Calibration and field evaluation of the Chemcatcher® passive sampler for monitoring metaldehyde in surface water

Glenn D. Castle[a], Graham A. Mills[b], Adil Bakir[a], Anthony Gravell[c], Melanie Schumacher[c], Ian Townsend[d], Lewis Jones[d], Richard Greenwood[e], Stuart Knott[f], Gary R. Fones[a,*]

[a] School of Earth and Environmental Sciences, University of Portsmouth, Burnaby Road, Portsmouth PO1 3QL, UK
[b] School of Pharmacy and Biomedical Sciences, University of Portsmouth, White Swan Road, Portsmouth PO1 2DT, UK
[c] Natural Resources Wales, NRW Analytical Services at Swansea University, Faraday Building, Swansea University, Singleton Campus, Swansea SA2 8PP, UK
[d] South West Water Limited, Peninsula House, Rydon Lane, Exeter EX2 7HR, UK
[e] School of Biological Sciences, University of Portsmouth, King Henry I Street, Portsmouth PO1 2DY, UK
[f] Anglian Water Group, Lancaster House, Lancaster Way, Ermine Business Park, Huntingdon, Cambridgeshire PE29 6XU, UK

ARTICLE INFO

ABSTRACT

Metaldehyde is a potent molluscicide. It is the active ingredient in most slug pellets used for crop protection. This polar compound is considered an emerging pollutant. Due to its environmental mobility, metaldehyde is frequently detected at impacted riverine sites, often at concentrations above the EU Drinking Water Directive limit of 0.1 µg L^{-1} for an individual pesticide. This presents a problem when such waters are abstracted for use in the production of potable water supplies, as this chemical is difficult to remove using conventional treatment processes. Understanding the sources, transport and fate of this pollutant in river catchments is therefore important. We developed a new variant of the Chemcatcher® passive sampler for monitoring metaldehyde comprising a Horizon Atlantic™ HLB-L disk as the receiving phase overlaid with a polyethersulphone membrane. The sampler uptake rate (R_s) was measured in semi-static laboratory (R_s = 15.7 mL day^{-1}) and in-field (R_s = 17.8 mL day^{-1}) calibration experiments. Uptake of metaldehyde was linear over a two-week period, with no measurable lag phase. Field trials (five consecutive 14 day periods) using the Chemcatcher® were undertaken in eastern England at three riverine sites (4th September-12th November 2015) known to be impacted by the seasonal agricultural use of metaldehyde. Spot samples of water were collected regularly during the deployments, with concentrations of metaldehyde varying widely (~ 0.03–2.90 µg L^{-1}) and often exceeding the regulatory limit. Time weighted average concentrations obtained using the Chemcatcher® increased over the duration of the trial corresponding to increasing stochastic inputs of metaldehyde into the catchment. Monitoring data obtained from these devices gives complementary information to that obtained by the use of infrequent spot sampling procedures. This information can be used to develop risk assessments and catchment management plans and to assess the effectiveness of any mitigation and remediation strategies.

1. Introduction

Metaldehyde is a solid, synthetic, neutral, non-chiral tetramer of acetaldehyde ($C_8H_{16}O_4$) and is used as a potent molluscicide. It is the active ingredient in most formulated slug pellets used commonly to eliminate infestations of slugs and snails on crops such as barley, oilseed rape and wheat [1]. It has been used for this purpose since the early 1940s. The amount of metaldehyde used in pellets varies between 1.5, 3.0 or 4.0% by weight. In the United Kingdom, it is estimated that 80% of arable farmers use metaldehyde, with ~ 460 t applied to fields between 2012 and 2015 [2]. Metaldehyde is predominantly used in the

early autumn to winter months when molluscs thrive in the wetter conditions [3]. Once applied to soil, metaldehyde degrades to acetaldehyde and CO_2, with a half-life reported to vary between 3 and 223 days [4,5]. Metaldehyde is polar and highly water soluble [6], with a low tendency to bind to soil [7] (Table S1). As a consequence, it readily runs off from land and enters surface waters particularly after rainfall events. Once in the aquatic environment, the degradation of metaldehyde is slowed significantly [7], hence, it is considered a semi-persistent pollutant.

The impact of metaldehyde in the aquatic environment has been reviewed recently [8]. Metaldehyde is detected regularly in surface

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waters in the UK with concentrations fluctuating seasonally. Frequently the concentration of metaldehyde exceeds the European Union's Drinking Water Directive limit of 0.1 µg L^{-1} for any pesticide (referred to within in the UK water industry as the prescribed concentration value (PCV) which is legally binding) [9]. Problems arise when such surface water bodies are used as capitation sources for potable drinking water supplies. Metaldehyde has also been detected in ground water (River Thames aquifer, Oxford, UK), above the PCV (0.73–1.00 µg L^{-1}) [10]. Due its physicochemical properties metaldehyde is difficult to remove from water using conventional drinking water treatment processes, such as granular or powdered activated carbon beds [11]. Whilst advanced treatment processes (e.g. use of ultra-violet/titanium dioxide oxidation processes) have potential to remove metaldehyde, these are expensive to operate commercially [8]. Therefore, alternative strategies (e.g. the 'Get Pelletwise' initiative promoted by the Metaldehyde Stewardship Group) or substituting metaldehyde for different molluscicides (e.g. ferric phosphate) are needed in order to protect river catchments [12,13]. Key to the successful delivery of these remedial environmental actions is the establishment of an effective surface water quality-monitoring programme for metaldehyde.

Typically, monitoring programmes rely on the collection of infrequent (e.g. weekly or monthly) spot (bottle or grab) samples of water (1–2 L) followed by analysis in the laboratory. The effectiveness of this approach is limited, particularly where concentrations of pollutants fluctuate significantly over short periods of time (e.g. hours to days), such as those associated with the sporadic application of pesticides. In order to gain a better temporal resolution, different approaches are required. Automated devices (e.g. ISCO – http://www.teledyneisco.com) allow for the frequent collection (hours to days) of water samples and can provide a higher temporal resolution. This equipment, however, has a high capital cost, requires regular maintenance and can be subject to damage or theft in the field [14]. The use of passive sampling devices can overcome many of these drawbacks, as they are relatively low-cost, non-mechanical, require no external power and are easily deployable in many field conditions.

A wide range of passive sampling devices is available to monitor different classes of organic pollutants found in surface waters [15]. These include semi-permeable membranes devices, polymer sheets (e.g. low-density polyethylene or silicone rubber) or Chemcatcher® for non-polar pollutants [16] and the polar organic chemical integrative sampler (POCIS) [17,18], o-DGT [19–21] and the polar version of the Chemcatcher® [22] for polar pollutants. Samplers comprise typically of an inert body housing a receiving phase selective for the compounds of interest, which is usually overlaid by a thin diffusion-limiting membrane. Devices can be deployed for extended periods (e.g. 1–4 weeks) where analytes are continually sequestered from the environment. Depending on the deployment regime, samplers can yield the equilibrium or the time-weighted average (TWA) concentration of a pollutant [23]. The former requires knowledge of sampler/water partition coefficient for the analyte of interest [23]. In order to measure the TWA concentration, the compound specific sampler uptake rate (R_s, normally expressed as the equivalent volume of water cleared per unit time (L day^{-1})) is required. R_s is determined typically in laboratory or in situ field calibration experiments. Mathematical models can also be used to predict uptake based on physicochemical properties [20,23].

We describe the development and evaluation of a new variant of the Chemcatcher® passive sampler for monitoring metaldehyde in surface water. This comprised a hydrophilic-lipophilic-balanced Horizon Atlantic™ HLB-L disk as the receiving phase overlaid with a polyethersulphone (PES) membrane. The R_s of metaldehyde was measured in laboratory and field calibration experiments. The performance of the device for measuring the concentration of metaldehyde was evaluated over a two week period alongside the collection of spot water samples at a number of riverine sites in eastern England, UK. To our knowledge this is the first time a passive sampling device has been used to quantify the concentrations of metaldehyde in surface water. The device has the

potential to be used in river catchment programmes to monitor the impact of this molluscicide and to provide improved, cost-effective information for the future development of environmental remediation strategies.

2. Experimental

2.1. Chemicals and glassware

Unless otherwise stated, chemicals and solvents were of analytical grade or better and were obtained from Sigma-Aldrich (Gillingham, England). Ultra-pure water was obtained from an in-house source (ELGA Purelab Ultra, Marlow, UK) and was used in all laboratory procedures. Metaldehyde (99% purity) and deuterated metaldehyde-d$_{16}$ (> 99 atom% deuterium) were purchased from Sigma-Aldrich and Qmx Laboratories Ltd. (Thaxted, UK) respectively. All glassware and apparatus were cleaned by soaking in 5% Decon 90 solution overnight (Decon Laboratories Ltd., Hove, UK), then washed with water and rinsed with methanol. Calibration standards and test solutions were prepared as described by [24].

2.2. Preparation of Chemcatcher® samplers

Three component PTFE Chemcatcher® bodies (Atlantic design) were obtained from A T Engineering (Tadley, UK). Components were cleaned initially by soaking overnight in a 2% Decon 90 solution and rinsed with water. This was followed by immersion (acetone) in an ultrasonic bath (10 mins), rinsed with water and dried at room temperature. Horizon Atlantic™ hydrophilic-lipophilic balanced (HLB-L) extraction disks (47 mm) (Arc Sciences Ltd., Alton, UK) were used as the receiving phase. Disks were washed by soaking in methanol overnight. Disks were then placed in an extraction manifold and pre-conditioned using methanol (50 mL) followed by water (100 mL) and stored in water prior to use. PES sheet (Supor® 200, 0.2 µm pore diameter) was obtained from Pall Europe Ltd. (Portsmouth, UK) and was used as the diffusion-limiting membrane. PES membrane circles (52 mm diameter) were punched by hand from the sheet and soaked in methanol overnight to remove traces of polyethylene glycol oligomers present as an artifact of the manufacturing process [25]. Afterwards, membranes were rinsed in water and then stored submerged in water until use. Devices were prepared by placing a HLB-L disk (smooth side uppermost) followed by the PES membrane onto the Chemcatcher® supporting plate, ensuring that no air bubbles were trapped in the interstitial space. The two components were secured in place by a retaining ring, which was tightened sufficiently in order to make a watertight seal. Assembled samplers were kept submerged in water (without the transport lid fitted) prior to use in order to prevent the HLB-L disks drying out. Performance reference compounds (PRCs) were not used.

2.3. Extraction of Chemcatcher® samplers

HLB-L disks were removed carefully from exposed samplers using solvent rinsed stainless steel tweezers with the PES membrane being discarded. The disks were placed onto solvent rinsed aluminium foil and allowed to dry at room temperature (48 h). The dried disks were placed in an extraction funnel manifold and metaldehyde eluted (under gravity) with methanol (40 mL) into a pre-washed glass vial (60 mL). HPLC grade water (1 mL) was added (as an analyte retainer) and the solution evaporated to ~ 0.5 mL using a Genevac 'Rocket' centrifugal rotary evaporator (Genevac Ltd., Ipswich, UK). The extract was transferred to a silanised glass vial (2 mL) and the volume adjusted to ~ 1 mL by the addition of methanol.

2.4. Instrumental analysis

Metaldehyde was quantified in all water samples by liquid

chromatography tandem mass spectrometry (LC-MS/MS) using an Agilent 1200RR LC system coupled to an Agilent 6460 tandem mass spectrometer (Agilent Technologies, Santa Clara, USA). The instrument was interfaced with an on-line solid-phase extraction system fitted with a Waters Oasis® HLB cartridge. The full analytical procedure has been described by Schumacher et al. [24]. Metaldehyde in extracts obtained from Chemcatcher® samplers was analysed using a similar procedure with the following modification. One hundred μL of extract (Section 2.3.) was added to a silanised glass auto-sampler vial containing water (900 μL) and 20 μL of internal standard solution (metaldehyde-d$_{16}$, 50 μg L^{-1}) and then analysed as for the water samples.

2.5. Laboratory measurement of sampler uptake rate

Preliminary experiments to investigate the sorption and recovery of metaldehyde from the HLB-L disks were undertaken. A river water sample (10 mL) collected as below was spiked (n = 11) with me-taldehyde to give environmentally relevant concentrations of 300 and 600 ng L^{-1} [26] and extracted under gravity using a pre-conditioned HLB-L disk held in an extraction funnel manifold. The above procedure was repeated with a second sample of river water from the same source. Metaldehyde was eluted and analysed as described above.

A 14-day laboratory calibration experiment was undertaken to de-termine the sampler uptake rate (R_s) for metaldehyde. Three hundred and fifty L of water was collected into a ∼ 400 L pre-cleaned poly-propylene vessel from the River Lliedi, Felinfoel near Llanelli, (latitude 51.6999°N, longitude −4.1446°W). The river water (dissolved organic carbon concentration = 3.34 mg L^{-1} and pH = 7.4) was stored in a temperature controlled room (5.0 ± 1.0 °C) and left to equilibrate prior to use. This value was selected, as it is typical of the temperature of rivers in the UK during late autumn to winter when metaldehyde is most prevalent in surface waters. The concentration of metaldehyde found in the river water was below the limit of quantification (LoQ = 20 ng L^{-1}) [24].

Uptake rate was measured in a calibration rig similar to that de-scribed by Vrana et al. [27], but using a semi-static system rather than a flow-through design. A pre-cleaned glass tank (300 × 300 × 400 mm) containing a rotatable PTFE carousel for holding up to 14 Chem-catcher® samplers on two layers was filled with 16 L of river water and allowed to pre-condition (∼ 18 h). Afterwards, the tank was drained and 14 devices placed into the carousel. The tank was refilled with river water (16 L) that had been spiked with metaldehyde, to give a nominal concentration of 1.7 μg L^{-1}. This concentration was chosen in order to sequester sufficient metaldehyde on the disk to enable quantification at early time points during the calibration experiment. This concentration is often exceeded in river catchments impacted by the molluscicide [26]. Using an overhead stirrer, the carousel was rotated at a speed of 20 rpm; giving a linear water velocity of ∼ 0.2 m s^{-1} over the face of the sampler bodies. This rotation speed was considered representative of water velocity at the riverine sites used for the subsequent field trials. Spiked water in the tank was drained and replenished every 24 h so as to ensure a relatively constant concentration of metaldehyde throughout the experiment. The concentration of metaldehyde in so-lution was measured before and after each tank replenishment in order to monitor the stability of the analyte during the trial. The small well on top of the Chemcatcher® body ensured that the PES membrane re-mained wet during these emptying and refilling operations.

One Chemcatcher® was removed from the carousel after exposures of 8, 24, 48, 72, 96, 120, 144, 168, 192, 216, 240, 264, 288, 336 h. A 'dummy' PTFE body was inserted into the position of each sampler removed from the carousel so as to maintain consistent hydrodynamic conditions in the tank. The temperature of the water was monitored throughout the duration of the study. A blank sampler exposed to the laboratory atmosphere was used to account for any background con-tamination during each operation. The mass of metaldehyde accumu-lated in the HLB-L disk from each exposure time was measured using

the analytical procedure described in Sections 2.3 and 2.4. These data were used to calculate R_S. PES membranes from the deployed Chem-catcher® samplers were also extracted and analysed using the same procedures.

2.6. In-field measurement of sampler uptake rate and field trials

Two types of field tests were undertaken alongside spot water sampling at several riverine locations in the east of England, where oil seed rape is grown extensively. These sites are known to be impacted by inputs of metaldehyde sometimes exceeding the PCV for drinking water. Firstly, R_s for the Chemcatcher® was measured 'in-field' at a site where the concentration of metaldehyde was known to be relatively constant. Here three replicate samplers were deployed for 14 days at a feeder tributary to a reservoir in the Anglian region between 4th–18th September 2015. Secondly, the performance of the sampler was eval-uated at three sites on the River Gwash between 4th September-12th November 2015. Samplers were deployed for five successive periods of 14 days at each of the three locations.

Triplicate Chemcatcher® samplers were used for each field deploy-ment. In order to protect the devices they were placed inside a bespoke stainless steel cage (A T Engineering). A chain was used to secure the cage to a mooring point along the river. This equipment ensured that the samplers remained fully submerged during the deployment period. Upon retrieval, the well in the body of the Chemcatcher® was filled with river water and sealed with the transport lid. Samplers were transported to the laboratory in cool boxes and stored at ∼ 4 °C until analysis. At each location, a field blank sampler was exposed during deployment and retrieval operations and was analysed as per the experimental samplers. Spot samples of river water (250 mL) were collected into pre-cleaned, screw-topped polyethylene terephthalate bottles at set periods (4th, 14th, 18th, 24th, 30th Sept; 7th, 14th, 21st, 28th Oct; 5th, 12th Nov 2015) during the sampler deployments and stored at ∼ 4 °C until analysis. Extraction and analysis were performed as described in Sections 2.3 and 2.4.

2.7. Theory of passive sampling

The theory of the uptake of a chemical by a passive sampling device is well known and has been described extensively elsewhere [15,23,28]. The uptake of an analyte over the time integrative (linear) period is as shown in Eq. (1).

$$Cw = \frac{M_{S(t)} - M_0}{R_S \times t} \tag{1}$$

Where: C_w = concentration (ng L^{-1}) of analyte in water

$M_{S(t)}$ = mass (ng) of analyte in Chemcatcher® receiving phase disk after exposure time t (day)

M_0 = mass (ng) of analyte in receiving phase disk of Chemcatcher® field blank

R_S = sampler uptake rate of analyte (L day^{-1})

For laboratory and 'in-field' calibration studies, R_s can be calculated from Eq. (1) using the slope ($M_{s(t)}\, t^{-1}$) of the regression of the mass in the sampler upon time (over the linear portion of the uptake data) and the concentration (C_w) in the water. Values for R_s can then be used in field trials to estimate C_w and this corresponds to the TWA concentra-tion of the chemical over the deployment period.

3. Results and discussion

3.1. Performance of the HLB-L receiving phase disk

The use of HLB-L disks as a receiving phase for the Chemcatcher® is new. This sorbent comprises a specific ratio of two monomers, hydro-philic N-vinylpyrrolidone and lipophilic divinylbenzene and provides high capacity for the retention of a wide range of polar analytes. Its use

with the Chemcatcher® for sequestering a wide range of pharmaceuticals and personal care products in waste water has been described [22]. This sorbent has been used extensively in the POCIS for monitoring a wide range of polar pollutants [29–31]. The POCIS uses a loose HLB sorbent powder ($\sim$ 200 mg) held between two PES membranes. The material can move and sag towards the base of the device during deployments altering the effective sampling area and hence uptake rates. This impacts on the robustness of the device [32]. The use of a commercially available bound receiving phase sorbent (e.g. Horizon Atlantic™ or Empore™ disks) can overcome this issue and gives better reproducibility.

As metaldehyde is a highly polar substance (log K_{OW} = 0.12) it was important to investigate its retention behaviour and recovery from the HLB-L disk. Results from batch extraction tests using spiked river water showed that this sorbent material was effective at retaining metaldehyde and that the compound could subsequently be eluted readily using methanol. Average recoveries (n = 11) for the duplicate river water samples spiked at 300 ng L^{-1} were 95.5% ($\pm$ 11.2% RSD) and 98.2% ($\pm$ 10.6% RSD) and at 600 ng L^{-1} were 92.7% ($\pm$ 4.1% RSD) and 95.5% ($\pm$ 4.7% RSD). These data indicated that this disk could be used as a receiving phase in the Chemcatcher® for the sequestration of metaldehyde.

3.2. Measurement of sampler uptake rate

3.2.1. Laboratory calibration

The water temperature (5.0 $\pm$ 1.0 °C) and concentration of metaldehyde in the test tank was stable over the 14-day period of the trial. The mean concentration measured (n = 11) each time before the tank was drained was 1.72 µg L^{-1} ($\pm$ 0.04 SD). The mean concentration measured (n = 13) each time after the tank was re-filled was 1.74 µg L^{-1} ($\pm$ 0.04 SD). A two-sample *t*-test showed that there was no significant difference (p = 0.161) between these two concentrations. A simple linear regression of the mass (ng) of metaldehyde accumulated in the disk on time of exposure (h) (Fig. S1) was highly significant (p < 0.001) and gave a good a fit (R^2 = 0.97). The slope of the linear regression equation was 1.13 (ng h^{-1}) giving a R_S = 15.7 mL day^{-1}. This would represent $\sim$ 220 mL of water cleared by the sampler over a typical 14 day field deployment. Unlike with many non-polar pollutants, longer field deployments for such highly mobile and often sporadic polar contaminants are unwarranted when investigating inputs into river catchments. The mass of metaldehyde found in the laboratory blanks was below the LoQ of the instrumental method. The intercept was -6.55 h (standard error 5.29, 95% confidence interval -17.23 to 4.14) and was not significantly different from zero indicating no lag phase in the uptake of metaldehyde caused by sorption of analyte to the polymeric diffusion limiting membrane. The absence of a lag phase was substantiated as no metaldehyde was detected in the PES membranes from the deployed Chemcatcher® samplers.

There is limited R_S data using the HLB-L disk as a receiving phase for the Chemcatcher®. Using such a device, Petrie et al. [22] determined the R_S values for 59 polar organic micropollutants (log K_{OW} -2.64 to 6.3) over a 9-day deployment in wastewater effluent. Sampler uptake rates ranged from 10 to 100 mL day^{-1}. Ahrens et al. [33] using an alternative receiving phase (SDB-RPS Empore™ disk) determined under laboratory conditions the Chemcatcher® uptake rates for 124 pesticides. R_S values varied between < 1–150 mL day^{-1}. Oasis® HLB sorbent has been used with the pharmaceutical variant of the POCIS (with an active sampling area approximately three times that of the Chemcatcher®) to sequester a wide range of polar pollutants and their associated sampler uptake rates (R_S = < 1–1000 mL day^{-1}) determined in the laboratory [33–35]. This wide variation in measured sampler uptake rates is a function of the physicochemical properties of the analyte and the conditions used for the calibration experiment. Taking these factors into consideration the sampler uptake rate measured for metaldehyde in our laboratory study falls within the range of previously reported R_S values for polar chemicals.

3.2.2. In-field calibration

The concentration of metaldehyde found in spot samples of water collected at the in-field calibration site on days 1, 10 and 14 was 35.2, 37.6 and 46.6 ng L^{-1}, respectively. The mass of metaldehyde accumulated in the receiving phase of the Chemcatcher® sampler (n = 3) after the 14 day deployment was 9.7, 9.8 and 10.3 ng. Using an average aqueous concentration (39.8 ng L^{-1}) over the exposure period this corresponded to R_S = 17.4, 17.6 and 18.6 mL day^{-1} (mean = 17.8 mL day^{-1}) for each device. Metaldehyde measured in the blank samplers was below the LoQ of the analytical method. The R_S values obtained using the two different approaches to calibration were in good agreement. A small variation between the R_S values can be expected. The water temperature in the laboratory tank was maintained at $\sim$ 5 °C, whilst the water temperature at the riverine site during early autumn was $\sim$ 13–14 °C. Higher temperatures increase the rate of diffusion and hence the uptake rate of an analyte and may account for the slightly higher R_S value found for the in-field study. Additionally, the water velocity in the laboratory study was maintained at $\sim$ 0.2 m s^{-1} and it is unlikely that a similar degree of turbulence appertained throughout the duration of the in-field calibration. However, the effect of water temperature and flow on the uptake of a wide range of polar analytes by the POCIS has been shown to be relatively small [36,37]. One solution to overcome issues associated with the variation of R_S with changing environmental conditions during field deployments is the use of PRCs. The effectiveness of this concept for use with polar passive samplers is not fully proven and alternative solutions such as the use of passive flow monitors (e.g. rate of dissolution of calcium sulphate casts) and increasing membrane resistance have been suggested and warrant further study [38,39].

3.3. Field evaluation of Chemcatcher®

The time period of the trial coincided with the agricultural use of metaldehyde (permitted in the UK between 1st August-31st December) within the catchment. The concentration of metaldehyde measured in the eleven spot samples of water taken during the three field trials is shown in Fig. 1(a-c). The values found were variable, ranging from $\sim$ 30-2900 ng L^{-1} and are representative of a river catchment in the UK impacted by high use of the molluscicide [26]. Higher peak concentrations were evident as the trial progressed, corresponding to increased application of metaldehyde to land for crop protection. On 28th October 2015 the concentration of metaldehyde found in spot samples of raw water at the three River Gwash sampling sites was between $\sim$ 10–30 times the permitted PCV for drinking water (Fig. 1(a-c)). Rainfall over this period is shown in Fig. 1(d). The rainfall fluctuated (0.00–11.32 mm), with a number of dry periods. It is difficult to link directly concentrations of metaldehyde found in the rivers to rainfall events during the trial as there is a number of additional influential factors (e.g. method and application rates of metaldehyde, croppage, field slope and drainage, soil type and moisture deficit) within the catchment that need to be taken into consideration [8].

Deployment of the Chemcatcher® samplers was restricted to 14 days as inputs of metaldehyde into river catchments are known to be episodic [8,26]. It was estimated that even for short periods of time (e.g. 1 day out of a total deployment period of 14 days at a concentration of metaldehyde of only 6 ng L^{-1}) sufficient sequestration of metaldehyde would be obtained for quantitative analysis. Additionally, restricting deployments to two weeks limited the degree of biofouling on the PES membrane of the sampler. TWA concentrations of metaldehyde were calculated using Eq. (1) and the R_S value measured in the laboratory calibration experiment (Section 3.2.1). The data for the three different field deployments are shown in Fig. 1(a-c). At all sites, there was an increase in the TWA concentrations as the trial progressed. The amount of metaldehyde found in the field blank samplers was below the LoQ.

It is difficult to compare directly the water quality data obtained using the two monitoring techniques, particularly where the
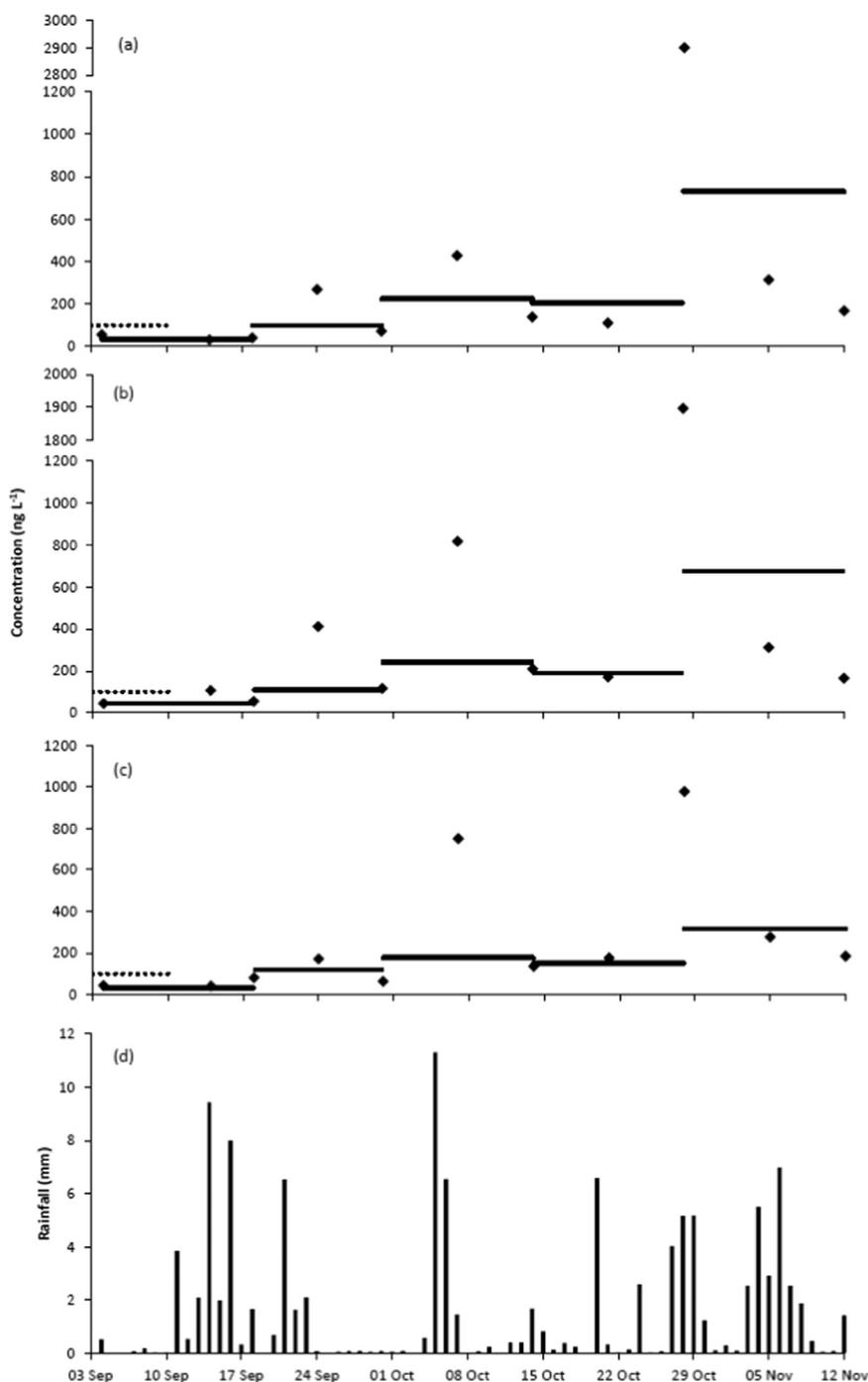
Fig. 1. Concentration of metaldehyde (ng L^{-1}) found in spot samples of water (◆) and time weighted average (TWA) values found with the Chemcatcher® passive sampler (——) at three sites (a, b, c) on the River Gwash (Rutland, UK) during the field trial. Rainfall (mm) in the Central England area (HadUKP - http://www.metoffice.gov.uk/hadobs/hadukp/) is shown in (d). The line (······) in (a-c) shows the European Union's Drinking Water Directive limit of 100 ng L^{-1} for a single pesticide.

concentration of pollutant is episodic [40,41]. Firstly, there is no information on how the concentration of metaldehyde varied in the time interval between collections of spot water samples. Secondly, recent evidence from field trials has shown polar passive samplers are unable to completely integrate stochastic events with rapidly changing concentrations of pollutants [42,43]. In this case the relatively low R_s values obtained for polar compounds may lead to an under-sampling of a pollution event. Due to its high polarity (log K_{OW} = 0.12) it is expected that metaldehyde will be freely dissolved in the water column, with no binding to particulate or dissolved organic matter present. During the first two weeks of the trial at all three locations there was good agreement between the data (concentration of metaldehyde < PCV) obtained by the two monitoring methods. At later periods when there was evidence of significant stochastic inputs of metaldehyde into the

catchment, this was reflected in higher TWA concentrations found using the Chemcatcher®. Here where there was an exceedance of the PCV found in spot samples this was also shown in the TWA values. One approach to improve the comparability of the data obtained by the two techniques is to increase the frequency of spot water sampling or the use of other monitoring methods such as time-triggered automated samplers or on-line systems [8]. These solutions, however, are expensive to employ within remote river catchments.

There has been recent interest in the use of passive sampling devices to detect pesticide inputs into river catchments. Such devices can provide information on the spatio-temporal occurrence, frequency and fluxes of pollutants within a river catchment. This information can assist in the development of remediation and risk assessment strategies [44–48]. Understanding diffuse and sporadic sources of pollutants

within river catchments is important where downstream waters are abstracted for use in the production of potable supplies. This is important for chemicals (such as metaldehyde, clopyralid and quinmerac) that are recalcitrant to remove to concentrations below the PCV using conventional drinking water treatment processes [8,49]. Such processes are expensive to operate and it is more cost effective to prevent the input of specific pollutants at source.

4. Conclusions

Deployment of Chemcatcher® devices in a river catchment in eastern England impacted by agricultural use of metaldehyde showed that they provide complimentary information to the currently used infrequent spot sampling procedures. Data from this study shows that the Chemcatcher® can have a role in river catchment investigations in identifying sources and fluxes of this problematic pesticide, particularly at locations where surface waters are abstracted for subsequent use in the production of potable supplies. Devices can also provide information useful in the management of designated Drinking Water Protected Areas (DrWPAs) and on the effectiveness of long-term remediation strategies (e.g. use of alternative molluscicides such as ferric phosphate). Further work using the Chemcatcher® to address these applications is presently on-going at a number of drinking water supply companies in the UK.

Acknowledgements

Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.talanta.2017.10.053.

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