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Pesticide Peak Discharge from Wastewater Treatment Plants into Streams During the Main Period of Insecticide Application: Ecotoxicological Evaluation in Comparison to Runoff

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In some rural regions, the input of agricultural chemicals from wastewater treatment plants (WWTPs) into streams can play a crucial role (Fischer et al. 1996; Seel et al. 1995). This applies preferably to regions in which these WWTPs treat both domestic wastewater and the rainwater from sealed surfaces. It has been suggested that pesticides entering WWTPs originate mainly from cleaning spraying equipment on farmyards, from which they are washed away during heavy rainfall events (Seel et al. 1996).

There have been only a few reports in the open literature concerned with the problems raised by WWTPs as a point source of pesticide pollution (Table 1). Although previous investigations included insecticides and fungicides, only herbicides were detected in daily or weekly composite samples (Neumann et al. 2002; Seel et al. 1995). During a 2-month investigation of 28 WWTP outlets, Seel (1995) found fungicides and insecticides in only one sample. Almost all studies undertaken so far employed a composite sampling design to assess the contribution of point sources to the total input of pesticides into streams. There is only one other study in which discrete peak sampling was also carried out (Cousins et al. 1995), during which only the insecticide lindane was detected.

Usually insecticides are more toxic to macroinvertebrates and fish than herbicides and fungicides (Baier et al. 1985, see also Table 2), thus for an ecological risk assessment of the effects on aquatic fauna it is important to know whether WWTPs play a role as input sources for insecticides. Because of the usually low application rates, high soil organic carbon sorption coefficients (KOC), and low half life time (DT50), insecticides would be expected to occur at low concentrations and only for short time periods in surface waters, making peak sampling methods necessary to detect them (Liess et al. 1999).

The aim of this paper was to monitor the pesticide peak contamination resulting from WWTPs with special emphasis on insecticides. For an ecotoxicological evaluation, our own data plus information from the literature for the point source WWTP were compared with data on nonpoint source surface runoff (exclusively

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Table 1. Survey of publications containing data on pesticides in the outflow from wastewater treatment plants (WWTP).

Total number of WWTP	Number of WWTP with detection of			Sampling			Max. Concentration (µg/L)		ref.
				period / date	Type		WWTP-effluent	downstream	
	H	F	I		C	P			
2	2	-	-	1 year	x		isoproturon: 42.0	n.m.	a
3	3	-	-	May - June	x		metamitron: 9.4	n.m.	b
n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	n.i.	lindane: 0.06	n.m.	c
28	28	1	1	April - May	x		metamitron: 29.8	n.m.	d
1	11	-	-	April – July	x		metamitron: 9.4	n.m.	e
1	1	-	-	April – May	x		isoproturon: 28.0*	isoproturon: 6.6	f
1	-	-	1	August		x	lindane: 0.12	lindane: 0.03	g
5	4	5	1	May -June.		x	isoproturon: 3.9	isoproturon: 3.6	h

H = herbicides; F = fungicides ; I = insecticides; C = composite; P = peak; n.i. = no information; n.m. = not measured; ref. = reference; * = calculated. a = Nitschke and Schüssler (1998); b = Seel et al. (1994) ; c = Stangroom et al. (1998) ; d = Seel et al. (1996) ; e = Neumann et al. (2002) ; f = Fischer et al. (1996); g = Cousins et al. (1995) ; h = this study.

literature data). Toxic loads were calculated to assess potential effects on macroinvertebrates in the receiving stream, using the toxic units (TU) concept according to Marking (1985).

MATERIALS AND METHODS

The sites investigated were five WWTPs and their receiving streams in an intensively cultivated region (3455-3515, 5580-5640 Gauss Krueger) southeast of Marburg (Hessen, Germany). The WWTPs under study receive not only domestic wastewater but also rainwater from sealed surfaces (e.g., farmyards) which is typical for the investigation area (Fischer et al. 1996; Seel et al. 1995).

Between April 24, and June 20, 2001, the streams were sampled during two rainfall-induced peak-discharge events (June 9 and 27) within the main period of

insecticide application (Table 2). Event-triggered samplers (Liess et al. 1999) were installed ca. 100 m upstream and 100 m downstream of the WWTP outlets. The pollution of WWTP outlets was characterized by taking a total of six discrete samples during elevated discharge according to the two above-mentioned rainfall events (3 discrete samples per each event taken at 2-hour intervals). Each water sample (1 L) was solid-phase extracted using RP 18-polarplus material (1 g; Baker). The residue was dissolved in hexane (1 ml) including the internal standard hexabromobenzene (250 pg/µL) and analyzed at the Institute for Ecological Chemistry of the Technical University of Braunschweig (Liess et al. 1999). Residues of 6 insecticides, 5 fungicides and 6 herbicides (Table 2) were analyzed by gas chromatography with electron capture detection and confirmed by gas chromatography-mass spectrometry. The detection limit for all substances was 0.05 µg/L.

In order to estimate the toxicity of the samples to the macroinvertebrate community, we used the toxic unit (TU) concept (Marking 1985). The toxicity of a pesticide is calculated by dividing the concentration of the detected substance by the 48 h EC50 or 48 h LC50 of the same compound for *Daphnia magna*.

RESULTS AND DISCUSSION

On June 9 and 27, two heavy rainfall events (9 mm/h and 10 mm/h) occurred, and for each event 3 samples were taken per WWTP outlet. The measured maximal pesticide concentrations are shown in Table 2. The highest concentrations were found for isoproturon (WWTP 1: 2.1 µg/L; WWTP 2: 3.5 µg/L; WWTP 4: 1.7 µg/L; WWTP 5: 3.9 µg/L). Out of the total of 17 substances for which analyses were carried out, 8 substances were found in the outputs from the WWTPs: 1 insecticide, 3 fungicides and 4 herbicides. The samples from the outlets of WWTP 1 and 5 to contained 7 and 6 pesticides, respectively, whereas at WWTP 2, 3 and 4 only up to 4 pesticides were detectable.

In the present study, the samples were taken on an event-triggered basis during the main period of application of insecticides and certain fungicides. Our objective was to look for insecticides and fungicides, because they are usually considerably more toxic to macroinvertebrates than herbicides (Table 2). It is likely that, as a result of their physicochemical properties (DT50, KOC) and the fact that smaller amounts are applied (Table 2), insecticides are more difficult to detect by means of composite sampling. Therefore discrete samples were taken during the peak-discharge from the WWTP outlets in the present study. Of the 30 samples collected, the insecticide pirimicarb was detected in one case at a low concentration (0.05 µg/L), and fungicides were found 34 times (max. concentration for azoxystrobin: 0.3 µg/L). Neumann et al. (2002), in contrast, could not demonstrate insecticides or fungicides at all in the outflow from WWTPs (analysis spectrum: 2 insecticides, 5 fungicides, 13 herbicides). Although the WWTPs in the present study, with their largely agricultural surroundings,

Table 2. Measured maximal pesticide concentrations (number of positive detections) in the wastewater treatment plant (WWTP) outflows.

	WWTPs (effluent samples[a])					Application[b]		$LC50_{48h}$
	1	2	3	4	5	Rate[g/ha]	period	*D. magna* µg/L[c]
Insecticides								
β-Cyfluthrin	n.d.	n.d.	n.d.	n.d.	n.d.	8	May/June	0.00014
λ-Cyhalothrin	n.d.	n.d.	n.d.	n.d.	n.d.	7	May/June	0.36
α-Cypermethrin	n.d.	n.d.	n.d.	n.d.	n.d.	8	May/June	0.2
Fenvalerate	n.d.	n.d.	n.d.	n.d.	n.d.	8	May/June	0.62
Parathion-ethyl	n.d.	n.d.	n.d.	n.d.	n.d.	146	May/June	1.43
Pirimicarb	0.05 (1)	n.d.	n.d.	n.d.	n.d.	150	May/June	16
Fungicides								
Azoxystrobin	0.20 (5)	0.30 (5)	n.d.	0,05 (1)	0.20 (6)	250	May	230
Epoxiconazole	0.05 (4)	0.05 (1)	n.d.	0.20 (1)	0.20 (6)	100	May	8,700
Fenpropimorph	n.d.	n.d.	n.d.	n.d.	n.d.	750	May	2,400
Kresoxim-methyl	n.d.	n.d.	n.d.	n.d.	n.d.	115	May	168
Tebuconazole	0.05 (2)	n.d.	0.05 (1)	0.05 (2)	n.d.	250	May	4,200
Herbicides								
Bifenox	n.d.	n.d.	n.d.	n.d.	n.d.	656	Jan.-April	660
Ethofumesate	0.30 (3)	n.d.	n.d.	n.d.	0.40 (5)	479	Jan.-April	13,500
Chloridazon	n.d.	n.d.	n.d.	n.d.	0.80 (6)	2,137	Jan.-April	50,100
Metamitron	0.30 (5)	n.d.	n.d.	n.d.	0.60 (4)	1,793	Jan.-April	5,700
Metribuzin	n.d.	n.d.	n.d.	n.d.	n.d.	525	Jan.-April	35,000
Isoproturon	2.10 (6)	3.50 (6)	n.d.	1.70 (5)	3.90 (6)	1,101	Jan.-April	580

[a] during two rainfall events (June 9 and 27, 2001) with 3 samples each (n.d. = not detected)

[b] Recommended median application rates and application period refer to the study area

[c] Median 48 h LC50 for Daphnia magna were extracted from the Aquire Database System of the US EPA

have a high potential for polluting the streams and the sampling technique used here is suitable for detecting insecticides and fungicides in the outflow from the plants, it can be inferred from our results that this route of entry is fairly insignificant for these categories of substances.

Herbicides, however, can enter the stream water in considerable amounts by way of WWTPs. In this study the highest concentration (isoproturon: 3.9 µg/L) and the largest number of positive results (46) were found for herbicides. In comparison to other studies (Table 1), however, the herbicide concentrations detected during this study were quite low. The likely reason is that sampling was carried out after the main period for herbicide application (Table 2).

The maximal pesticide concentrations measured in water samples during the study period at an upstream site above the WWTP and at a downstream site below the WWTP outlet are summarized in Table 3. The concentration of some pesticides was in most cases distinctly elevated downstream of the WWTP (Table 3, bold printed values). The increase in pesticide concentrations was greatest in streams 1, 4 and 5. In both streams 1 and 5, the concentrations of four substances were elevated, and in stream 4 three substances. Because the same pesticides were also present in the outflow of the WWTPs, in all cases, the increase in pesticide levels in the stream water can unequivocally be ascribed to the influence of the WWTPs. In stream 3, a decrease in concentration was measured below the WWTP because the inflowing WWTP water was almost uncontaminated and thus diluted the stream water.

Only very few publications have indicated the degree of contamination of both the WWTP outflow and the stream receiving this input (Table 1), and they are either restricted to a single substance (Cousins et al. 1995) or the data on pesticide concentrations in the receiving water are based in part on calculations (Fischer et al. 1996). In order to estimate the pollutant load from WWTPs with regard to the aquatic fauna, it appears recommended to measure directly the resulting in-stream contamination.

The overall toxicities calculated from the pesticide data show that the toxic load resulting from edge-of-field runoff is between 70 and 10^6 times higher than the load introduced by WWTP inputs (Table 4). In streams affected by surface runoff from cultivated fields, insecticides are measured in some cases in considerable concentrations. Schulz and Liess (1999a) give an overview of field studies of runoff-related insecticide input in small streams. One possible reason for the importance of edge-of-field runoff in terms of the associated risk to the aquatic fauna might be the direct input of pesticides during a rainfall event from field directly bordering surface waters. In comparison, the introduction of pesticides washed from farmyards into WWTPs during rainfall includes much longer time spans during which the compounds might be metabolized or sorbed. Furthermore, insecticides which are characterized by a relatively high toxicity (Table 2), are often present in edge-of-field runoff, while herbicides dominate in WWTP outlets.

Table 3. Measured maximal pesticide concentrations (µg/L) in stream water upstream and downstream of five wastewater treatment plants (WWTP) inlets.

	Streams (event triggered samples[a])									
	1		2		3		4		5	
	up	down	up	down	up	down	up	down	up	down
Pirimicarb	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Azoxystrobin	n.d.	**0.1**	n.d.	**0.05**	0.05	n.d.	n.d.	**0.05**	n.d.	**0.05**
Isoproturon	0.05	**0.1**	1.4	0.3	0.3	0.05	0.2	0.1	0.05	**3.6**
Tebuconazole	n.d.	**0.05**	n.d.	n.d.	0.05	n.d.	n.d.	**0.05**	n.d.	n.d.
Metamitron	0.05	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Epoxiconazole	n.d.	**0.05**	0.05	n.d.	0.1	n.d.	n.d.	**0.1**	n.d.	**0.05**
Ethofumesate	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Chloridazon	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	**0.1**

[a] upstream (up) and downstream (down) the WWTPs during two rain events (June 6 and 27, 2001) with one sample each (n.d. = not detected). Bold printed values indicate a concentration increase after the stream has passed the WWTP outlet

Table 4. Comparison of wastewater treatment plants and egde-of-field runoff with regard to the toxicity of resulting pesticide input expressed according to the toxic unit concept.

Route of entry	In-stream contamination		Reference
	TU[a]	Most toxic substance [µg/L]	
WWTP	0.00006	lindane: 0.03	Cousins et al. (1995)
WWTP	0.0064	isoproturon: 3.6	This study
WWTP	0.0137	isoproturon: 6.6	Fischer et al. (1996)
Runoff	0.224	parathion: 22.4	Zullei-Seibert (1990)
Runoff	4.2	parathion: 6.0	Schulz and Liess (1999a)
Runoff	10	fenvalerate: 6.2	Schulz and Liess (1999b)
Runoff	58	parathion: 83.0	Aufseß et al. (1989)

[a] toxic units of measured substances

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REFERENCES

Aufseß G, Beicht W, Bourquin H D, Hantge E, Heil J, Müller M J, Opfermann H, Riemer J, Zahn R K, Zimmer K H (1989) Investigations of the output of pesticides from vineyards of the Mosel-valley. In: Deutscher Verband für Wasserwirtschaft und Kulturbau e.V. (DVWK) (eds) Material loads in running water systems. Parey. Hamburg, Berlin, pp. 1-78 (in German)

Baier C, Hurle K, Kirchhoff J (1985) Data collection of pesticides in water bodies for risk assessment. Parey Verlag, Hamburg (in German)

Cousins I T, Watts C D, Freestone R (1995) Field measurement and modelling the fate of aniline and lindane in a UK lowland river. Environ Technol 16: 515-526

Fischer P, Bach M, Burhenne J, Spiteller M, Frede H-G (1996) Pesticides in running waters Section 3: Percentage of non-point and point entrees in a small stream. Deutsche Gewässerkundl Mittlg 40:168-173 (in German)

Liess M, Schulz R, Liess M H-D, Rother B, Kreuzig R (1999) Determination of insecticide contamination in agricultural headwater streams. Wat Res 33: 239-247

Marking L L (1985) Toxicity of chemical mixtures. In: Rand G M, Petrocelli S R (ed) Fundamentals of aquatic toxicology. Hemisphere, Washington, pp164-176.

Neumann M, Schulz R, Schäfer K, Müller W, Mannheller W, Liess M (2002): The significance of entry routes as point and non-point sources of pesticides in small streams. Wat Res 36: 835-842

Nitschke L, Schüssler W (1998) Surface water polution by herbicides from effluents of wastewater treatment plant. Chemosphere 36: 35-41

Schulz R, Liess M (1999a) A field study of the effects of agriculturally derived insecticide input on stream macroinvertebrate dynamics. Aquat Toxicol 46:155-176

Schulz R, Liess, M (1999b) Validity and ecological relevance of an active in situ bioassay using *Gammarus pulex* and *Limnephilus lunatus*. Environ Toxicol Chem 18: 2243-2250

Seel P, Knepper TP, Gabriel S, Weber A, Haberer K (1994) Entry of pesticides in a stream – attempt of drawing up a balance sheet. Vom Wasser 83: 357-372 (in German)

Seel P, Knepper TP, Gabriel S, Weber A, Haberer K (1996) Wastewater treatment plants as a main entry route for pesticides in a stream – drawing up a balance sheet for the entrees. Vom Wasser 86: 247-262 (in German)

Seel P, Lang S, Zullei-Seibert N (1995): Routes of entry of pesticides in surface waters. Wasserwirtschaft 85:28-33 (in German)

Stangroom SJ, Collins CD, Lester JN (1998) Sources of organic micropollutants to lowland rivers. Environ Technol 19: 643-666

Zullei-Seibert N (1990) Presence and provability of pesticides in raw and drinking water of Germany. Veröff Inst Wasserforsch GmbH Dortmund und der Dortmunder Stadtwerke AG, Dortmund (in German)