MONITORING OF PESTICIDES IN SUBSURFACE AND SURFACE WATER WITHIN AN AGRICULTURAL CATCHMENT IN SOUTHERN SWEDEN

J. KREUGER

Swedish University of Agricultural Sciences, Div. Water Quality Management, Dept. Soil Sciences, P.O. Box 7072, S-750 07 Uppsala, Sweden

ABSTRACT

A catchment in the southernmost part of Sweden was selected for intensive monitoring of pesticide occurrence in surface water. Information on farm management practices within this area was collected annually and most of approximately 40 pesticides used were included in the analytical procedures. Results showed large fluctuations in pesticide concentrations from day to day, with the highest concentrations occurring at the time of spraying, or later in the season associated with storm flow events. During the first three years of investigation a total of twenty-five different pesticides were detected in surface water leaving the catchment. Many of the pesticides were found over several months and some were found before the spraying season started. Transport calculations show that between 0.01-0.9% of an applied pesticide was transported in surface water leaving the catchment area.

INTRODUCTION

Monitoring programmes throughout the Nordic countries during the past eight years have detected 41 different pesticides (including 28 herbicides, 7 insecticides and 6 fungicides) occurring in surface waters in Denmark, Finland, Norway and Sweden, (Lundbergh *et al.*, 1994). For adequate exposure assessment, as a part of risk evaluation, good quality data is needed on pesticide exposure patterns and characteristics. The ecological effects of pesticides on flora and fauna in surface waters are dependent on both peak concentrations and the duration of exposure. The objective in many of the above monitoring studies has been to determine pesticide concentrations in surface waters on single occasions. This is inadequate for assessing the ecological risks posed by pesticides in surface waters. As a basis for exposure assessment and regulatory pollution control measurements, improved monitoring strategies are desirable. There is also a great need to increase our knowledge of transport pathways within a watershed, including processes (spills, runoff, leaching, drift, etc.) influencing stream water quality, to produce better guidance on minimising pesticide loss to water.

The overall objective of this study was to monitor the occurrence, temporal distribution and mass transport of pesticides to stream water from an intensively cultivated agricultural catchment.

MATERIAL AND METHODS

Catchment description

The Vemmenhög catchment is situated in the far south of Sweden, on the south-western plain of Skåne (Scania county), with undulating topography and glacial till-derived soils rich in chalk, crystalline rock and shale. The clay content of the till varies between 10-18%. The total thickness of the Quaternary deposits is 60-120 metres (Daniel, 1992). The catchment has an area of 8.55 km^2 consisting of 95% arable land, predominantly sandy loam in texture. Tile drainage systems are frequent within the area, with drainage water having a pH-value in

the range of 7.5-8.0. In the upper part of the catchment stream water is channelled through a large culvert. Water samples taken at the outlet of the culvert (site UT10) provide a measure of concentrations in drainage and runoff leaving fields and include losses from areas where pesticides are handled. At the discharge from the catchment (site LU12) the water has flowed 1.1 km from the culvert outlet. Samples taken at this site provide a measure of exposure not only to runoff and leaching, but also to drift, sedimentation, degradation and possible filling and washing of spraying equipment directly in the stream.

Agricultural practice in the watershed is comprised of a 4-year rotation with winter rape, winter wheat, sugar beet and spring barley on about 80 % of the area and with spring wheat, peas, oats, grass leys, winter barley, rye and spring rape on the remaining area. The total amount of pesticide applied within the catchment each year has been on average 1500 kg AI, with 80% applied during spring/early summer and 20% in the autumn. The pesticide usage during spring/early summer is dominated by herbicide applications (85%), but with the remainder made up of fungicides (12%), insecticides (2%) and growth regulators (1%). Autumn application is dominated by herbicides (99%). About 40 different AI's are used annually, but with only 10 of these accounting for 85% of total weight applied; 80-90% of pesticides used (by weight) were included in the analyses.

Measurements

Water outflow from the catchment area was continuously recorded by a water level gauge situated 200 m down stream from sampling location LU12. In April 1991 a Campbell datalogger was installed at sampling location LU12 to record water flow, using a submerged probe. Culvert flow rates at UT10 were measured using a 90-degree V-notch weir and an ISCO model 3210 ultrasonic sensor, starting in April 1993. Rainfall was recorded by two gauges within the catchment and at an official meteorological station located 6 km to the north-east.

Water samples were collected May-September, starting in 1990, using programmable automatic samplers (ISCO models 2700, 2700R and 3700FR), except at site UT10 where manual grab sampling during May-June was used during the first two years (1990-1991). With the automatic samplers, time paced samples were taken at daily or weekly intervals, each sample being a composite of sub-samples taken at 10-minute or houly intervals respectively. Between October 1992 and April 1993 additional sampling was carried out at UT10 to study pesticide transport during the winter period. To inhibit microbial degradation of the pesticides dichloromethane was added to the sample bottle in advance, plus distilled water to prevent evaporation losses of the dichloromethane. After completion of the sampling programme the samples were delivered to the laboratory within 48 hours and extracted within 24 hours of delivery.

Information on pesticide usage on a field scale (types of pesticide, amounts and application dates) and handling was collected annually from the 35 farmers operating within the area. Only one farm (2% of the area) did not participate. Non-farming residents within the catchment area were also interviewed about possible pesticide usage.

Analytical methods

Unfiltered water samples were analysed by two different procedures, the phenoxy acid method and the multiresidue method. In the former, phenoxy acids and related compounds were hydrolysed with alkali for one hour at 100°C. After acidification the acids were extracted with dichloromethane. Extractive alkylation with pentafluorobensylbromide and gas chromatography were conducted, as described by Åkerblom *et al.*, (1990). Confirmation was by gas chromatography and mass spectrometry (GC-MS), with a limit of detection in the range of 0.05-0.1 µg/l. Pesticides analysed by this method were bentazone, clopyralid, 2,4-D, dichlorprop, fluroxypyr, flamprop-M, ioxynil, MCPA and mecoprop.

With the multiresidue method semi-polar and non-polar pesticides were extracted with dichloromethane. Hydrophobic gel permeation clean-up and capillary column gas chromatography with selective detectors (GC-NP and GC-EC) were conducted according to Åkerblom *et al.*, (1990) and Andersson and Ohlin, (1986). Confirmation was by GC-MS, with a limit of detection in the range of 0.1-0.5 µg/l.

Quality assurance

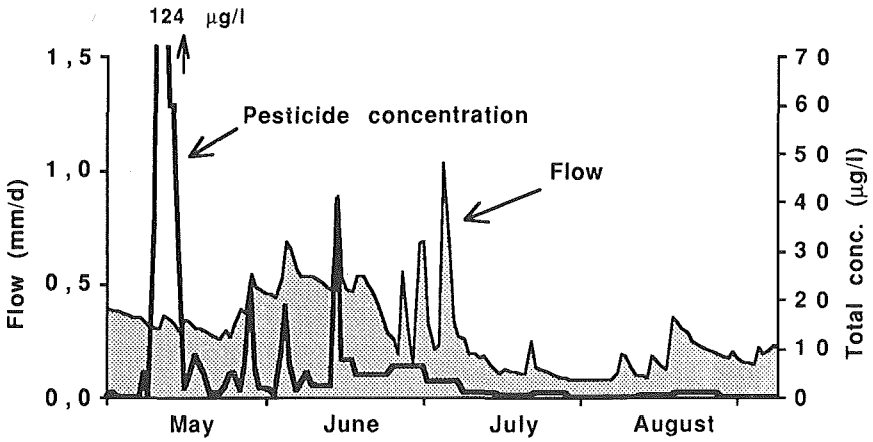
The possible loss of unstable compounds during the collection and transport procedure was evaluated in two separate studies, using 14 pesticides representing different intrinsic properties. In the first study spiked surface water samples were run through the ISCO model 2700R automatic water sampler in the field, testing the stability during the collection procedure (i.e. passage through the tubes of the sampling equipment) and during storage in the sampler (Kreuger, 1992). In the second study pesticide stability was tested under different storage conditions, (storage time, storage temperature and following dichloromethane addition), (Kreuger, 1994). The general conclusion of these studies was that the sampling and storage procedures used were adequate, with recoveries within the normal variance of the analytical procedures.

RESULTS AND DISCUSSION

Precipitation and discharge of water from the area showed great fluctuations between years, with high flow during the cold and rainy spring and early summer of 1991 and extremely low flow in 1992 when no precipitation fell for two months. 1990 was closer to the average, but with thunderstorms in June and July giving sudden high flow events.

In 1990 samples were collected daily during the first month of the investigation, (Figure 1). Results showed large fluctuations in pesticide concentration between days. The highest concentrations occurred during spraying in May without any large increase in discharge, indicating inputs from pesticide handling, (spills). Increases in concentration also occurred later in the season associated with storm flow events, indicating contributions from runoff and preferential flow. Surface runoff rarely occurs in this area due to the permeability of the soils, except in extreme situations with long periods of intense rainfall. In other investigations, subsurface flow through macropores has been shown to be a possible mechanism during storm flow, (Wilson *et al.*, 1990). Richard and Steenhuis, (1988),

FIGURE 1. Water flow and total pesticide concentration in discharge from the catchment in 1990.



demonstrated the importance of macropores on the concentration of a solute in tile drains, with a travel time of the solute to the tile drains of 3 to 4 hours.

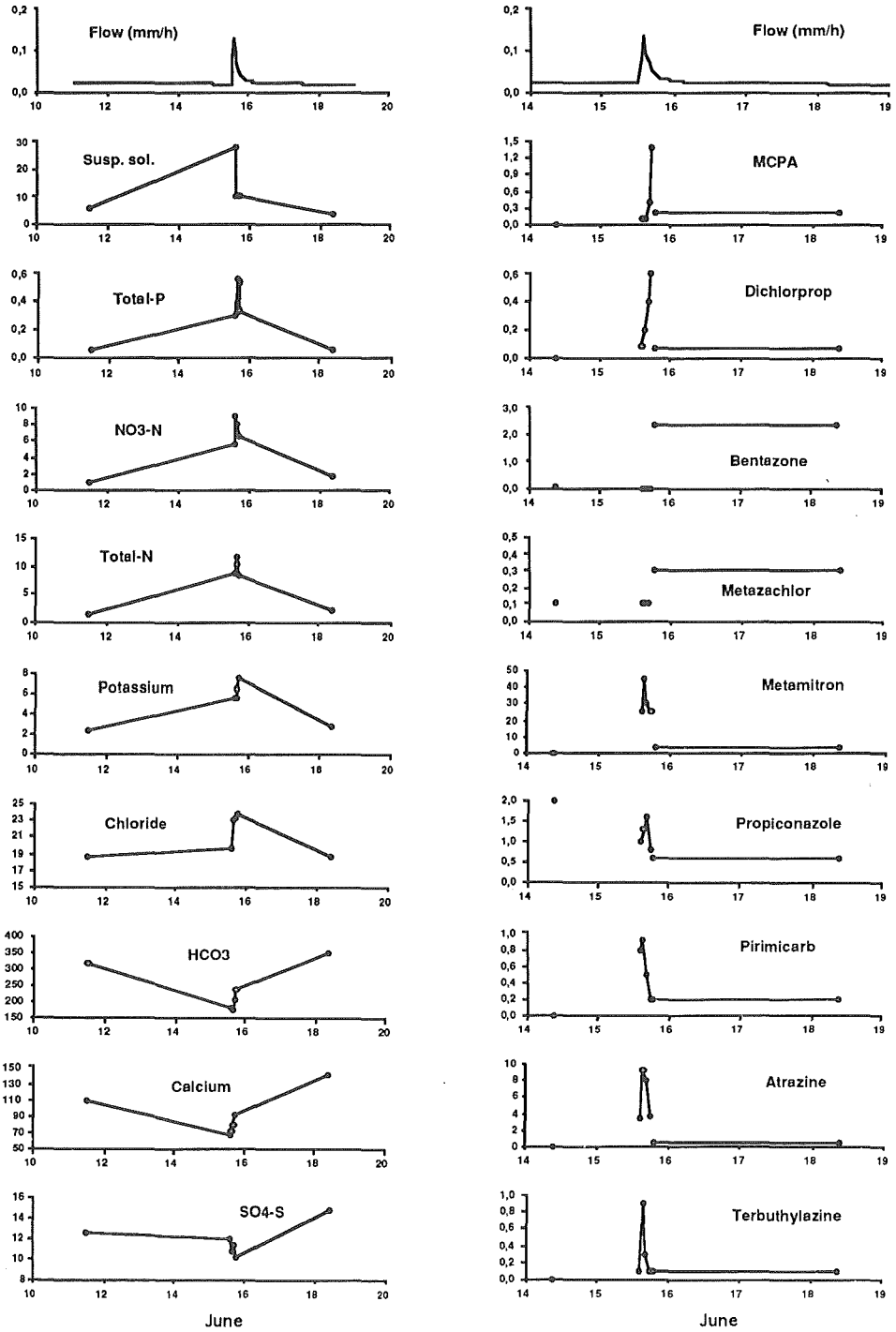
In order to study storm flow in more detail, samples were taken during an intense rainfall event on 15 June 1990. The event started at noon and within less than two hours 16 mm of precipitation had fallen. The first sample was taken as a grab sample at 14.30 when water flow was at its peak. This was followed by three composite samples collected at hourly intervals by the automatic water sampler, with 5 minute increments between the sub-samples, during the descending part of the hydrograph. Finally the automatic sampler collected a composite sample over the following 60 hours. To support the pesticide data, grab samples for analysis of nutrients and other constituents were also collected during the same period.

The results showed a very rapid increase and decrease in pesticide concentrations during the storm flow event (Figure 2). Peak concentrations for several of the pesticides were found in the second sample taken during the early stage of the descending hydrograph, 2.5-3.5 hours after the start of the rain event. A slightly different profile was shown by the phenoxy acids MCPA and dichlorprop with peak concentrations later in the hydrograph. The pesticide findings correlated well with the concentrations found for the nutrients potassium, nitrogen and phosphorus, showing maximum concentrations at the same time as most pesticides. In contrast, the reverse situation was found for other constituents, like sulphur, calcium, magnesium, sodium and bicarbonate, all of which showed a marked decrease in concentration during peak flow. A different response profile to the storm flow event was shown by bentazone and metazachlor, both of which did not show any change in concentration during peak flow, (bentazone 0.03-0.04 µg/l and metazachlor 0.1 µg/l). Both pesticides showed increased concentrations, however, in the last sample representing the end of the hydrograph and early base flow.

These findings indicate that pesticides and nutrients with peak concentrations coinciding with peak flow are easily translocated during a storm event with little interaction with the soil matrix and are either dissolved in the soil solution or bound to soil particles. Other constituents, e.g. calcium, are not readily transported and show a dilution effect. The slow response to storm flow for both bentazone and metazachlor could indicate that they were present in the soil solution in deeper soil layers and therefore not readily available during the initial stage of the subsurface flow process. These two chemicals have also been shown to persist in stream water for long periods at low concentrations and between seasons. Atrazine and terbuthylazine are only used in this area for occasional weed control on farmyards (1-3 farms per year per substance). The quick response of these two compounds during storm flow also demonstrates the influence of runoff from non-crop application.

A total of twenty-five pesticides were detected in stream water leaving the catchment area (LU12) throughout the sampling season (May-September) during the first three years of investigation. Many of the pesticides were found in water (at varying concentrations) over several months. MCPA, dichlorprop and metamitron were detected in the highest concentrations (40 µg/l, 20 µg/l and 45 µg/l respectively). Bentazone was the most frequently detected pesticide, followed by dichlorprop, terbuthylazine, MCPA, mecoprop and metazachlor. The results indicate an annual cycle of pesticides entering the stream water during the period of application, followed by a series of flushing events during storm flow periods. In 1992 the sampling period was extended into winter and continued until April 1993. Small amounts of pesticides (<2µg/l total concentration) were detected throughout the winter season. Pesticides were found at higher concentrations and with a longer duration in culvert water (UT10) than in water from the open part of the stream (LU12), perhaps illustrating that drift did not contribute to pesticide levels in the stream. Pesticides in the open part of the stream would also be subject to degradation, sedimentation and dilution by ground water inflow during base flow conditions.

FIGURE 2. Water flow and concentrations of nutrients (mg/l), suspended solids (mg/l) and pesticides (µg/l) at catchment outlet (LU12) during a storm flow event in mid-June 1990.



Suspended sediment samples and sediment cores were also collected to study the distribution of pesticides between the different matrices. Results showed that pesticides detected in the sediments mainly consisted of insecticides and fungicides. DDT was only found in the sediment cores (0-10 cm) and not in the suspended sediment samples. The fungicide `Tilt Top´ (fenpropimorph 75% and propiconazole 25%) is extensively used in the area. The less water soluble fenpropimorph was found at lower concentrations in water samples than propiconazole, but at higher concentrations in sediment samples. These findings illustrate the importance of accounting for pesticide distribution between the different matrices when setting up monitoring programmes.

Transport calculations show that between 0.01-0.9% of the different pesticides applied within the area were transported in the surface water leaving the watershed, with the non-crop, farmyard applied pesticides atrazine and terbuthylazine being transported in the largest quantities. This correlates well with estimations made in a study by Gomme *et al.*, (1991) who found that about 0.1% of the pesticides applied left the catchment via the river. The amount of atrazine transported from the same area was one order of magnitude higher than other pesticides.

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