



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



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## 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  $0.1 \mu\text{g L}^{-1}$  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 ( $R_s = 15.7 \text{ mL day}^{-1}$ ) and in-field ( $R_s = 17.8 \text{ mL day}^{-1}$ ) 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 ( $\sim 0.03\text{--}2.90 \mu\text{g L}^{-1}$ ) 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 ( $\text{C}_8\text{H}_{16}\text{O}_4$ ) 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  $\sim 460 \text{ t}$  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  $\text{CO}_2$ , 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  $0.1 \mu\text{g L}^{-1}$  for any pesticide (referred to within 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 ( $0.73\text{--}1.00 \mu\text{g L}^{-1}$ ) [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 ( $\text{L day}^{-1}$ )) 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- $\text{d}_{16}$  (> 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,  $0.2 \mu\text{m}$  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  $\sim 0.5$  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  $\sim 1$  mL by the addition of methanol.

### 2.4. Instrumental analysis

Metaldehyde was quantified in all water samples by liquid

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