



## A METHOD FOR MONITORING PESTICIDES BOUND TO SUSPENDED PARTICLES IN SMALL STREAMS

Mathias Liess \*, Ralf Schulz, Michael Neumann

Technical University Braunschweig  
Zoological Institute, Department of Limnology  
D-38092 Braunschweig, Spielmannstr. 7  
e-mail: M.Liess@tu-bs.de

(Received in Germany 5 January 1996; accepted 14 February 1996)

### Abstract

A Suspended Particle Sampler (SPS) is described with which pesticides bound to suspended particles can be readily monitored in small streams. Retention of the grain-size fraction below 0.02 mm grain diameter depends on the velocity of flow through the device, averaging 50% for 0.05 m s<sup>-1</sup> and 15% for 0.41 m s<sup>-1</sup>. The advantage of the SPS lies in its simple, economical construction and in the slight expenditure of time and effort needed to use it. Comparison with other methods of monitoring short-term pesticide contamination shows that the contamination values provided by the SPS describe the actual contamination dynamics considerably better than do the data obtained by conventional sampling of suspended sediments. Copyright © 1996 Elsevier Science Ltd

### Introduction

Streams with an agricultural catchment area are susceptible to unpredictable, brief pesticide inputs following precipitation, as a result of surface runoff (Wauchope, 1978). The pesticides introduced into the water are largely bound to suspended materials (Ghadiri & Rose, 1991). Even those pesticides dissolved in the water phase on entry are soon mostly adsorbed to suspended substances (Muir *et al.*, 1985). It is therefore essential to monitor the suspended materials in studies of the contamination of streams (Cooper, 1988; House *et al.*, 1992) and of its biological effects (Liess *et al.*, 1993). The maximal concentration of suspended substances is present only briefly, and hence can be quantified accurately only by event-controlled sampling. An economical alternative to this very elaborate method is to employ sedimentation vessels through which the water flows continuously. The disadvantage of this method is that it cannot be used to measure the exact maximal concentration, but instead gives the mean sediment contamination during the period from one emptying of the vessel to the next. The sedimentation vessels previously used are constructed as large, floating containers which thus are suitable only for use in fairly large rivers (Reinemann & Schemmer, 1994). In contrast, the Suspended Particle Sampler (SPS) described here is designed to be used in small streams. To evaluate the performance of the SPS, in the years 1993

and 1994 various sampling systems were used to monitor the insecticide contamination of a small stream with an agricultural catchment area. These systems are compared here with respect to the effort needed to operate them and their performance in measuring contamination of suspended materials.

## Methods

### Construction of the Suspended Particle Sampler (SPS)

The SPS (Fig. 1) is positioned in the stream so that the water flows through it (1, 5). It includes a ten-liter sedimentation vessel (3) made of glass. This vessel is seated in a stainless steel box (7) that is lowered into the sediment at the bottom of the stream. The box is closed by a cover plate (6) made of stainless steel. The box comes to rest with the cover plate in the same plane as the stream bed, to prevent mobilization of the stream sediment in the region of the inlet tube (2). In addition to the inlet tube, an outlet tube (4) is mounted in the cover plate. Both tubes are 34 mm in diameter. The inlet tube is closed at its upper end and has a slit measuring 25 x 5 mm in the wall facing upstream. As a result, a flow pressure is directed into the collecting vessel. The outlet tube is cut at an angle of 45 deg. at its upper end, forming an opening that faces downstream (5); this arrangement exerts suction on the collecting vessel. By rotating the outlet tube the magnitude of the suction effect can be changed, so that the velocity of flow into the inlet tube can be matched to the current of the stream. The height of the inlet opening can be adjusted to enable sampling at any desired level in the water. In the present study a height of three centimeters above the stream bed was chosen.

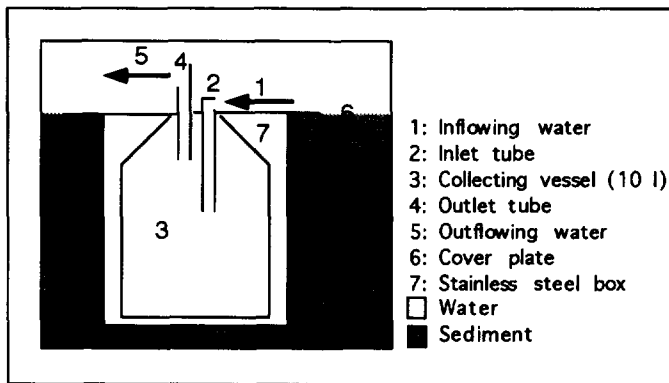


Figure 1:

Construction of the Suspended Particle Sampler (SPS).

### Determination of retention percentage

The grain-size-specific retention was determined in laboratory experiments for the flow velocities  $0.05 \text{ m s}^{-1}$ ,  $0.12 \text{ m s}^{-1}$ , and  $0.41 \text{ m s}^{-1}$ . For this purpose, 900 grams of dried stream sediment were added to 180 liters of water (i.e.,  $5 \text{ g l}^{-1}$ ); the grain-size composition of the sediment was as follows:  $<0.002 \text{ mm}$  - 12.0%;  $\geq 0.002 \text{ mm}$   $<0.006 \text{ mm}$  - 5.3%;  $\geq 0.006 \text{ mm}$   $<0.02 \text{ mm}$  - 17.1%;  $\geq 0.02 \text{ mm}$   $<0.06 \text{ mm}$  - 52.3%;  $\geq 0.06 \text{ mm}$   $<0.2 \text{ mm}$  - 4.4%;  $\geq 0.2 \text{ mm}$  - 9% (TOC: 8.3 %). This mixture was introduced to the sedimentation vessel through the inlet tube and the outflowing mixture, collected as it left the vessel through the outlet opening, was compared with the sediment retained in the SPS, with respect to grain-size distribution and quantity of sediments. The grain-size analysis was carried out after destruction of carbonate and humus, as described by Moschrefi (1983). The TOC was analyzed as described by Balesdent *et al.* (1988).

### **Study region**

The field studies were carried out in the Ohebach, a small headwater stream (base flow:  $10 \text{ l s}^{-1}$ ; peak discharge up to  $150 \text{ l}^{-1}$ ) in northern Germany. The dominant land use is agricultural, with no other sources of pollution. Sugar beets, winter barley and winter wheat are the most common crops. The catchment area comprises  $0.9 \text{ km}^2$  of slightly sloping (2%-4% gradient) fields of loess loam and clayey marl.

### **Pesticide analysis**

The suspended particles were analyzed with respect to pesticide content at the Institute for Ecological Chemistry of the Technical University of Braunschweig. The insecticides in the suspended sediments were extracted with acetone and purified by column chromatography with aluminium oxide. Those in the water samples were removed by solid-phase extraction ( $\text{C}_{18}$  columns). The measurements were made with GC-ECD and confirmed with GC-MS, with a quantification limit in sediment samples of  $1 \text{ } \mu\text{g kg}^{-1}$  for parathion,  $5 \text{ } \mu\text{g kg}^{-1}$  for fenvalerate; in water samples,  $0.01 \text{ } \mu\text{g l}^{-1}$  for parathion and  $0.05 \text{ } \mu\text{g l}^{-1}$  for fenvalerate.

### **Trials with different sampling methods**

So that the characteristics of the SPS could be compared with those of other methods, a variety of sampling methods were tested. The sediments and suspended materials collected in these trials were analyzed as described above; the outcomes are given in the Results.

### **Sediment - stream bed**

A spoon was used to scoop mixed samples of bottom sediment out of the layer extending from zero to two centimeters depth, at ten sites.

### **Suspended particles - runoff-triggered sampler**

A runoff-triggered sampler provided an accurate measurement of the maximal contamination of suspended particles, by sampling only the brief peak contamination levels during runoff events. The reduced conductivity of the stream water served as an indicator of runoff (Spalding & Snow, 1988; Walther, 1980). Every four minutes the conductivity was measured, and when a reduction by  $0.5\% \text{ min}^{-1}$  was observed, a 500-ml water sample was taken every eight minutes. In some samples the content of suspended sediments was too small for sediment analysis. In this case only the suspension-free water was analyzed.

### **Runoff collector at the field edge**

During the study year 1994, runoff collectors were set into erosion furrows at the top of the stream bank. This kind of collector consists of a 2.5-liter glass bottle buried so deeply that the rim of the bottle was 2 cm above ground level. The opening was covered with a metal strip to keep precipitation from entering directly. As rainwater drained away from the field into the brook, the water and the sediments it carried were caught in the bottle. Analysis of the runoff water can demonstrate the presence of insecticides, which are thus introduced into the brook.

## Results and Discussion

### Retention by the Suspended Particle Sampler

As expected, the amount retained by the SPS decreased with increasing rate of flow. Because pollutants become attached preferentially to the grain-size fraction below 0.02 mm grain diameter (Ghadiri & Rose, 1991), in evaluating retention properties particular weight was placed on the small grain sizes. With the highest flow velocity,  $0.41 \text{ m s}^{-1}$ , the retention rate was 15% for the grain-size fraction smaller than 0.02 mm. However, such rapid flow is rare in flatland streams. With the lower flow velocities tested here, the retention rate for this fraction was between 27% and 50%. The proportion of organic carbon retained, another parameter that is important regarding pesticide content (Adams *et al.*, 1992), was between about 40% and 60% for these currents.

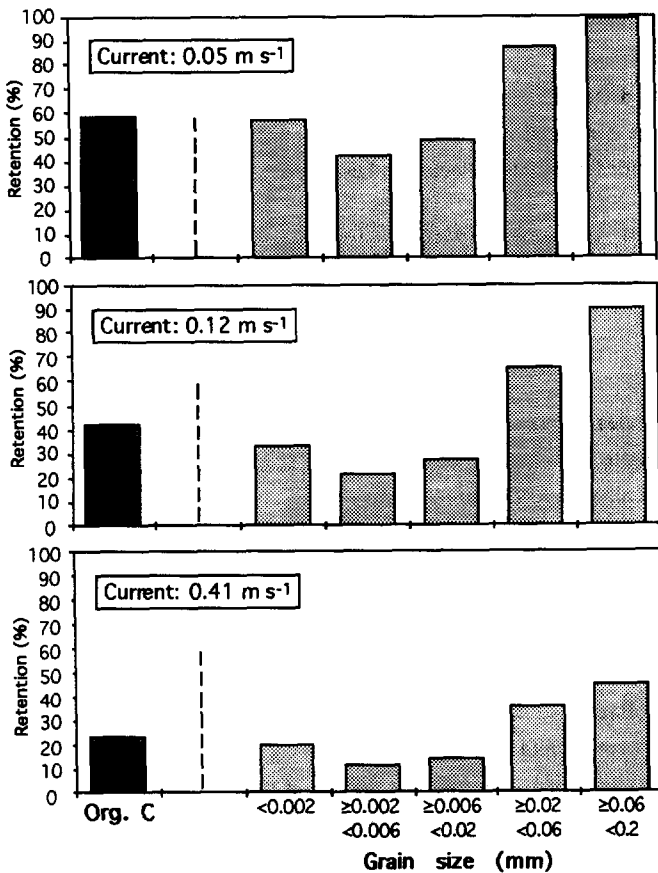


Figure 2:  
Retention by the Suspended Particle Sampler (SPS) for current velocities between  $0.05$  and  $0.41 \text{ m s}^{-1}$ .

### Comparison with other sampling systems

On June 8, 1994, as a consequence of a precipitation event, contaminants including the insecticide fenvalerate were introduced into the investigated stream from an agricultural area. The sediment eroded from the fields and accumulated in the stream-bank runoff collector was found to have a fenvalerate concentration of  $833 \mu\text{g kg}^{-1}$  dry

weight. In the following, this example is used as a standard for comparison of the stream contamination measured by the three sampling systems included in this trial.

The runoff-triggered sampler took samples of the suspended particles at the time when they were being introduced to the stream at the maximal rate. The suspended materials it collected during the June 8 event were contaminated with fenvalerate in the concentration  $302 \mu\text{g kg}^{-1}$ . The sediments collected by the SPS during the two-week period including this event, from May 26 to June 9, 1994, were contaminated with  $71 \mu\text{g kg}^{-1}$  fenvalerate. Analysis of the bottom sediment collected on June 9 gave a fenvalerate concentration of  $10.9 \mu\text{g kg}^{-1}$ . The suspended particles were thus more heavily contaminated than the stream bed, a finding also made by House *et al.* (1992). In the period just preceding the precipitation event, fenvalerate could not be detected in either the bottom sediment or the suspended particles. Fig. 3 represents graphically the contamination produced by the event, as measured by the three methods.

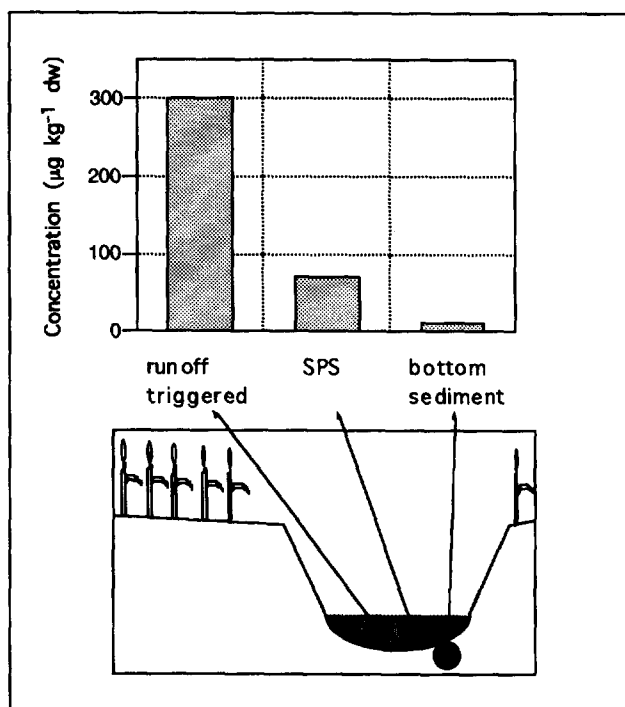


Figure 3:

Concentration of the insecticide fenvalerate associated with suspended particles and with bottom sediment of the Ohebach, following a surface runoff event on June 8, 1994. Results with various sampling methods (left to right):

- runoff-triggered sampler ( $302 \mu\text{g kg}^{-1}$ )
- SPS (Suspended Particle Sampler) ( $71.0 \mu\text{g kg}^{-1}$ )
- collection of bottom sediment ( $10.9 \mu\text{g kg}^{-1}$ )

#### Temporal dynamics of the insecticide contamination of suspended particles

The graphs in Figures 4 and 5 show the time course of the insecticide contamination of suspended particles measured during the years 1993 and 1994. In Fig. 4 the parathion contamination of the suspended particles, monitored with the SPS, is compared with the contamination of the bottom sediment. In the cases of massive input due to surface runoff (triangles indicate surface runoff events on May 27 and June 2, 1993) it is clear that the dynamic response of the suspended particles is more pronounced than that of the sediment. During the period of maximal pesticide input (beginning of June), the sediment was much less contaminated than the suspended material.

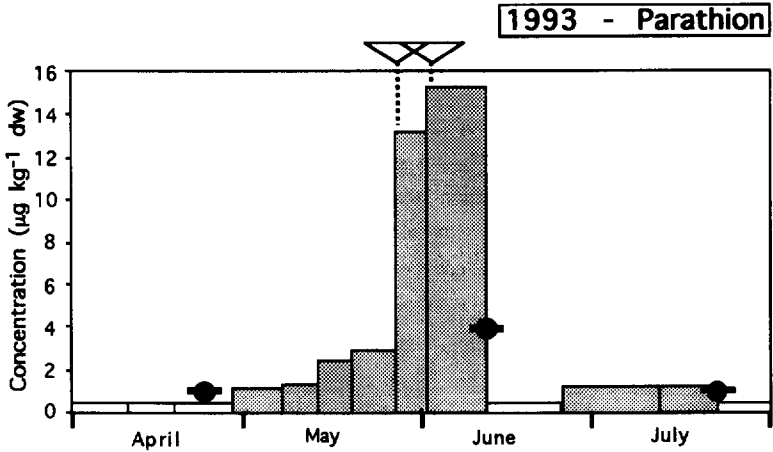


Figure 4:

Parathion contamination of the suspended materials as measured with the Suspended Particle Sampler (SPS, columns) and of the bottom sediment (black symbols); above the graph the times of surface runoff events are indicated by triangles. Limit of quantification  $1 \mu\text{g kg}^{-1}$ ; the white columns reaching  $0.5 \mu\text{g kg}^{-1}$  indicate that the insecticide was identified but could not be quantified.

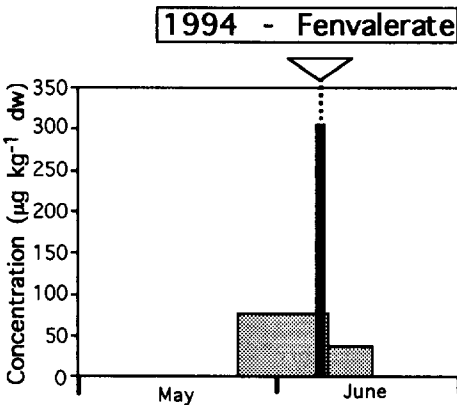
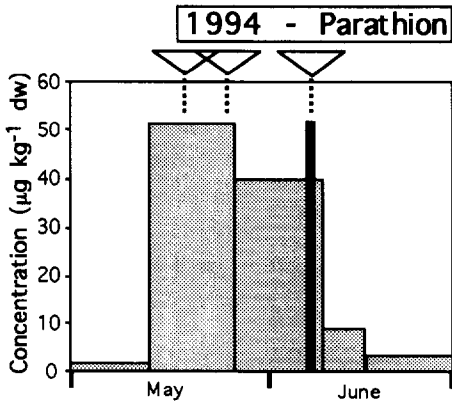


Figure 5:

Contamination of suspended materials as measured with the Suspended Particle Sampler (SPS, shaded columns) and with the runoff-triggered sampler (black columns). The times when surface runoff occurred are indicated by triangles above the graphs. Limits of quantification:  $1 \mu\text{g kg}^{-1}$  for parathion and  $5 \mu\text{g kg}^{-1}$  for fenvalerate.

Fig. 5 shows a comparison of the suspended-particle contamination measured in 1994 by two methods, the SPS and the runoff-triggered sampler, for the insecticides parathion and fenvalerate. The difference in the concentrations found by the two methods, exemplified by fenvalerate in Fig. 3, is evident for both insecticides here. The runoff-triggered sampler detects the most severe contamination of the suspended materials, but analysis is possible only if sufficient material has been collected during the relatively brief sampling period. In the case of parathion, the amount of suspended materials collected in the runoff-triggered sampler in May was too small to allow analysis. However, the parathion concentration in the water phase of these samples ( $6 \mu\text{g l}^{-1}$  on May 19;  $0.9 \mu\text{g l}^{-1}$  on May 26;  $0.2 \mu\text{l l}^{-1}$  on June 9) shows that this insecticide was introduced by the runoff. This conclusion was confirmed by the measurements with the stream-bank runoff sampler, which collected contaminated sediment from the field during all three events (indicated by triangles in the graphs; the parathion concentrations were  $724 \mu\text{g kg}^{-1}$  on May 19,  $154 \mu\text{g kg}^{-1}$  on May 26, and  $38.3 \mu\text{g kg}^{-1}$  on June 8; fenvalerate:  $833 \mu\text{g kg}^{-1}$  on June 8). Data from the runoff sampler also showed that fenvalerate was introduced to the stream only in June. Evidently, the fenvalerate input was substantially bound to the suspended sediments. In the sample taken immediately after that runoff event, on June 9, fenvalerate was found only in the suspended materials ( $302 \mu\text{g l}^{-1}$ ) and was not detectable in the water phase. As a conclusion of the results shown here we state that short-term pesticide contamination of streams with an agricultural catchment area could be well described by the SPS.

### Acknowledgments

This study is part of the Special Collaborative Programme 179 (Water and Matter Dynamics in Agroecosystems) and was supported by the German Society for the Advancement of Scientific Research (DFG).

### References

- Adams, W.J., R.A. Kimerle & J.W. Barnett Jr., 1992. Sediment quality and aquatic life assessment. *Envir. Sci. Technol.* 26: 1865-1875.
- Balesdent, J., G.H. Wagner & A. Mariotti, 1988. Soil organic matter turnover in long term field experiments as revealed by carbon-13 natural abundance. *Soil Science Society of America. Journal* 52: 118-124.
- Cooper, C.M., 1988. The toxicity of suspended sediments on selected freshwater invertebrates. *Verh. int. Ver. Limnol.* 23: 1619-1625.
- Ghadiri, H. & C.W. Rose, 1991. Sorbed chemical transport in overland flow. 2. Enrichment ratio variation with erosion processes. *J. envir. Qual.* 20: 634-642.
- House, W.A., J.E. Rae & R.T. Kimblin, 1992. Source-sediment controls on the riverine transport of pesticides. In B.B.C.P. Council (ed.) Brighton Crop Protection Conference: Pests and diseases 1992, Vol.1, International Conference Brighton England UK, Nov.19-22 1990. BCPC British Crop Protection Council, Farnham, UK: 865-870.
- Liess, M., 1993. Zur Ökotoxikologie der Einträge von landwirtschaftlich genutzten Flächen in Fließgewässer. Cuvillier, Göttingen, 133 pp.
- Liess, M., R. Schulz & U. Werner, 1993. Macroinvertebrate Dynamics in Ditches as Indicator for Surface Water Runoff - An Ecological Aspect for Assessment of Agricultural Impact on Running Water Ecosystems. *Modelling of Geo-Biosphere Processes* 2: 279-292.
- Moschrefi, N., 1983. Ein neues Verfahren der Schlämmanalyse für die Bestimmung der Korngrößenzusammensetzung. *Mitteilungen der Deutschen Bodenkundlichen Gesellschaft* 38: 115-118.
- Muir, D.C.G., G.P. Rawn & N.P. Grift, 1985. Fate of the pyrethroid insecticide deltamethrin in small ponds: A mass balance study. *J. agric. Food Chem.* 33: 603-609.
- Reinemann, L. & H. Schemmer, 1994. Neuartige Schwebstoffsammler zur Gewinnung von Schwebstoffen aus fließenden Gewässern. *Deutsche Gewässerkundliche Mitteilungen* 38: 22-25.
- Spalding, R.F. & D.D. Snow, 1989. Stream levels of agrochemicals during a spring discharge event. *Chemosphere* 19: 1129-1140.
- Walther, W., 1980. Prozess des Stoffabtrages und der Stoffauswaschung während und nach Starkregen in ackerbaulich genutzten Gebieten - 1. Bericht: Stoffabtrag. *Zeitschrift für Kulturtechnik und Flurbereinigung* 21: 65-74.
- Wauchope, R.D., 1978. The pesticide content of surface water draining from agricultural fields - a review. *J. envir. Qual.* 7: 459-472.