.5.		5	1.0	n.d.	d.	d.	n.d.	n.d.	n.d.
Sequential rain	29.5.		7	1.4	n.d.	n.d.	n.d.	d.	n.d.	n.d.
Sequential rain	29.5.		13	2.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	29.5.	20:23	23	4.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	29/30.5.		1	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	29.5.	18:33	1	0.0	d.	12	27	33	n.d.	n.d.
Tile roof	29.5.	18:58	2	0.2	d.	12	9	10	d.	n.d.
Tile roof	29.5.	19:04	3	0.4	d.	d.	d.	17	n.d.	n.d.
Tile roof	29.5.	19:13	6	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	29.5.	19:45	9	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	29.5.	03:19	12	3.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rain	8/9.6.		18.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	8.6.	19:05	1	0.2	n.d.	87	n.d.	64	29	11
Sequential rain	8.6.	19:20	2	0.4	n.d.	25	n.d.	42	24	13
Sequential rain	8.6.	19:41	3	0.6	n.d.	12	n.d.	19	12	n.d.
Sequential rain	8.6.	19:45	4	0.8	n.d.	11	n.d.	17	18	n.d.
Sequential rain	8.6.	19:48	5	1.0	n.d.	n.d.	n.d.	20	14	n.d.
Sequential rain	8.6.	19:55	6	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	8.6.	20:01	7	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	8.6.	20:07	8	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	8.6.	20:12	9	1.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	8.6.	20:19	10	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	8.6.	20:26	11	2.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	8.6.	20:29	12	2.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	8.6.	19:17	1	0.0	n.d.	n.d.	n.d.	74	30	n.d.
Tile roof	8.6.	19:45	2	0.3	n.d.	14	n.d.	13	34	n.d.
Tile roof	8.6.	19:52	3	0.4	n.d.	n.d.	n.d.	26	42	n.d.
Tile roof	8.6.	20:00	4	0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	8.6.	20:07	5	0.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	8.6.	20:13	6	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	8.6.	20:27	7	1.3	n.d.	n.d.	n.d.	n.d.	12	n.d.
Tile roof	8.6.	20:38	8	1.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.	10:58	1	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		2	0.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		3	0.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		4	0.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		5	1.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		6	1.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		7	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		8	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.	11:05	10	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		12	2.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		14	2.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		15	3.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.		16	3.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.	11:15	17	3.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Sequential rain	21.6.	11:20	19	3.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	21.6.	11:00	1	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	21.6.	11:02	2	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	21.6.	11:02	3	0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	21.6.	11:04	4	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

1995, all samples from Tüffenwies,
all concentrations in [ng/L]

	Date	Time	Sample [mm] No.	metazachlor	(R,S)-	(R,S)	2,4-D	MCPA	2,4,5-T	2,4,5-TP
					mecoprop	dichlorprop				
Tile roof	21.6.	11:05	5	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	21.6.	11:08	6	1.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	21.6.	11:11	7	2.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	21.6.	11:14	8	2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	21.6.	11:17	9	3.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rain	3.7.			20.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.	03:33	1	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.	03:41	2	0.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.	03:55	4	0.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.	04:02	5	1.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.		6	1.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.	04:28	7	2.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.		8	3.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.	05:04	9	3.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.		10	5.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.	09:37	11	7.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Flat roof	3.7.		12	9.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	02:30	1	0.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	02:31	2	0.2	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	02:32	3	0.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	02:35	5	1.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	03:18	7	2.1	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	03:28	11	4.7	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	03:35	15	9.3	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	03:44	17	12.9	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	05:38	19	16.6	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Tile roof	3.7.	08:37	20	18.4	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

never detected: atratone

n.a.: not analyzed; n.d.: not detected, < MDL; d.: detected, < LOQ

Appendix B raw, pesticide data, 1996, page 9

1996, all samples from Grütze,
all concentrations in [ng/L]

	Date	Time Start	Time End	[mm; L]	atra- zine	desethyl- atrazine	deisopropyl- atrazine	sim- zine	terbuthyl- azine	propa- zine	ala- chlor
Rain	15.-23.2.			20.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	7
Rain	20.-21.3.			2.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rain	21.-22.3.			11.0	n.d.	n.d.	n.d.	11	9	n.d.	n.d.
Rain	22.-29.3.			15.5	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rain	2.-11.4.			8.5	33	n.d.	n.d.	n.d.	9	n.d.	8
Rain	11.-17.4.			13.0	12	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rain	17.-29.4.			11.8	63	12	n.d.	15	6	n.d.	84
Rain	29.4.-2.5.			17.0	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	28
Rain	2.-3.5.			5.0	6	n.d.	n.d.	n.d.	n.d.	n.d.	17
Rain	7.-8.5.			15.5	34	n.d.	n.d.	n.d.	17	n.d.	50
Rain	8.-15.5.			21.5	14	6	n.d.	n.d.	7	n.d.	12
Rain	17.5.			4.0	196	65	35	20	48	n.d.	191
Rain	17.-21.5.			40.0	26	7	14	n.d.	5	n.d.	21
Rain	21.-24.5.			15.0	138	55	38	6	8	n.d.	52
Rain	25/26.5.	18:00	09:00	10.3	58	15	14	nd	nd	n.d.	12
Roof runoff	25.5.	20:00			52	21	27	9	d.	n.d.	10
Roof runoff	25.5.	20:20			34	12	21	7	n.d.	n.d.	6
Roof runoff	25.5.	20:50			39	22	25	6	n.d.	n.d.	6
Roof runoff	25.5.	21:10			64	38	35	7	d.	n.d.	11
Roof runoff	25.5.	21:44			71	41	48	7	d.	n.d.	12
Roof runoff	25.5.	22:13			73	36	41	9	d.	n.d.	11
Roof runoff	25.5.	23:21			70	35	39	8	d.	n.d.	11
Roof runoff	26.5.	06:10			48	24	28	8	d.	n.d.	10
Roof runoff	26.5.	09:25			48	26	33	7	d.	n.d.	9
Roof runoff	26.5.	13:21			35	19	30	4	n.d.	n.d.	6
Lysimeter Cm	25.5.	20:40	21:20	2.0	77	48	23	7	6	n.d.	10
Lysimeter Cm	25.5.	21:23	21:39	2.0	83	49	34	8	6	n.d.	12
Lysimeter Cm	25.5.	22:06	22:19	2.0	81	51	33	7	6	n.d.	11
Lysimeter Cm	25.5.	23:03	23:20	2.0	81	53	34	7	7	n.d.	11
Lysimeter Am	25.5.	18:45	21:26	2.0	76	49	24	8	7	n.d.	10
Lysimeter Am	25.5.	21:29	22:49	2.0	76	42	24	7	7	n.d.	12
Lysimeter Bh	25.5.	21:42	21:57	2.0	55	45	21	6	6	n.d.	10
Lysimeter Bh	25.5.	22:08	22:38	2.0	54	40	19	n.d.	6	n.d.	11
Lysimeter V	25.5.	19:15	22:33	2.0	55	37	14	n.d.	n.d.	n.d.	9
Lysimeter T	25.5.	18:45	23:50	1.1	49	31	16	n.d.	5	n.d.	8
Lysimeter U	25.5.	19:15	23:50	0.8	68	44	22	6	6	n.d.	8
Lysimeter Em	25.5.	20:10	20:27		75	32	26	8	4	n.d.	11
Lysimeter Em	25.5.	20:45	20:59		53	22	21	6	d.	n.d.	7
Lysimeter Em	25.5.	21:31	21:41		63	33	28	6	4	n.d.	9
Lysimeter Em	25.5.	22:11	22:25		72	38	30	7	4	n.d.	11
Lysimeter Em	26.5.	00:00	09:00		60	33	28	7	4	n.d.	10
Lysimeter Em	27.5.	09:00	14:00		39	28	25	4	d.	n.d.	11
Lysimeter Cv	25.5.	18:45	20:56		95	38	42	9	5	n.d.	14
Lysimeter Cv	25.5.	21:06	21:32		76	40	30	8	4	n.d.	9
Lysimeter Cv	25.5.	22:06	22:38		76	46	34	8	4	n.d.	10
Lysimeter Cv	25.5.	23:03	23:32		76	48	34	8	4	n.d.	9
Lysimeter Cv	26.5.	00:00	09:00		41	34	30	4	4	n.d.	16
Suction cups	26/27.5.	09:00	14:00	lower 3	53	38	31	6	d.	n.d.	12
Suction cups	26/27.5.	09:00	14:00	upper 3	45	35	32	5	d.	n.d.	12
Rain	26.-29.5.			17.0	22	9	13	n.d.	n.d.	n.d.	17
Rain	1.-2.6.			7.5	159	58	46	6	45	n.d.	24
Rain	12.6.			2.0	766	166	137	15	31	7	91
Rain	20.6.	11:00	12:00	0.3	903	140	n.d.	n.d.	n.d.	n.d.	n.d.
Rain	20.6.	15:45	16:00	0.3	277	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rain	20/21.6.	16:00	16:00	2.8	157	53	51	9	n.d.	n.d.	9
Rain	21/22.6.	18:50	10:00	30.5	13	n.d.	n.a.	n.d.	n.d.	n.d.	n.d.
Rain	22/23.6.	10:00	19:00	19.5	28	27	15	n.d.	5	n.d.	n.d.

1996, all samples from Grüze,
all concentrations in [ng/L]

	Date		Time		[mm; L]		atra-	desethyl-	deisopropyl-	sima-	terbutyl-	propa-	ala-
	Start	End	zine	atrazine	atrazine	zine	azine	azine	zine	azine	zine	chlor	
Roof runoff	20.6.	11:28		1178	388	272	52	28	12	24			
Roof runoff	20.6.	12:21		1098	324	188	55	21	10	n.d.			
Roof runoff	20.6.	12:35		703	231	138	45	10	8	n.d.			
Roof runoff	20.6.	12:58		527	245	115	33	11	6	n.d.			
Roof runoff	20.6.	13:15		338	166	75	n.d.	n.d.	n.d.	n.d.			
Roof runoff	20.6.	13:49		155	64	27	n.d.	n.d.	n.d.	n.d.			
Roof runoff	20.6.	15:48		380	111	n.d.	n.d.	n.d.	n.d.	n.d.			
Roof runoff	20.6.	15:51		265	85	n.d.	n.d.	n.d.	n.d.	n.d.			
Roof runoff	20.6.	19:52		326	133	n.d.	n.d.	n.d.	n.d.	n.d.			
Roof runoff	21.6.	13:47		431	193	235	n.d.	15	n.d.	n.d.			
Roof runoff	21.6.	13:53		342	96	66	n.d.	14	n.d.	n.d.			
Roof runoff	21.6.	13:55		296	58	64	n.d.	12	n.d.	n.d.			
Roof runoff	21.6.	13:58		295	81	81	n.d.	n.d.	n.d.	n.d.			
Roof runoff	21.6.	14:08		217	56	52	16	7	n.d.	n.d.			
Roof runoff	21.6.	14:39		146	64	29	n.d.	6	n.d.	n.d.			
Roof runoff	21.6.	15:20		238	139	113	n.d.	n.d.	n.d.	n.d.			
Roof runoff	21.6.	16:05		333	202	178	n.d.	10	n.d.	n.d.			
Roof runoff	21.6.	17:25		246	161	69	n.d.	5	n.d.	n.d.			
Roof runoff	21.6.	17:55		179	111	91	n.d.	9	n.d.	n.d.			
Roof runoff	21.6.	19:02		301	215	162	n.d.	9	n.d.	n.d.			
Roof runoff	21.6.	20:00		110	55	54	n.d.	7	n.d.	n.d.			
Roof runoff	21.6.	20:33		163	95	85	n.d.	n.d.	n.d.	n.d.			
Roof runoff	21.6.	22:15		123	78	74	n.d.	n.d.	n.d.	n.d.			
Roof runoff	22.6.	03:38		65	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
Roof runoff	22.6.	07:49		27	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
Roof runoff	22.6.	11:56		28	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
Roof runoff	22.6.	17:34		37	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
Roof runoff	23.6.	12:43		68	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
Roof runoff	23.6.	19:00		37	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.			
Lysimeter Cm	20.6.	14:05	14:05	2.0	329	171	n.a.	17	9	n.d.	105		
Lysimeter Cm	20.6.	14:07	15:16	1.9	234	154	134	12	7	n.d.	8		
Lysimeter Cm	21.6.	14:50	14:50	14.0	219	134	119	11	8	n.d.	9		
Lysimeter Cm	21.6.	15:19	15:22	2.0	246	190	173	14	9	n.d.	10		
Lysimeter Cm	21.6.	16:01	16:04	2.0	278	221	224	12	10	6	12		
Lysimeter Cm	21.6.	16:39	16:41	2.0	275	217	218	13	10	n.d.	15		
Lysimeter Cm	21.6.	17:16	17:18	2.0	268	216	223	15	10	5	10		
Lysimeter Cm	21.6.	17:58	18:00	2.0	220	193	187	13	10	n.d.	10		
Lysimeter Cm	21.6.	19:02	19:05	2.0	258	213	241	13	11	n.d.	11		
Lysimeter Cm	22.6.	10:00	10:01	2.0	30	23	n.a.	n.d.	n.d.	n.d.	5		
Lysimeter Cm	23.6.	19:10	19:12	2.0	42	34	29	6	n.d.	n.d.	6		
Lysimeter Cv	20.6.	14:14	14:14	2.0	424	184	72	n.d.	12	n.d.	19		
Lysimeter Cv	20.6.	14:15	15:19	1.4	240	115	53	n.d.	n.d.	n.d.	n.d.		
Lysimeter Cv	20.6.	15:57	16:22	1.7	234	49	73	n.d.	15	n.d.	19		
Lysimeter Cv	20.6.	16:23	18:25	1.8	285	46	79	n.d.	24	n.d.	19		
Lysimeter Am	20.6.	15:24	15:24	1.8	409	163	131	n.d.	10	n.d.	n.d.		
Lysimeter Am	20.6.	16:30	18:30	0.8	381	182	187	n.d.	13	n.d.	n.d.		
Lysimeter Am	21.6.	15:11	15:11	1.8	261	115	122	n.d.	8	n.d.	n.d.		
Lysimeter Am	21.6.	15:11	16:27	2.0	285	168	185	n.d.	n.d.	n.d.	n.d.		
Lysimeter Am	21.6.	16:27	17:40	2.0	302	186	206	n.d.	n.d.	n.d.	n.d.		
Lysimeter Am	21.6.	17:40	18:30	0.9	252	147	191	n.d.	n.d.	n.d.	n.d.		
Lysimeter Am	21.6.	18:30	19:15	1.5	287	193	215	n.d.	n.d.	n.d.	n.d.		
Lysimeter Am	23.6.	20:08	21:08	1.5	49	27	68	n.d.	n.d.	n.d.	n.d.		
Lysimeter Eh	20.6.	14:48	14:48	2.0	217	113	117	n.d.	n.d.	n.d.	n.d.		
Lysimeter Eh	21.6.	14:52	15:00	2.0	204	103	111	n.d.	n.d.	n.d.	n.d.		
Lysimeter Eh	21.6.	15:19	15:31	2.0	260	141	157	n.d.	n.d.	n.d.	n.d.		
Lysimeter Eh	21.6.	16:01	16:13	2.0	318	174	166	n.d.	n.d.	n.d.	n.d.		
Lysimeter Eh	21.6.	16:39	16:47	2.0	319	180	156	n.d.	n.d.	n.d.	n.d.		
Lysimeter Eh	21.6.	17:16	17:22	2.0	292	167	183	n.d.	n.d.	n.d.	n.d.		

Appendix B raw, pesticide data, 1996, page 15

1996, all samples from Grze,
all concentrations in [ng/L]

	Date	Time Start	S-		(R,S)-		P-		2,4-D	MCPA
			meoprop	End	dichlorprop	dichlorprop	dichlorprop	dichlorprop		
Rain	15.-23.2.				n.d.	n.a.	15	n.d.	n.d.	n.d.
Rain	20.-21.3.				n.d.	n.a.	5	n.d.	n.d.	n.d.
Rain	21.-22.3.				n.d.	n.a.	8	n.d.	n.d.	n.d.
Rain	22.-29.3.				n.d.	n.a.	13	n.d.	n.d.	n.d.
Rain	2.-11.4.				n.d.	n.a.	24	6	n.d.	16
Rain	11.-17.4.				n.d.	n.a.	19	n.d.	n.d.	15
Rain	17.-29.4.				n.d.	n.a.	59	n.d.	n.d.	n.d.
Rain	29.4.-2.5.				n.d.	n.a.	n.d.	n.d.	n.d.	n.d.
Rain	2.-3.5.				n.d.	n.a.	n.d.	n.d.	8	11
Rain	7.-8.5.				10	n.a.	106	11	23	27
Rain	8.-15.5.				13	n.a.	10	n.d.	n.d.	n.d.
Rain	17.5.				n.d.	n.a.	9	5	n.d.	n.d.
Rain	17.-21.5.				16	n.a.	5	n.d.	n.d.	n.d.
Rain	21.-24.5.				n.d.	n.a.	6	n.d.	n.d.	n.d.
Rain	25/26.5.	18:00	09:00		n.d.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	25.5.	20:00			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	25.5.	20:20			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	25.5.	20:50			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	25.5.	21:10			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	25.5.	21:44			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	25.5.	22:13			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	25.5.	23:21			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	26.5.	06:10			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	26.5.	09:25			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	26.5.	13:21			n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	25.5.	20:40	21:20		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	25.5.	21:23	21:39		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	25.5.	22:06	22:19		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	25.5.	23:03	23:20		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	25.5.	18:45	21:26		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	25.5.	21:29	22:49		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Bh	25.5.	21:42	21:57		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Bh	25.5.	22:08	22:38		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter V	25.5.	19:15	22:33		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter T	25.5.	18:45	23:50		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter U	25.5.	19:15	23:50		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Em	25.5.	20:10	20:27		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Em	25.5.	20:45	20:59		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Em	25.5.	21:31	21:41		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Em	25.5.	22:11	22:25		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Em	26.5.	00:00	09:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Em	27.5.	09:00	14:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	25.5.	18:45	20:56		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	25.5.	21:06	21:32		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	25.5.	22:06	22:38		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	25.5.	23:03	23:32		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	26.5.	00:00	09:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Suction cups	26/27.5.	09:00	14:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Suction cups	26/27.5.	09:00	14:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Rain	26.-29.5.				n.d.	n.a.	10	n.d.	n.d.	n.d.
Rain	1.-2.6.				6	n.a.	31	n.d.	n.d.	n.d.
Rain	12.6.				11	n.a.	28	n.d.	n.d.	n.d.
Rain	20.6.	11:00	12:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Rain	20.6.	15:45	16:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Rain	20/21.6.	16:00	16:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Rain	21/22.6.	18:50	10:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Rain	22/23.6.	10:00	19:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.

Appendix B raw, pesticide data, 1996, page 16

1996, all samples from Grze,
all concentrations in [ng/L]

	Date	Time	S-	(R,S)-	P-	S-	2,4-D	MCPA	
		Start	End	mecoprop	dichlorprop	dichlorprop	dichlorprop		
Roof runoff	20.6.	11:28		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	20.6.	12:21		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	20.6.	12:35		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	20.6.	12:58		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	20.6.	13:15		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	20.6.	13:49		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	20.6.	15:48		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	20.6.	15:51		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	20.6.	19:52		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	13:47		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	13:53		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	13:55		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	13:58		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	14:08		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	14:39		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	15:20		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	16:05		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	17:25		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	17:55		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	19:02		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	20:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	20:33		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	21.6.	22:15		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	22.6.	03:38		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	22.6.	07:49		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	22.6.	11:56		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	22.6.	17:34		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	23.6.	12:43		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Roof runoff	23.6.	19:00		n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	20.6.		14:05	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	20.6.	14:07	15:16	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	21.6.		14:50	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	21.6.	15:19	15:22	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	21.6.	16:01	16:04	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	21.6.	16:39	16:41	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	21.6.	17:16	17:18	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	21.6.	17:58	18:00	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	21.6.	19:02	19:05	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	22.6.	10:00	10:01	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cm	23.6.	19:10	19:12	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	20.6.		14:14	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	20.6.	14:15	15:19	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	20.6.	15:57	16:22	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Cv	20.6.	16:23	18:25	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	20.6.		15:24	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	20.6.	16:30	18:30	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	21.6.		15:11	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	21.6.	15:11	16:27	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	21.6.	16:27	17:40	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	21.6.	17:40	18:30	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	21.6.	18:30	19:15	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Am	23.6.	20:08	21:08	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Eh	20.6.		14:48	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Eh	21.6.	14:52	15:00	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Eh	21.6.	15:19	15:31	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Eh	21.6.	16:01	16:13	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Eh	21.6.	16:39	16:47	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.
Lysimeter Eh	21.6.	17:16	17:22	n.a.	n.d.	n.a.	n.a.	n.d.	n.d.

Appendix B raw, pesticide data, 1996, page 17

1996, all samples from Grze,
all concentrations in [ng/L]

	Date	Time	S-		(R,S)-		R-		S-		2,4-D	MCPA
			Start	End	mecoprop	dichlorprop	dichlorprop	dichlorprop	dichlorprop			
Lysimeter Eh	21.6.	17:58	18:05	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter Eh	21.6.	19:03	19:11	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter Eh	23.6.	20:08	20:44	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter Ev	21/22.6.	18:30	10:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter Bm	21/22.6.	18:30	10:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter Bm	23.6.	20:08	20:23	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter Fm	23.6.	19:10	19:14	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter Dm	21.6.	16:34	18:30	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter V	20/21.6.		18:25	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter V	21/22.6.	18:26	10:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter V	22/23.6.	10:00	19:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter U	20/21.6.		18:25	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter U	21/22.6.	18:26	10:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter U	22/23.6.	10:00	19:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter T	21/22.6.	18:26	10:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Lysimeter T	22/23.6.	10:00	19:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Suction cups	20.6.	12:00	19:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Suction cups	21.8.	07:30	19:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Suction cups	21/22.6.	19:00	10:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Suction cups	21/22.6.	19:00	10:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Suction cups	22/23.6.	10:00	19:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Suction cups	22/23.6.	10:00	19:00	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Suction cups	23/24.6.	19:00	08:30	n.a.	n.d.	n.a.	n.a.	n.a.	n.a.	n.d.	n.d.	
Rain	23.6.-30.6.			n.d.	n.a.	14	5	n.d.	n.d.	n.d.	n.d.	
Rain	30.6.-1.7.			n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	1.-2.7.			n.d.	n.a.	n.d.	5	n.d.	n.d.	n.d.	n.d.	
Rain	2.-3.7.			n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain				n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	7.-8.7.			7	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	8.7.			n.d.	n.a.	21	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	8.-9.7.			n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	9.-18.7.			5	n.a.	8	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	18.-24.7.			8	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	24.-29.7.			8	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	29.-31.7.			n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	1.-9.8.			7	n.a.	8	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	9.-19.8.			12	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	19.-27.8.			n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	27.8.-16.9.			n.d.	n.a.	6	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	16.9.-14.10.			n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	14.-18.10.			n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	
Rain	18.-22.10.			n.d.	n.a.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	

never detected: atratone, 2,4,5-T, 2,4,5-TP

n.a.: not analyzed, n.d.: not detected, < MDL, d: detected < LOQ

1997, all samples from Dübendorf,
all concentrations in [ng/L]

	Date	Time	Sample [mm]	(R,S)-	R-	S-	2,4-D	MCPA
	Start	No.		dichlorprop	dichlorprop	dichlorprop		
Sequential rain	26.4.	02:00	0.2	38	n.a.	n.a.	156	53
Sequential rain	26.4.	02:04	0.4	23	n.a.	n.a.	92	39
Sequential rain	26.4.	02:07	0.6	16	n.a.	n.a.	55	26
Sequential rain	26.4.	02:11	0.8	11	n.a.	n.a.	38	17
Sequential rain	26.4.	02:22	1.0	10	n.a.	n.a.	34	18
Sequential rain	26.4.	02:29	1.2	n.d.	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	02:40	1.6	n.d.	n.a.	n.a.	23	11
Sequential rain	26.4.	02:48	2.0	n.d.	n.a.	n.a.	16	d.
Sequential rain	26.4.	02:57	2.4	n.d.	n.a.	n.a.	14	n.d.
Sequential rain	26.4.	03:06	2.8	n.d.	n.a.	n.a.	12	n.d.
Sequential rain	26.4.	03:13	3.2	n.d.	n.a.	n.a.	11	n.d.
Sequential rain	26.4.	03:28	3.6	n.d.	n.a.	n.a.	13	n.d.
Sequential rain	26.4.	03:56	4.0	n.d.	n.a.	n.a.	14	n.d.
Sequential rain	26.4.	04:02	4.4	12	n.a.	n.a.	18	11
Sequential rain	26.4.	04:40	4.8	n.d.	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	04:55	5.2	n.d.	n.a.	n.a.	10	n.d.
Sequential rain	26.4.	05:04	5.6	n.d.	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	05:08	6.0	n.d.	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	05:13	6.4	n.d.	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	05:23	6.8	9	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	05:28	7.2	n.d.	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	05:39	8.2	n.d.	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	05:47	9.2	n.d.	n.a.	n.a.	n.d.	n.d.
Sequential rain	26.4.	06:41	10.0	n.d.	n.a.	n.a.	n.d.	n.d.

never detected:

deisopropylatrazine, propazine, atratone

dimethenamid, acetochlor, metolaxyl, metazachlor

(R,S)-mecoprop, 2,4,5-T, 2,4,5-TP

n.a.: not analyzed, n.d.: not detected, < MDL, d.: detected, < LOQ

1997, all samples from Dübendorf,
all concentrations in [µg/L]

	Date	Time Start	Sample [mm] No.	2,4-DNP	DNOC
Rain	4.4.		2.0	3	1.69
Rain	21.4.		8.2	n.d.	0.53
Rain	26.4.		9.3	n.q.	0.227
Sequential rain	26.4.	02:00	0.2	3.801	n.q.
Sequential rain	26.4.	02:04	0.4	3.006	n.q.
Sequential rain	26.4.	02:07	0.6	2.328	n.q.
Sequential rain	26.4.	02:11	0.8	1.809	n.q.
Sequential rain	26.4.	02:22	1.0	1.812	n.q.
Sequential rain	26.4.	02:29	1.2	1.448	n.q.
Sequential rain	26.4.	02:40	1.6	0.667	n.q.
Sequential rain	26.4.	02:48	2.0	0.509	n.q.
Sequential rain	26.4.	02:57	2.4	0.462	n.q.
Sequential rain	26.4.	03:06	2.8	0.724	n.q.
Sequential rain	26.4.	03:13	3.2	1.006	n.q.
Sequential rain	26.4.	03:28	3.6	0.713	n.q.
Sequential rain	26.4.	03:56	4.0	1.100	n.q.
Sequential rain	26.4.	04:02	4.4	1.231	n.q.
Sequential rain	26.4.	04:40	4.8	0.791	n.q.
Sequential rain	26.4.	04:55	5.2	0.648	n.q.
Sequential rain	26.4.	05:04	5.6	0.380	n.q.
Sequential rain	26.4.	05:08	6.0	0.404	n.q.
Sequential rain	26.4.	05:13	6.4	0.288	n.q.
Sequential rain	26.4.	05:23	6.8	0.565	n.q.
Sequential rain	26.4.	05:28	7.2	0.347	n.q.
Sequential rain	26.4.	05:39	8.2	0.350	n.q.
Sequential rain	26.4.	05:47	9.2	0.107	n.q.
Sequential rain	26.4.	06:41	10.0	0.166	n.q.
Rain	28.4.		15.5	n.d.	n.d.
Rain	30.4.		8.0	n.d.	n.d.
Rain	6.5.		2.2	n.d.	n.d.
Rain	7.5.		8.3	n.d.	n.d.
Rain	8.5.		9.0	n.d.	0.086
Rain	20.5.		10.6	n.d.	n.d.
Rain	4.6.		2.6	n.d.	n.d.
Rain	9.6.		5.0	n.d.	n.d.
Rain	12.6.		8.9	n.d.	0.297
Rain	13.6.		1.9	n.d.	0.277
Rain	14.6.		11.3	n.d.	0.141
Rain	17.6.		0.8	n.d.	n.d.
Rain	18.6.		4.5	0.540	0.211
Rain	19.6.		5.0	n.d.	0.184
Rain	20.6.		7.2	n.d.	0.184
Rain	21.6.		1.4	n.d.	0.088
Rain	22.6.		20.0	n.d.	0.047
Rain	23.6.		12.5	n.d.	0.047
Rain	24.6.		9.1	n.d.	0.206
Rain	25.6.		1.4	n.d.	d.
Rain	26.6.		4.9	n.d.	d.
Rain	28.6.		2.1	n.d.	n.d.
Rain	29.6.		8.0	n.d.	0.076
Rain	30.6.		6.9	n.d.	0.076
Rain	3.7.		0.8	n.d.	0.193
Rain	4.7.		8.0	n.d.	0.111
Rain	5.7.		9.7	n.d.	0.111
Rain	6.7.		21.3	n.d.	0.151

1997, all samples from Dübendorf,
all concentrations in [$\mu\text{g/L}$]

	Date	Time Start	Sample No.	[mm]	2,4-DNP	DNOC
Rain	7.7.			7.9	n.d.	0.151
Rain	11.7.			0.7	1.782	0.771
Rain	18.7.	after midnight		7.0	1.005	0.625
Sequential rain	18.7.	after midnight +		0.3	0.686	1.039
Sequential rain	18.7.	1.00 min		0.5	1.137	0.798
Sequential rain	18.7.	1.50 min		0.8	0.183	0.643
Sequential rain	18.7.	2.00 min		1.0	0.634	0.556
Sequential rain	18.7.	2.50 min		1.3	0.716	0.569
Sequential rain	18.7.	3.00 min		1.5	1.137	0.697
Sequential rain	18.7.	3.50 min		1.8	0.929	0.65
Sequential rain	18.7.	4.00 min		2.0	0.884	0.649
Sequential rain	18.7.	4.50 min		2.3	1.131	0.725
Sequential rain	18.7.	5.00 min		2.5	1.444	0.757
Sequential rain	18.7.	5.38 min		2.8	0.782	0.501
Sequential rain	18.7.	5.75 min		3.0	0.707	0.476
Sequential rain	18.7.	6.13 min		3.3	0.77	0.531
Sequential rain	18.7.	6.88 min		3.8	0.771	0.515
Sequential rain	18.7.	7.63 min		4.3	0.726	0.53
Sequential rain	18.7.	8.38 min		4.8	0.739	0.501
Sequential rain	18.7.	9.13 min		5.3	0.854	0.583
Sequential rain	18.7.	14.33 min		5.8	0.94	0.66
Sequential rain	18.7.	15.00 min		6.3	0.975	0.564
Sequential rain	18.7.	23.00 min		6.8	1.051	0.674

n.q.: not quantifiable, n.d.: not detected, < MDL, d.: detected, < LOQ

1997, samples from Grütze, and Burgdorf
all concentrations in [µg/L]

	Location	Date	Time Start	Time End	[mm; L]	R-mecoprop	S-mecoprop
Rain	Grütze	18-19.6.	12:00	12:30	14.3	0.02	0.02
Rain	Grütze	19-22.6.	12:30	13:00	48.2	0.03	0.03
Roof runoff	Grütze	18.6.	00:04			0.08	0.05
Roof runoff	Grütze	18.6.	00:08			0.05	0.04
Roof runoff	Grütze	18.6.	00:12			0.14	0.11
Roof runoff	Grütze	18.6.	00:20			0.91	0.62
Roof runoff	Grütze	18.6.	00:29			1.40	0.96
Roof runoff	Grütze	18.6.	01:02			1.67	1.19
Roof runoff	Grütze	18.6.	02:03			1.94	1.41
Roof runoff	Grütze	18.6.	02:51			2.39	1.73
Roof runoff	Grütze	18.6.	03:38			2.46	1.73
Roof runoff	Grütze	18.6.	05:29			2.04	1.44
Roof runoff	Grütze	18.6.	12:17			2.25	1.58
Roof runoff	Grütze	18.6.	14:24			2.61	2.48
Roof runoff	Grütze	18.6.	17:10			5.82	5.70
Roof runoff	Grütze	19.6.	03:06			18.10	18.42
Roof runoff	Grütze	19.6.	11:52			0.73	0.74
Roof runoff	Grütze	19.6.	15:34			6.89	6.99
Roof runoff	Grütze	19.6.	15:48			6.62	6.31
Roof runoff	Grütze	19.6.	16:09			5.81	5.63
Roof runoff	Grütze	19.6.	16:42			3.68	3.44
Roof runoff	Grütze	19.6.	17:22			2.67	2.57
Roof runoff	Grütze	19.6.	18:00			2.47	2.40
Roof runoff	Grütze	19.6.	18:34			2.07	2.02
Roof runoff	Grütze	19.6.	19:32			2.11	2.08
Roof runoff	Grütze	19.6.	20:54			2.03	2.06
Roof runoff	Grütze	19.6.	23:22			3.28	3.36
Roof runoff	Grütze	20.6.	05:10			3.55	3.61
Roof runoff	Grütze	20.6.	08:22			1.90	1.93
Roof runoff	Grütze	20.6.	10:12			2.21	2.31
Roof runoff	Grütze	20.6.	12:00			2.73	2.85
Roof runoff	Grütze	20.6.	14:48			0.72	0.54
Roof runoff	Grütze	21.6.	10:12			7.37	6.52
Roof runoff	Grütze	21.6.	19:58			1.33	1.42
Roof runoff	Grütze	21.6.	22:18			0.85	0.91
Roof runoff	Grütze	22.6.	01:24			1.28	1.42
Roof runoff	Grütze	22.6.	05:44			1.12	1.25
Roof runoff	Grütze	22.6.	08:30			1.08	1.21
Roof runoff	Grütze	22.6.	12:50			1.10	1.23
Roof runoff	Grütze	22.6.	14:06			0.96	1.01
Roof runoff	Grütze	22.6.	17:40			1.67	2.06
Roof runoff	Grütze	23.6.	07:26			16.94	18.08
Roof surface water	Grütze	18.6.	12:50			0.06	0.07
Roof surface water	Grütze	20.6.	12:00			0.30	0.33
Roof surface water	Grütze	23.6.	07:30			2.64	3.41
Lysimeter Cv	Grütze	20.6.		12:00	3.0	0.50	0.51
Lysimeter Ch	Grütze	20.6.		12:00	20.0	0.46	0.48
Roof 1 runoff	Burgdorf	25.6.	0:00:00	0:12:30	0.5	20.87	20.02
Roof 1 runoff	Burgdorf	25.6.	0:22:28	0:25:38	0.5	18.89	18.99
Roof 1 runoff	Burgdorf	25.6.	0:29:42	0:32:09	0.5	17.78	18.01
Roof 1 runoff	Burgdorf	25.6.	0:35:53	0:38:30	0.5	16.06	16.33
Roof 1 runoff	Burgdorf	25.6.	0:45:55	0:48:39	0.5	18.07	18.64
Roof 1 runoff	Burgdorf	25.6.	0:57:00	1:05:30	0.5	18.23	19.10
Roof 1 runoff	Burgdorf	25.6.	1:14:48	1:18:41	0.5	16.29	17.07
Roof 1 runoff	Burgdorf	25.6.	1:35:58	1:40:28	0.5	16.26	17.08
Roof 1 runoff	Burgdorf	25.6.	1:59:30	2:04:30	0.5	16.41	17.26

1997, samples from Gröze, and Burgdorf
all concentrations in [$\mu\text{g/L}$]

	Location	Date	Time		[mm: L]	R-mecoprop	S-mecoprop
			Start	End			
Roof 1 runoff	Burgdorf	25.6.	2:25:52	2:31:25	0.5	15.93	16.62
Roof 1 runoff	Burgdorf	25.6.	2:55:15	3:01:40	0.5	15.95	16.60
Roof 1 runoff	Burgdorf	25.6.	3:28:58	3:36:00	0.5	15.47	16.10
Roof 1 runoff	Burgdorf	25.6.	3:56:20	4:04:05	0.5	17.01	17.41
Roof 1 runoff	Burgdorf	25.6.	4:26:38	4:35:15	0.5	16.85	17.27
Roof 1 runoff	Burgdorf	25.6.	5:12:30	5:23:05	0.5	17.51	17.78
Roof 3 runoff	Burgdorf	25.6.	0:00:00	0:07:50	0.5	2.94	3.22
Roof 3 runoff	Burgdorf	25.6.	0:09:25	0:10:10	0.5	1.67	2.36
Roof 3 runoff	Burgdorf	25.6.	0:11:10	0:11:20	0.5	0.60	0.84
Roof 3 runoff	Burgdorf	25.6.	0:14:00	0:14:40	0.5	0.90	1.14
Roof 3 runoff	Burgdorf	25.6.	0:17:02	0:17:48	0.5	0.78	0.94
Roof 3 runoff	Burgdorf	25.6.	0:21:08	0:22:12	0.5	0.67	0.75
Roof 3 runoff	Burgdorf	25.6.	0:26:01	0:27:22	0.5	0.77	0.82
Roof 3 runoff	Burgdorf	25.6.	0:31:07	0:32:40	0.5	0.80	0.83
Roof 3 runoff	Burgdorf	25.6.	0:39:40	0:46:07	0.5	0.67	0.69
Roof 3 runoff	Burgdorf	25.6.	0:53:01	1:01:10	0.5	0.53	0.57
Roof 3 runoff	Burgdorf	25.6.	1:19:45	1:53:00	0.5	0.34	0.37
Roof 3 runoff	Burgdorf	25.6.	2:46:00	3:25:00	0.5	1.56	0.79

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Curriculum Vitae

Date of birth: November 9, 1967

Citizen of Zürich and Schwarzenberg (LU), Switzerland

- 1974 - 1982 Primary and secondary school
- 1982 - 1986 Mathematisch-Naturwissenschaftliches Gymnasium Rämibühl, Zürich
- 1986 Matura type C (mathematics and natural sciences)
- 1987 Military service
- 1987 - 1992 Studies in environmental sciences at ETH Zürich
- 1989 - 1990 Practical training at the Institute of Marine Research in Bergen, Norway
- 1992 Diploma thesis with PD Dr. Karl Fent (EAWAG): Inhibition of hepatic microsomal monooxygenase system by organotins *in vitro* in freshwater fish
- 1992 Diploma in environmental sciences
- 1993 Proficiency course at the Australian College of English, Sydney, Australia, Certificate of Proficiency in English (Grade B)

Literature review on the induction of cytochrome P450 as a biomarker for environmental contamination in aquatic ecosystems; EAWAG
- 1994 - 1997 Graduate student in the group of Prof. Dr. René P. Schwarzenbach, and teaching assistant in the environmental sciences department at ETH Zürich