COMPARISON OF PESTICIDE MONITORING TECHNIQUES USING PASSIVE SAMPLES AND AUTOMATIC WATER SAMPLERS IN A SWEDISH STREAM

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There is an increased need for water administrations today to monitor watercourses to comply with the Water Framework Directive. Taking occasional grab samples is simple, but results in a snapshot picture of pesticide occurrence in the water. Pesticide concentrations are known to vary rapidly in running waters and it is therefore difficult to interpret the results from single grab samples. Taking more frequent and/or composite samples requires on the other hand the installation of automatic sampling equipment, which is more expensive and also time consuming.
An alternative, lo-tech, approach is the use of passive samplers with simple cartridges mounted in the stream attached to a pole. The cartridge, containing an adsorbing material and a tracer salt, is left in the stream for 1-3 weeks and then sent to the laboratory for analysis. In this study we used Sorbicells from the company Sorbisense A/S in Denmark.
Parallel sampling using both passive samplers and conventional automatic water samplers were carried out in a small agricultural stream (16 km^2, 89% arable land) in southern Sweden during a nine weeks period in 2010 (June-July and September). Pesticide monitoring has been carried out in this stream since 2002 within the Swedish national monitoring programme. The regular program includes weekly, time proportional, composite water samples analysed for 111 pesticides by the university laboratory (OMK). The analytical program for the passive samples was run by the OMEGAM laboratory in the Netherlands and included 50 of these pesticides. Only pesticide findings exceeding the limit of quantification (LOQ) is included in this summary. The LOQ stated by the laboratories was equal for 12 of the 50 pesticides analysed in parallel, whereas 35 of the pesticides had a lower LOQ in the analyses performed by OMK while OMEGAM had a lower LOQ for three of the pesticides. A total of nine parallel samples were collected.
A total of 16 compounds were detected, with 8 of these being detected using the passive samplers and 13 using the automatic, regular, sampler (Table 1). If limiting the comparison to findings above the lowest common LOQ a total of eight pesticides were detected also with the regular sampler, although only five in common with both methods. Another 12 pesticides were detected in the regular samples using the full analytical programme by OMK (not shown in the table), with azoxystrobin, clopyralid, glyphosate, quinmerac and thiacloprid being the most frequently detected pesticides (6-9 findings).
The total concentration in each parallel sample is presented in Figure 1 (restricting the calculation to findings exceeding a common LOQ for each pesticide). On most occasions the total concentration in the time proportional sample exceeded that of the passive sample, but on two occasions the passive sampling measured higher concentration of pesticides. This was due to findings of elevated concentrations of prochloraz, 0.38 and 0.20 µg/l, respectively, on these occasions without corresponding findings in the regular samples. This pesticide is registered in Sweden for use in cereals and oilseed rape

Table 1. Pesticides detected in stream water during 2010 above the limit of quantification (LOQ) in the regular samples and in the passive samples

Pesticides	No. of findings in regular samples[1]	No. of findings in passive samples	LOQ in regular samples	LOQ in passive samples
BAM[2]	3 (0)	0	0.01	0.07
bentazone	9 (9)	8	0.01	0.01
cyprodinil	1 (1)	0	0.01	0.02
diuron	1 (0)	0	0.005	0.01
fluroxipyr	2 (1)	0	0.02	0.05
imidacloprid	3 (0)	0	0.01	0.05
isoproturon	5 (0)	0	0.002	0.01
MCPA	3 (0)	0	0.01	0.05
metalaxyl	3 (1)	1	0.01	0.2
metazachlor	9 (4)	5	0.002	0.02
metribuzin	8 (6)	1	0.01	0.02
penkonazole	0 (0)	2	0.01	0.02
pirimicarb	5 (1)	0	0.002	0.01
prochloraz	0 (0)	2	0.01	0.2
propiconazole	2 (1)	3	0.01	0.03
prosulfocarb	0 (0)	1	0.01	0.01

[1] Figure in brackets represents the number of findings if using the same LOQ as that of the passive samples.
[2] 2,6-dichlorobenzamide (a degradation compound of the herbicide dichlobenil).

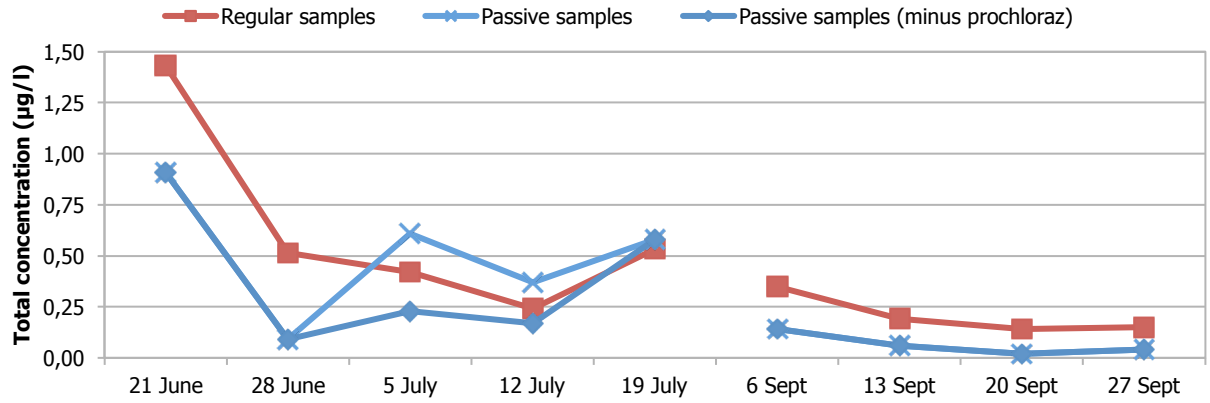

Figure 1. The total concentration (µg/l) of pesticides in each sample from both the regular and the passive samples (based on findings exceeding a common LOQ for each pesticide).

plants during early summer. In the catchment prochloraz was applied in late May on 25 ha. There were a few rainy days the week before the sampling started, but after that there was no rainfall event until the 17th of July. It is therefore difficult to explain why prochloraz was detected in elevated concentrations in two samples preceding this rain event. The regular sampling did not detect any prochloraz in any of the samples despite a limit of detection well below this level (0.003 µg/l). There was no interference registered in the chromatograms for this compound in the analysis of the regular samples and in the spiked samples (natural water) included in each analytical run prochloraz could be detected without any problems. Hence, one possible explanation might be that the material in the passive samplers interferes with the analytical methods for some of the pesticides, creating false positives.

The method to use passive sampling is promising since it offers a relatively cheep and simple sampling method. However, the results from this study indicates that there are certain features that needs to be improved, since the overall analytical results demonstrate little correlation between the two techniques, with only five out of the overall 16 detected pesticides being identified by both sampling procedures. Bentazone was consistently detected in higher concentrations in the regular samples (on average 5 times), whereas metazachlor was consistently detected in lower concentrations (on average 4 times) in the regular samples compared to the passive samples, thus indicating no particular consistency in either method to over- or underestimate pesticide concentrations in this investigation.

Furthermore, our experience was that the passive sampling technique is not quite as straightforward as might have been expected. One crucial aspect to consider was the selection of the right size of the sampling cartridge, which depends on the expected water flow at the location during the sampling season, something that might be difficult to predict if no previous water flow recordings or modelling results are at hand. Another important aspect with the passive samplers used in this study it that the calculation of pesticide concentrations in µg/l is highly dependent on the amount of salt released during the sampling period, a feature that can be quite sensitive and dependent on selecting the right sampling size. One other problem that might occur is dead leaves or other wastes getting stuck in the opening of the cartridge, which means that the sample will not represent the time that you expect. In our investigation we suspect that this might have happened during one week, since we were able to compare the results with a flow measuring station at the sight.

KEY WORDS: pesticide monitoring, passive sampling technique, aquatic environment, surface water.

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