

Can elevated pesticide concentrations in sediments indicate past acute pollution events?

Vincent Pettigrove¹, Silvia Mohr², Lena Reiber³, Stephen Marshall¹, Bryant Gagliardi¹, Stefan Meinecke²

1. Centre for Aquatic Pollution Identification & Management, The University of Melbourne, Vic., 3010, AUSTRALIA

2. Federal Environmental Agency, Schichauweg, 58, 12307, Berlin, GERMANY

3. Helmholtz Centre for Environmental Research, Leipzig, 04318, GERMANY



Introduction

Pesticides are usually measured in surface waters but their presence in sediments is often ignored. Several Australian studies have found the concentrations of many pesticides, including hydrophilic ones, can be 100 to 1,000 times higher than in overlying waters. This raised the question whether sediments can act as passive samplers and could indicate recent acute pesticide events that would be missed in ambient monitoring programs. We therefore conducted an experiment to test whether an acute pesticide event could be detected in surficial and deeper sediments and to determine how long these pesticides may persist in sediments.

We selected five pesticides that have been commonly detected in south-eastern Australia (Schaefer et al, 2011; CAPIM, unpublished data): these being the herbicides simazine and atrazine, the fungicides myclobutanil and pyrimethanil and the insecticide imidacloprid.

Mesocosm Experiment

- 2 X 104 m long outdoor recirculating flumes located at the FSA Artificial Stream and Pond Simulation Facility of the German Federal Environmental Agency were used to conduct the experiment (Figure 1)
- Each flume contained 11.27 m³ of sediment at a depth of 15 cm and a surface area of 59 m²
- Each flume contained four pools (1.2 X 2.7 m) with a fine sediment and sand mixture. Two pools had sediments containing 0.1% organic carbon (d.w.) and two pools had sediments containing 0.9% carbon (Figure 2). The remainder of the stream beds were composed of mineral sand.
- Two wooden logs were inserted at each pool to induce vertical flux (Figures 3 & 4)
- Pre-experiments were conducted using uranine tracer to determine optimal velocity to maximize vertical flux (Figure 3)
- The waters of each stream were spiked with the pesticides for 12 hours and the streams were covered to prevent photolysis of the pesticides.
- After 12 hours the spiked waters were replaced with clean waters
- The concentrations of pesticides in the streams were monitored for the next 400 hours



Figure 1: Stream mesocosm used for this experiment. The frames are suspending logs over the four pools present in the mesocosm



Figure 2: Preparing sediments for the experiment



Figure 3: A pool section



Figure 4: Use of uranine to illustrate vertical flux of surface waters

Results

Pesticide Uptake in Sediments

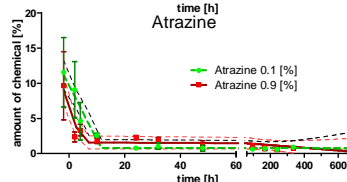
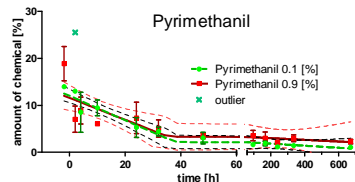
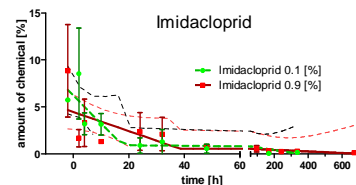
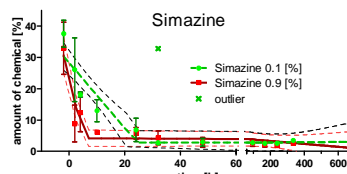
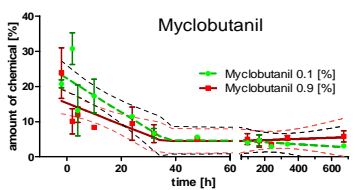
- After 10 hours of exposure to spiked surface waters all 5 pesticides were present in sediments
- Sediment concentrations were 5 to 35% of surface water concentrations
- Similar concentrations were present in sediments with 0.1 and 0.9 % carbon (Table 1)
- 2 hours after spiked waters were replaced with clean waters, the concentrations of pesticides in sediments were variable in 0.1% carbon and 57 to 87% less in 0.9 % carbon (Table 1)

Pesticide	Spike Concentration µg/L	% carbon Sediment (mg/kg)		% Sed/Water
		-2 h	2 h	
Myclobutina	101.89	0.1	21.2	31.3
		0.9	24.3	10.3
Pyrimethanil	102.04	0.1	14.3	19.3
		0.9	19.3	7.2
Simazine	29.69	0.1	11.2	7.8
		0.9	9.8	2.7
Atrazine	29.63	0.1	3.4	2.7
		0.9	2.9	0.7
Imidacloprid	50.9	0.1	2.9	4.3
		0.9	4.6	0.9

Table 1: Pesticide concentrations in water and sediments before (-2 hr) and 2 hr after the spiked waters were replaced with clean waters

Persistence of pesticides in surficial sediments

- **Myclobutanil, pyrimethanil, simazine & atrazine** were present in surficial sediments 4 days after the spiked waters were removed. Their concentrations remained constant from days 4 to 14. There was no discernable difference in concentrations between 0.1 and 0.9 % carbon sediments.
- **Imidacloprid** (Figure 8) was present in surficial sediments at Day 4 in sediments with 0.9% carbon but was below detection limits in the 0.1% sediment. The concentrations in the 0.9% carbon sediment remained constant from Days 4 to 14.



Concentrations (mg/kg) in surficial sediments after 336 hr

% Carbon	0.10%	0.90%
Pyrimethanil	1.5	3.1
Myclobutinal	3.6	5.5
Simazine	1.0	0.8
Atrazine	0.3	0.2
Imidacloprid	0.1	0.2

Discussion

- All five pesticides did persist in sediments for up to 600 hours (25 days) after being exposed to spiked surface waters. Therefore sediments can be effective passive samplers of pesticides including acute pollution events
- Persistence and distribution of pesticides in sediments varied between pesticides
- It is difficult to understand the ecological impact of pesticides measured in conventional passive samplers, whereas their concentrations in sediments do have ecological meaning
- The current study demonstrates that sediments could provide some information on pesticide pollution in the past 25 days. In the field the persistence of pesticides in sediments will be influenced by local conditions such as sediment composition, flows, the presence of biofilms, stream size, weather and in-stream habitat. Therefore, there would need to be an assessment of local streams to determine the period of time streams was may effective passive samplers

Acknowledgements

We thank Dr Rüdiger Berghahn, Dr Claudette Kellar, Stefan Loth and Ronny Schmiediche. This project was funded by the Victorian Government through the Victorian Science Agenda

References

Schaefer R.B, Pettigrove V.J, Rose G, Allinson G, Wightwick A, von der Ohe PC, Shimta J, Kuhne R, Kefferd B.J (2011). Effects of pesticides monitored with three sampling methods in 24 sites on macroinvertebrates and microorganisms. *Environmental Science and Technology* 409:2055-2063