Bull. Environ. Contam. Toxicol. (1993) 50:1–7

Environmental
Contamination
and Toxicology

Pesticide Retention by a Programmable Automatic Water/Suspended-Sediment Sampler

S. Smith, Jr.

USDA-ARS National Sedimentation Laboratory, Water Quality & Ecology
Research Unit, in cooperation with the Mississippi Agricultural & Forestry
Experiment Station, P.O. 1157, Airport Road, Oxford,
Mississippi 38655-1157, USA

The most accurate method of determining the mean suspended-sediment concentrations in streamflow is probably depth-integration. However, this manual method is extremely laborious, time-consuming, and costly (Murphree et al. 1972). To overcome these difficulties, automatic pumping-type, suspended-sediment samplers were developed and field tested (Hansen 1966, Miller et al. 1969, Welch et al. 1971). These included various research models with names such as the XPS-62, PS-66, PS-67, Chickasha sediment sampler, and PS-69. The PS-69 was thoroughly tested by pesticide researchers and found to be suitable for evaluating the transport of relatively water-insoluble pesticides in suspended sediment/agricultural runoff (Parr et al. 1974). However, these same researchers cautioned that additional testing of automatic pumping samplers needed to be conducted "where there are extremely low concentrations of suspended sediment (organic and inorganic) such as under minimum tillage, resulting in very high pesticide-sediment ratios, and particularly where more highly water-soluble pesticides are employed. Considerable adsorption by sampler components might occur."

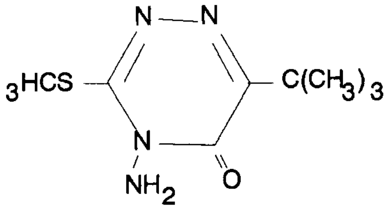
This paper reports results of extensive pesticide laboratory studies to determine the magnitude of pesticide retention by a commercially-available automatic pumping sampler (ISCO Model 2710) in common use today in water quality research. The studies are part of a major research effort at the USDA-ARS National Sedimentation Laboratory to determine the effects of conservation tillage practices on surface and ground water quality in the loessial uplands of north Mississippi. Mention of a pesticide does not constitute a recommendation for use by the U.S. Dept. of Agriculture nor does it imply registration under FIFRA as amended. Names of products are included for the benefit of the reader and do not imply endorsement or preferential treatment by the U.S. Dept. of Agriculture.

Send reprint requests to S. Smith, Jr. at the above address.

MATERIALS AND METHODS

Grenada silt loam (fine-silty, mixed, thermic Glossic Fragiudulfs; Ap horizon, 0-13 cm; pH 6.0; 1.5% organic matter), obtained from the Nelson Research Farm in Tate county, Mississippi, was air-dried, passed through a 0.5-mm sieve, and used as sediment in these studies. Gas chromatographic analysis revealed no detectable residues of any of the pesticides under investigation. Pesticides used (Figure 1) were analytical-grade and included: metribuzin (4-amino-6-*tert*-butyl-4,5-dihydro-3-methylthio-1,2,4-triazin-5-one), a systemic preemerge/postemerge triazine herbicide; chlorpyrifos (*O*,*O*-diethyl *O*-3,5,6-trichloro-2-pyridyl phosphorothioate), a broad-spectrum soil/foliar organophosphorus insecticide; and metolachlor [2-chloro-6'-ethyl-*N*-(2-methoxy-1-methylethyl)acet-*o*-toluidide] a selective preemerge/preplant-incorporated acetamide herbicide. Pesticide-sediment-water mixtures of 30-L volumes, ranging from 0.05 to 20 ppm of pesticide (μg/g sediment) and from 100 to 10,000 ppm of sediment (mg/L water) were formulated in 38-L stainless steel milk cans. Pesticide:sediment ratios thus ranged from 1:20 to 1:200,000. A predetermined amount of each pesticide, from stock solutions, was delivered in ethyl acetate to the appropriate weight of sediment (oven-dry basis). After thorough mixing on a roller mill and allowing the ethyl acetate to volatilize (about 16 h), the pesticide-sediment mixture was transferred to the milk can containing 30 L distilled water. The mixture was then stirred continuously and vigorously for 0.3 h to ensure complete suspension of the sediment, and a 0.9-L sample was directly removed for pesticide and sediment analysis. With continued stirring, the Isco sampler was immediately backflushed for about 15 sec and 0.9 L of the mixture was pumped through the sampler and into a glass container, also for pesticide and sediment analysis. After another 15-sec backflush, 0.9 L of distilled water was pumped through the sampler and collected for pesticide and sediment analysis to assess the amount of pesticide and sediment immediately recoverable from the sampler. At 3.0 h the sampling process was repeated. Each pesticide-sediment-water mixture (treatment) was replicated three times.

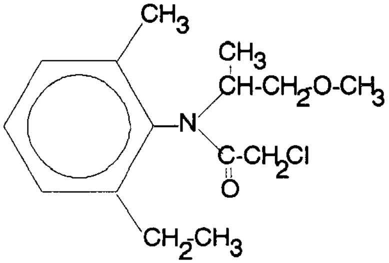
Samples were separated into water and sediment phases via 0.45-μm Millipore filtration. Aliquots (1000-8000 mL) of the water phase were extracted with 25 mL ethyl acetate and 1 g KCl by sonification for 1 min. The extracts were partitioned in separatory funnels and the water discarded. The ethyl acetate portion was dried over anhydrous Na_2SO_4 and brought to an appropriate volume (often < 1 mL) for gas chromatographic (gc) analysis. The sediment from Millipore filtration was air-dried (24 h), weighed, and extracted with 100 mL distilled water and 25 mL hexane by sonification for 1 min. The extract was transferred to a separatory funnel and the water phase discarded. The hexane phase was dried over anhydrous Na_2SO_4 and brought to an appropriate volume for gc analysis. The ethyl



METRIBUZIN

S_{H_2O}=1200 ppm*

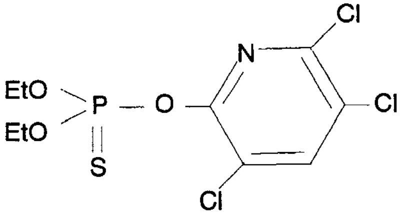
K_{oc}=24 cc/g**



METOLACHLOR

S_{H_2O}=530 ppm*

K_{oc}=181 cc/g**



CHLORPYRIFOS

S_{H_2O}=ca. 2 ppm*

K_{oc}=6070 cc/g**

* Water solubility from Royal Society Chemistry 1987.

** Organic carbon partition coefficient from Jury et al. 1987.

Basic structures and selected properties of pesticides used.

acetate and hexane extracts were analyzed using a Tracor model 540 gc equipped with a ^{63}Ni electron capture detector, a Hewlett-Packard model 3396A integrator, and a 15 m X 0.53 mm J & W Scientific DB210 (1.0 µm film thickness) column. The carrier gas was ultra-high purity helium at 12.7 cc/min and the column makeup and detector purge gas was ultra-high purity nitrogen at 60 and 10 cc/min, respectively. Column oven, inlet, and detector temperatures were 180, 240, and 350 C, respectively. Under these conditions, retention times were 1.54, 2.02, and 3.17 min for metribuzin, chlorpyrifos, and metolachlor, respectively. Mean extraction efficiencies, based on fortified samples, were >90 % for all three pesticides from both water and sediment. Pesticide residues were confirmed with a Tracor model 702 nitrogen-phosphorus detector. The gc analysis system was upgraded for the second and third replications of each treatment. Upgrades included a Dynatech Precision GC-411V autosampler for unattended sample injections and a PE Nelson 2700 chromatography data handling system consisting of a Model 970 interface, Turbochrom 3^{TM} software, and a microcomputer with color printer for automated quantification and reporting of pesticide peak data including gas chromatograms. A multi-level calibration procedure was used with standards and samples injected in triplicate. Calibration curves were updated every tenth sample.

RESULTS AND DISCUSSION

Table 1 shows the recovery of metribuzin from the pesticide-sediment-water mixtures pumped through the Isco automatic sampler following 0.3 and 3.0 h stirring times. These percent recoveries were calculated based on the amounts of metribuzin present in the water and sediment after the mixtures traversed the sampler compared to the amounts before. Metribuzin recoveries were essentially complete for all pesticide and sediment concentrations except one. At a metribuzin concentration of 0.05 ppm (µg/g) sediment and a sediment concentration of 100 ppm (mg/L) water, only about 50-60% (water phase concentration of 0.0017 - 0.0026 µg/L) of the metribuzin present in the water before the mixture traversed the sampler was recovered. The unrecovered metribuzin was lost to the sampler, probably by sorption to the silicone tubing used in the sampler's intake line, peristaltic pump line, and outflow line. The distilled water rinses of the sampler contained no quantifiable metribuzin residues, however, traces of metribuzin were apparent from the gas chromatograms.

The recovery of chlorpyrifos from these same pesticide-sediment-water mixtures under the same conditions as for metribuzin is presented in Table 2. Chlorpyrifos recoveries were essentially complete for the sediment phase at all concentrations used. No chlorpyrifos was found in the water phase except at the highest pesticide treatment level of 10 ppm and the two lower sediment treatment levels of 100 and 1000

Table 1. Recovery of metribuzin from pesticide-sediment-water mixtures pumped through the ISCO sampler following 0.3 and 3.0 h stirring times.

Pesticide conc.	Sediment conc.	Pesticide/ Sediment ratio	Pesticide recovery* Water phase 0.3 h	3.0 h	Sediment phase 0.3 h	3.0 h
ppm			%			
0.05	1000	1:20000	94±2	95±1	100±1	96±1
0.05	100	1:2000	52±3	59±2	98±1	96±1
0.05	10000	1:200000	99±1	98±3	98±3	99±2
0.5	1000	1:2000	95±1	98±2	97±1	98±1
0.5	100	1:200	98±4	97±2	91±3	96±3
0.5	10000	1:20000	101±2	100±2	98±1	96±2
5	1000	1:200	96±3	99±1	94±2	95±1
5	100	1:20	105±6	97±1	98±1	95±3
5	10000	1:2000	94±1	96±4	99±3	96±3

* Mean ± standard deviation of 3 replications.

ppm. The only losses (recoveries of 77-81%, equivalent to water phase concentrations of 0.128-0.162 μg/L) of chlorpyrifos to the sampler were from the water phase of the mixture in which the pesticide/sediment ratio was highest (1:10). The finding of no chlorpyrifos in the water phase in all but two of the mixtures is not surprising considering its relatively low water solubility (S_{H2O}) of ca. 2 ppm (Royal Society of Chemistry 1987) and its relatively high organic carbon partition coefficient (K_{oc}) of 6070 cc/g (Jury et al. 1987). This K_{oc} for chlorpyrifos reflects its inherently very strong tendency to be partitioned toward the soil sediment phase.

Metolachlor recoveries (Table 3) were similar to those of metribuzin. The only loss of metolachlor to the sampler was from the water phase of the mixture which had the lowest metolachlor concentration (0.2 ppm) in sediment and the lowest sediment concentration (100 ppm) in water. The magnitude of this loss was about 30% (recoveries of 69-73%, equivalent to water phase concentrations of 0.0104 - 0.0122 μg/L).

No losses of sediment to the sampler could be detected in these studies. The programmed sampler backflushing operations were very efficient in thoroughly clearing out the intake, pump and outflow lines.

In summary, the losses of pesticides to the sampler in these studies were very small but quantifiable. However, under certain conditions, losses could be as high as 40-50%. As an added precaution, new tubing should be installed periodically

Table 2. Recovery of chlorpyrifos from pesticide-sediment-water mixtures pumped through the ISCO sampler following 0.3 and 3.0 h stirring times.

Pesticide conc.	Sediment conc.	Pesticide/ Sediment ratio	Pesticide recovery Water phase 0.3 h	3.0 h	Sediment phase 0.3 h	3.0 h
ppm			%			
0.1	1000	1:10000	U[*]	U	98±1	94±1
0.1	100	1:1000	U	U	95±2	93±3
0.1	10000	1:100000	U	U	103±3	95±3
1	1000	1:1000	U	U	92±1	99±1
1	100	1:100	U	U	98±2	96±2
1	10000	1:10000	U	U	98±5	97±4
10	1000	1:100	97±1	101±3	99±1	96±2
10	100	1:10	77±3	81±1	89±1	98±4
10	10000	1:1000	U	U	103±5	97±1

[*] U = undetectable (water phase concentration < 0.0003 μg/L)

Table 3. Recovery of metolachlor from pesticide-sediment-water mixtures pumped through the ISCO sampler following 0.3 and 3.0 h stirring times.

Pesticide conc.	Sediment conc.	Pesticide/ Sediment ratio	Pesticide recovery Water phase 0.3 h	3.0 h	Sediment phase 0.3 h	3.0 h
ppm			%			
0.2	1000	1:5000	92±4	99±5	89±4	96±2
0.2	100	1:500	73±2	69±2	104±5	99±3
0.2	10000	1:50000	89±4	92±3	98±4	94±1
2	1000	1:500	88±3	102±1	99±1	93±4
2	100	1:50	96±2	93±1	94±3	96±2
2	10000	1:5000	94±2	96±4	90±1	91±4
20	1000	1:50	96±3	98±2	94±1	99±2
20	100	1:5	96±4	96±2	96±2	94±4
20	10000	1:500	98±3	102±4	95±4	98±4

in these types of samplers because tubing tends to become more sorbent as a result of wear and aging. Aged tubing that becomes contaminated would have the potential to transfer pesticides to otherwise pesticide-free samples via desorption.

These types of samplers function exceptionally well for collecting water and suspended-sediment samples. However, field researchers attempting to study pesticide transport in runoff/streamflow should conduct, with the pesticides that they may encounter, preliminary studies similar to one reported in this paper.

Acknowledgments. I thank Mr. Blake Sheffield for his able assistance in conducting these studies.

REFERENCES

Hansen EA (1966) Field test of an automatic suspended-sediment pumping sampler. Trans ASAE 9:738-743

Jury WA, Focht DD, Farmer WJ (1987) Evaluation of groundwater pollution potential from standard indices of soil-chemical adsorption and biodegration. J Environ Qual 16:422-428

Miller GE, Allen PB, Welch NH, Rhoades, ED (1969) The Chickasha sediment sampler. ARS Publ 41-150

Murphree CE, McDowell LL, Bolton GC, Bowie AJ (1972) Field performance and evaluation of two automatic suspended sediment pumping samplers. Miss Water Res Conf Proc p 1-17. Miss State Univ, State College, Miss

Parr JF, Willis GH, McDowell LL, Murphree CE, Smith S (1974) An automatic pumping sampler for evaluating the transport of pesticides in suspended sediment. J Environ Qual 3:292-294

Royal Society of Chemistry (1987) Agrochemicals Handbook 2nd ed. Nottingham, England

Welch NH, Allen PB, Rhoades ED (1971) Field tests of pumping-type sediment samplers. Trans ASAE 14:1122-1125

Received October 8, 1991; accepted July 13, 1992.