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General Purposes



The evaluation of human exposure to pesticides needs sampling devices that provide reliable measurements, that are easy to handle, and that are economical. The aim of this study was to develop a passive sampler to analyze outdoor air for pesticides, and to inform about potential human exposure to pesticides in the respective environments. The sampling device will use adsorption of pesticides on tubes containing adsorbing materials (XAD-2[®] resin) in proportions allowing an extraction via ASE (accelerated solvent extraction) using little or no organic solvents. This study should be seen as a first attempt to test the applicability of the developed passive samplers for the collection of atmospheric pesticides. The samplers were exposed for an entire year on monthly basis in the open atmosphere of two source sites where pesticides are applied, and three receptor sites where no application takes place.

Materials and Methods



Figure 1. Photo of a passive air sampler and its shelter (behind)

Tubes of adsorb were made at dimensions compatible with the extraction by ASE (direct introduction into 100 mL ASE 300 cells) and allowing an easy manipulation in the field. These tubes of adsorb have to be protected towards climatic hazards (wind, rain, ...) when exposed in the field, and shelters were made as shown on figure 1. The tubes of adsorb were filled with resin XAD-2[®]. This resin was used as it showed very good retention of the monitored atmospheric pesticides (Dobson *et al.*, 2006).

SPME analysis was made with two GC-MSMS runs since some pesticides are better extracted at 30 °C and others at 90°C at the following conditions :

SPME conditions :	
TEMPERATURE :	30°C and 90°C (two independent extractions on the same vial)
DURATION :	45 min.
IMMERSION MODE :	(for both extractions)
FIBER :	PDMS/DVB
CONSTANT STIRRING DURING EXTRACTION	

After exposition, the sampling tubes were extracted following the outline presented below :

ASE conditions :

SOLVENT :	acetonitrile
HEAT :	7 min.
STATIC :	15 min.
FLUSH :	100 %
PURGE :	300 sec.
CYCLES :	3
PRESSURE :	1500 psi (103.38 bar)
TEMPERATURE :	150 °C

Evaporation of solvent to 1 mL in a rotary evaporator

Recoveries of extraction were higher than 70 % for all pesticides.

Preparation of the sample for SPME extraction :

- after concentration, 0.5 mL of the extract were dissolved in 19.5 mL of milli-Q water
- addition of Tecnazen at 100 µg.L⁻¹ as internal standard
- addition of 144 mg of NaCl (2 % saturation)

Pesticides were analyzed using a VARIAN GC 3400 CX equipped with a mass spectrometer SATURN IV (ion trap). All pesticides were analyzed by MSMS in EI mode. Detection limites varied from 0.05 to 6 ng/sampler with variabilities ranging from 7.2 to 19.7 % (intra-day) and from 9.3 to 22.5 % (inter-day).

Results and Discussion

SPME analysis. SPME was chosen for the analysis as this considerably reduces the detection limits, as shown in table 1.

Table 1: Comparison of detection limits for some selected pesticides

pesticide	Limits of detection [ng/sampler]	
	liquid injection	SPME
Cyprodinil	24	0.125
Fenoxycarb	75	5.0
Trifloxystrobin	147	1.25
Flusilazole	93	1.25
Bifenthrin	25	0.125
Tebufenpyrad	83	1.25
Aclonifen	150	0.125
Fenrimol	35	0.125
S-Metolachlor	26	1.25
Spiroxamine	36	1.25
Captan	36	5.0

The passive samplers were exposed on five outdoor sites (figure 2), of which two are source sites and three are receptor sites. Sampling was done at monthly basis for the five sites. Some examples of results are given in figures 3 and 4.

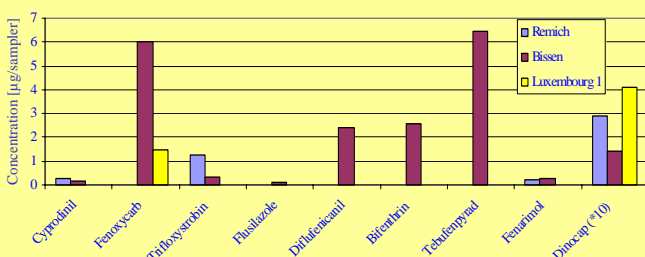
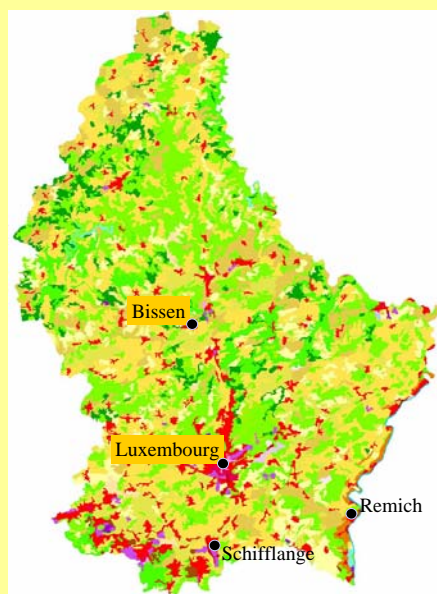


Figure 3. Concentrations measured on three sites (2 source sites, 1 receptor site) in July 2008. Following pesticides were also detected, but at concentrations below the limit of quantification: Aclonifen (Remich), Clofentezin, S-Metolachlor (Bissen), Spiroxamine, Cyprodinil and Trifloxystrobin (Luxembourg 1).

Figure 3 shows that the passive sampler is well adapted to the monitoring of spatial variations of pesticides, and figure 4 shows that it also allows the analysis of temporal variations. The results prove that the passive sampler is sensitive enough to allow the detection and quantification of very low concentrated pesticides found in the atmosphere of receptor sites, and does not saturate in higher contaminated atmospheres found at source sites.



Source sites:

Bissen (agriculture)
Remich (viticulture)

Receptor sites:

Luxembourg (2 sites)
Schifflange

Figure 2. Localisation of the sampling sites

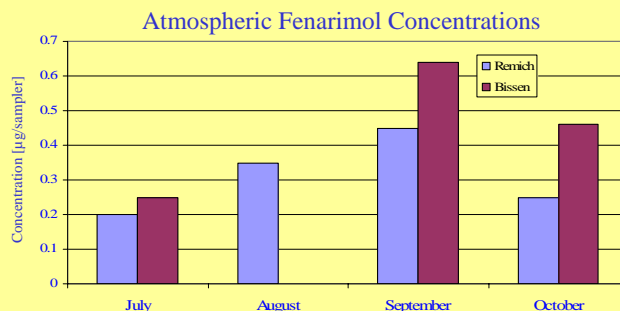


Figure 4. Temporal variations measured for Fenarimol on both source sites from July to October 2008.

Conclusions and Perspectives

Although the sampling campaign has an exploratory character, passive sampling seems to be a good and efficient alternative to conventional active sampling for the characterisation of the atmospheric contamination by pesticides and their spatial and temporal variations. The obtained results show that the developed sampler is well adapted to the sampling of atmospheric pesticides and allows to analyze spatial and temporal variations of pesticides in air. A next step in the development of the samplers is their calibration in open and closed atmospheres using an air generator. In a third step they will be used on fields in a large scale experiment.