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Occurrence of plant protection products in rivers and groundwater

- As part of national environmental assessment, the occurrence of plant protection products in Swedish water courses is being monitored. In 2005, plant protection products were found in all water samples from streams in the four small catchment areas investigated.
- Compounds that are widely used within the areas as well as compounds that have not been used for many years were both found in the streams.
- The concentration of plant protection products varied during the season, but the common trend was for higher peaks

in the spring and early summer than in the autumn.

- Rain soon after spraying of plant protection products increases the risk of higher concentrations in water courses.
- Between 15 and 20 compounds were found at least once a year in concentrations that might carry a risk for algae and fauna colonising water courses.
- In the Scania area, where measurements have been carried out since the beginning of the 1990s, concentrations have been reduced by 90%.



Tramlines in sugarbeet, the stream in Västergötland and a buffer zone along a water course.

wedish agriculture uses approximately 1 500 tonnes of chemicals (plant protection products) per year and these chemicals play an important role in ensuring high yields. However, use of plant protection products also carries the risk of toxic compounds leaching out into the surrounding environment. The occurrence of plant protection products in Swedish water courses is therefore being monitored as part of national environmental monitoring programme (Factfile 1). The aim of environmental monitoring is to record the concentrations and types of plant protection products being lost to water courses and to assess the effects of different agricultural policy decisions on such losses.

Highest concentrations in spring and early summer

In 2005, we found 2-27 different compounds per water sample from streams in the catchment areas. We found residues of compounds that are used frequently, but also of those that have not been used in Sweden for a number of years. The concentrations of chemical residues vary during the season; in the spring and early summer there are often peaks with somewhat higher concentrations than are found in the autumn (Figure 2). This is primarily because most plant protection products are applied in the spring and early summer. In addition, there is often more water in the streams in autumn, which means that the compounds present are diluted to lower concentrations.

Weather and point sources affect losses

Losses to streams are strongly affected by how soon and how heavily it rains after chemicals are applied in the field. We have seen on a number of occasions that when rain falls soon after spraying, a pulse of plant protection products can be found in streams. The reason is that the compounds do not have time to be adsorbed or degraded, but are dissolved by the rainwater and transported down through the soil and out via drainage pipes. Certain compounds that are not

FACTFILE 1

Swedish environmental monitoring programme

Environmental monitoring of plant protection products on a national level began in Sweden in 2002, with funding from the Environmental Protection Agency. Four small catchment areas (800–1700 hectares) were selected to represent four large agricultural regions in Sweden. These catchments lie in Scania, Halland, Östergötland and Västergötland and in all four areas, around 90% of the land is used for agriculture.

The water in the streams is collected weekly from May to November using automatic sampling equipment and the samples are analysed for around 80 different substances. Farmers in the catchment areas are interviewed about their cropping. Groundwater and sediments are also sampled. Two rivers in Scania and a site for collection of rainwater are also included in the environmental monitoring (see Figure 1).



FIGURE 1. Catchment areas, rivers and rainwater collection site for Swedish environmental monitoring progamme.

very soluble in water can be transported on particles moving with the water in or on the soil and out to water courses. The concentrations in the stream in Västergötland reached a strong peak $(17.3 \text{ }\mu\text{g/l})$ in June. The compound contributing most to this peak was bentazone. Since none of the farmers had used this compound on an agricultural field within the area, the losses were most likely from a point source. A point source means that the loss does not come from the compound being transported through the soil profile but instead taking a short-cut to the water course. This can be the result of e.g. accidents, spillages or carelessness. It is very important that farmers do all they can to avoid point sources.

Losses usually small

We also measure water flow in the streams, i.e. the amount of water passing through them. This information is then used to calculate the amount of plant

Cumulative concentration (µg/l)

protection products transported from the area. This in turn can be compared with the amount of chemicals used in the area in order to calculate the percentage loss. The percentage loss varies both between years and between areas but in general, less than 0.2% of the total amount used in an area is transported out via water courses. For individual compounds the loss can be somewhat greater in individual cases, up to 1%, usually when higher concentrations are found during periods of high flow.

The most common products dominate

Herbicides against weeds are normally used much more frequently than insecticides and fungicides. Herbicides are also the compounds found most frequently in water courses (Figure 3). The six most commonly found compounds are all herbicides, and they are also among the ten most commonly used in the areas. For Sweden as a



FIGURE 2. Cumulative concentration of plant protection products in the four catchment areas during 2005.

whole, these compounds are also among the 15 bestsellers. A high level of use generally increases the risk of a compound being found in the water, since it is likely to give rise to concentrations that can be detected in the analyses.

Bentazone was found in all water samples from all four catchments in 2005, and this has also been the picture in previous years. Bentazone is found in the product Basagran, a herbicide used in e.g. leys and peas. It is generally regarded as a mobile compound and therefore it is only permitted for use in the spring.

Glyphosate alone represents over a third of total Swedish sales of plant protection products. Within the catchments, this compound was found in 80% of samples in 2005, and the detection frequency for the entire period 2002-2005 was also 80%. The percentage loss of glyphosate was 0.01-0.23% in the catchment areas in 2005. Measured as number of detections per 10 kg active ingredient used in all areas, glyphosate has a lower value than a number of other compounds, which indicates that there are other compounds with greater losses relative to their level of use.

Banned compounds also found

Several of the detected compounds included in Figure 3 are no longer permitted for use in Sweden, namely terbuthylazine, terbutryn, benazolin, atrazine, lindane and the degradation compounds DEA, DETA and BAM. Most of these are found only in trace amounts, i.e. in concentrations just above the limit of detection. A look back over the measurements from recent years shows that the number of detections of terbutylazine has decreased continuously since measurements began in 2002.

A possible reason why we are still finding old compounds is that they Detection frequency (%)



FIGURE 3. | Detection frequencies for compounds detected in more than 10% of the samples analysed during 2005. □=concentration at trace level (i.e. below LOQ); \square =concentration above LOQ, but below 0.1 µg/l; \square =concentration above 0.1 µg/l.

may have leached to the shallow groundwater during the period they were in use. When a compound ends up in the groundwater, decomposition is quite slow (because there are fewer micro-organisms in deeper soil layers). Groundwater flowing into streams can then carry chemical residues with it. During the summer months in particular, the water flowing in streams mostly consists of groundwater, since any rain that falls is often taken up by plants or evaporates to the air.

It is also interesting to see which compounds are widely used but not detected so frequently. Metamitron is one of the ten most sold compounds in Sweden, but it was only detected in 25% of water samples. However, the average concentration of these detections was 0.6 μ g/L, which is relatively high compared with other substances. Aclonifen, phenmedipham and prosulfocarb are also used in relatively large amounts, but these compounds were not detected at all, or only in low concentrations on a few occasions, during 2005.

Concentrations over the limits

Finding a compound frequently does not necessarily mean that it is one of

TABLE I. | Number of compounds, number of samples and number of detects with concentrations exceeding the guideline values (GV), 2002–2005.

2002 2003 2004 2005 Compounds above GV (No.) 15 12 16 21	0					
Compounds above GV (No.) 15 12 16 21		2002	2003	2004	2005	
Samples above GV 54 (51%) 39 (37%) 34 (32%) 39 (43° Detects above GV 96 (<1%)	Compounds above GV (No.) Samples above GV Detects above GV	15 54 (51%) 96 (<1%)	12 39 (37%) 68 (<1%)	16 34 (32%) 63 (<1%)	21 39 (43%) 59 (<1%)	

the major threats to algae and fauna in the streams. To get an idea of the possible impact of different compounds, water quality objectives (guideline values) have been developed (Factfile 2). Bentazone, which was found in all samples, has a guideline value of 40 μ g/l and this was not exceeded on any occasion during 2005. However, the guideline value of 21 other plant protection products were exceeded at some time during 2005 (Table 1). Comparing all surface water samples from both the streams and rivers included in environmental monitoring, the guideline value for at least one compound was exceeded in 40% of samples. At the same time, less than 1% of the total number of possible detections (number of samples multiplied by number of compounds analysed) exceeded the guideline value.

Pyrethroids, a group of insecticides, have low guideline values (i.e. they are very toxic for aquatic organisms) of down to $0.0001 \,\mu g/l$, which is below the detection limit. This means that every time a pyrethroid was detected, its guideline value was automatically exceeded.

Better analytical methods

We found more compounds exceeding their guideline value in 2005 than in previous years. This was mainly due to improved analytical methods, i.e. lower detection limits, for certain compounds, including the pyrethroid group. Excluding these, only flurtamon was new for 2005 compared with previous years.

FACTFILE 2

Guideline values

Swedish water quality objectives (so called guideline values) were developed by the Swedish Chemicals Inspectorate as part of their work within the environmental objective "A non-toxic environment".

The guide-line values specifies the highest con-centration of a compound at which negative effects are not expected. Guideline values have been set for about 100 compounds. When a guideline value is being calculated, a safety factor is included and both chronic and acute effects are taken into consideration.

The compounds that most frequently exceeded their guideline values were isoproturon and terbuthylazine. These were found on 7-8 occasions in streams and rivers during 2005. As mentioned above, terbuthylazine is no longer registered for use in Sweden. Compared with the first year in which samples were taken (2002), the number of detections of terbuthylazine above the guideline value was considerably lower in 2005.

Isoproturon is a component of the products Arelon Flytande, Cougar and Tolkan, which are used against weeds, mainly in autumn-sown crops. These products are largely used during the autumn, but sometimes also in spring. Autumn spraying carries an increased risk of leaching, partly because the temperature is lower, which means that degradation is slower, and partly because there is downwards transport of water in the soil profile in the autumn. Isoproturon has a guideline value of 0.3µg/l and also in 2004 it was the compound most frequently exceeding its guideline value.

Findings in groundwater

We take groundwater samples from two sites per catchment and from each

 TABLE 2. | Some examples of permissible compounds detected, their tradenames, areas of use, amounts sold in 2005 and guideline value for occurrence in surface water.

Compound	Tradename (example)	Used against	Sales 2005 (tonnes)	Guideline value (µg/l)
aclonifen	Fenix	weeds	23	0.2
alpha-cypermethrin	Fastac	insects	1	0.001
bentazone	Basagran	weeds	20	40
esfenvalerate	Sumi-alpha	insects	2	0.0001
phenmedipham	Betanal	weeds	30	2
glyphosate	Roundup	weeds	629	10
isoproturon	Arelon, Cougar, Tolkan	weeds	70	0.3
quinmerac	Butisan Top, Fiesta	weeds	5	100
metamitron	Goltix	weeds	84	1
metazachlor	Butisan, Nimbus	weeds	29	0.2
prosulfocarb	Boxer	weeds	22	0.9

site groundwater is extracted from two depths. Sampling takes place four times per year. All samples are taken in the shallow groundwater with the deepest pipe extending to ca six metres under the soil surface.

In 2005, residues of plant protection products were found at low concentrations in all four catchment areas. In the previous year, no residues were detected in the areas in Östergötland and Halland. Most detections in 2005 were in the Scania area, where nine different compounds were found. Four of these came from products that have not been used in Sweden for several years. Low concentrations of metazachlor and bentazone were found on several occasions and in several of the groundwater pipes. During autumn 2004 quinmerac was found, at most in a concentration of 0.32 μ g/l, at one of the sites in the Västergötland catchment. In continued sampling during 2005, quinmerac was found in all samples from the site except one, but the concentrations had decreased to 0.05 $\mu g/l$ or below.

Decreasing concentrations in Scania

Weather conditions and use of plant protection products vary between years and make it difficult to see whether leaching of chemicals is increasing or decreasing with so few years of data. In Scania, however, measurements started in 1990 and during the 1990s concentrations of plant protection products in the stream decreased by 90%. This decrease was due to e.g. farmers being given advice on how to avoid point sources and stricter regulations being introduced for sugarbeet growing. We know very little about the effects of plant protection products found in water courses on the flora and fauna of that environment. This is an area that requires more research. The fact that the maximum limits are being exceeded is a sign that there is a risk of damage by these plant protection products.

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