Use of passive sampling devices for monitoring emerging contaminant metaldehyde

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Abstract

Metaldehyde is the active ingredient in 80% of slug pellets used globally. Metaldehyde is not phytotoxic and is used by arable farmers to protect crops such as cereals, oilseed rape, and potatoes and has been identified as an emerging contaminant by NORMAN. High mobility and extensive use allow metaldehyde to enter surface waters where it has been detected above the EU Drinking Water Directive limit of 0.1 μg/L. Water quality monitoring programs rely on the collection of infrequent (2-4 weeks) high volume spot/grab water sampling. This is expensive and time-consuming and can miss sporadic inputs having serious implications for water quality management. We have developed a new variant of the Chemcatcher® (an easy to use, low-cost passive sampling device) for a suite of polar pesticides including metaldehyde which utilises a hydrophilic/lipophilic balance sorbent (Horizon Atlantic HLB-L) as the receiving disk. Initial trials for the metaldehyde Chemcatcher® were undertaken at three catchment sites along the river Thames, where previous spot sample data shows drastic fluctuations in metaldehyde concentrations over time. Spot sample concentrations were measured at concentrations of 71- 309 ngL^{-1} during the two week deployment interval, with the Chemcatcher® demonstrating a TWA concentration 159 ng L^{-1} (with good agreement to the mean concentration of spot samples). It was therefore determined that the Metaldehyde Chemcatcher® can provide accurate reporting and act as a supplement for metaldehyde monitoring programmes.

Keywords: Metaldehyde, Chemcatcher® passive sampler, Surface water, Calibration, In Situ sampling rate.

1. Introduction

Metaldehyde is an active ingredient in most proprietary forms of slug pellets used to protect crops such as oilseed rape and cereals. Metaldehyde is generally applied in the autumn and winter months when molluscs thrive in the wet weather conditions (Green, 1996). Due to its extensive application (FERA, 2013) (1,300 t in 2008-2011, in the UK) and high mobility, metaldehyde has the propensity to enter surface waters during these months. UK water companies must monitor concentrations in surface waters designated for drinking water capitation in compliance with the Drinking Water Directive - 1998/83/EC.(Council Directive, 1998).

Monitoring programmes undertaken by UK water companies have detected concentrations of metaldehyde exceeding 100 ng L^{-1} (limit set by the Drinking Water Directive) during the autumn, necessitating research into alternative removal and remediation techniques. Currently, no cost effective or viable procedures exist for the removal of metaldehyde from water. Despite alternative technologies being promoted (Spieser & Kistler, 2002) (e.g. use of ferric phosphate as a molluscide), metaldehyde is still applied on a large scale in agriculture. In order to determine diffuse sources of metaldehyde that are released to surface waters, effective monitoring techniques are needed.

The current technique for monitoring metaldehyde in surface water is spot (grab or bottle) sampling, followed by analysis in the laboratory. Often the effectiveness of this approach is challenging, particularly where concentrations fluctuate over time. Passive sampling devices (PSDs) have been identified as a method to measure these intermittent fluctuations of metaldehyde as they can deployed in the field for extended periods: days to weeks. Data obtained from PSDs can be used to inform and improve existing models and management plans to determine the sources, distribution, and fate of metaldehyde within river catchments.

2. Methods

2.1 Field trials

The Chemcatcher® passive sampler, developed at the University of Portsmouth, can monitor a range of pollutant classes (Paschke *et al.*, 2006; Schumacher *et al., 2016)* by altering the configuration of the receiving phase towards the analyte of interest. A Chemcatcher® with an Atlantic^{TM} HLB SPE disk (Horizon Technologies) overlain with a polyethersulfone membrane has been developed to

sequester metaldehyde in surface waters. Utilising conventional laboratory extraction techniques liquid chromatography coupled with a triple quadropole mass spectrometer (LC/MS/MS) disk extracts can be analysed (Kingston *et al.,* 2000). Once calibrated it can provide a time weighted average (TWA) concentration for metaldehyde in water. Initial trials for the 'metaldehyde' Chemcatcher[®] were undertaken at two sites in the River Thames catchment, where previous spot sample data showed fluctuations in metaldehyde concentrations over time. Chemcatchers were deployed in triplicate for a period of two weeks. Spot samples were taken at the start of each deployment and on a weekly basis. Laboratory trials have shown that the device gives a linear uptake of metaldehyde over 14 day deployment period. The uptake rate (R_s) estimated was ~ 0.016 L/day.

The TWA average concentration (CW in ng L^{-1}) for metaldehyde can be calculated using Equation 1:

$$Cw = \frac{M_S - M_0}{R_S \times t} \qquad \text{Equation 1}$$

where:

M_S = mass of metaldehyde on Chemcatcher[®] receiving phase disk (ng)

M_0 = mass of metaldehyde on field blank Chemcatcher[®] disk (ng)

R_S = sampling rate of metaldehyde (L/day)

t = Chemcatcher[®] deployment period (days)

3. Results

2.3. Field trials

Figures 2 and 3 show the comparison of spot sample concentrations taken at days 1, 7 and 14 with Chemcatcher[®] TWA concentrations over the two week deployment period at both sites (X and Y).
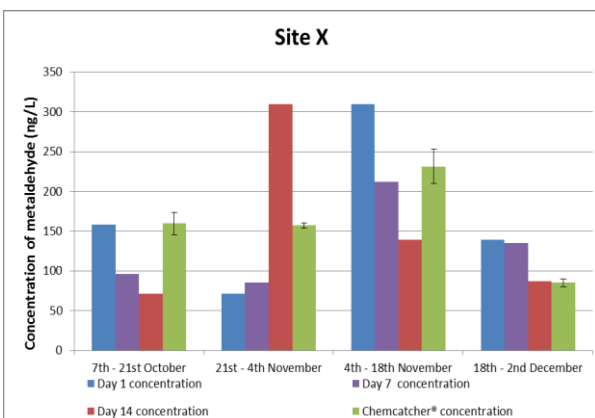

Fig. 2. Comparison of spot sampling and Chemcatcher[®] TWA results for site X.

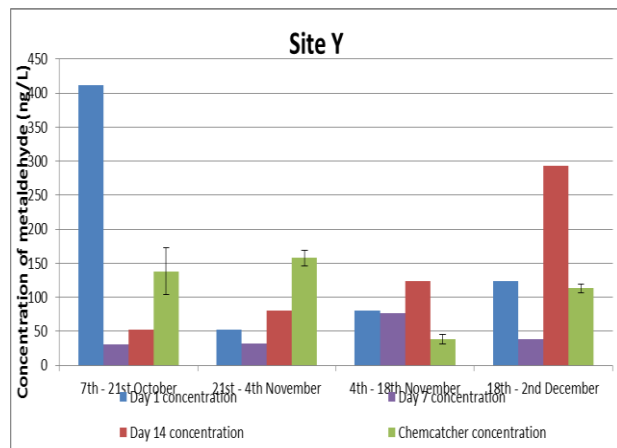Both figures show metaldehyde concentration fluctuation due to diffusive input.

Fig. 3. Comparison of spot sampling and Chemcatcher[®] TWA results for site Y

Table 2 shows the extent of metaldehyde fluctuations with large standard deviations (n=3) observed in the spot samples at both sites X and Y. Chemcatcher® results show a relatively good agreement with the mean concentration of the spot samples for each deployment.

Table. 2. Time weighted average concentration of metaldehyde found at each site after each deployment compared with average spot sample concentrations measured.

Deployment period (2015)	Site	Average (TWA) (ng L^{-1})	Average spot sample (ng L^{-1})
7th-21st Oct	X	159 ± 24	109 ± 45
	Y	138 ± 60	165 ± 214
21st-4th Nov	X	157 ± 6	155 ± 134
	Y	157 ± 20	55 ± 24
4th-18th Nov	X	231 ± 37	220 ± 85
	Y	39 ± 11	93 ± 26
18th-2nd Dec	X	85 ± 9	120 ± 29
	Y	113 ± 11	151 ± 130

4. Discussion and Conclusions

4.3 Field trials

The data provided shows that with the use of the Chemcatcher[®] passive sampler, the risk in missing spikes in metaldehyde with spot samples will diminish. The Chemcatcher[®] will continuously sequester water for a 14 day period. This amounts to 14 days of data, compared to a spot sample which will collect data for approximately 10 seconds for each bottle. This allows Chemcatcher[®] to capture metaldehyde inputs that only some of the spot samples capture. This initial pilot study shows promise for

the Chemcatcher® in being a useful tool for monitoring metaldehyde and for providing data for river catchment management plans.

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Acknowledgments

Disclosures

Unpublished data from Thames Water has been used in this study hence the need for sites X and Y.