Irene Wittmer, environmental scientist and doctoral student in the Environmental Chemistry department.
Co-author: Michael Burkhardt

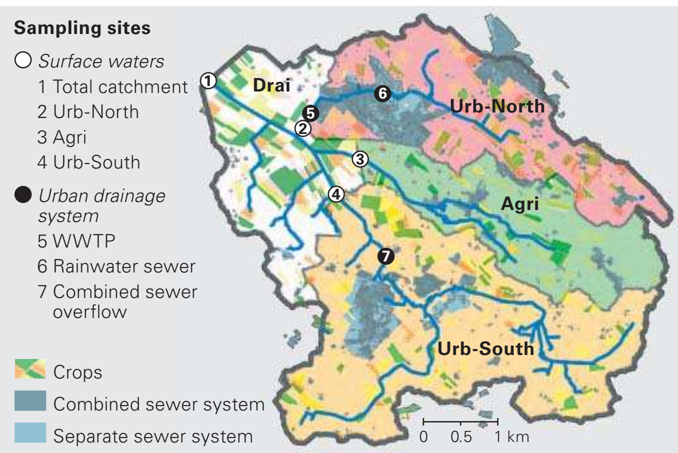
Dynamics of biocide and pesticide input

Biocides and pesticides are used to control harmful organisms in agriculture and in urban areas. But how do these substances ultimately find their way into natural waters? And is agriculture in fact the main source of water pollution? These questions are being investigated by Eawag researchers in various projects.

Agriculture was long regarded as the main source of pesticide input to surface waters. Accordingly, the agricultural use of pesticides is clearly regulated, and people who work with these substances require a licence to do so. When Switzerland's agricultural policy was reshaped around 15 years ago, one of the goals defined was a 50 % reduction in pesticide input. Although pesticide use declined by 25–30 % from 1992 to 2004 [1], agricultural pesticides still contribute to water pollution, despite all the regulations in force.

Input of biocides and pesticides from urban areas. At the same time, initial studies carried out at the end of the 1990s indicated that pesticides, such as the herbicide mecoprop, can also originate from urban areas [2]. In some cases, pesticides are chemically identical to biocides used in urban areas (see Box). On the basis of sales figures, however, it was assumed that the quantities of biocides and pesticides used in urban areas are much lower than in the agricultural sector. The fact that this underestimated the amounts actually used was demonstrated when estimates of consumption were first published in 2007. At approx. 2000 tonnes per year, the level of biocide use in urban areas of Switzerland (excluding alcohol- and chlorine-based disinfectants) [3] is roughly comparable to agriculture, where around 1300 tonnes of pesticides are applied [4]. Eawag is therefore studying in detail the contributions of urban and agricultural sources of water pollution.

Fig. 1: Overview of the study area and the seven sampling sites.
Urb = urban land use, Agri = mainly agricultural use, Drai = drained area.
Degree of urban land use: Agri < Drai < Urb-South < Urb-North.



Amounts of pesticides used. In a large-scale project, biocide and pesticide flows are to be assessed in a selected study area. The catchment, covering a total area of 25 km^2, is close to the Greifensee. It comprises 470 hectares of farmland, as well as two communes (12,000 inhabitants) sharing a wastewater treatment plant (WWTP). The area was divided into four subcatchments (Fig. 1) – one with mainly urban (Urb-North) and one with agricultural land use (Agri) and two with mixed use (Urb-South, Drai). During major rain events in 2007, numerous water samples were collected at four sampling sites in watercourses and three sites in the urban drainage system (WWTP outlet, combined sewer overflow, rainwater sewer). The samples were analysed for a series of biocides and pesticides (see Table on p. 10).

First, however, we conducted surveys on the amounts of pesticides used: almost all the farmers (95 %) and a manageable number of urban households (60 of 1800) were surveyed in the study area. It was found that isoproturon was the pesticide most used for agricultural purposes (107 kg applied), followed by glyphosate, atrazine and terbuthylazine (74, 64 and 42 kg). Four other substances (mecoprop, mesotrione, sulcotrione and diazinon) were used in quantities between 2 and 13 kg.

Pesticides were used in 80 % of the households surveyed, largely to protect roses from insects. In addition, 20 % of the respondents reported that – in spite of a legal prohibition (of which they were unaware) – they also used pesticides on driveways. Surprisingly, in the 60 households, 45 different agents were used, including three of the substances covered by our study – mecoprop, diazinon and glyphosate. Our extrapolation indicated that urban areas are thus not to be neglected as a source of pesticides. As yet, we cannot draw any conclusions concerning the use of biocides; this will first need to be roughly estimated on the basis of consumption figures and product information.

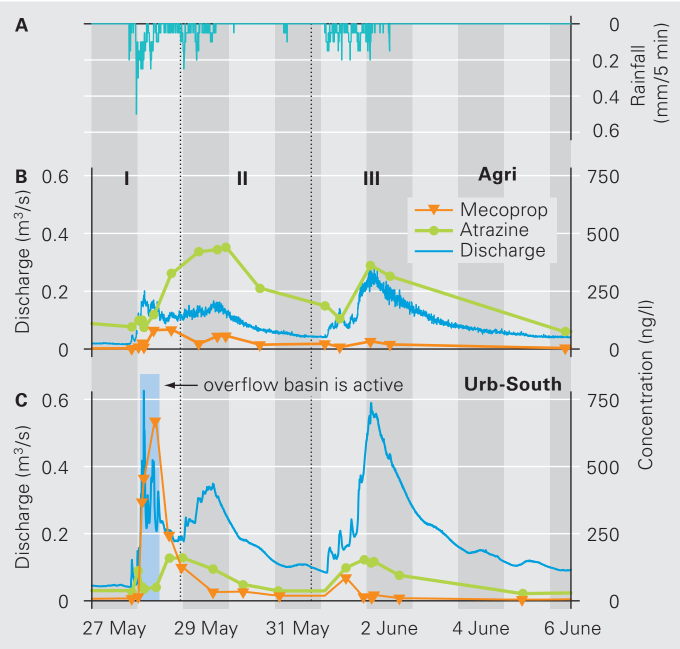


Fig. 2: Concentrations of mecoprop and atrazine measured in two watercourses during rain events between 27 May and 6 June 2007. Rainfall is shown (A), as well as data from the sampling sites in the predominantly agricultural subcatchment Agri (B) and the mainly urban subcatchment Urb-South (C).

Biocides and pesticides transported by rainwater. Pesticides and biocides used outdoors can be washed out and transported into surface waters by rainwater. The example selected here – rain events that occurred at the end of May/beginning of June (Fig. 2A) – illustrates the different concentration dynamics of substances released from an urban and an agricultural area. Curves are shown for atrazine (a substance used exclusively in the agricultural area) and mecoprop (mainly used in the urban area; see Table). These rain events coincided with the agricultural application period for atrazine. The following conclusions can be drawn:

► The discharge dynamics differ markedly for the Agri and Urb-South subcatchments (blue curves in Fig. 2B + C). In the agricultural area, the three peak discharges caused by the rainfall are considerably lower, as water is absorbed and subsequently released by the unsealed soils. In the urban area, by contrast, water runs off the sealed surfaces (roads, paved areas, roofs) without any delay. Some of this runoff drains directly into receiving waters via rainwater sewers, while the remainder enters the combined sewer system and reaches the WWTP via overflow basins. In the case of very heavy rainfall, however, excess water is discharged from the combined sewer overflow tanks directly into the stream. This was the case for the first peak discharge in the Urb-South subcatchment (Fig. 2C).

► Atrazine concentrations rise as stream discharge increases (green curves in Fig. 2B + C). This applies not only for the agricultural area but also, albeit to a lesser extent, for the mixed-use Urb-South area.

► In the urban receiving waters, concentrations of mecoprop (orange curve in Fig. 2C) rise sharply in association with the overspill from the combined sewer overflow basin. Thereafter, the overflow is no longer active and mecoprop concentrations remain low during the two subsequent peak discharges. In the agricultural area, meanwhile, mecoprop concentrations in the stream are only slightly increased during all three phases (Fig. 2B). This is presumably also due to losses from the small number of settled areas in the subcatchment. Similar concentration dynamics were observed for the biocides carbendazim and diuron, also typically used in urban areas.

For rain events in general, therefore, it can be said that increased contamination of natural waters with agricultural pesticides usually occurs during the application season, whereas substances with biocidal and pesticidal effects can enter waters from urban areas throughout the year (cf. Fig. 3A + B). Apart from this rainfall-related input, however, there are constant losses from urban areas and temporary increases in concentrations from agricultural sources. For example, we measured elevated diazinon concentrations in WWTP effluents all year round (> 50 ng/l), and on several occasions, we observed massive increases in pesticide concentrations (up to 20,000 ng/l atrazine), most likely attributable to inappropriate handling or disposal.

Urban areas: a significant contribution to water pollution. As well as studying concentration dynamics, the composition of loads can be assessed in order to determine the relative importance of agricultural and urban sources for the occurrence of substances in natural waters. In the case of the rain event at the end of May, the two agriculturally influenced subcatchments play an important role in the composition of the atrazine load, while the combined sewer overflow and the WWTP (dark brown and dark blue areas in Fig. 3A) contribute virtually nothing to this load. In contrast, the predominantly urban subcatchment contributes decisively to the

Biocides and pesticides

Biocides and pesticides are used to control unwanted organisms. Put simply, while pesticides serve to protect plants, biocides are used for all other types of application (protecting walls and facades, preserving wood, controlling household pests, etc.; see Table). The approval of active substances is regulated by the Biocidal Products Ordinance (VBP) and the Plant Protection Products Ordinance (PSMV). Biocides and pesticides enter natural waters via various pathways. In agricultural areas, pesticides enter watercourses from fields via surface runoff or drainage flows and as a result of inappropriate handling or disposal of spray mixtures. Substances used in urban areas enter surface waters via sewer systems.

mecoprop load observed during the same event. The WWTP and the combined sewer overflow account for up to 25 % of the total load. Measurements of the two substances in the autumn indicate that the atrazine load is extremely low, while the mecoprop load remains high. In addition, the mecoprop load exhibits the same pattern as in the spring. This shows that the sources of mecoprop remain more or less constant. It is not yet clear, however, whether this input is attributable to urban applications (gardening season from May until the end of September) or to constant losses from flat roofs and foundation sealing membranes.

Flat roofs: a possible source of mecoprop. The fact that mecoprop is indeed released from flat roofs is demonstrated by another Eawag study. The herbicide is used to prevent root penetration in bitumen sheets (roofing felt) on flat roofs. A large proportion of the mecoprop is leached out in roof runoff. As several million square metres of flat roofs sealed with bitumen membranes are constructed in Switzerland each year, it is not surprising that mecoprop is ultimately also found in numerous surface waters. It enters these waters either directly via rainwater sewers or in "treated" wastewater – the elimination of mecoprop at WWTPs is only 10–30 %.

Our studies have now shown that, with two more modern root protection agents based on the ethyl hexyl ester (Herbitect®) and the octyl ester of mecoprop (Preventol®B5), hydrolysis and leaching are reduced, compared with the traditional product based on the polyglycol ester (Preventol®B2) (Fig. 4). Leaching behaviour is also influenced by the composition of bitumen sheets – the content and quality of bitumen, polymer and mineral filler: in products with a higher bitumen content, leaching was reduced by another 50 %. In recent years, the concentrations of mecoprop added to bitumen have already been reduced by about half. A further reduction would only be possible if efficacy was still assured, but there is uncertainty as to where the threshold for efficacy lies.

Educating consumers and modifying chemical compositions to minimize losses. Our findings clearly demonstrate that both agricultural and urban applications of biocides and pesticides lead to water pollution. But how can such losses be minimized in the future? One option is to improve the management of biocides and

Applications of the various biocides and pesticides studied. The levels of importance assigned to the individual substances are based on the concentrations measured in the study area (Fig. 1).

important agricultural | less important agricultural | important urban | less important urban | not detected

		Urban: constant	Urban: seasonal	Agricultural: seasonal
		Biocide	**Pesticide**	**Pesticide**
Agricultural	Sulcotrione			Chinese silver grass, maize
	Mesotrione			Maize
	Atrazine			Maize[1]
	Terbuthylazine			Pomaceous fruit, maize
Urban and agricultural	Isoproturon	Facades, preservatives, etc.		Cereals
	Glyphosate		Lawns, railway lines, roadsides, etc.	Fallows, fruit, meadows, pastures
	Mecoprop	Flat roofs[2], foundation sealing membranes	Gardens, lawns, driveways[3], roadsides, etc.	Cereals, Chinese silver grass, fruit, meadows, pastures
	Diazinon	Unknown sources, flea collars[4]	Roses, fruit, ornamentals, gardens	Fruit, sugar beet, rape, vegetables, cut flowers
	Diuron	Facades, preservatives, etc.		Fruit, asparagus, bushes, vines
	Carbendazim	Fungicides for bathrooms, facades, etc.		Fruit, vegetables, rape, potatoes, sunflowers
Urban	Terbutryn	Fungicides for bathrooms, facades, etc.		
	Irgarol	Antifouling coatings, facades, etc.		
	IPBC	Preservatives, wood protection products, etc.		
	Isothiazolinone	Preservatives, facades, etc.		

[1] The sale of atrazine has been prohibited since December 2008. However, farmers are allowed to use up existing stocks until December 2011.
[2] Although mecoprop is not legally classified as a biocide, it can be considered equivalent in terms of its effects.
[3] Although this type of application is illegal, it was confirmed in our survey.
[4] In flea control products, diazinon is neither a biocide nor a pesticide, but a veterinary medicine..

pesticides. There is great potential here, especially with regard to the use of pesticides in urban areas, since many consumers are not familiar with the proper use of these agents – or aware of existing prohibitions. However, there is also room for improved management of pesticides in the agricultural sector, even though training and information are available. But it will be more difficult to minimize diffuse losses from agricultural sources. Often, these losses may even derive from a small proportion of the total field area [5]. For this reason, an Eawag project is currently seeking to identify those agricultural areas where the risk of losses is particularly high.

Another way of reducing losses is to improve the chemical composition of products. In the case of mecoprop in bitumen sheets, this has already been done. "At source" measures are required in applications of this kind, where water pollution cannot be effectively reduced by conventional treatment processes since most of the runoff does not even reach the WWTP. Last year, after three decades in which only Preventol®B2 was used in bitumen sheets, the three main manufacturers modified their formulations to include Herbitect® and Preventol®B5 in the light of our findings. According to recent recommendations issued by the Federal Office for the Environment (FOEN) on mecoprop in bitumen roofing sheets, roof runoff should be infiltrated through a microbially active soil layer to avoid contamination [6]. In addition, the manufacturers and the FOEN recommend that root-resistant sheets should only be used on genuine green roofs; they are not generally required on gravel-covered or bare roofs. Over the long term, all these measures combined could prevent 96–98 % of mecoprop leaching, thus leading to a reduction in water pollution.

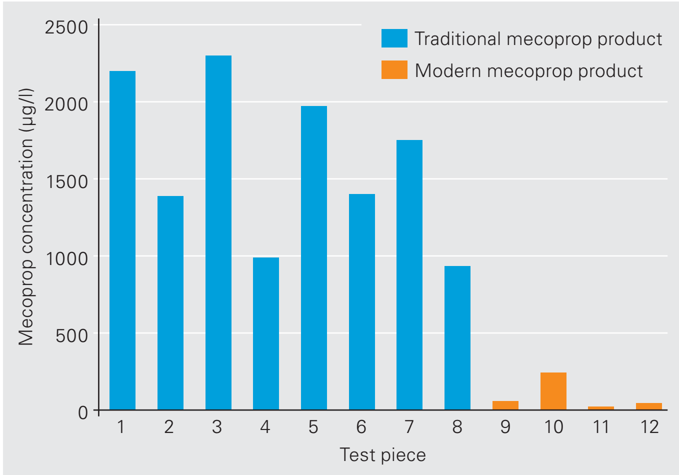


Fig. 4: Leaching of mecoprop from bitumen sheets.

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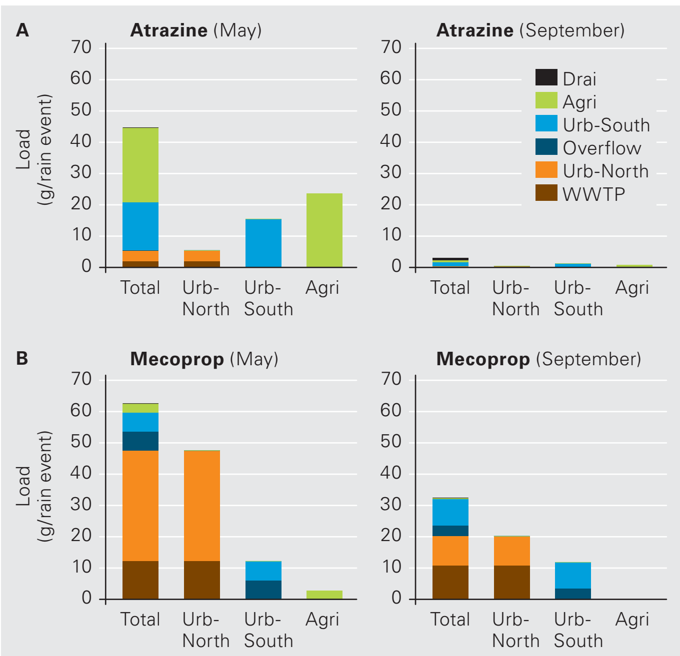

Fig. 3: Comparison of loads of atrazine (A) and mecoprop (B) measured at six different sampling sites (cf. Fig. 1) during rain events in May (60 mm rainfall) and in September (35 mm rainfall).

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