Bull. Environ. Contam, Toxicol. (1999) 62:55-62

Bulletin of Environmental Contamination and Toxicology

Agricultural Inputs of Pesticide Residues to Stream and Pond Sediments in a Small Catchment in Southern Sweden

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Received: 16 October 1998/Accepted: 8 November 1998

Pesticide residues in bottom sediments of streams draining agricultural land can be a useful indicator of the entry of pesticides, from crop production applications, into aquatic systems (Stewart et al. 1977). The presence and magnitude of such residues may be influenced by a number of factors including runoff potential and intrinsic properties of the pesticides. Most currently used pesticides will leave the field in dissolved form, with only pesticides with very low water solubilities (less than 1 mg/L) or strong ion-exchange capabilities with clay minerals (e.g. paraquat) entering surface waters in runoff attached to suspended soil particles (Wauchope 1978; Larson et al. 1997). While in the stream, phase-transfer processes can move the pesticides from one environmental matrix to the other, with sorption to sediments and volatilization being the most important processes (Larson et al. 1997). Chemicals associated with particles are generally less available for biodegradation and are not available for volatilization to the atmosphere.

In an investigation of pesticide water contamination of rural ponds in Canada, Frank et al. (1990) found that 63% of the investigated pond waters were contaminated with pesticides. The findings were mainly a result of surface runoff following storm events and airborne spray drift, but also accidental spills, resulting in high residue concentrations, were found. Furthermore, they found pond sediment to contain pesticide residues higher than those detected in water. For example, three ponds with atrazine residues of between 0.7 and 8.9 µg/L in the water had sediment levels of 28 to 50 µg/kg (Frank et al. 1990). However, there are only a limited number of studies where a range of currently used agricultural pesticides have been examined in sediments (Albanis et al. 1994; Fletcher et al. 1994; Bester and Hühnerfuss 1996; Miles and Pfeuffer 1997) and none reported from the Nordic countries. The objective of this study was to determine concentrations of commonly used pesticides in stream and pond sediment from a small agricultural catchment in southern Sweden, and to relate findings of these pollutants with those occurring in stream water from the same area.

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MATERIALS AND METHODS

The investigation was carried out in the Vemmenhög catchment located in the very south of Sweden. It forms the upper reach of the Vemmenhög Stream drainage basin which empties into the Baltic Sea. The catchment has undulating topography with glacial till-derived soils rich in chalk. It has an area of 9 km^2 consisting of 95% arable land, with sandy loam soils dominating. Extensive tile-drainage systems have been installed within the area. Throughout the upper part of the catchment, runoff and drainage water is charmeled through a large culvert. The culvert water empties into a small open stream that stretches 1.1 km to the outlet of the catchment. Just north of the outlet the stream has been widened to form a small, 0.2-0.4-m deep, pond (~ 0.1 ha). In the center of the catchment there is one larger pond (~ 0.5 ha) with the outflow connected to the culvert system, but with no flow-through. The pH-value of drainage and stream water is within the range 7.5-8.0. Monitoring of pesticide occurrence in stream water from the catchment was initiated in 1990. A detailed description of the catchment and pesticide usage in the area, along with water sample collection procedures have been given in Kreuger (1996; 1998).

Bed sediment samples using a coring device were collected on June 18, 1991 at four different sites within the catchment (Figure 1): a) in the pond in the center of the area (P04); b) in the stream, 200 m south of the culvert outlet (UT10); c) in the northern part of the pond (OD11) situated in the stream close to the catchment outlet; and d) in the southern part of the pond at LU12. A small boat was used to obtain samples from the ponds. The cores were collected using a coring device made of stainless steel and acrylic plastic tubing, 60 cm in length, and 7.5 cm o.d. and 7 cm i.d. The tubing was reinforced with a sharp edge of stainless steel at the bottom end. To facilitate the sampling procedure, the core was equipped with a frame of 3.0 kg of exchangeable weights. At the top end of the corer a vertically movable lid allowed air to vent during coring insertion, and during core extraction it maintained, by tight closure, a vacuum, thus holding the sediment in place. After extraction of the core the sediment was transferred to a glass bottle, selecting the upper 10 cm of the sediment column by means of an extruding rod (except at site UT10 where the upper 5 cm were collected). At each location, five different cores, collected some meters apart, were mixed into one glass bottle. The bottles were returned to the laboratory within 48 hours and stored at -18°C prior to analysis.

In addition to the above, samples of the mobile sediment fraction were collected on three occasions from sediment traps located at LU12, the collection periods being May-July and June-July in 1990 and July-August in 1991. During the 1991-period, mobile sediment was also collected close to OD11, just before the stream enters the small pond. The sediment was trapped in glass jars placed in the bottom

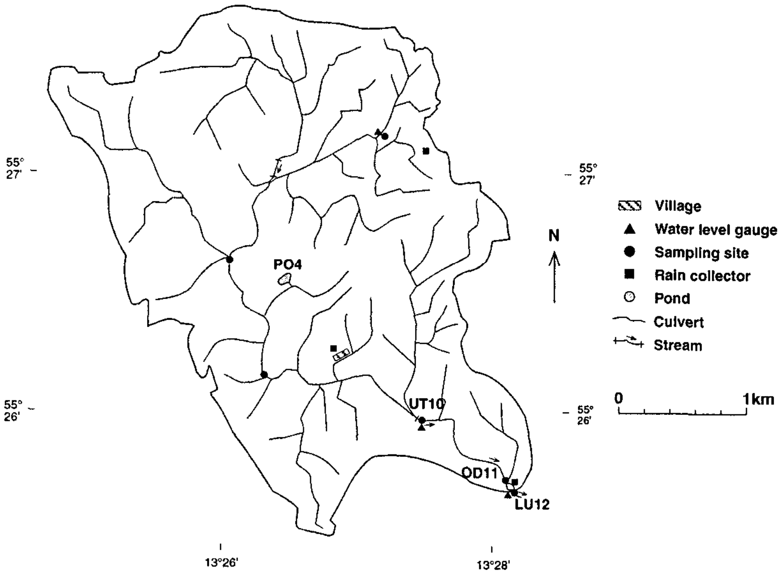

Figure 1. Location of sampling sites in the catchment area.

sediment with the opening a few centimeters above the sediment surface. Five jars were used for each integrated sample.

Analysis was carried out using two different procedures, one for ‘acidic’ compounds and one for semi-polar and non-polar compounds. Wet sediment samples were extracted twice with 1) ethanol (with ammonia) for ‘acidic’ compounds followed by addition of sodium hydroxide and hydrolysis at basic conditions and thereafter acidification to $\text{pH} < 2$ followed by partitioning into dichloromethane; and 2) calcium chloride and acetone/dichloromethane for semi-polar and non-polar compounds. The analyses were thereafter conducted according to procedures used for water samples as described by Åkerblom (1990) and, briefly, also by Kreuger (1998), using gas chromatography with selective detectors and mass spectrometry (GC/MS) after liquid-liquid extraction and, for the semi- and non-polar compounds, hydrophobic gel permeation clean-up. With these methods, 26 different pesticides were included in the analyses. Analytical limits of determination are presented in Table 2. The recovery efficiency for ‘acidic’ substances was 71-95% (±12-28). For the other substances the recovery was within the range 71-115% (±12-27), except for fenpropimorph (51±31) and *p,p*’-DDT (59±19) that had a lower recovery than the other pesticides. None of the reported results were corrected for recovery efficiency. The results are stated as µg/kg dry weight (dw) of sediment.

RESULTS AND DISCUSSION

Concentrations of detected pesticide residues are given in Table 1 for both bed sediments and the mobile sediment fraction. Since pesticide occurrence in sediments is a reflection of applied amounts and also transport from surrounding areas during a relatively long period of time, the amount of pesticides used within the catchment, along with the average concentration of pesticides occurring in stream water during May-July 1990 and 1991 are given in Table 2. These results are taken from Kreuger (1996).

Altogether eleven pesticides were identified in the sediment samples collected within the catchment (Table 1). The most frequently detected pesticides in both sediment types were the fungicides fenpropimorph and propiconazole, and the insecticide fenvalerate. DDT was detected in all four bed sediment samples, but not in the mobile sediment samples. The maximum concentration of the four most frequently detected pesticides were: fenpropimorph - 200 µg/kg; ΣDDT - 98 µg/kg; fenvalerate - 80 µg/kg and propiconazole - 80 µg/kg. Highest total pesticide concentrations were found in the small pond at the catchment outlet (site LU12) with a maximum concentration of 350 µg/kg.

The fungicide fenpropimorph was the only pesticide detected in all samples. Fenpropimorph was applied to cereals in this catchment area in a commercial product also including propiconazole (the proportions being fenpropimorph 75% and propiconazole 25%). Although applied in larger quantities, the less water soluble fenpropimorph was found at lower concentrations in water samples than propiconazole (Table 2), but at higher concentrations in sediment samples.

DDT, withdrawn from the Swedish market in 1970 and totally banned in 1975, was detected in bed sediment cores at all sites (2-98 µg ΣDDT/kg) and with the highest concentration detected in the pond in the central part of the catchment (PO4) (Table 1). This pond with stagnant water during the summer months receives water through runoff and drift from neighboring fields and atmospheric deposition and has no flow-through by the stream. DDT was not found in the mobile sediment fraction translocated with stream flow. Technical DDT is largely comprised of *p,p'*-DDT (- 80%), but also of *o,p'*-DDT (~15%) (Buffin 1998), and is slowly decomposed to the main metabolites *p,p'*-DDE and *p,p'*-DDD. In the bed sediment samples from the stream, with ΣDDT ranging from 2-10 µg/kg, *p,p'*-DDE was the dominant component of the DDT family, accounting for an average of 45% of ΣDDT, whereas *p,p'*-DDT and *p,p'*-DDD accounted for an average of 25% and 30%, respectively. However, in the pond in the central part of the catchment (PO4) with ΣDDT of 98 µg/kg, *p,p'*-DDE accounted for only 10% of ΣDDT, whereas *p,p'*-DDT and *p,p'*-DDD constituted 50% and 40%, respectively.

Table 1. Concentration of pesticides detected in sediment samples collected in 1990 and 1991

Pesticide	Location/mobile sediment[a]				Location/bed sediment[a]			
	LU12[b] 1990	LU12[b] 1990	OD11 1991	LU12 1991	PO4 1991	UT10 1991	OD11 1991	LU12 1991
∑DDT	n.d.[c]	n.d.	n.d.	n.d.	98	4	2	12
dichlorprop	n.d.	2	n.d.	n.d.	n.d.	(1)	(1)	2
diuron	n.a.[d]	n.a.	(1)	2	n.d.	3	2	3
fenpropimorph	200	200	10	40	40	20	30	200
fenvalerate	70	60	n.d.	20	n.d.	30	10	80
MCPA	n.d.	n.d.	n.d.	n.d.	n.d.	2	(1)	(1)
mecoprop	n.d.	n.d.	n.d.	n.d.	n.d.	2	(1)	3
methabenzthiazuron	n.d.	n.d.	n.d.	20	n.d.	30	20	n.d.
permethrin	n.a.	n.a.	n.d.	2	n.d.	(1)	2	3
prochloraz	n.a.	n.a.	n.d.	n.d.	n.d.	60	n.d.	n.d.
propiconazole	80	60	(5)	20	n.d.	20	20	30
∑ Pesticides	350	322	16	104	138	173	89	334

[a] Concentrations are given in µg/kg dw. Values in parentheses are below the limit of determination, but above the method detection limit, and are therefore only indicative.
[b] Samples collected during May-July and June-July, respectively.
[c] n.d. = not detected.
[d] n.a. = not analyzed.

The insecticide fenvalerate, which was never detected in the water samples during 1990-1991, was found in both bed sediment and mobile sediment samples (10-80 µg/kg). Fenvalerate and DDT were the only two pesticides detected in sediment cores collected from five rivers in this region in 1986, with DDT detected in three out of the five rivers at 3- 17 µg ΣDDT/kg and fenvalerate in one of the rivers at 40 µg/kg (*Kreuger, unpublished data*).

The insecticide permethrin was detected on one occasion in a water sample (1.9 µg/L) collected at site LU12 in 1990, but was not included in the analysis of the suspended sediment samples collected that year. In 1991, permethrin was found in all bed sediment cores collected in the stream and also in the mobile sediment collected at site LU12 at 1-3 µg/kg (Table 1). However, it was never detected in any of the water samples in 1991. A similar result was shown by the herbicide diuron, that was detected in culvert discharge in 1990 and in sediment samples in 1991 at 1-3 µg/kg. The herbicide detected at the highest concentration was methabenzthiazuron (20-30 µg/kg), with findings in bed sediment samples from sites UT10 and OD11 in June 1991, and with findings also in the mobile sediment collected at site LU12 during July-August 1991.

Table 2. Applied amounts of selected pesticides in the catchment during spring/early summer each year, time-weighted mean concentration in stream water at site LU12 during May-July each year, general limit of determination (LOD) in sediment samples, average concentration of detections in sediments and values for different compound properties measured at 20-25°C

		Used amount (kg)		Water conc. (µg/L)		LOD	Sediment conc.	Solubility[b]	log Pow[c]	DT50[d]
Substance	Type[a]	1990	1991	1990	1991	µg/kg dw	µg/kg dw	(mg/L)		(days)
atrazine	H	f.y.[e]	f.y.	0.27	0.10	20-80	n.d.[e]	33	2.5	41
bentazone	H	30	9	0.67	0.14	2	n.d.	570	-0.5	12
clopyralid	H	<1	2	n.d.	n.d.	5	n.d.	143	-2.6	37
cyanazine	H	10	9	0.09	0.03	20-100	n.d.	171	2.1	14
cyfluthrin	I	<1	<1	n.d.	n.d.	20	n.d.	0.002	6.0	116
2,4-D	H	3	n.u.[e]	0.02	n.d.	2	n.d.	600	2.6	7
DDT	I	n.u.	n.u.	n.a.[e]	n.a.	2	28	0.006	6.2	2000
deltamethrin	I	<1	<1	n.d.	n.d.	20	n.d.	0.0002	4.6	23
dicamba	H	<1	n.u.	n.d.	n.d.	2	n.d.	6500	-0.2	14
dichlorprop	H	188	141	1.07	0.61	2	2	350	1.8	23
diuron	H	f.y.	n.u.	s.o.[e]	n.d.	1	2	36	2.9	135
ethofumesate	H	25	10	n.a.	0.09	30	n.d.	50	2.7	245
fenpropimorph	F	103	136	s.o.	0.09	10	93	4	4.1	54
fenvalerate	I	2	n.u.	n.d.	n.d.	5	45	0.01	5.0	80
isoproturon	H	14	n.u.	s.o.	0.22	30	n.d.	65	2.5	17
MCPA	H	234	188	1.79	0.75	2	2	734	0.5	7
mecoprop	H	73	60	0.26	0.80	2	2	734	0.1	10
metamitron	H	314	182	2.53	0.20	100	n.d.	1700	0.8	30
metazachlor	H	5	n.u.	0.86	0.01	10-30	n.d.	430	2.1	77
methabenzthiazuron	H	46	25	0.02	0.05	10-100	23	59	2.6	135
pendimethalin	H	17	n.u.	n.d.	n.d.	60	n.d.	0.3	5.2	100
permethrin	I	n.u.	n.u.	s.o.	n.d.	2	2	0.2	6.1	38
pirimicarb	I	44	6	0.22	0.02	20	n.d.	3000	1.7	120
prochloraz	F	15	28	n.a.	n.d.	50-100	60	34	4.1	21
propiconazole	F	35	47	0.46	0.15	10	34	100	3.7	55
terbuthylazine	H	f.y.	f.y.	0.20	0.11	30-50	n.d.	9	3.2	45

[a] H = Herbicide; F = Fungicide; I = Insecticide.

[b] Values for water solubility from Tomlin (1997) - for DDT from Mackay et al (1997). If possible, a value obtained at ~ pH 7 was selected.

[c] Values for octanol-water partition coefficient from Tomlin (1997) - for DDT from Mackay et al (1997). If possible, a value obtained at ~ pH 7 was selected.

[d] Values for average half-life in soil from Tomlin (1997) - for cyfluthrin, metamitron and methabenzthiazuron from Linders et al. (1994), for DDT from Mackay et al. (1997).

[e] f.y. = farm yard application, no information on used amounts; n.d. = not detected; n.u. = not used; n.a. = not analyzed; s.o. = only detected on single occasions.

The phenoxy acid herbicides dichlorprop, MCPA and mecoprop, applied in large quantities within the catchment, were present in some sediment samples at 1-3 µg/kg. Some of the pesticides, notably the triazines, metamitron, methabenzthiazuron, pendimethalin and prochloraz, had higher limits of determination than the other compounds and may therefore have been undetected or detected less frequently than if they had been measured at a lower level.

The results demonstrate the importance of pesticide distribution between matrices. Pesticides detected at the highest concentrations in sediment samples were either not detected or detected only at low levels in water samples collected in the stream at LU12 during the same period. In water samples collected at UT10, before the water had passed the open part of the stream, some of these pesticides could be detected more frequently.

Six out of nine pesticides having a log P_{ow}-value above 3.5 were detected in the sediment samples despite quite limited use or, in the case of DDT and permethrin, no use at all during the investigation period. Only fenpropimorph was applied in larger amounts comparable to those of the phenoxy acids. The three undetected pesticides with a high log P_{ow}-value had either very limited use (< 1 kg/yr) or a high limit of determination (pendimethalin) and none were detected in the water samples. Of the remaining 17 pesticides included in the investigation, having a log P_{ow} below 3.5, only five were detected. These were the phenoxy acids (applied in large quantities) detected at a low level in the sediments and also diuron and methabenzthiazuron, both of which had a longer soil dissipation half-life than most of the other pesticides.

Pesticide occurrence in sediments could result in adverse effects on sediment living organisms. Denitrifying microorganisms are of particular concern since they contribute to reduce the nitrogen load from agricultural land to eutrophicated lakes and coastal waters. In a study by Svensson and Leonardson (1992), they demonstrated the inhibitory effect of the fungicide fenpropimorph on denitritication in lake sediments from southern Sweden, whereas the denitrifying microorganisms were unaffected by addition of the insecticide fenvalerate.

Acknowledgments. Financial support for this work by the Swedish National Chemicals Inspectorate, the Swedish Environmental Protection Agency and the Environmental Foundation of the Malmöhus county council is gratefully acknowledged. Göran Areskoug assisted in collecting the samples and Dr Lars Bergstrom gave valuable comments on the manuscript.

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