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A qualitative sampling method for monitoring water quality in temporary channels or point sources and its application to pesticide contamination

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Abstract

A water-sampling device to monitor the quality of water periodically and temporarily flowing out of concrete tubes, sewers or channels is described. It inexpensively and easily enables a qualitative characterization of contamination via these point-source entry routes. The water sampler can be reverse engineered with different sizes and materials, once installed needs no maintenance, passively samples the first surge, and the emptying procedure is short. In an agricultural catchment area in Germany we monitored an emergency overflow of a sewage sewer, an outlet of a rainwater sewer and two small drainage channels as input sources to a small stream. Seven inflow events were analysed for 20 pesticide agents (insecticides, fungicides and herbicides). All three entry routes were remarkably contaminated. We found parathion-ethyl concentrations of 0.3 $\mu g\,l^{-1}$, diuron up to 17.3 $\mu g\,l^{-1}$, ethofumesate up to 51.1 $\mu g\,l^{-1}$, metamitron up to 92 $\mu g\,l^{-1}$ and prosulfocarb up to 130 $\mu g\,l^{-1}$.

Keywords: Herbicides; Fungicides; Insecticides; Small streams; Point sources; Sewage plant; Rainwater sewer; Pipes

1. Introduction

Streams receive inflow via a wide range of entry routes. Besides non-point sources there are various point sources like drainage channels, outlets from industrial plants or sewage plants and sewers or concrete tubes. Monitoring of the water quality in continuous outlets can easily be done by hand sampling. However, taking water samples at outlets with a high variability in time or even with periodic and temporary inflow events is difficult (Liess and Schulz, 2000). These events occur only after rainfall or emergency overflows during a short period of time. Hence, they can only be monitored with event-controlled samplers. As is known from non-point sources (Spalding and Snow, 1989; Schulz, 2001), the highest contamination and the poorest water quality can be expected for the first surge, which is nearly impossible to sample by hand. Therefore an ideal water sampler should be easy to install with no maintenance needed and should sample mainly the first surge of an inflow event. Such a sampling method is known only for the agricultural edge-of-field runoff (Schulz et al., 1998).

Even in catchment areas where intensive agriculture is practised, for certain pesticides classes the point sources can cause a stronger contamination than the non-point sources (Fischer et al., 1996; Mohaupt et al., 1999).

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Wastewater treatment plants are known to be a major point source of pesticides (Seel et al., 1996). Neumann et al. (2002) found the outlets from farmyards to be responsible for an average of 24 g pesticides during an application period, presumably caused by cleaning the spraying equipment. In this study we describe a qualitative sampling device, which was used to monitor the pesticide contamination of a rainwater sewer, an emergency overflow of a sewage sewer and two temporary drainage channels.

2. Methods

2.1. Construction of the water-sampling device

The water sampler is built from a glass tube (∅: 7 cm) that is 60 cm long and has been sealed on both ends (Fig. 1, 1). The resulting sampling volume is 1.3 l. The inflow opening (Fig. 1, 2) is only 2 cm wide, 0.5 cm high and is positioned at a height of 6 cm. The sampler is placed parallel to the current with the opening through which the water enters at the posterior end. This approach prevents the opening from becoming occluded by drift material in the stream water. At the front end a pipe, 3 cm long and 0.5 cm wide, is placed on top of the sampler body (Fig. 1, 3) to allow air to leave the sampler during the passive filling procedure. The water sampler was attached at the bottom of the concrete tubes and the lined channels. This was done during dry periods. They were fixed in position by steel straps (Fig. 1, 4). The sampler could easily be taken out and replaced after the emptying procedure.

2.2. Study area

Near Viersen in the Niederrheinische Bucht in Nordrhein-Westfalen (NRW) in Germany the catchment area of the Nette was investigated. Intensive agriculture prevails in the catchment area of this small stream: predominantly grain and potatoes (each 25% of the total area), then sugar beet (19%) and maize (14%), other vegetable crops (4%) and grassland plus pasture (6%). The sampling was done while pesticide application to the fields was most intensive, from mid-April to mid-July 1998. We used the sampling method described here to monitor the water quality in an emergency overflow of a sewage sewer, the outlet of a rainwater sewer and two small drainage channels as input sources to the stream. The outlets of both sewers were 80 cm concrete tubes. The drainage channels were 50 cm wide and were lined with wooden planks at the bottom and both sides. All entered the stream through the embankments. The water samplers were installed at the beginning of the investigation. Whenever water flowed through the entry routes into the stream, the water sampler passively filled up with water. Hence, it had to be emptied after every inflow event. To ensure this, the status of the water sampler was routinely monitored once a week as well as directly after rainfall events. For cleaning, the water sampler was rinsed with acetone after each sampling.

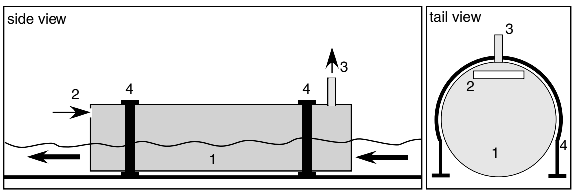

Fig. 1. Construction of the water-sampling device: (1) body of sampler with a length of 60 cm and a diameter of 7 cm; (2) inflow opening with a width of 2 cm, a height of 0.5 cm, disposed 6 cm above the bottom of the sampler; (3) deaeration pipe 3 cm long and 0.5 cm wide; (4) steel straps for fixation.

2.3. Pesticide analysis method

All water samples were concentrated by solid-phase extraction (RP-C18) directly after sampling and then stored at −18 °C. At the end of the investigation period the Institute for Ecological Chemistry of the Technical University of Braunschweig analysed our selected samples by a GC/MS method similar to that described by Liess et al. (1999). Tests were carried out for two insecticides (fenvalerate and parathion-ethyl) and five fungicides (azoxystrobin (= pyroxystrobin), kresoxim-methyl, epoxiconazole, fenpropimorph, propiconazole). Of the 13 herbicides of interest, atrazine and simazine are prohibited for agricultural use. Terbuthylazine, metazachlor, chloridazon, ethofumesate, metamitron, isoproturon, prosulfocarb, metribuzin, and metobromuron are currently used agricultural herbicides. The samples were also tested for bromazil (= imazalil) and diuron, although these are not used agriculturally. The detection limits reached 0.1–0.5 $\mu g\,l^{-1}$ depending on the matrix loading. The detection limit for metobromuron and diuron was 1 $\mu g\,l^{-1}$.

3. Results and discussion

3.1. Evaluation of the sampling device

The water sampler was applicable to monitor the input sources over a relatively long period of time and thus took water samples from all inflow events that exceeded the height of the opening. Once it has been filled with water through the small openings, the replacement and the mixing of the sample with the flowing water is negligible even under strong current. The water sampler is cheap to construct and easy to handle, with no mov-

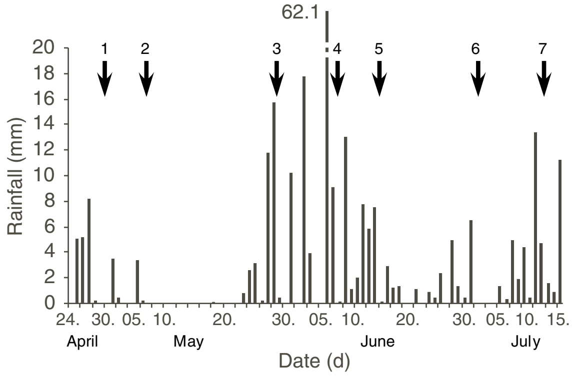

Fig. 2. Amount of daily rainfall (mm) during the investigation period. The arrows indicate the seven selected inflow events in the entry routes from which water samples were taken and analysed for pesticides.

able components. The construction material should be selected with regard to the substances of interest. Here, we used glass as a rather inert material, because pesticides have high tendency to become bound to plastic materials. The sampling volume used here was 1.3 l, but for other purposes the water sampler can be dimensioned as-needed. Once installed, the water sampler needed no maintenance. The use of straps for mounting shortened and simplified the emptying procedure.

During the investigation period several relatively strong rainfall events occurred (Fig. 2). A total of 13 samples were taken at the rainwater sewer (RS), nine (C1) and eight (C2) samples at the drainage channels and four samples at the emergency overflow of the sewage sewer (SS). Here we present the results from the sampling of seven rainfall events. They were selected, because they caused the most inflow events in the considered entry routes. Table 1 gives the concentrations of pesticides found in the water samples. Three rainfall events did not cause an inflow event at the emergency overflow of the sewage sewer, so no sample (n.s.) was available. This demonstrates that this entry route causes inflow only after heavy rainfall, lasting long enough that the capacity of the wastewater treatment plant is exceeded. The other entry routes caused inflow events for all of the seven rainfall events considered, but seven samples were not analysed (n.a.). Three water samples had a specific conductivity between 364 and 693 $\mu S\,cm^{-1}$ and all other samples had values lower than 100 $\mu S\,cm^{-1}$. The low conductivity values prove that the inflow was mainly composed of rainwater.

3.2. Pesticide contamination in the rainwater sewer

In the water of this entry route 17 pesticides were found. All samples were contaminated with minimally three and maximally 14 pesticides. The concentrations of the herbicides were particularly high, with atrazine at 10.5 $\mu g\,l^{-1}$, terbuthylazine at 19.5 $\mu g\,l^{-1}$, prosulfocarb at 8.3 $\mu g\,l^{-1}$ and diuron at 11.2 $\mu g\,l^{-1}$. Fungicides were found at the end of May and June in rather low concentrations. The insecticide parathion-ethyl was detected once.

In the sewage systems of many small villages an effort is made to separate sewage and rainwater, so that the rainwater need not be treated. The rainwater sewer studied here collects the water drained from the eaves of buildings, the streets and the paved surfaces of a small village. Our analyses show that such a rainwater sewer can carry pesticides into streams. The real cause of this entry route for pesticides is probably the cleaning of spraying equipment on the paved farm yard (UBA, 1997).

3.3. Pesticide contamination in the drainage channels

Three water samples from the channel C1 and five from C2 were analysed and 14 pesticides were found. Extremely high herbicide concentrations were found nearly permanently with peak concentrations at 130 $\mu g\,l^{-1}$ for prosulfocarb, 92 $\mu g\,l^{-1}$ for metamitron and 51.1 $\mu g\,l^{-1}$ for ethofumesate. Diuron was found once with 17.3 $\mu g\,l^{-1}$. Insecticides were not found at all and fungicides were found infrequently with concentrations up to 5.5 $\mu g\,l^{-1}$ for propiconazole.

The contamination found in the drainage channels has to rate as extremely high. The pesticides in this entry route are probably introduced by field drainage pipes (Kladivko et al., 1999; Gentry et al., 2000) and by runoff (Schulz et al., 1998) from the adjacent agricultural fields.

3.4. Pesticide contamination in the sewage sewer

Four of the seven investigated rainfall events caused inflow from this entry route into the stream. All samples were contaminated with at least one herbicide and a maximum of 11. Herbicides were found nearly continuously with concentrations up to 9.4 $\mu g\,l^{-1}$ for metamitron and 5.4 $\mu g\,l^{-1}$ for ethofumesate. Diuron was found at levels up to 2 $\mu g\,l^{-1}$. No insecticides or fungicides were detected.

The sewage sewer carries the sewage entering a sewage plant. After heavy precipitation the input flow exceeds the capacity of the sewage plant and causes an emergency overflow into the stream. This could be prevented only by increasing the temporary storage capacity of the plant. The introduction of unclarified sewage to a body of water as a source of agricultural pesticides has attracted little attention till now. The causes are the cleaning of the spraying equipment on paved farmyards (UBA, 1997) and the handling of

Table 1
Pesticide concentration (μg l^{-1}) in the entry routes after seven rainfall events

Event #	1				2				3				4				5				6				7			
Point source	RS	C1	C2	SS	RS	C1	C2	SS	RS	C1	C2	SS	RS	C1	C2	SS	RS	C1	C2	SS	RS	C1	C2	SS	RS	C1	C2	SS
Date	n.a.	n.a.	28.4	n.s.	6.5	n.a.	6.5	n.s.	29.5	29.5	29.5	29.5	6.6	6.6	6.6	6.6	12.6	n.a.	12.6	15.6	1.7	1.7	n.a.	n.s.	08.7	n.a.	n.a.	11.7
Conductivity (μS cm^{-1})	–	–	100	–	267	–	180	–	250	157	131	207	693	164	78	237	543	–	109	364	152	127	–	–	281	–	–	408
Parathion-ethyl (0.005)			–		–		–		–	–	–	–	–	–	–	–	0.3		–	–	–	–			–			–
Azoxystrobin (–)			–		–		–		0.2	–	–	–	0.2	0.7	2.6	–	–		–	–	–	0.6			–			–
Kresoxim-methyl (–)			–		–		–		0.2	–	–	–	0.3	–	–	–	0.2		–	–	–	–			–			–
Epoxiconazole (–)			–		–		–		0.4	–	0.5	–	0.4	–	2.4	–	0.3		–	–	–	–			0.2			–
Fenpropimorph (–)			–		–		–		–	0.3	–	–	0.1	0.2	–	–	–		–	–	–	–			–			–
Propiconazole (–)			0.6		–		–		0.4	–	–	–	0.9	1.1	5.5	–	–		1.2	–	–	–			–			–
Atrazine (–)			–		10.5		–		3.5	–	–	0.3	0.2	0.2	–	0.2	0.3		–	–	0.2	0.3			–			0.3
Simazine (0.1)			–		0.2		–		0.9	–	–	–	–	–	–	0.3	–		–	–	–	–			–			–
Terbuthylazine (0.5)			–		8.9		–		3	0.2	–	0.3	2.9	0.7	–	1.7	19.5		–	–	3	0.8			–			–
Metazachlor (0.4)			–		–		–		–	–	–	–	5	–	–	0.2	0.1		1.9	–	–	–			–			–
Chloridazon (10)			–		1		15.4		0.5	–	10.2	0.6	2.6	–	8.6	2.7	–	1.6	0.5	–	–	–						–
Ethofumesate (–)			51.1		0.4		16.9		2.1	2.3	29.3	1.6	3.4	0.4	15.7	5.4	0.3		1.8	0.5	–	18.9			–			–
Metamitron (–)			57.9		0.7		15.7		2.2	6	92	9.4	9.1	0.7	31.3	7.1	0.6		2.5	2.2	0.6	7.4			0.3			–
llsoproturon (0.3)			0.5		1.7		2		2	2	0.47	0.2	2.5	2.2	–	0.2	–		–	–	0.2	1.5			–			–
Prosulfocarb (–)			0.5		–		130		8.3	6	17.5	1.4	7.7	1.4	10.8	0.8	0.9		2.1	0.3	0.9	1.5			–			–
Metribuzin (–)			–		1.4		25.4		2.5	1.3	18.9	1.5	2.9	0.5	5.8	0.4	1.9		1.8	–	–	0.5			0.23			–
Metobromuron (–)			–		–		5.1		–	–	1.4	–	–	–	3.4	–	–		–	–	–	–			–			–
Diuron (0.05)			–		–		–		1.9	–	–	–	–	–	–	2	–		–	–	11.2	17.3			–			–

Fenvalerate and bromazil were not found at all. RS: rainwater sewer; C1, C2: drainage channel one and two; SS: sewage sewer; n.a.: sample not analysed; n.s.: no sample; –: below detection limit; values in bracket refer to the quality targets for aquatic communities (μg l^{-1}) from the German Federal Environmental Agency.

pesticide containers at wash basins after agricultural or private use (Seel et al., 1996).

Overall we found remarkable pesticide contamination in the entry routes we considered. In Germany no target value for pesticides in entry-route water is available at all. For stream water the Federal Environmental Agency has recently published a proposal with quality targets for 35 pesticides (UBA, 1999). Of the 20 pesticide agents investigated here only eight (Table 1) have such a quality target. We found that seven (chloridazon, diuron, isoproturon, metazachlor, parathion-ethyl, simazine, terbuthylazine) of these exceeded the quality target. The pesticide contamination via the investigated entry routes can be evaluated as significant. The concentrations found for the three pesticide classes correlate with the amount applied on average in the catchment area during the investigation period (Neumann et al., 2002). Herbicides caused the highest contamination and were applied at a rate of 1.5 $kg\,ha^{-1}$, while fungicides were only applied at 0.18 $kg\,ha^{-1}$. Insecticides were on average only used at 0.0002 $kg\,ha^{-1}$ in the catchment area and detected only once.

4. Conclusion

- The water-sampling device presented here monitors the water quality of point sources periodically entering surface water. It demonstrates whether an inflow event occurred at all and at the same time passively samples the inflow event to specify the relative pesticides levels.
- Besides the output from wastewater treatment plants, the emergency overflow of sewage sewers and the outlets of rainwater sewers and small drainage channels can be regarded as point sources of pesticides to streams.

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