

## **PESTICIDE MONITORING AT THE CATCHMENT SCALE IN SWEDEN**

**ADIELSSON S., TÖRNQUIST M., KREUGER J.**

Swedish University of Agricultural Sciences, Department of Soil Sciences, P.O. Box 7014, SE-750 07 Uppsala, Sweden

E-mail. Stina.Adielsson@mv.slu.se

### **ABSTRACT**

Environmental monitoring of pesticides in Sweden started during the mid-1980s. Today's monitoring programme includes intensive sampling from four small rivers draining catchments of 8-16 km<sup>2</sup> dominated by arable land. Water samples are time integrated and analysed for approximately 80 substances representing a majority of the pesticides applied in the area.

Results from the beginning of the 1990s revealed concentrations of up to 200 µg/l for single pesticides, sometimes with high concentrations as a result of accidental spillages. During recent years concentrations in stream water have decreased by more than 90%, even though the amounts of pesticides used in the area have not decreased. The reduction in concentration was a result of information campaigns directed to farmers in the area and political measures. Today most samples have a total concentration of pesticides below two micrograms per litre. An index was applied in an attempt to compare potential toxicity for the aquatic organisms between the catchments and over the years.

Today the main transport pathway for pesticides is assumed to be through the soil profile and thus differences in pesticide behaviour in relation to their intrinsic properties can be addressed. Using multiple linear regression it was possible to find significant functions explaining up to 99% of the variability of pesticide leaching for individual years.

**KEY WORDS:** monitoring, leaching, point sources, toxicity index, pesticide properties.

### **INTRODUCTION**

Environmental monitoring of pesticides in Sweden started during the mid-80s as short term, research based investigations of possible occurrence of pesticides in streams and rivers. Today it includes several monitoring sites with sampling in different matrixes such as surface water, ground water, sediments and precipitation. The Swedish Environmental Protection Agency is the authority responsible for the pesticide monitoring. The programme is performed by the Division of Water Quality Management, in collaboration with the Section of Organic Environmental Chemistry, at the Swedish University of Agricultural Sciences (SLU).

The aim of the Swedish pesticide monitoring programme is to quantify and follow variations of pesticides in time and space, both regarding concentrations and transported amounts. Results from the monitoring programme have been used in different ways. One was to combine detected concentrations with toxicity values into a pesticide toxicity index. Another way was in a statistical study investigating to which extent different intrinsic properties can be used to predict pesticide losses to stream water, using data from 1997-2003 (Adielsson, 2005). A similar study was made on monitoring data from 1990-1994 (Kreuger & Törnqvist, 1998).

## MATERIAL AND METHODS

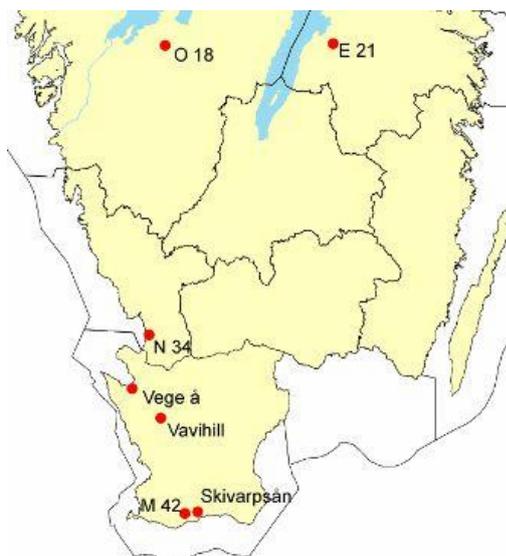


Figure 1. Map of monitoring sites in Sweden.

The monitoring programme on pesticides is mainly focused on four intensive study areas, E21, M42, N34 and O18 in Figure 1. The areas represent major agricultural regions in Sweden. Beside these, two rivers and one site for precipitation sampling is included. The intensive study areas are catchments (8-16 km<sup>2</sup>) dominated by agriculture. Surface water samples are taken during the cropping season as weekly time-integrated samples, collected with refrigerated automatic ISCO-samplers. Samples are analysed for approximately 80 substances. In one area (M42) sampling started in 1990 and in the other three areas sampling started in 2002. Samples of shallow groundwater (3-6 m) and stream sediments are also collected from these areas. Great emphasis is given to collecting information (through interviews with the farmers) on agricultural practices within the catchments, including detailed data on pesticide usage. More information is presented in Kreuger (1998) and in Adielsson & Kreuger (2007).

Monitoring data from the Vemmenhög catchment (M42) was used in a statistical analysis in order to explore possible relations between pesticide intrinsic properties and occurrence in stream water. Data from the monitoring programme was used to calculate the yearly percentage loss rate (transported amounts divided by applied amounts) for 1997-2003. Only pesticides used in amounts of at least three kilograms per season were included. Monitoring data including 20 different pesticides were subjected to stepwise multiple linear regression analysis to express loss rate as a function of different pesticide properties (or a combination of these). The properties included were the sorption coefficient ( $k_{oc}$ ), the degradation half-life ( $DT_{50}$ ), water solubility ( $S_w$ ) and the octanol-water partition coefficient ( $\log P_{ow}$ ). A more detailed description is available in Adielsson (2005).

## RESULTS

Monitoring results obtained from the Vemmenhög catchment (M42) during the first years revealed elevated concentrations (up to 200 µg/l for single pesticides) and also pesticide residues entering the stream without preceding rainfall, clearly a result of accidental spillage when filling or cleaning the spraying equipment on surfaces with drainage in direct connection to the stream. Investigations also demonstrated very high concentrations (up to 2000 µg/l) in run-off water entering surface water inlet wells on farmyards close to areas where filling of sprayers had taken place and, also, where the farmyard had been treated with herbicides to keep it free of weeds. A more detailed presentation of the results has been reported elsewhere (Kreuger, 1998).

During recent years there has been a significant decrease in pesticide concentrations in stream water leaving the catchment. The results demonstrate a considerable reduction in overall pesticide findings in the stream, with concentrations down by more than 90% (Figure 2). The most notable decrease in concentration levels and transported amount occurred in 1995, coinciding with the onset of the information efforts that first took place in the area before the

1995 application season. This was followed by economic incentives introduced by the government and the industry in 1998. Further information on risk mitigation measure is given by Kreuger & Nilsson (2001).

It is interesting to note that the amounts applied within the catchment have been relatively constant throughout the monitoring period. The decreasing levels of pesticides in stream water from the catchment area can primarily be attributed to an increased awareness amongst the farmers on better routines for the correct handling of spraying equipment and application procedures

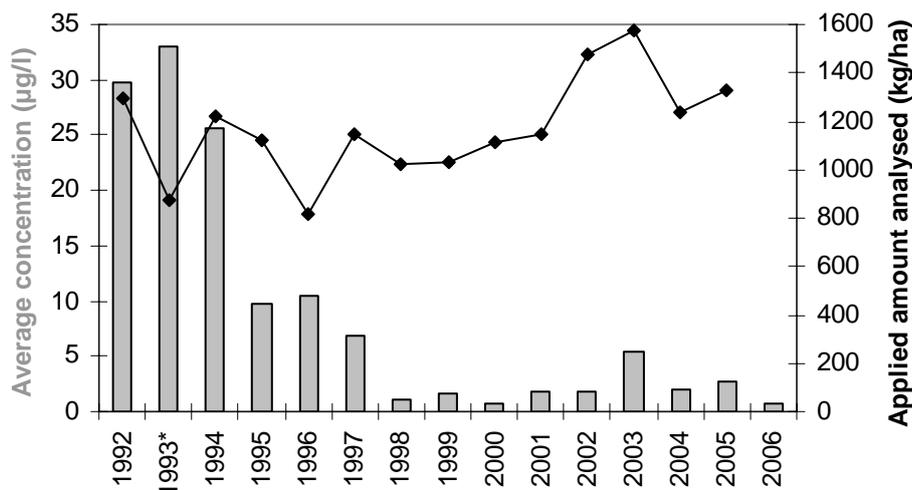
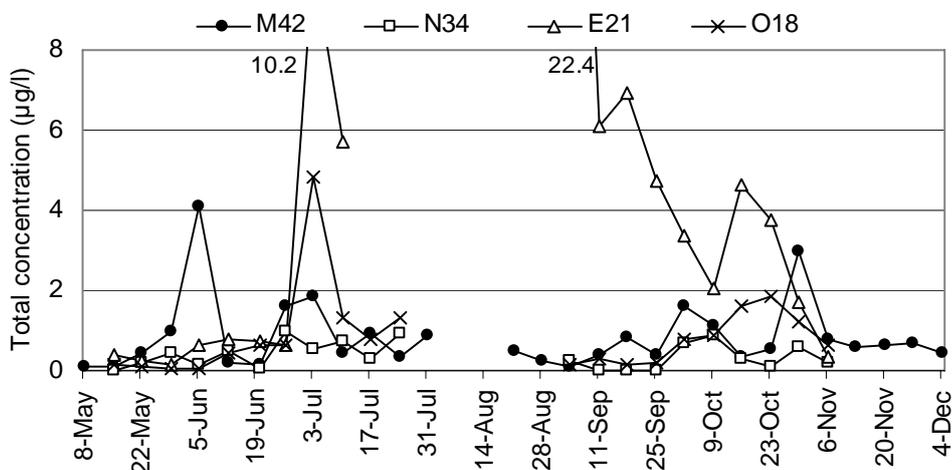


Figure 2. Average total pesticide concentration (bars) in the Vemmenhög catchment during May-September 1992-2005 (\*only May-June) and amounts applied of the pesticides included in the analysis (line).

How the other three catchments compare to the Vemmenhög catchment can be seen in Figure 3. The concentration of pesticides in the rivers varies somewhat over the year, with intense rainfall soon after pesticide application as one main contributing factor for elevated concentrations in stream water. The total concentration per sample ranges between zero and 22 µg/l, normally the concentration is below two micrograms per litre.



Total concentration (weekly average) of pesticides ( $\mu\text{g/l}$ ) from the four monitoring areas M 42, N 34, E 21 and O 18 during the monitoring period in 2006. The two peaks exceeding  $8 \mu\text{g/l}$  measured 10.2 and  $22.4 \mu\text{g/l}$  respectively.

The concentration alone does not provide information on potential toxicity of the water. Different pesticides are toxic at different concentration levels. The Swedish Chemicals Agency has developed surface water quality objectives (WQO) for a number of pesticides (methods described in Asp et al., 2004). The WQO gives the maximum concentration of each pesticide that is calculated not to cause negative effects on aquatic organisms. Dividing measured concentrations for a substance with its WQO and summarizing for each sample or season results gives an index describing potential toxicity (PTI = Pesticide Toxicity Index) (Asp & Kreuger, 2005). The index was calculated for the areas within the monitoring programme (Figure 4). There are differences between the areas, with O18 having the lowest PTI during all years, while E21 has an index value that varies considerably. PTI calculated for the Vemmenhög catchment (M42) shows that not only has the concentrations decreased, but also the potential risk for aquatic organisms is continuing to decrease.

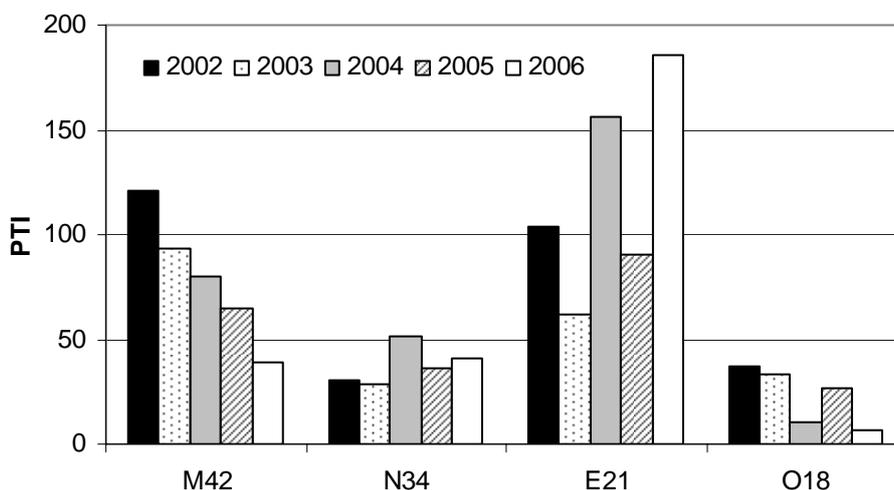


Figure 4. Pesticide toxicity index for the areas within the Swedish monitoring programme 2002-2006.

Point sources are usually considered to contribute significantly to pesticide leaching. In the Vemmenhög catchment the transport losses have decreased mainly due to reduction of point sources. With less point sources one would expect the pesticide properties to be of vital importance for the extent to which a pesticide leach. Using multiple linear regression analysis to study the influence of intrinsic properties on pesticide losses to water, it was possible to find significant functions at  $P > 0.05$  for all years (Table 1). However for three of the years (1997, 1999 and 2001), the  $r^2$  value was less than 45% and there were no consistency in parameter selection.  $DT_{50}$  and  $k_{oc}$  were included in all the best functions, for years with high  $r^2$  values. The quota of  $DT_{50}$  and  $k_{oc}$  was the variable that was chosen most often. The highest single  $r^2$  value was found in 2002 where a function containing  $DT_{50}/k_{oc}$  and  $S_w$  had an  $r^2$  value of 99% ( $P < 0.0001$ ). Grouping the years, the best function explained 69% of the variation ( $P < 0.0001$ ).

When the functions were used for predicting pesticide losses for other years, the data selection was slightly different; pesticides applied in amounts less than three kilograms per hectare were included but where there was a zero loss rate, the substance was excluded. The highest model

efficiency found was 0.56 using a function developed on grouped data from 1997-2000, predicting for 2001-2003.

Table 1. Results from statistical analysis, with the variables that were included in the best possible functions, their significance level, rate of explanation and number of substances included in the analysis, data from M42

Year	Variables	P	r <sup>2</sup>	r <sup>2</sup> ad <sup>#</sup>	n
1997	S <sub>w</sub> *	0.025	0.41	0.35	12
1998	DT <sub>50</sub> /k <sub>oc</sub> , log P <sub>ow</sub> , GUS, log S <sub>w</sub> *	0.006	0.80	0.71	13
	DT <sub>50</sub> /k <sub>oc</sub> , log P <sub>ow</sub> , S <sub>w</sub> *	0.003	0.78	0.70	13
	DT <sub>50</sub> /k <sub>oc</sub>	0.006	0.51	0.47	13
1999	log k <sub>oc</sub> *	0.030	0.45	0.40	10
2000	k <sub>oc</sub> , log P <sub>ow</sub> , S <sub>w</sub> , log DT <sub>50</sub> *	0.021	0.82	0.69	11
	log S <sub>w</sub> *	0.012	0.52	0.47	11
2001	log P <sub>ow</sub> *	0.036	0.37	0.30	13
2002	DT <sub>50</sub> /k <sub>oc</sub> , S <sub>w</sub> *	<0.0001	0.99	0.98	9
	DT <sub>50</sub> /k <sub>oc</sub>	<0.0001	0.95	0.95	9
	DT <sub>50</sub> , S <sub>w</sub> *	0.020	0.73	0.64	9
2003	DT <sub>50</sub> /k <sub>oc</sub> , DT <sub>50</sub> *	0.0004	0.76	0.71	14
	DT <sub>50</sub> /k <sub>oc</sub> , S <sub>w</sub>	0.005	0.62	0.54	14
97-03	DT <sub>50</sub> /k <sub>oc</sub> , log P <sub>ow</sub> *	<0.0001	0.69	0.66	20
	DT <sub>50</sub> /k <sub>oc</sub>	<0.0001	0.62	0.60	20

# The rate of explanation adjusted for the number of variables included.

\* Results from stepwise procedure.

## DISCUSSION

The decrease in pesticide concentrations in stream water from the Vemmenhög catchment (M42) is not explained by a decreasing pesticide usage (Figure 1), but rather by mitigation efforts by farmers during the mid 1990's followed by economic incentives introduced by the government and the industry in 1998. Farmers were educated and the awareness of risks related to pesticide use was improved. With these efforts point sources could be considerably decreased. Concentrations in the other three areas are in the same range as the Vemmenhög catchment. There are always variations between areas and between years due to climate and different use of pesticides.

There is a general lack of knowledge concerning the potential risk posed by a multitude of different pesticides occurring in a field situation. However, to theoretically compare possible risk of toxic exposure between monitoring areas and long term development an index (PTI) was used. Two of the areas seem to have a lower toxicity index than the others (Figure 3), but numbers vary somewhat over the years. The downward trend in M42 is partly due to decreasing amounts of some old hazardous substances that have been entering the river through addition of ground water. E21 had a rather high index value in 2006, because some of the high concentration peaks in Figure 2 also included substances that were exceeding their WQO.

The results from the statistical analysis imply that long-term leaching to a large extent is influenced by the pesticide properties DT<sub>50</sub> and K<sub>oc</sub>, i.e. when the influence of point sources has been reduced. Pesticide properties can only be expected to influence transport through the soil

profile which is why it is important to reduce point sources before it is possible to find relations to pesticide properties.

## CONCLUSION

Based on data from long-term monitoring, it was demonstrated that the transported amounts of pesticides were decreased by 90% due to education of farmers on best management practices and political measures taken. The amount of pesticides in the area during the same period has been quite constant. Using multiple linear regression based on results from the same area it was possible to find significant functions explaining up to 99% of the variability for individual years, based on pesticide properties. The highest model efficiency was 0.56. The result implies that a large part of the long term leaching could be explained by pesticide properties when the influence of point sources had been eliminated.

## ACKNOWLEDGEMENTS

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