

# Point- and Nonpoint-Source Pesticide Contamination in the Zwester Ohm Catchment, Germany

Karin Müller,\* Martin Bach, Holger Hartmann, Michael Spiteller, and Hans-Georg Frede

## ABSTRACT

Reducing pesticide loads in surface waters implies identifying the pathways responsible for the pollution. The current study documents the pesticide contamination of the river Zwester Ohm, a 4917-ha catchment in Germany with 41% of the land used for crop production. Discharges and concentrations of 19 pesticides were measured continuously at three locations for 15 mo. The load detected at the outlet of the catchment amounted to 9048 g a.i. The losses represent 0.22% of the pesticides applied by the farmers. The contamination showed a seasonal pattern following the pesticide application times. The wastewater treatment plant system (WWTPS) in the catchment (two wastewater treatment plants [WWTP], 14 combined sewer overflows (CSO), four CSO tanks) emits during dry weather periods purified sewage and during storm events sewage mixed with stormwater runoff into the river. The contribution by the WWTPS to the pesticide load was defined as point-source pollution (PSP). The load was dominated by PSP with at least 77% of the total pollution. No significant interdependencies between intrinsic properties of the pesticides, hydrometeorological factors, and the loads occurring in the stream could be found. Therefore, it is not possible to predict PSP for other catchments based on the results from this study. Whereas 65% of the total load entered the river via the WWTP, a portion of 12% was attributed to the CSO. The study points out that the influence of CSO on PSP should be taken into account in future catchment studies in areas with comparable agricultural structure.

THE USE OF pesticides is indispensable for conventional labor-extensive farming systems. Pesticides guarantee high production levels and quality standards, but they are also partially lost to the atmosphere and hydrosphere of agroecosystems. As pesticides are toxic by nature, they can endanger the aquatic ecosystem and diminish its quality as a drinking water supply. The general public is, therefore, concerned about the possible effects of pesticides on ecosystems and human health.

Recent monitoring programs have found the presence of pesticide residues in surface and ground water bodies in Europe (Albanis et al., 1998; Barcelo et al., 1996; Carter, 1999). The EC Drinking Water Directives (80/778/EC, 98/83/EC) stipulate the requirement that not a single pesticide should exceed  $0.1 \mu\text{g L}^{-1}$  in drinking water. Minimization of water contamination is preferable to avoid noncompliance with legislation and the costs of water treatment. A sound understanding of pesticide dynamics in the environment is a prerequisite for any

effective prevention and management strategy. Water pollution originates from two different sources: point and nonpoint sources. In the literature this terminology is not used consistently (DeCoursey, 1985; Frank et al., 1982; Léon et al., 2001; Mohaupt et al., 2000; Novotny, 1988). In accordance with Léon et al. (2001) and Mohaupt et al. (2000), in this paper point-source pollution is defined as the discharge of a discrete identifiable source, such as a waste pipe. The pesticide load, which is contributed to a stream by a wastewater treatment plant system (WWTPS) including emissions by wastewater treatment plants (WWTP) and combined sewer overflows (CSO), is referred to as PSP. These loads result from disposal of pesticides and filling and cleaning of spraying equipment on farmyards during dry weather periods, as well as from washing off pesticide residues from impervious areas (farmyards, streets, roofs, etc.) during storm events. On the other hand, transport processes such as soil surface runoff, interflow, preferential flow, leaching, atmospheric depositions, and spray drift lead to nonpoint-source pollution (NPSP).

In the past, intensive field studies were carried out to characterize the main pathways by which a pesticide might be transported through the soil into surface waters. Much effort has been invested in understanding the spatial and temporal fate of pesticides in soils (Flury, 1996). Most studies have focused on plot scales (Gaynor et al., 1995; Kladviko et al., 1991). The main objectives of catchment studies have been to monitor the occurrence of pesticides in surface waters (Donnelly and Ferrari, 2001; Dubrovsky et al., 1998; Fenelon and Moore, 1998; Harman-Fetcho et al., 1999; Laroche and Gallichand, 1995; Pereira et al., 1996; Williamson et al., 1998) or to calculate the total load of pesticides in surface waters (Bach and Frede, 1996; Isenbeck-Schröter et al., 1998; Larson et al., 1995, 1999). In other studies, the relative importance of different nonpoint-source contributions to the total load has been characterized (Ng and Clegg, 1997; Rawn et al., 1999). Catchment studies differentiating between point and nonpoint-source pesticide contamination are fewer in number. Most of these investigations are limited to small catchments (Fischer, 1996; Mason et al., 1999) or to only the dominant application period (Seel et al., 1994). Frank et al. (1982) identified runoff as a predominant mechanism for the entrance of pesticides into surface waters from investigations of 11 watersheds in Ontario. But during the main pesticide application periods, PSP contributed 82% to the total load. Up to now the contribution of CSO to the pesticide PSP of surface waters has not been taken

**Abbreviations:** CSO, combined sewer overflows; LC, liquid chromatography; NPSP, nonpoint-source pollution; PSP, point-source pollution; SP, sampling point; WWTP, wastewater treatment plants; WWTPS, wastewater treatment plant system.

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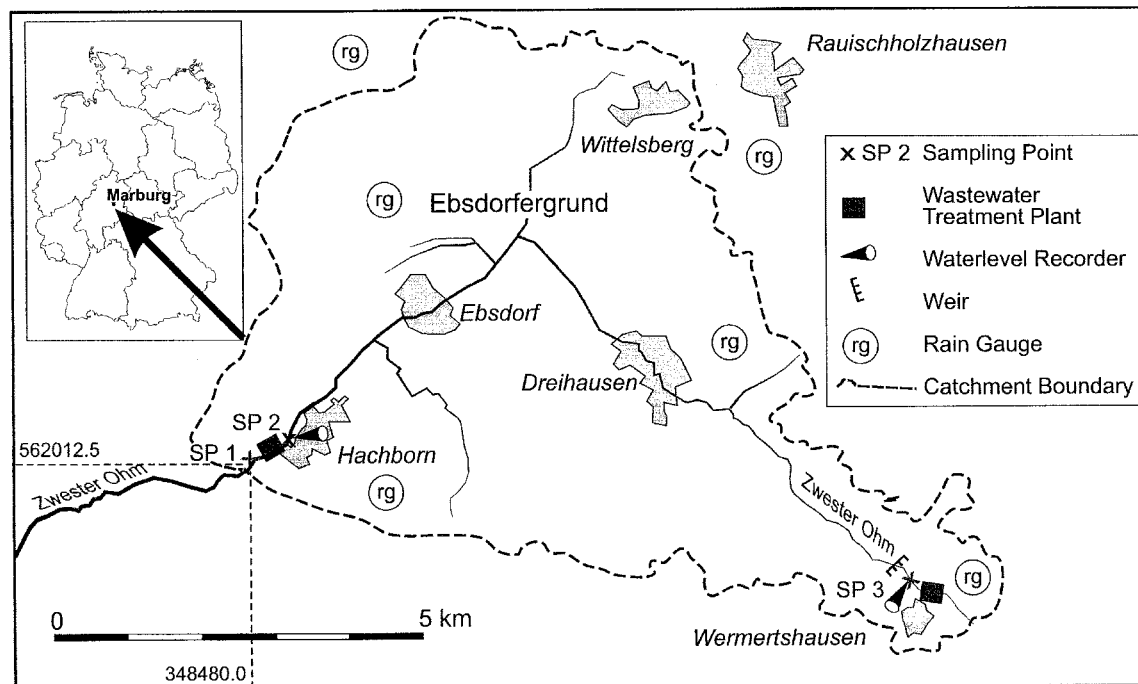


Fig. 1. Location of sampling sites in the catchment area.

into consideration, in spite of the fact that nearly all catchments in Europe are drained by a mixed sewage system (Mulliss et al., 1996).

The objective of the project described in this paper was to determine annual input and output of pesticides for a typical mesoscale agricultural catchment in Germany. Furthermore, the relative importance of normal field use of pesticides, referred to as NPSP, and of handling of pesticides and sprayers on impervious areas (PSP) for the detected pesticide loads was determined.

## MATERIALS AND METHODS

### Catchment

The investigated catchment, totaling 49.7 km<sup>2</sup>, is located in a low mountain range in the middle of Germany (federal state Hessen, county Marburg-Biedenkopf), 10 km south of the city Marburg, in the municipality Ebsdorfergrund. The catchment is drained by the river Zwester Ohm (Fig. 1). The boundaries of the catchment, as well as the flownet of the Zwester Ohm, were calculated by means of the model TOPAZ 1.2 (Topographic Parameterization; Garbrecht and Martz, 1995). The database used was a digital elevation model (625-m<sup>2</sup> grids)

Table 1. Field crops surveyed for pesticide use pattern in the catchment.

Crop	Area	
	ha	%
Winter wheat ( <i>Triticum aestivum</i> L.)	686	34
Winter barley ( <i>Hordeum vulgare</i> L.)	481	24
Rye ( <i>Secale cereale</i> L.)	106	5
Summer barley	50	3
Oat ( <i>Avena sativa</i> L.)	159	8
Oil rape seed ( <i>Brassica napus</i> L.)	278	14
Maize ( <i>Zea mays</i> L.)	81	4
Sugar beet ( <i>Beta vulgaris</i> L.)	48	2
Root crops	117	6
Total	2006	100

with a vertical resolution of 5 m ( $\pm 3$  m) (Nöhles, 2000). The catchment has an undulating topography and is located 200 to 400 m above sea level. The climatic conditions are characterized by an average annual precipitation of 585 mm and an average temperature of 8°C.

Luvisols, Cambisols, and Stagnic Gleysols (FAO system) are the main soil types in the catchment, depending on the parent material and the ground water level. Soils derived from loess are dominating. Based on the SCS curve number method (USDA, 1972) the soils in the catchment were classified into hydrologic groups. Soils of the hydrologic group C are dominating, which are silt and clay loams with a low infiltration capacity, prone to runoff. About 23% of the arable area is tile drained.

The landuse in the catchment (1997–1998) was mapped, supported by photos of aerial surveys at a scale of 1:5000 (Hessisches Landesvermessungsamt Wiesbaden, 1990). The information gained was digitalized with the geographic information system ERDAS IMAGINE 8.3 (Fa. Geosystems, Munich), which showed that about 41% of the land was used for crop production, with another 20% fallow land and pastures, and 30% forest. The crop rotation systems are dominated by winter cereals (Table 1), reflecting the extensive character of agriculture in the region.

### Pesticide Usage

The rural catchment is inhabited by 9600 persons of which 164 are farmers, with an average farm size of 27 ha. Farmers living in the catchment were asked to complete a questionnaire concerning the farm, the crops, and the pesticide usage (type of pesticide applied, dosage, dates of spraying). This was done three times for each of the application periods in the investigation period (spring 1997, fall 1997, spring 1998). About 75% of the farmers with 69% of the arable land participated in the investigation. Using the results from the inquiry and from mapping of the landuse in the catchment the pesticide usage for the entire catchment was inferred from data on crop acreage and the average application rates of pesticides on specific

**Table 2.** Applied amount and farm-specific and unit-area loading of the Zwester Ohm catchment during the investigation period (10 Mar. 1997–31 May 1998).

Pesticide	Area†	Y <sub>x</sub> ‡	Loading		Specific load	
	ha	kg	g	g ha <sup>-1</sup>	% of Y <sub>x</sub>	g farm <sup>-1</sup>
Atrazine	94	–	87.4	0.93	–	0.53
Carbetamide	280	41	293.0	1.05	0.71	1.79
Chlortoluron	1435	–	19.5	0.01	–	0.12
2,4-D	1435	–	11.8	0.01	–	0.07
Dichlorprop-P	1435	610	535.2	0.37	0.09	3.26
Dimefuron	280	21	139.3	0.50	0.66	0.85
Diuron	–	–	1126.9	–	–	–
Fenpropimorph	1435	116	16.8	0.01	0.01	0.1
Isoproturon	1435	2029	4606.0	3.21	0.23	28.09
MCPA	1435	321	825.1	0.57	0.26	5.03
Mecoprop-P	1435	263	239.6	0.17	0.09	1.46
Metamitron	58	40	246.1	4.24	0.62	1.50
Metazachlor	280	111	468.6	1.67	0.42	2.86
Metolachlor	94	–	340.9	3.63	–	2.08
Pirimicarb	–	–	nd§	–	–	–
Simazine	–	–	39.0	–	–	–
2,4,5-T	1435	–	11.3	0.01	–	0.07
Terbuthylazine	94	47	24.4	0.26	0.05	0.15
Triadimenol	280	–	16.7	0.06	–	0.10
Total	–	–	9047.6	–	–	–
Total¶	1867	3599	7881.7	4.22	–	48.06

† Area of the relevant crops for which the pesticide was used.

‡ Applied amount of the pesticide.

§ Not detected.

¶ Simazine and diuron are not used in agriculture and are not considered.

crops by probabilistic statistics (Müller, 2000). Non-agricultural applications of pesticides are difficult to quantify, but Der Rat von Sachverständigen für Umweltfragen (1998) estimated that in 1997, agricultural applications accounted for 80% of the total nationwide pesticide usage. Only 9% of the catchment has urban character (settlements, streets); therefore, non-agricultural pesticide applications were neglected in this study.

The estimated total amount of pesticides applied within the catchment during the investigation period amounted to 4600 kg a.i. with 61 different compounds contributing to this total. Pesticides included in the analyses of this study represented 78% of the total amount applied. The overall pesticide use was dominated by herbicides (92%) and 68% of the total pesticide amount was applied in spring. Details on the pesticide usage are presented in Table 2.

### Identification of Input Pathways for Pesticides into the River

The WWTPS in the catchment features two WWTP, 14 CSO, and four combined sewer overflow tanks. During dry weather periods the sewage delivered to the two WWTP originates from households and farms located in the catchment, which are all connected to the WWTPS. The purified sewage is emitted into the stream via the WWTP. During storm events pesticides that accumulate on impervious surfaces within the catchment boundaries (roofs, streets, farmyards, etc.) are washed off into the WWTPS. Stormwater runoff is mixed with sewage in the sewer. This mixed water is emitted into the river after its purification in the WWTP. The CSO and the combined sewer overflow tanks are activated only if a critical discharge in the sewer is exceeded. The surplus of mixed water is either stored in the combined sewer overflow tanks until discharge conditions in the sewer are back to normal and then routed to the WWTP for purification, or it is emitted into the river without passing the WWTP by the CSO, which are located all over the catchment.

During dry periods, the PSP of the Zwester Ohm catchment could be determined directly by analyzing water samples upstream and downstream of the WWTP (sampling sites SP 1,

SP 2, and SP 3 in Fig. 1): The detected pesticide load at SP 3 entered the stream via the WWTP in Wermertshausen. Here, NPSP can be excluded, as the catchment of this sampling point is mainly used for pastures. Not a single arable field is adjacent to the stream. The contribution of the WWTP, located in Hachborn, to the PSP was calculated by subtracting the detected loads at the sampling site directly upstream of the WWTP from the loads found downstream from the WWTP (Fig. 1). Since the distance between the two sampling sites was only about 500 m, NPSP on this part of the stream could be excluded.

During storms it was not possible to measure the PSP directly. The 14 CSO could act as point sources for pesticides by emitting sewage mixed with stormwater runoff to the stream. The empirical model MOMENT 4.0 (Brandt-Gerdes-Sitzmann-Wasserwirtschaft GmbH, 1997) was applied to calculate the overflow volumes from the CSO. The model is not capable of computing pesticide concentrations in the effluents. When a pesticide load was determined at the sampling site SP 2 and an overflow volume from the CSO was modeled for the same day, the pesticide load was identified as PSP.

### Surface Water Sampling

The investigation period extended to 15 mo covering two spring application periods and one fall application period (10 Mar. 1997–31 May 1998). Throughout this period surface water samples were collected continuously at three sampling sites in daily time steps (Fig. 1). The sampling was performed with automatic samplers (ISCO [Lincoln, NE] 3700), with each sample being a composite of subsamples taken at 10-min intervals. Samples were collected in glass bottles washed with methanol. To inhibit dissipation of the pesticides during the collection period, water samples were cooled to 4°C. Each day the samples were delivered to the laboratory and were kept frozen at –20°C until analysis. During the main application periods every daily sample was analyzed, but during the remainder of the year the samples were combined to weekly samples. The water samples were analyzed for 19 pesticides of relevance for the area (Table 3).

**Table 3. Physico-chemical properties of the pesticides included in the investigation (Huber, 1998), recovery rates, and limits of detection.**

Common name	Chemical name (IUPAC)	$K_{oc}$	$DT_{50}$	$RR^{\dagger}$	$LOD^{\ddagger}$
		$L\ kg^{-1}$	$d$	%	$\mu g\ L^{-1}$
Atrazine	6-chloro- <i>N</i> <sup>2</sup> -ethyl- <i>N</i> <sup>4</sup> -isopropyl-1,3,5-triazine-2,4-diamine	100§	60§	91.0	0.04
Carbetamide	( <i>R</i> )-1-(ethylcarbamoyl)ethyl carbanilate	10¶	60¶	97.1	0.03
2,4-D	2,4-dichlorophenoxyacetic acid	38	10	91.3	0.04
Chlorotoluron	3-(3-chloro- <i>p</i> -tolyl)-1,1-dimethylurea	235	27	98.8	0.01
Dichlorprop-P	( <i>R</i> )-2-(2,4-dichlorophenoxy)propanoic acid	20	12	91.4	0.02
Dimefuron	3-[4-(5- <i>tert</i> -butyl-2,3-dihydro-2-oxo-1,3,4-oxadiazol-3-yl)-3-chlorophenyl]-1,1-dimethylurea	145¶	50¶	97.0	0.01
Diruon	3-(3,4-dichlorophenyl)-1,1-dimethylurea	800	68	97.9	0.02
Fenpropimorph	(±)- <i>cis</i> -4-[3-(4- <i>tert</i> -butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine	3400	31	97.2	0.05
Isoproturon	3-(4-isopropylphenyl)-1,1-dimethylurea; 3- <i>p</i> -cumenyl-1,1-dimethylurea	85	12	96.1	0.04
MCPA	(4-chloro-2-methylphenoxy)acetic acid; 4-chloro- <i>o</i> -tolylxyacetic acid	55	15	84.3	0.03
Mecoprop-P	( <i>R</i> )-2-(4-chloro- <i>o</i> -tolylxy)propionic acid	20	9	93.7	0.03
Metamitron	4-amino-4,5-dihydro-3-methyl-6-phenyl-1,2,4-triazin-5-one; 4-amino-3-methyl-6-phenyl-1,2,4-triazin-5(4 <i>H</i> )-one	156	21	93.8	0.05
Metazachlor	2-chloro- <i>N</i> -(pyrazol-1-ylmethyl)acet-2',6'-xylylidide	80	6	97.7	0.01
Metolachlor	2-chloro-6'-ethyl- <i>N</i> -(2-methoxy-1-methylethyl)acet- <i>o</i> -toluidide	200	39	88.7	0.02
Pirimicarb	2-dimethylamino-5,6-dimethylpyrimidin-4-yl dimethylcarbamate	53§	7§	92.8	0.03
Simazine	6-chloro- <i>N</i> <sup>2</sup> , <i>N</i> <sup>4</sup> -diethyl-1,3,5-triazine-2,4-diamine	201	57	88.2	0.04
2,4,5-T	2,4,5-trichlorophenoxyacetic acid	80§	30§	87.1	0.02
Terbutylazine	<i>N</i> <sup>2</sup> - <i>tert</i> -butyl-6-chloro- <i>N</i> <sup>4</sup> -ethyl-1,3,5-triazine-2,4-diamine	250	70	88.5	0.02
Triadimenol	(1 <i>RS</i> ,2 <i>RS</i> ; <i>1RS</i> ,2 <i>RS</i> )-1-(4-chlorophenoxy)-3,3-dimethyl-1-(1 <i>H</i> -1,2,4-triazol-1-yl)butan-2-ol	360	110	98.1	0.02

<sup>†</sup> Recovery rate.

<sup>‡</sup> Limit of detection.

§ Hornsby (1992).

¶ Tomlin (1994).

### Discharge and Rainfall Measurement

At two sampling sites (SP 2 and SP 3) the water-stage heights  $h$  were recorded continuously on Ott (Kempton, Germany) R20 water level recorders. By means of calibration functions delineating the relation between stage height  $h$  and discharge  $Q$ , each measured stage height was related to a discharge.

At SP 2 the discharge was determined indirectly by measuring the flow velocities at a cross-sectional area with an Ott Flügel C2 flow meter. The measured velocities were transformed to discharges according to the mean-section method proposed by Herschy (1995). A second-order polynomial function was applied describing the relation between discharge and height:

$$Q = 0.5 - 3.45h + 6.5h^2 \quad [1]$$

with a resulting  $r^2$  of 0.96 and a standard deviation of  $0.05\ m^3\ s^{-1}$ . An estimated error for the measurements was calculated according to the rules of error propagation by Gauss (Herschy, 1995) and amounted to 8%. By adding the measured effluents of the wastewater treatment plant in Hachborn to the discharge at SP 2, the streamflow at the outlet of the catchment (SP 1) was indirectly determined. At SP 3 river discharges were measured using a 90-degree V-notch weir. To describe the relationship between measured height  $h$  and discharge  $Q$  for the weir a square root equation was used (Dyck and Peschke, 1989) with a resulting  $r^2$  of 0.97 ( $n = 79$ ) and an estimated error of the measurements of 17%.

Daily rainfall data were collected at six locations (Fig. 1) and interpolated according to the Thiessen polygon method (Maniak, 1993).

### Pesticide Analysis

In Germany, phenoxy acid herbicides are exclusively applied during spring; therefore, only the water samples collected during the spring application periods were analyzed for these compounds. The remaining pesticides were determined in every water sample. Each water sample collected during the

spring application periods was divided into two subsamples of 500 mL, as the analysis of the phenoxy acid herbicides (2,4-D, dichlorprop-P, MCPA, mecoprop-P, 2,4,5-T) was carried out separately. The extraction of the pesticides was performed according to the methods described by Janssen et al. (1995). The pH values of the samples were adjusted to 1.8 and 7.5 for the analysis of the phenoxy acid herbicides and the other compounds, respectively. To increase the ionic strength of the water samples,  $20\ mg\ mL^{-1}$  NaCl was added to the 500-mL samples. After filtering the samples, the extraction of the pesticides was performed by solid phase extraction. Polar Plus cartridges with a 1-g sorbent mass were used for extracting the phenoxy acid herbicides, while RP-C<sub>18</sub> cartridges with a 500-mg sorbent mass were used for all other compounds (all cartridges from Baker, Gross-Gerau, Germany).

The samples for pesticide recoveries were prepared by adding known amounts of the pesticides to tap water samples. The recovery efficiencies are presented in Table 3. None of the reported values was corrected for the analytical recovery efficiencies.

The analysis is described in detail elsewhere (Hartmann et al., 1998). Two different procedures were applied, one for the nonpolar and semipolar pesticides and the other for the five phenoxy acid herbicides included in this study. Liquid chromatography (LC) was carried out with a Gynkotek (Germering, Germany) Model P580 pump. High performance liquid chromatography (HPLC) was either coupled directly to UV detection (UV340S; Gynkotek) or to tandem mass spectrometry (MS-MS) with a Finnigan (San Jose, CA) MAT TSO 7000 triple quadrupole mass spectrometer for quantification of the five phenoxy acid herbicides. In the first case, the pesticides were separated on a 50-mm by 4.6-mm-i.d. Alltech (Deerfield, IL) Altima column filled with 5- $\mu m$  C18 reversed phase packing. Isocratic LC elution was performed using 30% Millipore (Bedford, MA) water including 1% formic acid and 85% acetonitrile with a flow rate of  $0.6\ mL\ min^{-1}$ . For the MS-MS technique, we used a Macherey & Nagel (Düren, Germany) C18 column (125 mm long, 2-mm diam.). For the isocratic LC elution, the same solvents were used with a flow rate of 0.25

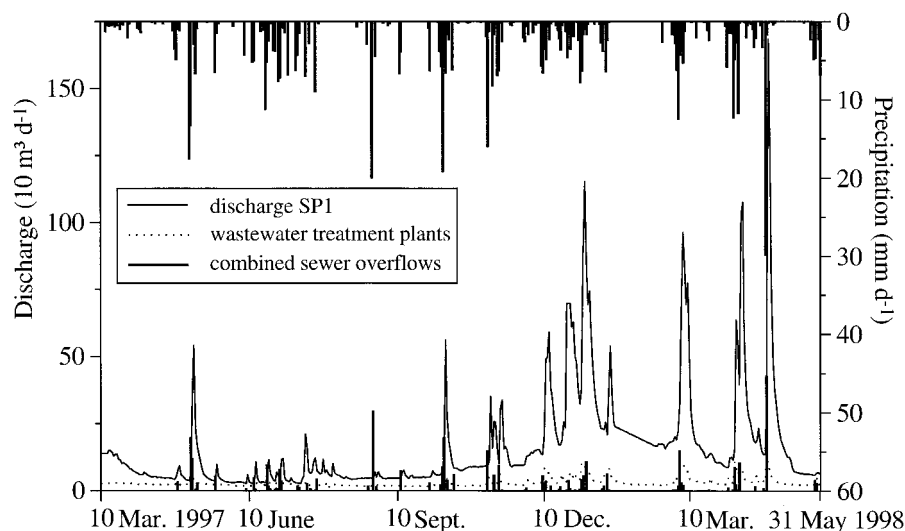


Fig. 2. Pattern of rainfall, natural discharge of the Zwesters Ohm, and human effluents consisting of the discharges of the two wastewater treatment plants, 14 combined sewer overflows, and four combined sewer overflow tanks.

$\text{mL min}^{-1}$ . The column temperature was in both cases  $30^\circ\text{C}$ . The limits of detection were determined according to Frehse and Thier (1991) and are presented in Table 3.

### Calculation of Pesticide Loads

Daily mass loads of pesticides  $L_t$  passing the different sampling sites were calculated by multiplying the daily streamflow volumes  $Q_t$  by the mean daily stream pesticide concentrations  $C_t$ . Concentrations below the detection limit were treated as 0. Therefore, calculated loads represent minimum estimates. The measured daily values were summed up for the whole investigation period to approximate the total pesticide offsite movement from the catchment.

## RESULTS

### Catchment Hydrology

From 10 Mar. to 31 Dec. 1997, the catchment received 387 mm of rain, significantly less than the average annual rainfall of 508 mm for this period. Apart from October and November all months were unusually dry. In contrast the following spring was extremely wet (Fig. 2). The flow volume at the outlet of the catchment amounted to  $7.9 \times 10^6 \text{ m}^3$  in the investigation period (Fig. 2). Discharge mirrored the precipitation pattern. A runoff coefficient of 9% was calculated applying the hydrograph separation method by Wittenberg (1999). Mainly during spring and summer 1997 emissions of the WWTPS dominated the total discharge of the Zwesters Ohm. On single days they reached a maximum fraction of 55% of the total stream discharge. For the entire investigation period nearly 15% of the total stream discharge could be attributed to the two WWTP. According to the simulations with the model MOMENT 4.0, 77 rainfall events led to the direct emission of sewage by at least one of the 14 CSO into the Zwesters Ohm. The CSO emissions accounted for 1.5% of the total stream discharge.

The simulations performed with the model MOMENT 4.0 could not be verified, as no discharge mea-

surements at the CSO were carried out. For German combined sewer systems, Hamm et al. (1991) determined 18% as an average percentage of the total sewage emitted directly into flowing waters by CSO. According to the simulations in the catchment of the Zwesters Ohm this percentage totaled 19%.

### Pesticide Occurrence in the Zwesters Ohm

Results of the analysis of 264 water samples taken at the outlet of the catchment are presented in Fig. 3 and Table 4. The presence of pesticides in water was unevenly distributed throughout the investigation period. The seasonal variation in pesticide concentrations in surface water showed a marked increase during the main application periods for pesticides, which is in line with findings by Baker and Richards (1990), Kreuger et al. (1999), Rawn et al. (1999), Thurman et al. (1991), and Tisseau et al. (1996).

The median concentrations of detections varied between  $0.05 \mu\text{g L}^{-1}$  for 2,4,5-T and  $0.41 \mu\text{g L}^{-1}$  for metazachlor and exceeded (with the exception of pirimicarb, terbuthylazine, 2,4-D, and 2,4,5-T) the EU drinking water quality criteria of  $0.1 \mu\text{g L}^{-1}$ . Pirimicarb was the only pesticide that was not detected. Isoproturon was present in 65% and diuron in 59% of the analyzed samples collected at the outlet of the catchment. The two urea derivatives were detected with the highest frequency. The highest individual concentration measured was  $23.2 \mu\text{g L}^{-1}$  for isoproturon and occurred in October (Fig. 4). Other pesticides with high detection rates were metamitron (52%), dichlorprop-P (38%), MCPA (32%), mecoprop-P (33%), and metazachlor (33%). The median of the detected dichlorprop-P concentrations was higher than those of the other phenoxy acid herbicides. This matches the highest application amount of 610 kg among the phenoxy acids (Table 2). For the two herbicides carbetamide and dimefuron, which were only applied in a combination product Pradone Combi (Feinchemie Schwebda GmbH, Eschwege,

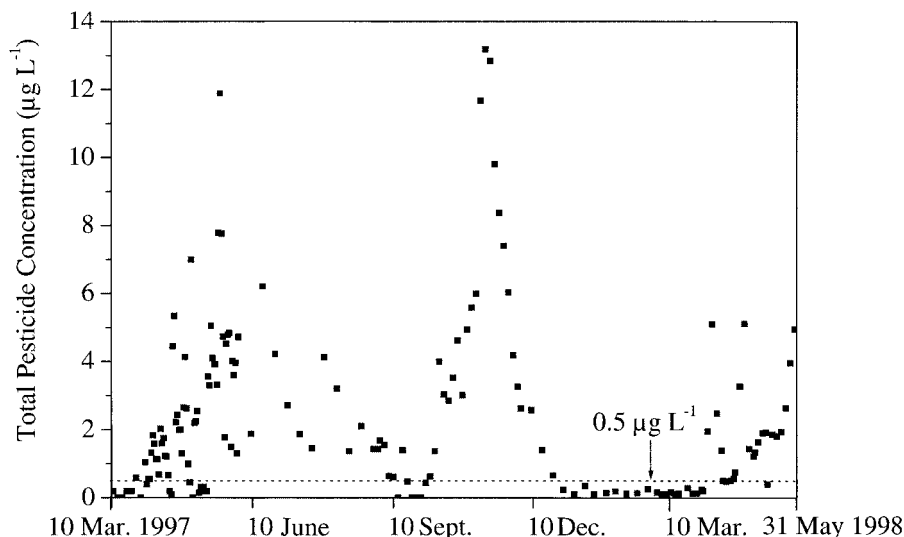


Fig. 3. Sum of concentrations of all pesticides analyzed of the water samples taken from the Zwester Ohm during the investigation period (10 Mar. 1997–31 May 1998). The dashed line delineates the drinking water quality objective for the sum of all pesticides set by the EC.

Germany), comparable median concentrations of 0.15 and 0.17  $\mu\text{g L}^{-1}$ , respectively, were observed. Nevertheless, the concentrations for carbetamide showed a wider dispersion, with a maximum concentration of 1.95  $\mu\text{g L}^{-1}$ . This can be explained by the lower affinity of carbetamide for adsorption to soil (Table 3). All other pesticides were rarely detected. The lower frequency of detection can be related to the lower use of these pesticides in the catchment (Table 2), but it is also influenced by the chemical and physical properties of the compounds, as well as the methods of their agricultural application.

During the investigation period total losses of the measured pesticides amounted to 9048 g and ranged from 11 g for 2,4-D and 2,4,5-T to 4606 g for isoproturon (Table 2). Unit losses ranged from 0.01  $\text{g ha}^{-1}$  for fen-

propimorph to 4.24  $\text{g ha}^{-1}$  for metamitron, a herbicide intensively applied to sugar beet.

## DISCUSSION

### Pesticide Loads

Pesticide loads are a better indicator of pesticide contamination than concentrations and allow comparison with other studies, especially if they are expressed as a fraction of the pesticide applied. The approach neglects residue carryover within the soil, which was shown for example for atrazine by Frank et al. (1982) from analysis of 11 watersheds in southern Ontario. But for modern pesticides used in Europe, both the intrinsic properties of the pesticides and the low amounts applied result in a minimization of the carryover problem. In Table 2, calculated fractional losses for this study are summarized. The losses ranged from 0.01% for fenpropimorph and 0.71% for carbetamide and agreed with published values for European countries by, for example, Kreuger (1998) and Fischer (1996).

The seasonal distribution of the pesticide loads is represented in Fig. 5. Carbetamide and metazachlor were mainly transported during fall, the main application period for these herbicides used in oil rape seeds. In contrast, the peak of the dimefuron pollution with a higher sorption coefficient (Table 3) was mainly detected during winter, with a time lag to its application. The seasonal distributions of the two urea derivatives isoproturon and diuron reflect their application patterns. Whereas isoproturon is an agricultural herbicide, diuron is a non-agricultural total vegetation control herbicide, which is mainly applied during spring and summer. The phenoxy acid herbicides were only analyzed in spring. The wet spring in 1998 led to higher pollution levels than the spring 1997 application period.

Stepwise multiple linear regression analysis was used to identify predictive equations for pesticide losses. The stepwise procedure of the statistical analysis program

Table 4. Number of pesticide detections, detection frequency, and concentrations observed in samples collected at the outlet of the catchment (SP 1) during the investigation period (10 Mar. 1997–31 May 1998, 448 d).

Pesticide	Number of detections	Detection frequency <sup>†</sup>	Median	Range
		%		
Atrazine	34	8	0.19	0.13–1.68
Carbetamide	79	18	0.15	0.14–1.95
Chlortoluron	9	2	0.33	0.31–0.37
2,4-D	3	2	0.07	0.05–0.19
Dichlorprop-P	63	38	0.26	0.04–1.75
Dimefuron	57	13	0.17	0.05–0.44
Diuron	264	59	0.20	0.04–5.09
Fenpropimorph	1	<1	1.92	1.92–1.92
Isoproturon	293	65	0.21	0.05–23.18
MCPA	52	32	0.20	0.06–4.17
Mecoprop-P	54	33	0.14	0.05–0.79
Metamitron	43	52	0.16	0.06–1.28
Metazachlor	148	33	0.41	0.05–6.12
Metolachlor	96	21	0.28	0.04–2.09
Pirimicarb	0	0	–	–
Simazine	16	4	0.28	0.13–0.55
2,4,5-T	3	2	0.05	0.05–0.07
Terbutylazine	14	3	0.06	0.05–1.59
Triadimenol	2	<1	1.30	1.00–1.60

<sup>†</sup> In general, 448 d are set as a total of 100%, with the exception of metamitron (analyzed 10 Mar. 1998–31 May 1998, 82 d) and the phenoxy acid herbicides (analyzed 10 Mar.–31 May 1997 and 1998, 164 d).

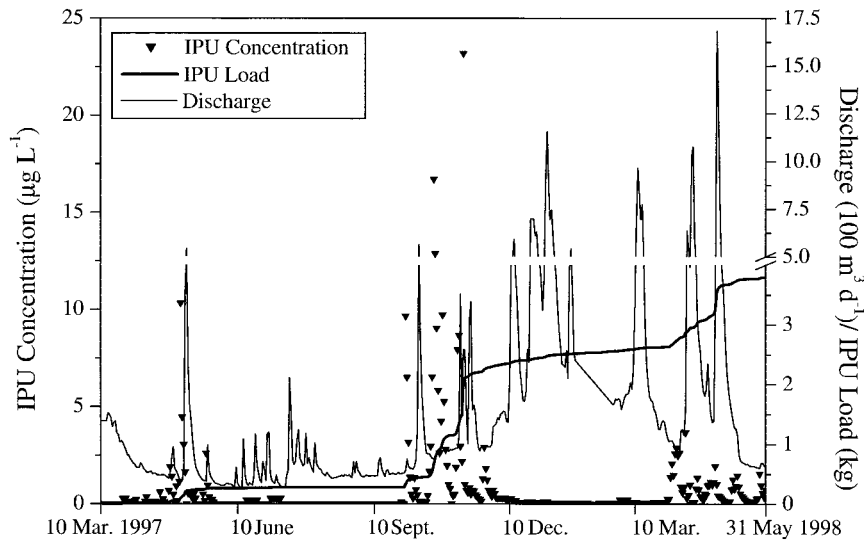


Fig. 4. Pattern of the total discharge, the detected concentrations, and the resulting cumulative load of isoproturon (IPU) in the Zwerster Ohm during the investigation period (10 Mar. 1997–31 May 1998).

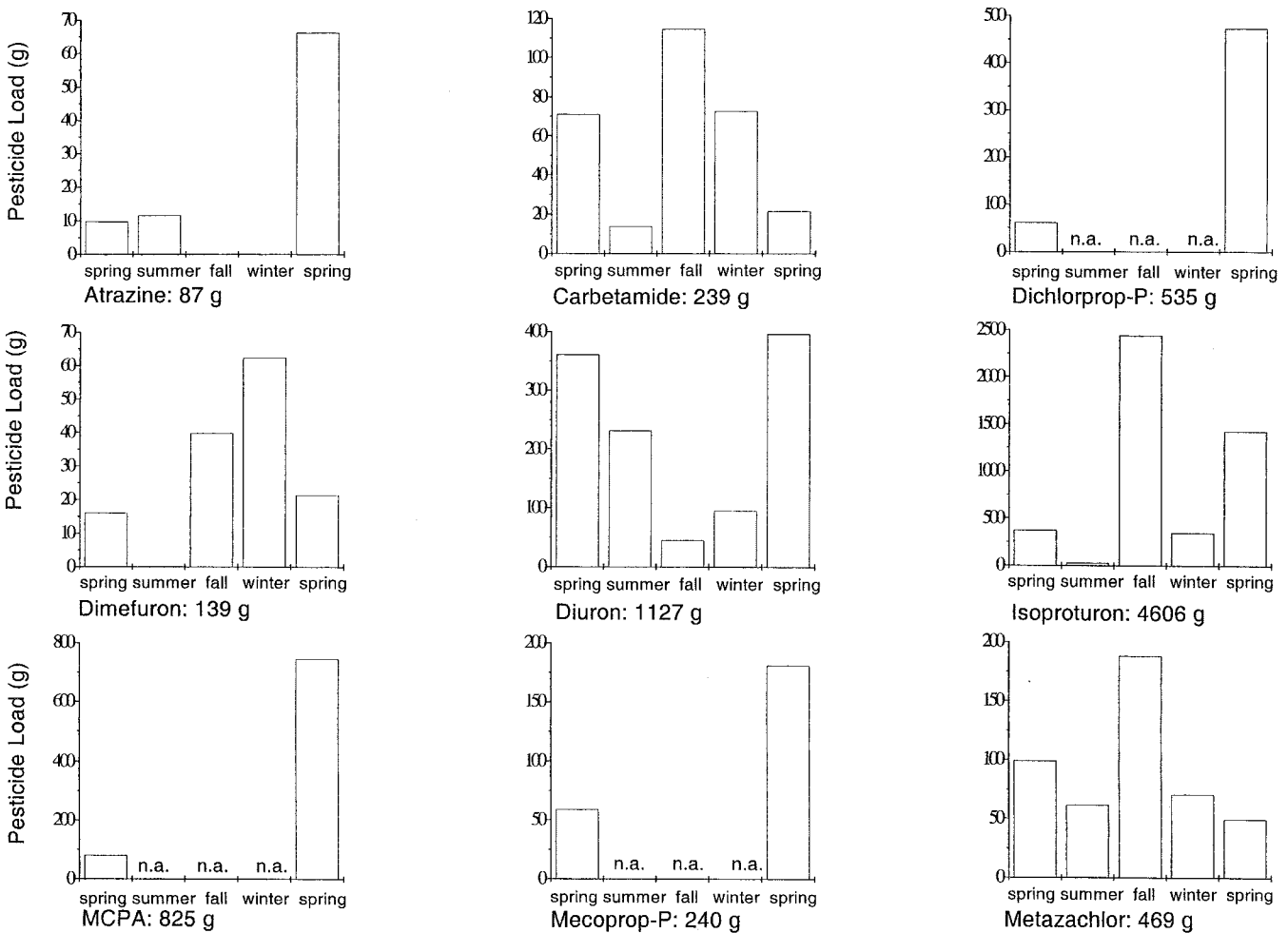


Fig. 5. Seasonal distribution of the loading for different pesticides during the investigation period (10 Mar. 1997–31 May 1998). Note the different scales of the ordinates and the fact that the phenoxy acid herbicides were only analyzed in spring.

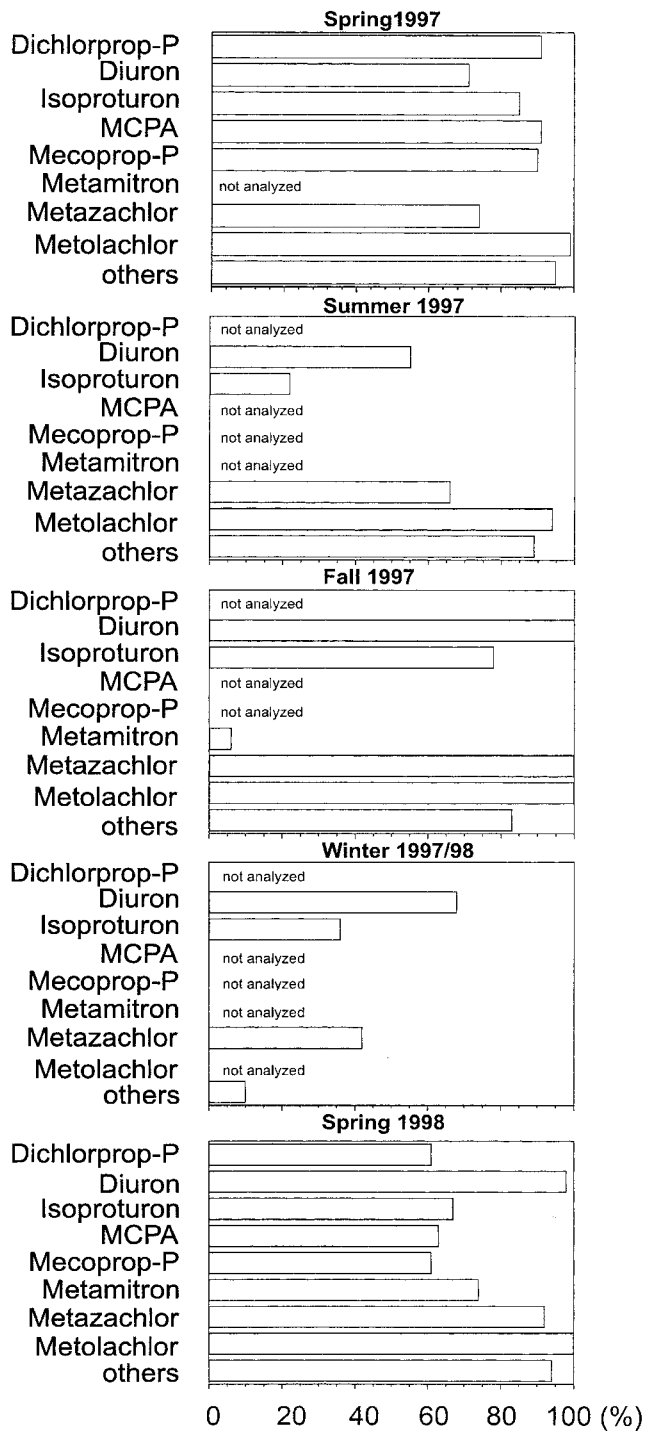


Fig. 6. The point-source pollution as a percentage of the total load during different seasons.

SAS 6.12 (SAS Institute, 1985) performs a multiple regression in which parameters (pesticide properties like  $K_{oc}$ ,  $DT_{50}$ , water solubility, and quantities applied) are added or subtracted from the regression, depending on the contribution of the tested parameter on the resulting  $r^2$ . In the final model, the pesticide amount applied ( $Y_x$ ) in kilograms was the only significant variable at a significance level of  $\alpha = 0.001$ . For the nine herbicides with defined application amounts (carbetamide, dichlor-

prop-P, dimefuron, isoproturon, MCPA, mecoprop-P, metamitron, metazachlor, and terbuthylazine) the best regression model was:

$$L_t = -286.84 + 1.95Y \quad [2]$$

with a calculated  $r^2$  of 0.91. The importance of this variable was already delineated by Kreuger and Törnqvist (1998) for a small catchment in southern Sweden. In their studies the quantities applied were responsible for 50 to 85% of the determined variability of the surface water pollution. The statistical analysis of the data from the midwestern rivers in the USA by Battaglin and Goolsby (1997) also supports this. In all of their analyses the amount of pesticide applied was significantly related to the detected concentrations. Whereas the study of Battaglin and Goolsby only involved two chemical classes (triazines and acid amides), the study presented in this paper covered a larger number of dissimilar compound classes.

### Nonpoint-Source Pollution

The temporal pattern of the isoproturon loads is presented in Fig. 4. The load reached its minimum level during summer, a time period that was characterized by low concentrations and discharges. During winter, the loads increased due to higher flow rates, which are typical of winter rainfall climates. The maximum daily loads were measured during fall, which represents the main application period for isoproturon. The loads of the wet spring 1998 exceeded those of the preceding spring. Comparisons of the chemograph with the hydrograph revealed that the highest detected concentrations were independent of the peak discharges of the river.

In a Spearman rank-order correlation analysis for the daily measurement sets of the three application periods, using the concentrations of all different pesticides considered in this study, the estimated flow at SP 1 and the measured rainfall revealed no significant correlation between any of the variables ( $\alpha = 0.01$ ). The highest pesticide concentrations occurred during periods of very low flow. These flow rates were too low to be due to storm events causing runoff.

### Point-Source Pollution

To further elucidate the source of pesticide contamination, samples of the Zwester Ohm were taken at different sampling sites (Fig. 1). The wastewater treatment plant close to the outlet of the catchment had the strongest effect on the pesticide contamination of the Zwester Ohm. The Wilcoxon test for differences between measurement pairs was performed ( $\alpha = 0.1\%$ ) and revealed significant differences between the loads of the water samples upstream and downstream of the wastewater treatment plant close to the outlet of the catchment (SP 1 and SP 2, Fig. 1). The overall pesticide load was dominated by PSP with at least 77% of the total load (6968 g a.i.). On an average, the two WWTP accounted for 84% of the PSP, with the remainder due to the CSO. The approach to classify pesticide loads as PSP or NPSP

tends to overestimate PSP, as during storms not only the WWTPS responds to rainfall, but also the catchment by soil surface runoff, interflow, and drainage. The approach is justified since all grab water samples taken randomly from the CSO during storm events throughout the investigation period displayed high concentrations of various pesticides (maximum concentration:  $6.6 \mu\text{g L}^{-1}$  isoproturon). Moreover, even when assuming that no pesticides enter the stream by CSO, PSP still accounts for 65% of the total pesticide contamination. The PSP during dry weather periods accounted for 54% of the total PSP fraction. The contribution of point sources to the total pesticide load has to be considered as a serious factor for surface water pollution.

Management strategies for ameliorating water quality need improved information about the pesticide occurrence and the relevance of all different input pathways on a catchment scale. The results show that the agricultural structure of a catchment, the site conditions, and application methods, for example, have to be taken into account, but also, the WWTPS and in particular the sewage disposal system by farmers should be recorded in future investigations. However, river monitoring programs are restricted to a limited number of watersheds. Potential causalities between pesticide PSP and easily accessible parameters such as number of field sprayers operated in a catchment would allow prediction of PSP in other catchments.

A specific load of 43 g a.i. was calculated for each field sprayer in the Zwester Ohm catchment considering all 14 analyzed pesticides that were used by agriculture. This normalized load per field sprayer is higher than the loads per farm calculated in the short-term investigations by, for example, Bach and Frede (1996), Fischer (1996), and Seel et al. (1994): 30 g considering 13 pesticides, 15 g considering six pesticides, and 11 g considering four pesticides, respectively. Comparisons of normalized loads are critical to the layout of the studies (e.g., variance in the number of pesticides analyzed and length of investigation time). However, even comparing the pesticide loads caused by PSP in the catchment of the Zwester Ohm in the two consecutive springs of this study showed significant differences, with a pesticide load of 9 and 19 g per field sprayer in the spring applications of 1997 and 1998, respectively.

Depending on the season, between 27% (winter 1997 total of 171 g) and 96% (spring 1998 total of 3561 g) of the total load entered the stream via the WWTPS. These differences were even more pronounced when analyzing the transport pathways for individual pesticides during the different investigated application periods. For individual pesticides the contribution to point sources ranged from 3% for chlortoluron during fall 1997 to 100% for dimefuron during spring 1997 (Fig. 6). The PSP was very variable and appeared to be merely coincidental. The physical-chemical properties of the pesticides, as well as hydrometeorological parameters, were only of minor importance for the PSP, as no significant interrelations between these parameters were found.

The careless handling of spraying equipment and material on paved areas, such as the farmyards, leads to

pesticide residues in the WWTPS (Ganzelmeier, 1998). The reduction of pesticides during the purification process in a WWTP appears to be minor (Seel et al., 1994). Because hardly any reduction of the pesticide loads through the WWTP is achieved, avoiding PSP is desirable.

## CONCLUSIONS

The dataset presented in this paper provides a detailed account of the seasonal trends of 19 herbicides in surface waters over a 15-mo period. The total load was dominated by a single herbicide, isoproturon. The majority of the pesticide load entered the stream during dry weather periods via the WWTPS as PSP. Of the pesticides lost to the river during the investigation period (10 Mar. 1997–31 May 1998), 77% were the result of PSP. However, on a seasonal basis, PSP ranged between 27 and 96% of the total load. As no significant interdependencies between intrinsic pesticide properties, hydrometeorological factors, and the detected loads could be established, it is not possible on the basis of this dataset to predict PSP for other catchments.

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## REFERENCES

- Albanis, T.A., D.G. Hela, T.M. Sakellarides, and I.K. Konstantinou. 1998. Monitoring of pesticide residues and their metabolites in surface and underground waters of Imathia (N. Greece) by solid-phase extraction disks and gas chromatography. *J. Chromatogr. A* 824:59–71.
- Bach, M., and H.-G. Frede. 1996. Pflanzenschutzmittel in Fließgewässern. Teil 1: Monitoring im Lahngebiet. *DGM*. 40(3):110–114.
- Baker, D.B., and R.P. Richards. 1990. Transport of soluble pesticides through drainage networks. p. 241–270. *In* D.A. Kurtz (ed.) Long range transport of pesticides. Lewis Publ., Chelsea, MI.
- Barcelo, D., S. Chiron, A. Fernandez-Alba, A. Valverde, and M.F. Aloendurada. 1996. Monitoring pesticides and metabolites in surface waters and groundwater in Spain. p. 237–253. *In* M.T. Meyer (ed.) Herbicides—Metabolites in surface and groundwater. Am. Chem. Soc., Washington, DC.
- Battaglin, W.A., and D.A. Goolsby. 1997. Statistical modeling of agricultural chemical occurrence in midwestern rivers. *J. Hydrol.* 196: 1–25.
- Brandt-Gerdes-Sitzmann-Wasserwirtschaft GmbH. 1997. Dokumentation des EDV-Programmsystems MOMENT, Vers. 4.0. Darmstadt, Germany.
- Carter, A.D. 1999. Pesticide contamination of water sources and the monitoring data across the EU. p. 11–20. *In* A.A.M. Del-Re et al. (ed.) Proc. of the XI Symp. Pestic. Chem., Cremona, Italy. 11–15 Sept. 1999. La Goliardica Pavese, Pavia, Italy.
- DeCoursey, D.G. 1985. Mathematical models for nonpoint water pollution control. *J. Soil Water Conserv.* 40:408–413.
- Der Rat von Sachverständigen für Umweltfragen. 1998. Flächendeckend wirksamer Grundwasserschutz—Ein Schritt zur dauerhaften Entwicklung. Sondergutachten. Metzler-Poeschel, Stuttgart, Germany.
- Donnelly, C.A., and M.J. Ferrari. 2001. Summary of pesticide data from streams and wells in the Potomac River Basin. Open File Rep. 97-666. U.S. Geol. Survey, Reston, VA.
- Dubrovsky, N.M., C.R. Kratzer, L.R. Brown, J.M. Gronberg, and

- K.R. Burow. 1998. Water quality in the San Joaquin-Tulare Basins, California, 1992-95. Circ. 1159. U.S. Geol. Survey, Reston, VA.
- Dyck, S., and G. Peschke. 1989. Grundlagen der Hydrologie. VEB Verlag für Bauwesen, Berlin.
- Fenelon, J.M., and R.C. Moore. 1998. Transport of agrichemicals to ground and surface water in a small central Indiana watershed. *J. Environ. Qual.* 27:884-894.
- Fischer, P. 1996. Quantifizierung der Eintragspfade für Pflanzenschutzmittel in Fließgewässern. Ph.D. diss. Justus-Liebig-Universität, Giessen, Germany.
- Flury, M. 1996. Experimental evidence of pesticides through field soils—A review. *J. Environ. Qual.* 25:25-45.
- Frank, R., H. Braun, M. van Hove Holdrinet, G. Sirons, and B. Ripley. 1982. Agricultural and water quality in the Canadian Great Lakes Basin: V. Pesticide use in 11 agricultural watersheds and presence in stream water, 1975-1977. *J. Environ. Qual.* 11:497-505.
- Frehse, H., and H.P. Thier. 1991. Die Ermittlung der Nachweisgrenze und Bestimmungsgrenze bei Rückstandsanalysen nach dem neuen DFG-Konzept. *GIT Fachz. für das Lab.* 35:285-291.
- Ganzelmeier, H. 1998. Proper cleaning of sprayers. p. 91-98. *In* T. Robinson (ed.) Managing pesticide waste and packaging. BCPC Symp. Proc. no. 70. Kent, UK. 30 Mar.-1 Apr. 1998. BCPC, Farnham, UK.
- Garbrecht, J., and L.W. Martz. 1995. TOPAZ—An automated digital landscape analysis tool for topographic evaluation, drainage identification, watershed segmentation and subcatchment parameterization. USDA Natl. Agric. Water Lab., Durant, OK.
- Gaynor, J.D., D.C. McTavish, and W.I. Findlay. 1995. Atrazine and Metolachlor loss in surface and subsurface runoff from three tillage treatments in corn. *J. Environ. Qual.* 24:246-256.
- Hamm, A., D. Gleisberg, W. Hegemann, K.H. Kraut, G. Metzner, F. Sarfert, and P. Schleypen. 1991. Stickstoff- und Phosphoreinträge in Oberflächengewässern aus punktförmigen Quellen. p. 765-799. *In* A. Hamm (ed.) Studie über Wirkungen und Qualitätsziele von Nährstoffen in Fließgewässern. Acad. Skt. Augustin.
- Harman-Fetcho, J.A., L.L. McConnell, and J.E. Baker. 1999. Agricultural pesticides in the Patuxent River, a tributary of the Chesapeake Bay. *J. Environ. Qual.* 28:928-938.
- Hartmann, H., J. Burhenne, and M. Spittler. 1998. Trace determination of pesticides in water by coated capillary micro extraction (CCME) and reversed-phase high performance liquid chromatography. *Fresenius Environ. Bull.* 7:96-102.
- Hersch, R.W. 1995. Streamflow measurement. E&FN Spon, London.
- Hessisches Landesvermessungsamt Wiesbaden. 1990. Orthophoto maps of the whole Hessen territory. Dep. for Land and Surveys, Wiesbaden, Germany.
- Hornsby, A.G. 1992. Site-specific pesticide recommendation: The final step in environmental impact prevention. *Weed Technol.* 6:736-742.
- Huber, A. 1998. Belastung der Oberflächengewässer mit Pflanzenschutzmitteln in Deutschland-Modellierung der diffusen Einträge. Ph. D. diss. Justus-Liebig-Universität, Giessen, Germany.
- Isenbeck-Schröter, M., M. Kofold, B. König, T. Schramm, E. Bedbur, and G. Mattheß. 1998. Auftreten von Pflanzenschutzmitteln in Oberflächengewässern und im Grundwasser. *Grundwasser.* 2:57-66.
- Janssen, A., M. Keuter, D.M. zu Altenschildesche, A. Ritzkopf, and W. Treder. 1995. Chromatographische Pestizidbestimmung entsprechend der Trinkwasserverordnung—Teil I: Anreicherung mittels Festphasenextraktion. *GIT Fachz. Lab.* 5:417-424.
- Kladviko, E.J., G.E. van Scoyoc, E.J. Monk, K.M. Monk, and W. Pask. 1991. Pesticide and nutrient movement into subsurface tile drains on a silt loam in Indiana. *J. Environ. Qual.* 20:264-270.
- Kreuger, J. 1998. Pesticides in stream water within an agricultural catchment in southern Sweden, 1990-1996. *Sci. Total Environ.* 216: 227-251.
- Kreuger, J., M. Peterson, and E. Lundgren. 1999. Agricultural input of pesticide residues to stream and pond sediments in a small catchment in southern Sweden. *Bull. Environ. Contam. Toxicol.* 62:55-62.
- Kreuger, J., and L. Törnqvist. 1998. Multiple regression analysis of pesticide occurrence in streamflow related to pesticide properties and quantities applied. *Chemosphere* 37:189-207.
- Laroche, A.M., and J. Gallichand. 1995. Analysis of pesticide residues in surface and groundwater of a small watershed. *Trans. ASAE* 38:1731-1736.
- Larson, S.J., P.D. Capel, D.A. Goolsby, S.D. Zaugg, and M.W. Sandstrom. 1995. Relations between pesticide use and riverine flux in the Mississippi River Basin. *Chemosphere* 31:3305-3321.
- Larson, S.J., R.J. Gilliom, and P.D. Capel. 1999. Pesticides in streams of the United States—Initial results from the National Water-Quality Assessment Program. *Water-Resour. Investigations Rep.* 98-4222. U.S. Geol. Survey, Reston, VA.
- Léon, L.F., E.D. Soulis, N. Kouwen, and G.J. Farquhar. 2001. Non-point source pollution: A distributed water quality modelling approach. *Water Res.* 35:997-1007.
- Maniak, U. 1993. Hydrologie und Wasserwirtschaft—Eine Einführung für Ingenieure. Springer Verlag, Berlin.
- Mason, P.J., I.D.L. Foster, A.D. Carter, A. Walker, S. Higginbotham, R.L. Jones, and I.A.J. Hardy. 1999. Relative importance of point source contamination of surface waters: River Cherwell catchment monitoring study. p. 405-412. *In* A.A.M. Del-Re et al. (ed.) Proc. of the XI Symp. Pestic. Chem., Cremona, Italy. 11-15 Sept. 1999. La Goliardica Pavese, Pavia, Italy.
- Mohaupt, V., M. Bach, and H. Behrendt. 2000. Overview on diffuse sources of nutrients, pesticides and heavy metals in Germany—Methods, results and recommendations for water protection policy. p. 419-428. *In* Proc. 4th Int. Conf. Diffuse Pollution, Bangkok, Thailand. 16-21 Jan. 2000. IAWQ, Bangkok, Thailand.
- Müller, K. 2000. Diffuse und punktuelle Pflanzenschutzmittel-Einträge in Fließgewässern: Messungen und Modellierung. Ph.D. diss. Justus-Liebig-Universität, Giessen, Germany.
- Mulliss, R.M., D.M. Revitt, and R.B. Shutes. 1996. The impacts of urban discharges on the hydrology and water quality of an urban watercourse. *Sci. Total Environ.* 189/190:385-390.
- Ng, H.Y.F., and S.B. Clegg. 1997. Atrazine and metolachlor losses in runoff events from an agricultural watershed: The importance of runoff components. *Sci. Total Environ.* 193:215-228.
- Nöhles, I. 2000. Landnutzungsklassifikation mit multitemporalen Landsat TM-Szenen in einer kleinstrukturierten Agrarregion. Ph.D. diss. Justus-Liebig-Universität, Giessen, Germany.
- Novotny, V. 1988. Diffuse (nonpoint) pollution—A political, institutional and fiscal problem. *J. Water Pollut. Control Fed.* 60:1404-1413.
- Pereira, W.E., J.L. Domagalski, F.D. Hostettler, L.R. Brown, and J.B. Rapp. 1996. Occurrence and accumulation of pesticides and organic contaminants in river sediment, water and clam tissues from the San Joaquin river and tributaries, California. *Environ. Toxicol. Chem.* 15:172-180.
- Rawn, D.F.K., T.H.J. Halldorson, W.N. Turner, R.N. Woychuk, J.-G. Zakrevsky and D.C.G. Muir. 1999. A multi-year study of four herbicides in surface water of a small prairie watershed. *J. Environ. Qual.* 28:906-917.
- SAS Institute. 1985. SAS user's guide: Statistics. 5th ed. SAS Inst., Cary, NC.
- Seel, P., T.P. Knepper, S. Gabriel, A. Weber, and K. Haberer. 1994. Einträge von Pflanzenschutzmitteln in ein Fließgewässer—Versuch einer Bilanzierung. *Vom Wasser.* 83:357-372.
- Thurman, E.M., D.A. Goolsby, M.T. Meyer, and D.W. Koplin. 1991. Herbicides in surface waters of the Midwestern United States: The effect of spring flush. *Environ. Sci. Technol.* 25:1794-1796.
- Tisseau, M.A., N. Fauchon, J. Cavard, and T. Vandeveld. 1996. Pesticide contamination of water resources: A case study—The rivers in the Paris region. *Water Sci. Technol.* 34:147-152.
- Tomlin, C. 1994. The pesticide manual. 10th ed. British Crop Protection Council, The Royal Soc. of Chem., Farnham, UK.
- USDA. 1992. National engineering handbook. USDA, Washington, DC.
- Williamson, A.K., M.D. Munn, S.J. Ryker, R.J. Wagner, J.C. Ebbert, and A.M. Vanderpool. 1998. Water quality in the Central Columbia Plateau, Washington and Idaho, 1992-95. Circ. 1144. U.S. Geol. Survey, Reston, VA.
- Wittenberg, H. 1999. Baseflow recession and recharge as nonlinear storage processes. *Hydrol. Processes* 13:715-762.