1   **Trends in the use of passive sampling for monitoring polar pesticides in water**

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32 **Abstract**

33 The presence of polar pesticides in environmental waters is a growing problem. After application their

34 migration into the aqueous phase is promoted by their high water solubility. Transport processes are

35 usually complex and inputs are generally stochastic; this makes monitoring of this class of pesticides

36 challenging using low volume spot samples of water. Recently there has been a trend to use passive

37 samplers to monitor pesticides in river catchments as it is an *in-situ* time integrative sampling

38 technique. The three main types of device used for this purpose are, Chemcatcher®, POCIS and o-

39 DGT. This article reviews the fate and current state-of-the-art for monitoring polar pesticides in

40 aqueous matrices. Principles and the theory of passive sampling and strategies for passive sampler

41 design and operation are presented. Advances in the application of passive sampling devices for

42 measuring polar pesticides are extensively critiqued; future trends in their use are also discussed.

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47 **Abbreviations**

48 aqueous concentration (c_W); contaminants of emerging concern (CECs); deployment time (t);

49 diffusion membrane (DM); diffusive layer (DL); dissolved organic carbon (DOC); drinking water

50 quality standards (DWQS); environmental quality standard (EQS); ethylene-vinyl acetate (EVA);

51 limit of detection (LOD); limit of quantification (LOQ); mode of action (MoA); natural organic

52 matter (NOM); *n*-octanol-water distribution coefficient (D_{OW}); *n*-octanol-water partition coefficient

53 (K_{OW}); organic carbon-water partition coefficient (K_{OC}); passive flow monitors (PFMs); passive

54 sampling device (PSD); performance reference compounds (PRC); plant protection products (PPPs);

55 polyethersulphone (PES); polysulphone (PSU); polytetrafluoroethylene (PTFE); sampled analyte

56 mass (m_S); sampler-water partition coefficient (K_{SW}); sampling rate (R_S); solid-phase extraction

57 (SPE); stir bar sorptive extraction (SBSE); time-weighted average (TWA); TWA concentration

58 (c_{TWA}); water boundary layer (WBL); Water Framework Directive (WFD); α-amino-3-hydroxy-5-

59 methyl-4-isoxazolepropionic acid (AMPA).

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1. Introduction

Polar pesticides, defined here as pesticides with an *n*-octonol-water distribution coefficient (log D_{OW}) < 4.5, are contaminants of emerging concern (CECs) [1]. Recent advances in analytical techniques have enabled the detection of CECs in the environment at trace concentrations (ng L^{-1} to µg L^{-1}). CECs have now been detected in waters globally [2]. Knowledge of the environmental presence and fate of CECs is often limited and the risk CECs pose to human and ecological health is not well understood [3]. Polar pesticides encompass numerous fungicides, herbicides, insecticides and other biocides, with new chemism continually developed [4]. The European Union is becoming increasingly aware of the risk posed by polar pesticides, resulting in the inclusion of several in their list of priority pollutants (e.g. diuron) [5,6]. Worldwide only 26% of jurisdictions have equivalent monitoring programmes for environmental pesticide residues [7].

Polar pesticides (including biocides) are used in agriculture, domestically and industrially, and may enter the aquatic environment through several pathways [1]. Polar pesticides have differential environmental persistence and mobility and temporal variation in usage and landscape processes (i.e. precipitation) result in a dynamic fluctuation in aqueous concentrations [8]. Current monitoring programmes rely on spot samples. However, spot sampling only provides a 'snapshot' of analyte concentration at the time of sampling and may not accurately capture variation over time [9]. Additionally, spot sampling may not achieve limits of quantification (LOQ) for all pesticides present in a sample [10]. Another method, passive sampling, relies on *in-situ* accumulation of analytes within a receiving phase during an exposure in sampled waters. Passive sampling overcomes many of the limitations of spot sampling and can provide additional information through time-weighted average (TWA) or equilibrium concentrations of the freely dissolved pesticide fraction [11]. A range of passive sampling devices and receiving phases is available with selectivity for different polar pesticides [12]. This paper briefly discusses the environmental fate of polar pesticides and presents the theory of passive sampling, before reviewing recent applications of passive sampling of polar pesticides in water. Passive sampling techniques for monitoring hydrophobic (non-polar) pesticides was recently reviewed by Taylor et al. [12].

2. Polar pesticides in the environment

2.1 Pesticide use and classification

A pesticide is any product intended to prevent harm caused by pests such as plants, fungi, and insects. This encompasses plant protection products (PPPs) used in agriculture, as well as biocides with public health, veterinary or industrial applications [4]. Most agricultural land globally is treated with pesticides, with usage undergoing a 20-fold increase since 1960, a trend set to continue until 2050, in line with increasing worldwide demand for food [13]. Pesticides vary in terms of their physical and

96 chemical properties and are normally classified according to their chemical group, mode of action
97 (MoA) and target pest. Development of new pesticides is driven by the need for new MoA often in
98 response to developed pest resistance [4]. Over time changes in pesticide usage occur as compounds
99 are approved, banned or become obsolete [11]. There are now hundreds of pesticides in current use
100 and a greater number of legacy compounds; for example the European Union pesticides database
101 contains < 1300 compounds, of which approximately 500 have approval [14]. Table 1 shows use,
102 approval and toxicity [15] [16] for a range of commonly used polar pesticides.

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2.2 Polar pesticides in environmental waters

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105 The fate of polar pesticides in the environment is a function of their physicochemical properties, the
106 environmental compartment of residence and transport processes that take place in each
107 environmental compartment [17,18]. To describe the fate of persistent and mobile organic compounds
108 Reemtsma et al. [10] conceptualize a partially closed system with pollution sources, pathways,
109 environmental compartments and barriers. Figure 1 is an adaptation of this concept for a partially
110 closed system appropriate for pesticide fate (i.e. a river catchment). Sources, environmental
111 compartments and attenuation, transport and retention within the system are presented.

112

2.3 Sources

113

114 Environmental sources of polar pesticides and biocides vary widely and include application in
115 agriculture, amenities (e.g. herbicides on railways and road margins) and households (e.g. in gardens
116 and insecticide treatments for pets) [19]. Factors relating to pesticide use, such as, dose, frequency,
117 timing of application and other effects (e.g. spray drift, drain flow, run-off and infiltration), facilitate
118 initial mobilisation from the site of application [18]. Generally, polar pesticides enter the environment
119 through multiple routes, primarily through diffuse sources due to use in agriculture [18]. Additional
120 contributions to diffuse pollution result from improper handling or disposal, which may permit
121 movement to sewers, ground waters and surface waters [20]. A strong seasonal pattern in usage is
122 observed for most pesticides used in agriculture, caused by seasonal differences in cropping and pest
123 stress [21]. Where areas of high use and potential for mobilisation intersect in a catchment, pollution
124 hotspots making a disproportionately large contribution to pesticide load are probable [18].

125

2.4 Mobility

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127 The affinity for water (solubility) and other interacting phases (sorption) largely determine mobility of
128 polar pesticides [10]. Mobility is not a measure of solubility, but of the preference for aqueous phases
129 over non-polar phases; as such the partition or distribution coefficient between n-octanol and water
130 (K_{OW} and D_{OW} respectively) and organic carbon and water (K_{OC}) are more accurate predictors of

131 mobility [17]. Log K_{OW} is a good approximation of log K_{OC} for neutral pesticides [22]. Alongside
132 coefficients describing partitioning and distribution, other metrics attempt to provide information
133 about environmental fate. Many of these metrics (see Table 2) are derived from predicted values of
134 these coefficients (e.g. K_{OW}). Such predicted values often disagree depending on the calculation
135 method [23]; for example log K_{OW} of actetamiprid, predicted using two different software
136 programmes   is   either   0.62   or   2.55   (http://www.chemspider.com/Chemical-
137 Structure.184719.html?rid=0a73594e-a785-4ffc-b321-136f5b0bdd66). As such the mobility of a
138 compound in the environment cannot be precisely determined through modelling.

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142   *2.5 Persistence*

143 Environmental concentrations of polar pesticides are a reflection of ongoing input, and attenuation
144 occurring through elimination and dilution [20]. Persistence describes resistance to elimination
145 through transformation or removal, that supports longevity in the environment [10,22]. Pseudo-
146 persistence often occurs where the rate of input supports ubiquity in the environment, despite
147 attenuation. Table 2 shows attenuation processes within each environmental compartment.
148 Transformation can occur through microbial degradation in soil, ground, surface and waste waters,
149 chemical oxidation (e.g. in drinking water treatment process such as chlorination and ozonation),
150 photodegradation and hydrolysis [1,11,24]. Removal may occur through sorption to solid surfaces.
151 Metabolites and transformation products may be chemically similar, to the parent compounds, and/or
152 persistent [1]. Persistence in each environmental compartment can be significantly different.

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155   *2.6 Stochastic processes affecting pesticide fate*

156 Pesticide fate in the environment is subject to a high degree of uncertainty over space and time
157 [18,20,25] due to the interaction of:

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159 i)   Anthropogenic, climatic and biotic factors, affecting pesticide use, mobilisation, transport and
160   attenuation.

161 ii) The geological and topological features of the landscape, and the hydrological regime and
162   connectivity of waters.

163 iii) Hydraulic (e.g. suspension of sediments under high flow or stratification of water column
164   under low flow), physiochemical and compositional qualities of aqueous phases.

165 As a consequence of these uncertainties, the dynamics of pesticide fate in the environment are
166 fundamentally complex and fluctuation in aqueous pesticide concentrations may appear random. To
167 simplify and understand pesticide fate it is useful to consider the factors contributing to the
168 uncertainty in mobilisation, transport and attenuation within each compartment separately, which are
169 shown in Table 2. Within this context, any position in a hydrological system exists at a confluence of
170 pesticide transport pathways, originating throughout the upstream catchment (see Figure 1), resulting
171 in pesticide mixes derived from temporally and spatially diverse sources [19]. Increasing hydrological
172 complexity and catchment size, compound the stochastic nature of pesticide flux and the challenge of
173 characterising pesticide pollution at downstream locations. Most current monitoring involves
174 infrequent low volume spot (bottle or grab) sampling; this approach neglects the majority of pesticide
175 flux. More representative sampling methods are required to detect peak concentrations due to short-
176 term events and long-term trends. Time integrative methods such as passive sampling are becoming
177 increasingly favoured within pesticide monitoring programmes.

178

179 ## 2.7 Regulation of pesticide residues in water

180 Regulatory limits are set for pesticide concentrations in water and other environmental matrices such
181 as, residential air, soil and food. These vary by matrix and correspond to the risk identified during
182 pesticide authorisation or reauthorisation [26]. Limits in water are often generic for groups of
183 compounds such as pesticides [22]. In the European Union regulatory limits and monitoring
184 requirements for pesticides in surface water are contained within the Water Framework Directive
185 (WFD) and its daughter directives [5,27–30]. Through implementation of the WFD the European
186 Union aimed to achieve good ecological and chemical status for water bodies throughout Europe by
187 2015, since revised to 2027 [31]. Secondary legislation and amendments to the WFD have set
188 environmental quality standards (EQSs) for priority substances and (generic) drinking water quality
189 standards (DWQS); $0.1\ \mu g\,L^{-1}$ for pesticides and relevant pesticide transformation products, and 0.5
190 $\mu g\,L^{-1}$ for the total of these [6]. Twenty pesticides including several polar pesticides are priority
191 substances, these are generally monitored monthly in all water bodies [11]. Several polar pesticides
192 are also included in the first and second Watch Lists [29] and may become priority substances in the
193 future [6]. Through a delegation of powers, Member States are now encouraged to set EQS for
194 catchment specific pollutants to be included in monitoring. This has been undertaken for several polar
195 pesticides in the UK (see Table 1 for examples). To achieve good chemical status a water body must
196 comply with both maximum allowable and annual average EQS determined through spot sampling,
197 the only approved method [32]. As of 2019, there has been a modest increase in the number water
198 bodies achieving good status, with legacy pesticides responsible for poor chemical status in many
199 failing water bodies [31]. As relatively few polar pesticides are priority or Watch List substances,
200 pesticide occurrence in drinking water is a higher priority in the European Union. The intrinsic

mobility and persistence of certain polar pesticides allows them to pass through drinking water treatment processes, with many frequently detected at elevated concentrations (> DWQS) in treated drinking water, for example the molluscicide, metaldehyde [33]. Regulatory standards and monitoring of pesticides in water in other jurisdictions is often decentralised and based on established guidelines [26].

3. Monitoring of polar pesticides in water

Monitoring of environmental waters is undertaken to obtain qualitative and quantitative information about the biological chemical, hydrological and toxicological status of waters [34]. In the case of polar pesticides this is typically achieved through representative sampling and subsequent analysis (chemical and/or toxicological) within monitoring programmes [34]. Such programmes may be undertaken in commercial, research or regulatory contexts. The requirements of data quality and assurance prescribe the precision, accuracy and sensitivity of sampling and analytical methods. The requirements of data representativeness and availability of resources, determine the spatial and temporal resolution of sampling [34]. The number and identity of pesticides included in the monitoring suite may be informed by legislation, based on known or suspected presence or in screening approaches expanded to all compounds amenable to the selected analytical methods [19].

3.1 Design of monitoring programmes

There is no universal methodology for monitoring polar pesticides. The timing and frequency of sampling, location and number of sampling sites, and the duration of monitoring are all important considerations [11,19,34]. The frequency of sampling and duration of monitoring should consider the dynamic range of pesticide concentration and variability over time to ensure that peak concentrations are not missed, and long-term trends are correctly interpreted [35]. Likewise, the timing of sampling should consider the hydrological system and the influence of events such as rainfall to peak concentrations [36–38]. For example, flow proportional sampling and Lagrangian sampling are often used to accommodate diurnal flow patterns in waste water treatment plants [39], and the travel time between upstream and downstream surface water sites [25], respectively. Monitoring of ground waters may be appropriate at lower frequencies [40]. When selecting sampling locations, it is important to consider the information sampling seeks to provide (e.g. source appointment or describing fate), to ensure this is discriminated within results, and to minimise replication [36]. Increasing the temporal and spatial resolution of sampling will increase data representativeness. In practice workability, time and cost often restrict this [41].

3.2 Comparison of sampling methods

Sampling can be integrative or discrete [34]. Methods can be integrative of flow, time or both [36]. Whilst discrete methods can be representative of the progression in time and/or flow through recurring sampling that is proportional to evolving conditions [42]. Multiple discrete samples can be analysed separately to provide a time series describing concentration fluctuations [43], or pooled to obtain a composite value [42]. Whole water sample collection may be manual, automated or on-line [43]. Sampling may seek to capture different quantities of aqueous pesticides such as, total or dissolved concentration, load or distribution, or qualitative confirmation of the presence of a pesticide [19,32,40]. Comparable results are often possible with different methods, and method performance, versatility, practically, cost and expertise should be considered to select the most appropriate approach [42–45]. Practical handling considerations include the sampling frequency, the equipment transported to field or left *in-situ*, and the need to prepare the site before sampling (e.g. power supply) [43]. The monitoring programme of the WFD mandates spot sampling, however, use of passive sampling is recommended if large temporal variation in concentrations may reduce the representativeness of spot sampling (alone) [42]. Discussing monitoring under the WFD, Allan et al. [34] acknowledge that no sampling method is appropriate in all situations, with each providing different, often complimentary, information. Spot sampling remains the default choice in most pesticide monitoring programmes, despite its lack of temporal representativeness [11]. Table 3 shows attributes of a variety of discrete and integrative sampling methods. The current trend within pesticide monitoring is use of time-integrative methods such as passive sampling. Most studies investigate surface waters, where passive sampling has been extensively compared with other methods. Passive sampling has also been evaluated alongside on-line, automated and spot sampling in a drinking water supply works [43], with exposures occurring in a range of matrices, for example, waste waters [46] and ground waters [47]. Trends in the applications of passive samplers for pesticide monitoring are reviewed in Section 5. The principles underpinning passive sampling are presented in Section 4.

4. Passive sampling of polar pesticides

A recent review of passive sampling of hydrophobic organic compounds [48] presents the monitoring principles for non-polar pesticides. At present, knowledge of the theory underpinning passive sampling of polar organic compounds, such as polar pesticides, is less developed. The absence of a complete mechanistic understanding prevents modelling of uptake and accumulation in polar devices [49,50]. Whilst available models do predict uptake and accumulation within acceptable error for some compounds and conditions, examples of divergent accumulation behaviour occur throughout the literature. Researchers have been unable to attribute, or distinguish, the contribution of phenomena responsible for this variation within, and between, studies [51]. Principles derived from absorption of non-polar organic compounds, a process occurring through partitioning, underpinned the initial theory

271   for passive sampling of polar organic compounds. Passive accumulation of polar compounds occurs
272   through adsorption, the result of concentration dependant interactions between solute and sorbent
273   leading to bond formation [49]. As such the equivalence of the principles of non-polar/polar passive
274   sampling is not always appropriate, for example, the existence of isotropic exchange between bulk
275   and receiving phases for any analyte is uncertain and examples of anisotropic exchange are not well
276   understood [44,52,53]. The following sections introduce the basic theory and range of passive
277   sampling devices (PSDs) used to monitor polar pesticides.

278

4.1 Theory of passive sampling

280   Passive sampling is any technique where mass flux driven by differential chemical potential, causes
281   transfer and retention of contaminants present in a bulk phase of the sampled medium, in/to the
282   receiving phase of a device placed within said medium [54]. Mass flux will continue in the presence
283   of a positive gradient in chemical potential between bulk and receiving phases (i.e. until
284   thermodynamic equilibrium is reached) [48]. Mass flux of freely dissolved analytes from bulk to
285   receiving phases occurs over successive interfacial layers [49]. These layers can include:

286

287   $$\text{WLB}_{\text{sW/DM}} > \text{Fouling film} > \text{DM/DL} > \text{WBL}_{\text{DM/iW}} > \text{WBL}_{\text{iW/S}} > \text{Sorbent}$$

288

289   Where $\text{WLB}_{\text{sW/DM}}$ is the external water boundary layer (WBL) between sampled water and diffusion
290   membrane (or layer). Fouling film refers to any accumulation of sediment and biotic matter formed on
291   the sampling surface during exposure. DM/DL refers to a diffusion membrane (DM) or layer
292   (hydrogel) (DL) separating sorbent and sampled water. $\text{WBL}_{\text{DM/iW}}$ and $\text{WBL}_{\text{iW/S}}$ refer to any WBL
293   present between the DM ($\text{WBL}_{\text{DM/iW}}$) and sorbent ($\text{WBL}_{\text{iW/S}}$) and interstitial water within the sampler.
294   Sorbent describes the receiving phase of the sampler. The device used largely determines the
295   existence and/or importance of transport through each layer. Resistance to mass transfer in each layer
296   is analyte specific and may limit uptake. The extent of any rate limiting effect is determined by the
297   sampler configuration and ambient conditions [55]. When equating resistance to mass transfer over all
298   interfacial layers (i.e. the resistance to mass transfer of uptake), resistance to mass transfer in
299   sequential layers is normally assumed to be additive [56]. It is typically appropriate to consider only
300   the external WLB, DM/DL and sorbent, in approaches using three compartment first order kinetic
301   models [57–59].

302   Some devices promote mass flux (direction of diffusion gradient) occurring perpendicular to the
303   water/sampler boundary and uniform across the sampling face. The design of other devices may

304   permit lateral diffusion, or the formation of variable diffusion gradients where the relative position of

305   layers is not uniform throughout the device, or shifts (e.g. when the sampler moves in the water

306   column) [50,60]. Accumulation in the receiving phase follows first order kinetics, occurring in linear,

307   then curvilinear regimes, ending at equilibrium. In the linear uptake regime, accumulation is time

308   integrative and responsive to changes in aqueous concentration. The rate of mass flux and length of

309   linear and curvilinear regimes, as well as the point at which equilibrium is attained, is specific to the

310   analyte, sampler composition and geometry (configuration), and the ambient conditions during

311   sampling. It must be determined and validated for each polar pesticide in each setting [61]. Many

312   devices have been developed to monitor polar pesticides, with design and operation, optimised to

313   achieve sensitivity and selectivity over exposures of various time lengths. Typically, passive sampling

314   of polar pesticides is undertaken in the linear regime, and the sampled analyte mass (m_S) is related to a

315   TWA concentration (c_{TWA}) in the sampled water over a deployment time (t) through knowledge of the

316   analyte sampling rate (R_S), using first order kinetic models [57,62], from which the following

317   equation (Equation 1) can be derived:

318

319                                   $$c_{TWA} = m_S/(R_S\ t)$$ (Equation 1)

320

321   R_S is a theoretical volume of water sampled per unit time and must be determined for each

322   combination of analyte and device. During the linear regime the aqueous concentration (c_W)

323   corresponds to the rate of accumulation in the sorbent (as R_S should not change). Differences in the

324   speed of transport over layers between sampled water and sorbent, result in analyte specific lag-

325   phases before a change in c_W is registered as accumulation in the sorbent. Lag-phases of between

326   several minutes and days are common. Subsequent increases or decreases in the rate of accumulation

327   following a change in c_W may also experience a lag-phase [46,63,64]. Large lag-phases reduce the

328   accuracy of c_{TWA} during short exposures (< 10 days) [46]. In the curvilinear regime, the rate of

329   accumulation reduces, approaching an asymptote at equilibrium, when solute-sorbent bond formation

330   ceases to be energetically favourable, or assuming isotropic exchange, sorption and desorption are

331   equal (or a mixture of both, producing no net accumulation if exchange is anisotropic). Under what

332   circumstances such bonds are reversible (i.e. desorption) is poorly understood [50]. Equilibrium

333   sampling of polar pesticides is uncommon and may be inappropriate for adsorption-based devices.

334   Use of passive samplers in the qualitative chemical or toxicological monitoring of pesticides, such as

335   screening or bioassays, does not require knowledge of R_S and is growing in popularity [40,46,65,66].

336   It is still necessary to confirm the suitability of the device over the exposure length and aqueous

337   concentration range before devices can be used to monitoring pesticides in water. This is normally

338   performed through calibration experiments.

4.2 Types of passive sampler

Three types of device are predominantly used to monitor polar pesticides, namely the, Chemcatcher®, o-DGT and POCIS [67]. These passive samplers typically operate in the linear/integrative mode for monitoring polar pesticides and not in the equilibrium mode. However, if deployed for long periods of time (~months) they will move into the equilibrium phase and thus unable to elucidate TWA concentrations. The choice of diffusive membrane/layer and receiving phase is made to alter the performance of each device. The following sections and Table 4 present practical aspects of the design, handling, performance and availability of samplers used to monitor polar pesticides. Values for LOQ, sensitivity, R_S and linear period (i.e. integrative time) contained in Table 4 are taken from selected calibration studies. These values are indicative of performance and should be used only to compare device configurations. R_S values reported in the literature often disagree. Reviews of Chemcatcher® [68,69], polar organic compound integrative sampler (POCIS) [49], and o-DGT [70], assemble data from multiple sources and discuss the inter-comparability of values for each device.

i)   Chemcatcher®

The Chemcatcher® comprises a reusable three-part polytetrafluoroethylene (PTFE) body (base plate, retaining ring and transport lid) housing a commercially available solid-phase extraction (SPE) disk (Empore™/AttractSPE™/Atlantic™) receiving phase, overlain with a DM. Sorbent chemistry and DM composition and structural properties (e.g. membrane thickness or pore size) are selected based on affinity for monitored pesticides and required performance (e.g. integrative time or LOQ). Since Kingston et al. [71] developed the Chemcatcher® several iterations of the design have occurred, with two designs in current use. Each design has an internal volume and sampling area that accommodates SPE disks with diameters of either 52 mm (Atlantic design) or 46 mm (Empore design). Repeatability is aided through use of DMs and receiving phases with known properties (e.g. thickness, pore size, sorbent mass and distribution). The main differentiation between the Chemcatcher® and other devices is the use of commercially available SPE disk receiving phases. Whether this differentiation is advantageous or restrictive is a matter of opinion, as the uniformity in device properties, could equally be considered in terms of the lack of ability to optimise sorbent mass or use mixed sorbents, as is seen with other samplers. Likewise, fewer sorbent chemistries are available in the SPE disk format than in granular forms. What is certain is that the simplicity of preparation and handing means that performance bias resulting from user proficiency is less likely to occur than with POCIS, and to a much greater extent o-DGT. Occasionally improvised Chemcatcher® type devices are also used [72], however, problems resulting from the inconsistency of construction of such devices have been reported (e.g. DM losing contact with disk) [46]. Only one face of the receiving disk of the Chemcatcher® is in contact with the DM, however, improvised POCIS type devices containing SPE disks with two sampling surfaces are used occasionally [12]. A polyethersulphone (PES) DM is

375 normally used for monitoring polar pesticides, however, other polymers such as polysulphone (PSU)

376 have been used [72]. The geometric properties of the DM such as pore size, porosity, tortuosity, and

377 membrane thickness may be different between studies with pores of 0.2 or 0.45 μm typical [58] and

378 0.1 μm used infrequently [12]. Sometimes no DM is used, and the receiving phase is exposed directly

379 in the sampled water. This will effect performance (e.g. reducing lag-phases and integrative periods),

380 and may complicate sample clean-up, or increase uncertainty [73]. Naked disks outside the housing

381 are also used as samplers, these are considered separately, as the area of sorbent disk exposed to

382 sampled water has been shown to alter performance [74]. SPE disks used in Chemcatcher® are usually

383 polymeric with moieties able to interact with solutes through polar, non-polar and ionic bond

384 formation [58]. Generally. methanol is the preferred choice of solvent for eluting pesticides from the

385 SPE disks used in Chemcatcher® devices [39]. In the past n-octadecyl disks were used to monitor

386 polar pesticides [12], however, the improved performance of newer polymeric sorbents, mean these

387 are now preferred. Unlike POCIS and o-DGT miniaturised versions of the Chemcatcher® have not

388 been developed.

389

390   ii) POCIS

391 The POCIS contains granular sorbent sandwiched between two DMs, held in place by two stainless

392 steel rings screwed together to form a seal. The internal sorbent is loose and does not fill the

393 interstitial space. Distribution of sorbent within the sampler may change throughout deployments and

394 the area in contact with the DM, is likewise, subject to change [50,61]. As the interstitial space is not

395 filled it is convenient to increase the mass of sorbent within a device, however, sorbent mass of 200-

396 230 mg is typical. Polymeric sorbents are used to monitor polar pesticides, but carbonaceous sorbents

397 are sometimes mixed with polymeric sorbents to improve performance. A variety of sorbents have

398 been shown to have broad affinity for polar pesticides, whilst other sorbents have specific affinity for

399 certain compounds for example a molecularly imprinted polymer sorbent has been developed to

400 monitor glyphosate and α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA) [75]. Two

401 standardised versions of the POCIS: POCIS-pharms and POCIS-pest contain polymeric, or a mix of

402 carbonaceous and polymeric sorbents, respectively. Despite names that suggest suitability for

403 monitoring different classes of compounds both devices are used to monitor polar pesticides.

404 Typically, methanol is used to extract the pesticides from the sorbent [42]. Ahrens et al. [12] found

405 that each version of the POCIS had affinity for a similar number of compounds (106 or 110 of 124

406 investigated), over the a similar range (log K_{OW} -1.9 to 5.2 or -1.9 to 5.3), with similar sorption

407 capacity (sampler and water partition coefficient (K_{SW})) of (log K_{SW} of 4.78 L kg^{-1} or 4.56 L kg^{-1}).

408 PES DMs with pore sizes of 0.1 μm and combined sampling area of 41 cm^2 are typically used to

409 monitor polar pesticides [58], Miniaturised POCIS have also been used with a reduced surface area

410 (16 cm^2) and 0.45 μm pores [58]. Other studies have investigated larger sampling areas (95 cm^2) [76],

411 and the effect of varying sampling area and sorbent mass [77]. Nylon DMs with pores of 30 μm have

412 also been investigated, and were shown to reduce lag-phases [63]. The POCIS is vulnerable to

413 damage as DMs have no solid support and can be punctured during deployments. Lose sorbents must

414 be weighted and conditioned for each device and preparation is more complicated than Chemcatcher®.

415 Conditioning and elution of sorbents is typically undertaken in an SPE column.

416

417   iii) o-DGT

418 o-DGT is a recent variant of the DGT sampler, developed to monitor organic compounds in water and

419 sediment with several variants used to monitor polar pesticides [70]. The o-DGT uses granular

420 sorbents. The mass of sorbent used in each device deviates between studies, however, between 300-

421 350 mg of sorbent is typical. These may be polymeric, carbonaceous or inorganic, such as the TiO_2

422 sorbent developed to monitor glyphosate and AMPA [78]. The important distinction from both

423 Chemcatcher® and POCIS is the use of hydrogel diffusive and binding layers to control analyte uptake

424 and stabilise and ensure constant distribution of sorbent within the device. The binding layer

425 containing sorbent sits at the base of a plastic housing and is overlain by the diffusive layer, held in

426 place by a cap with an aperture exposing the diffusive layer surface to sampled waters. Following use

427 the analytes are eluted from the binding disk using methanol [70]. o-DGT was developed to reduce

428 the influence of ambient conditions on analyte uptake and the requirement to perform calibration for

429 each compound. This is achieved as the resistance to mass transfer in the diffusive layer is similar to

430 the WBL, and as the thickness is far greater, typically 0.75 mm, variation in WBL thickness does not

431 impact R_S significantly. Diffusive layers of between 0.4 and 2 mm have been investigated whilst the

432 sampling area is typically 3.1 cm^2. Larger devices with sampling areas of 4.91 cm^2 [78] and 45 cm^2

433 [79] have been used. Binding layer thickness typically mirrors the diffusive layer, although different

434 hydrogels are often used for each layer (1.5% agarose or 15% polyacrylamide). The thickness of each

435 layer must be precise, and the distribution of sorbent equal, as inaccuracy in either may extend or

436 reduce the length of the diffusional path within the device or promote lateral diffusion, altering

437 uptake. As such preparation of o-DGT requires high user proficiency to avoid bias and is more time

438 consuming than other devices. Ready constructed o-DGTs can be purchased to avoid this bias. To

439 reduce the effect of ambient conditions on device performance o-DGT sacrifices sensitivity and

440 sampling rates meaning LOQ are higher than POCIS and Chemcatcher®. Upscaling of the device

441 would enable reduced LOQ but is complicated by the vulnerability of hydrogel layers to grazing,

442 mechanical damage and dissolution, which prohibits larger sampling areas. One solution to protect the

443 hydrogel layers during deployments is the inclusion of a protective filter or membrane. A range of

444 membranes (cellulose acetate, cellulose ester, Nylon and PES) has been evaluated and were found to

445 suppress uptake [80,81]. Commenting on use of protective membranes, Guibal et al. [70] proposed

446 two points to consider before use:

447

"1: target analytes and their potential interaction with the membrane (several compounds are often targeted and there is no "universally" inert membrane). 2: knowledge of the site of field deployment (including seasonal changes) to evaluate the risk of biofilm development and the relevance using naked o-DGT."

It is probable that use of protective membranes may reintroduce some of the uncertainty associated with transport over layers that the o-DGT tries to avoid. If lower LOQ are desired, multiple devices can be deployed in parallel and extracts combined for analysis.

iv) Other devices

A range of other devices has been used to monitor polar pesticides. These include silicone rubber, sheets [82,83] or stir bar sorptive extraction (SBSE) rods [84,85]. Silicone hollow fibre membranes containing nitric acid have been used to monitor triazine herbicides [86] and silicone sheets with various embedded SPE sorbents have been evaluated [87], and used to monitor equilibrium concentrations of polar pesticides in rivers [88]. Microporous polyethylene tubes filled with hydrogel embedded polymeric [89] and inorganic sorbents [90] have been exposed in river waters to monitor polar pesticides over a broad range of affinities (for different sorbents), or glyphosate and AMPA, respectively. Ethylene-vinyl acetate (EVA) coated Ti sheets have been used to monitor selected pesticides in coastal waters [91]. Other studies have used sorbents typically used in devices such as the Chemcatcher® but without the DM separating sorbent from the sampled water. This has mainly been done where it is desirable to increase the sensitivity of the device when monitoring episodic flux of polar pesticides [92] or when monitoring ground waters [47]. Ground water has also been monitored with an activated carbon sorbent contained in a steel mesh [93]. Aside from use of naked SPE disks in monitoring ground water or episodic pollution, it is unclear if any other devices currently used offer improved performance over the Chemcatcher®, POCIS or o-DGT. Use of naked disks to monitor short duration events, typical of polar pesticide pollution, may be particularly suitable, as the dynamic range and rate of mass flux can be large. For this reason, use of equilibrium devices based on silicone rubber alone or with embedded sorbent probably offers little improvement over discrete sampling methods, as the time to equilibrium is typically several days (i.e. the response time of the device is greater than fluctuation in environmental concentrations). Such devices may be suitable for monitoring other polar organic contaminants with stable environmental concentrations. New devices that remove some of the limitations the Chemcatcher®, POCIS or o-DGT would be welcome.

4.3 Calibration

Calibration experiments are undertaken to establish device performance for specific analytes and exposure conditions. The length of time-integrative accumulation must exceed the duration of sampling and follow first order kinetics. Accumulation in the sorbent should be proportional and

485 responsive to fluctuating concentrations. Calibration should characterise any lag-phases. Calibration

486 of multiple analytes can be performed simultaneously. This is done through laboratory or *in-situ*,

487 exposure within water in which the analyte concentration is known. In most laboratory calibrations

488 samplers are exposed within an analyte fortified matrix, representative of the ambient conditions

489 during field exposure. Devices are removed and analysed at regular intervals (1-2 days) and the

490 fortified matrix is regularly (i.e. static renewal) or continuously (i.e. flow through systems) replaced.

491 Alternative approaches inferring analyte uptake by measuring analyte depletion (i.e. static depletion)

492 are occasionally used. However, analyte losses due to volatilisation, degradation, and sorption to the

493 DM and surfaces within the calibration system reduce the accuracy of such calibrations [49]. There

494 are currently no universally agreed calibration protocols and by necessity, each calibration system is

495 bespoke. This has frustrated the reliability of laboratory derived R_S which often disagree [49,50].

496 Ahrens et al. [12] characterised performance of five devices in laboratory calibrations experiments for

497 124 polar pesticides, showing broad affinity for different configurations. Alternatively, *in-situ*

498 calibrations may be performed in the field were aqueous concentrations are regularly checked with

499 discrete sampling alongside analysis of samplers at regular intervals to convert the mass sampled to

500 R_S [94,95]

501 Quality control during calibration studies and field exposures typically includes duplicate or triplicate

502 deployment of samplers and a number of blanks to identify contamination during sorbent conditioning

503 (solvent blank), construction, (construction blank) and field handling (field blank). A current trend for

504 *in-situ* calibration is use of a variety of methods alongside each other to monitor non-steady state

505 events [9,37,73,74]. Non-steady state conditions have also been replicated in laboratory calibrations;

506 such approaches may help identify confidence intervals for passive sampling data, important for

507 passive sampling of stochastic pesticide pollution. Vermeirssen et al. [57] found that lag-phases of

508 certain moderately hydrophobic pesticides (diazinon and diuron) occurred following increases and

509 decreases in aqueous concentration in a flow-through system, reducing the integrative performance

510 the greater the duration of the lag-phase in relation to the length of exposure. Bernard et al. [96]

511 investigated the integrative performance of POCIS through several static renewal calibrations with

512 fluctuating concentrations of variable intensity and duration. Uptake was linear for most pesticides

513 with lag-phases in accumulation differing based on analyte polarity. Shaw et al. [97] found sampler

514 configuration effected integrative performance with DMs preferable over longer exposures. Naked

515 SPE disks exposed to fluctuating concentrations of atrazine and allowed to equilibrate where found to

516 attain isotherms proportional to the sampling surface area of the disk, not the mass of sorbent.

517 Typically, R_S values are greatest in POCIS as this device has the largest available surface area.

518 Chemcatcher® has the next largest surface area and lower R_s lower values compared to POCIS. This

519 was shown by Townsend et al. when assessing uptake of acidic herbicides [21]. o-DGT has the

520 smallest surface area and hence the lowest uptake rate of these three passive samplers. However

521 device composition, geometry and ambient conditions will all affect the uptake rate in practice. The
522 mass of sorbent and sampling surface area alongside the sorbent to sampling surface area ratio can be
523 used to approximate R_S values for devices of similar composition (i.e. same type and thickness of
524 diffusive layer or membrane) [21]. Such approximations would be imprecise and compound specific
525 as the contribution of different stages in the uptake process to rate limitation for different analytes will
526 produce diverging responses to any change in device configuration. This complexity and uncertainty
527 reinforce the need for device calibration and improved quality assurance and control in passive
528 sampling of polar analytes.

529

530 *4.4 Environmental factors effecting uptake*

531 The properties of the DM and sorbent do not change, however, ambient conditions influence and limit
532 the rate of transport across interfacial layers, and accumulation in the sorbent [98]. Such rate limiting
533 effects either, alter the transport distance or resistance to mass transfer, or influence the rate at which
534 the component mechanisms of transport/uptake occur. Changes in transport distance or resistance to
535 mass transfer can be caused by variation in the thickness of the external WBL or the formation of
536 fouling films [99]. Whilst temperature and matrix composition may also influence solute diffusion
537 [79], speciation [100], or interaction with surfaces of DM and sorbent [101]. Additionally, amenable
538 metabolic pathways or sorption sites present in fouling films may attenuate mass flux, suppressing
539 accumulation in the sorbent [99]. Pesticide use and mobilisation is associated with seasonal and
540 episodic climatic conditions that may also cause rate-limiting effects. These must be overcome,
541 estimated, or preferably quantified, to improve accuracy of quantitative results and identify any
542 uncertainty.

543   i)   Flow

544 The WBL is a region of stationary water at the sampler-water boundary. Analyte transfer across this
545 region occurs only by diffusion. WBL thickness is determined by turbulence at the sampling surface,
546 which is typically greater at higher flow rates, however, translating measured flow to turbulence at the
547 sampler surface is difficult [102]. o-DGT hydrogels are homogeneous and have a similar resistance to
548 mass transfer as the WBL, and it is appropriate to consider the latter as an extension of the former
549 comprising a single compartment [70]. Changes in the thickness of the WBL are normally negligible
550 compared to the thickness of diffusive and binding gels and the rate limiting effect of flow should not
551 exceed 20% of R_S for o-DGT as a result [103]; with the exception of stagnant conditions where
552 significant WBLs have been observed [104]. Diffusion across the WBL is often dominant in limiting
553 uptake in POCIS [49] and Chemcatcher® [46], however, the flow dependency of R_S is not always
554 observed [54,95,105]. At present no approach can adequately compensate for flow effects on R_S.
555 Although, empirical approaches to determining R_S in quiescent and turbulent conditions such as that

556 adopted by Poulier et al. [11] have been used to establish confidence intervals for c_{TWA} of pesticides to

557 support use of POCIS in regulatory monitoring. Likewise, passive *in-situ* methods relating dissolution

558 of gypsum balls to flow rate to infer WBL thickness have been demonstrated, but are not routinely

559 used at present [102,106]. Compounding the challenge of understanding the effect of flow on R_S is the

560 failure to adequately report the hydrodynamic conditions in calibration experiments [50].

561   ii) Fouling

562 The presence of fouling layers composed of microbial flora and fauna and deposited particles on the

563 surface of samplers may alter the resistance to mass transfer and uptake rates. When monitoring polar

564 pesticides exposures exceeding 21 days are less common, reducing the potential for excessive fouling.

565 Lissalde et al. [55] found that POCIS exposed for 14 days in positions parallel or perpendicular to

566 flow, both experienced slight fouling that obstructed DM pores. Accumulation of a range of pesticides

567 and metabolites was statistically similar for both exposure positions. The PES DM used in POCIS and

568 Chemcatcher® resists fouling more than polymeric materials used in other device [62]. Challis et al.

569 [104] noted fouling on o-DGT over 21 days, but no apparent effect on the uptake of a range of

570 pesticides. The composition and thickness of each fouling film is unique, however, [48], and the

571 potential for fouling should always be minimised as any effects on uptake are not understood and may

572 be situational. Harman et al. [107] found that uptake decreased for certain hydrophobic analytes (log

573 K_{OW} 4-6) in pre-fouled POCIS compared to co-deployed un-fouled devices, whilst uptake of more

574 hydrophilic analytes increased. Uptake of thiacloprid in Chemcatcher® was unaffected by fouling on

575 the DM, but fouling on naked disks suppressed uptake, potentially due to interference with the sorbent

576 moieties, impeding analyte uptake and/or recovery [99]. Djomte et al. [108] induced heavy fouling on

577 POCIS through addition of suspended sediments (3600 ppm) to deionised water to compare uptake of

578 12 polar pesticides in PES and Oasis™ HLB of fouled and unfouled devices exposed for 10 days.

579 Visible fouling of DMs increased throughout exposure to suspended sediments. Comparison of DMs

580 prior to exposure and at 10 days under microscopy, confirmed that unfouled DMs remained in the

581 same condition throughout the experiment, whilst fouled DMs were extensively soiled with visible

582 obstruction of (some) pores. Sultana et al. [24] suspected suppressed performance reference

583 compounds (PRC) elimination of POCIS deployed in raw water (drinking water treatment) resulted

584 from fouling but could not rule out other factors (e.g. matrix composition). The consequences of

585 fouling on performance may differ depending on the identity of sampled pesticides and the

586 composition of fouling layers and when fouling does occur the consequence for all sampled analytes

587 should be assessment separately.

588   iii) Temperature

589 Generally, diffusion increases with temperature. The effect of temperature on R_S is less clear,

590 however, with enhanced uptake observed in laboratory exposures [109], contrasting with uptake

591   unaffected by temperature in field exposures [95]. Yabuki et al. [98] found R_S of 43 pesticides in

592   POCIS increased between, 18, 24 and 30 °C, whilst five more hydrophobic pesticides displayed the

593   opposite trend. Two-fold changes in R_S in response to temperature are possible, but any effect may

594   depend on the contribution of diffusion, partitioning and adsorption to rate limitation, which is not

595   understood in POCIS or Chemcatcher® at present. In o-DGT, diffusion within hydrogel layers is rate

596   limiting. Challis et al. [104] recently proposed a method to correct for the effect of temperature on

597   uptake in o-DGT devices.

598   iv) Matrix composition

599   Speciation of ionisable pesticides is pH dependant. pH was found to effect uptake of acid herbicides

600   in o-DGT containing Oasis™ HLB or Oasis™ MAX [110] and Oasis™ HLB or Sepra™ ZT [101].

601   Stroski et al. [101] attributed this to differential proclivity of species for solute-sorbent interactions

602   leading to sorption as uptake of neutral pesticides was unaffected by pH. The effect of pH on solute-

603   sorbent interactions for ionizable pesticides has also been highlighted in Chemcatcher® [58,72] and

604   POCIS [111], with ion-exchange sorbents displaying superior performance for ionised species. The

605   possibility of competition at sorption sites, complex formation and enhanced adsorption (e.g. salting

606   out) due to interference from other matrix components has been suggested [67], however, salinity was

607   not found to effect equilibrium adsorption isotherms in Oasis™ HLB [112]. Likewise nitrate [111] did

608   not influence pesticide uptake in POCIS. Charlestra et al. [53] performed batch experiments to

609   investigate the influence of natural organic matter (NOM) on uptake in POCIS for three moderately

610   hydrophilic pesticides expected to partition to NOM. However, no effect on R_S was observed.

611   Mazzella et al. [61] investigated the potential of dissolved organic carbon (DOC) to influence PRC

612   desorption rates through competition with PRCs, detecting no effect. Suggesting that although solutes

613   capable of competition with PRCs were absent in sampled waters, this did not intimate their non-

614   existence elsewhere. The effect of such competition on PRC correction is unclear, as the dynamics of

615   solute-sorbent bond formation are not understood. Interference in glyphosate and AMPA

616   accumulation in samplers containing TiO_2 sorbents has been inconsistently observed in waters with

617   different metal cation compositions [90]. PSDs are occasionally used to monitor the removal of polar

618   pesticides in treatment process waters where oxidising agents such as ozone and chlorine [113], or

619   electrolytes such as Ca^{2+}, Na^+, and Cl^- [114], are present. Oxidation could suppress analyte uptake, or

620   cause degradation of sorbed molecules. The presence of electrolytes in solution has been

621   demonstrated to influence the sorption affinity of ions to oppositely charged SPE sorbents [114], such

622   an effect could alter uptake to ion exchange sorbents during passive sampling. However, the effect of

623   such oxidants and electrolytes in process waters on sampler performance has not been investigated.

624

625

5. Applications of passive sampling for polar pesticides

Tables 5-8 present recent applications of passive sampling for polar pesticides. For each study, monitored analytes and sampler configuration are summarised alongside a short description of research methods and objectives. The following analyte types are listed in the tables: acid herbicides, fungicides, herbicides, insecticides and molluscicides. Herbicides includes plant growth regulators. Insecticides includes insect repellents. Metabolites means any pesticide transformation product. For brevity the chemical class or name of pesticides is only provided if convenient. Applications covered include event monitoring in sewer overflows [92] and floods [37,74] and evaluation of passive samplers over larger temporal [38] and spatial [115,116] scales. Other applications include the qualitative characterisation of aqueous pesticides has included screening in, ground water [40,76,117] and surface water [118], and comparison with quantitative analysis of sampler extracts [65,95]. Field applications including device performance has been extensively investigated in comparative studies assessing various PSDs [8,12,36,89,119], and other sampling methods [8,9,42,43,84,115] for pesticides in a range of aqueous matrices. Other field applications have focused on passive sampling within the context of regulatory monitoring [11,32,120], and to optimise strategies to characterise pesticide flux and identify analytes originating from episodic or continuous sources within passive sampling data [35,116]. A significant portion of the literature for each PSD concerns calibration and performance, including the influence of ambient conditions on uptake [103,108,121]. Approaches to data quality and assurance have included development and evaluation of methods for PRC correction [52,61,123] and discussion of challenges of the PRC approach [51], use of passive flow monitors (PFMs) [106] and modelled analyte uptake [23,124,125].

6. Conclusions and future trends

Over the last decade, passive sampling of polar pesticides has seen preferential use of POCIS and Chemcatcher®. The introduction of o-DGT marked a divergence from previous sampler designs due to its internal hydrogel layers. It was hoped that by adopting hydrogels, a homogenous material with known diffusional properties, o-DGT would reduce measurement uncertainties arising from analyte uptake within traditional sampler designs. However, o-DGT measurement was found to be vulnerable to lower sensitivity and reduced integrative ability (slow responsiveness). This diminished the suitability of o-DGT for monitoring stochastic pesticide flux.

Trends in the use of alternative devices (e.g. SBSE), were promoted due to user familiarity (used in sample separation), and compatibility with simplified analytical methods for extraction and analysis. However, such devices have only been validated over relativity short deployments and may be

661 unsuitable for monitoring pesticide flux over longer exposures. As such kinetic or equilibrium
662 application of such devices is unlikely to be representative of non-steady state pesticide pollution. Use
663 of sorbent embedded SR (mixed polymer) to sample hydrophobic and polar pesticides in same device
664 has been demonstrated. However, with the need manufacture the sorbent embedded polymer in house,
665 this seems like an unnecessary complication, offering no improvement over parallel exposure of
666 sorbent and SR independently. Other novel designs have incorporated a range of design features taken
667 from established devices with novel materials and geometries. For example, microporous
668 polyethylene tubes combining the diffusive gels and sorbents used in o-DGT enveloped by a porous
669 barrier with a rigid structure, have been developed to overcome vulnerability of hydrogels whilst
670 increasing the sampling area associated with standard o-DGT designs.

671 Predicting future trends in sampler use is difficult, as past decisions to include devices in monitoring
672 were often made based on the habit or past experience of each research group, rather than objectively.
673 Past trends in Chemcatcher® and POCIS development, have focused on novel materials (e.g. DMs or
674 sorbents) expanding the devices to new compounds, recalcitrant to previously available
675 configurations. Whilst methods with broad affinity have continued, largely unchanged, these are
676 exemplified by certain Chemcatcher® and POCIS configurations in continual use, since the initial
677 development of these devices. Future improvements to device configuration will continue with the
678 availability of novel materials, producing incremental expansions in chemical affinity and sensitivity
679 of Chemcatcher® and POCIS. Past deployments in many cases, did not address the causes of
680 uncertainty within passive sampling (e.g. ambient conditions). In future continued failure to address
681 the sources of uncertainty common to polar passive sampling, will allow these uncertainties to
682 propagate in future monitoring programmes. This will frustrate efforts to increase wider acceptance of
683 passive sampling. Recent application of passive sampling has seen devices deployed in surface water,
684 drinking water and ground water, however, use within regulatory monitoring is currently prevented by
685 gaps in the theoretical understanding of the mechanisms occurring during passive sampling, and the
686 absence of validated methods to ensure precision and reproducibility of passive sampling data. In the
687 absence of novel sampler configurations the popularity of Chemcatcher® and POCIS for monitoring
688 polar pesticides will likely continue.

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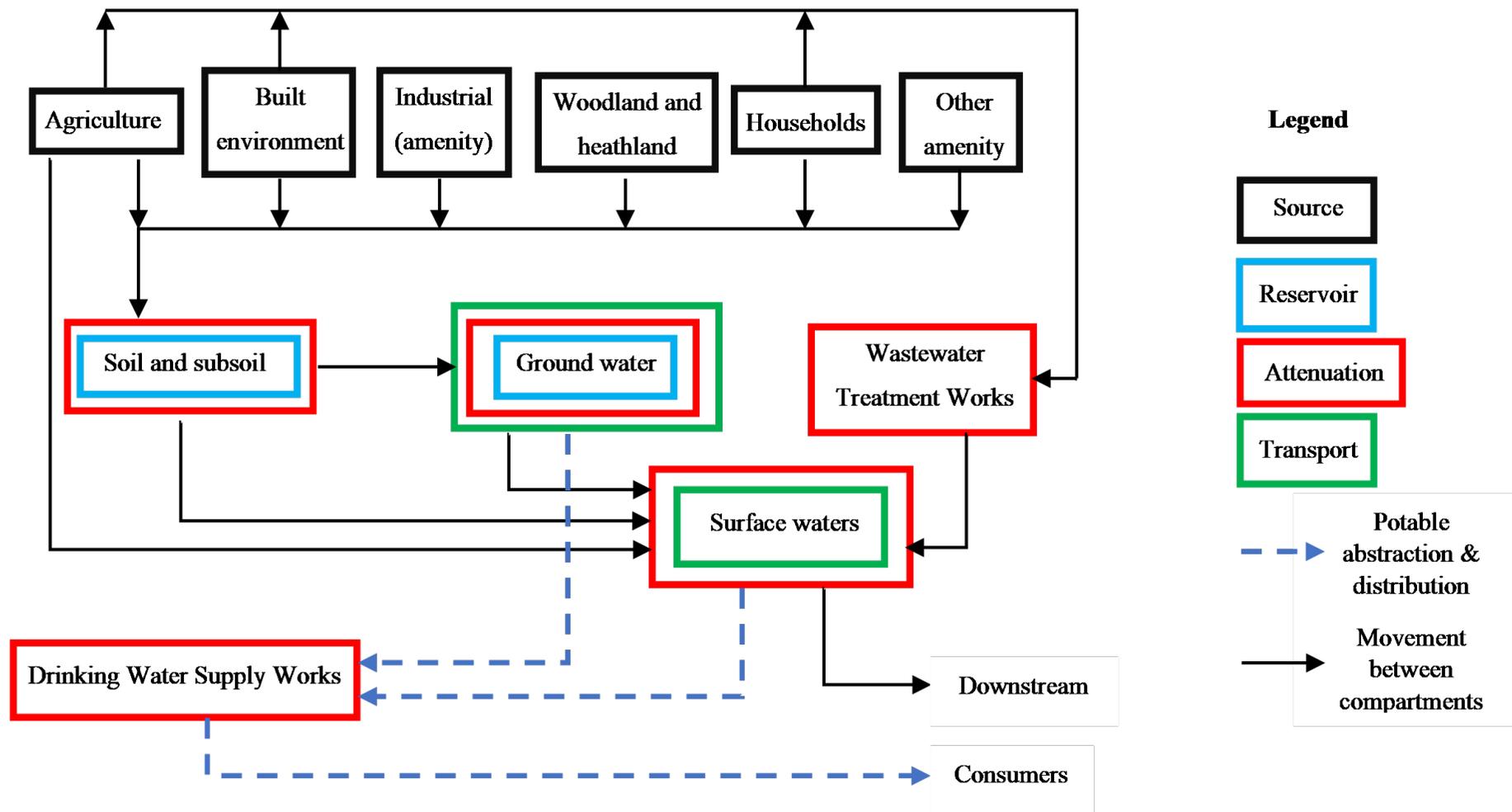
Figure 1. Pesticide sources and processes influencing their fate in different compartments of a simplified water cycle in a partially closed system, such as a river catchment. Adapted from Reemtsma et al. [10].

Table 1 Examples of properties and application of polar pesticides.

Chemical Class	MoA	Type	Applications	Authorisation (EU)	Comments
Neonicotinoids					
Clothianidin	nAChRs agonist	Insecticide	OSR, corn, fruit, potatoes, ornamentals	Restricted	Outdoor use ban.
Imidacloprid	nAChRs agonist	Insecticide	Cereals, potatoes, beet, lawns, maize	Restricted	Outdoor use ban.
Thiacloprid	nAChRs agonist	Insecticide	Apples, pears, carrots, parsnip, brassicas, potatoes, OSR, peas	Approved (CfS)	Candidate for substitution EDC
Triazines					
Atrazine	PSII inhibitor	Herbicide	Pre/post-emergence: Corn, sorghum, turf, asparagus	Expired	Not used since 2010, WFD Priority Substance, still detected in groundwaters and surface water, as well as a number of transformation products.
Simazine	PSII inhibitor	Herbicide	Fruit, vines, hops, legumes	Expired	WFD Priority Substance
Terbuthylazine	PSII inhibitor	Herbicide	Maize, sorghum, fruit, vines, roads, railways, industrial sites	Approved	UK approval withdrawn
Azoles					
Ipconazole	SS inhibitor	Fungicide	Root and leafy vegetables, brassicas, cereals, sunflower	Approved	PAN listed HHS
Propiconazole	ES inhibitor	Fungicide	Mushroom, corn, sorghum, oats, fruit	Expired	Ban March 2020
Tebuconazole	SS inhibitor	Fungicide	Cereals, vines, onions, peas, peppers	Approved (CfS)	Also used as a plant growth regulator.
Urea					
Linuron	PSII inhibitor	Herbicide	Carrots, parsnips, cereals, peas, ornamentals	Expired	UK aaEQS 2 ug/L, MAC 20 ug/L
Isoproturon	PSII inhibitor	Herbicide	Cereals	Expired	Banned 2016, not used since 2011. WFD Priority Substance: aaEQS:0.3 ug/L; MAC 1.0 ug/L. UK aaEQS 2 ug/L, MAC; 20 ug/L. WHO drinking water guideline; 0.009 mg/L
Chlorotoluron	PSII inhibitor	Herbicide	Cereals, potatoes, maize, vegetables, fruit	Approved (CfS)	UK aaEQS; 2 ug/L, MAC; 20 ug/L.
Carboxamide					
Boscalid	DhyE inhibitor	Fungicide	Vegetables, brassicas, onions, garlic, peas, carrots, turnips, fruit	Approved	
Asulam	DhyE inhibitor	Herbicide	Fruit, hops, pasture, amenity, moorland, woodland	Withdrawn	Subject to PIC regulations. *Emergency approval bracken.
Bhenoxy					
2,4-D	Synth Aux			Approved	
MCPA	Synth Aux	Herbicide	Cereals, grass, linseed, asparagus	Approved	Non-statutory standards EA: 12 ug/L; WHO drinking water guideline: 0.002 mg/L
Mecoprop-p	Synth Aux	Herbicide	Post-emergence: lawns, amenity, cereals	Approved	
Pyridine					
Clopyralid	Synth Aux	Herbicide	Cereals, turf, ornamentals, fallow land, industrial sites	Approved	
Fluroxypyr	Synth Aux	Herbicide	Grass, pasture, cereals, orchards, vines	Approved	
Quaternary					
Paraquat	PSI inhibitor	Herbicide	Lucerne, legumes, hops, vines, potatoes, amenity, industrial	Withdrawn	PAN Dirty Dozen; Chemical subject to PIC regulations
Diquat	PSI inhibitor	Herbicide	Potatoes, OSR, fruit, vines, sunflowers, legumes, carrots, beet	Expired	PAN listed HHC
Chlormequat	-	PGR	Cereals, ornamentals, tomatoes, cabbage, cauliflower, radish	Approved	
Misc.					
Quinmerac	Synth Aux	Herbicide	OSR, cereals, beet	Approved	PAN listed HCC
Glyphosate	ESPS inhibitor	Herbicide	Agriculture (many uses), industrial and amenity sites	Approved	PAN listed HCC

Abbreviations: acetylcholinesterase (AchE); candidate for substitution (CfS); endocrine disrupting compound (EDC); nicotinic acetylcholine receptors (nAChRs); mode of action (MoA); maximum allowable concentration (MAC); sterol synthesis (SS); photosystem I (PSI); photosystem II (PSII); DeHydrogenase (DhyE); Synthetic Auxin (Synth Aux); Very long chain fatty acid (VLCFA); highly hazardous chemical (HHC); pesticide action network (PAN); Water Framework Directive (WFD); World Health Organization (WHO).

Table 2 Environment fate of polar pesticides: Properties of compartments and chemicals, pathways, attenuation and uncertainty.

Compartment	Inward pathways	Compartment properties	Attenuation	Chemical properties	Uncertainty
Soil (days-weeks)	- Application - Improper handling, disposal and cleaning of pesticide products and equipment.	- Soil composition and structure (e.g. clay content). - Distance to and interaction with water table. - Microbiome - Subsurface flow and field drains	-Sorption to soil - Photolysis (surface) - Microbial metabolism (aerobic and anaerobic)	- Log K_{oc} (sorption) - Log K_{ow} (solubility) - Ionisation (sorption and solubility) - DT_{50} Soil - Groundwater ubiquity score (GUS) describes the likelihood of a compound to infiltrate to water table	- Usage variation because of differential pest stress and cropping patterns. - Diurnal and annual variation in climatic condition will impact biological activity - Variation in soil moisture and precipitation and resulting runoff to surface waters before compounds enter the soil structure.
Ground water (months-years)	- Infiltration from soil, surface water and sewers	- Flow regime. - Redox potential. - Microbiome - Composition and porosity of aquifer matrix.	- Sorption to aquifer matrix - Microbial metabolism	- Log K_{oc} (sorption) - Log K_{ow} (solubility) - Ionisation (sorption and solubility)	- Metabolite formation. - Farming practices which effect infiltration, such as soil compaction or drainage.
WWTW (hours)	- Sewers, residency in sewers is inconsistent and will vary with distance and flowrate.	- Level of treatment (primary, secondary and tertiary) - Types of processes - Process operation	-Sorption to sediments -Microbial metabolism Aerobic and anaerobic -Oxidation	- Log K_{oc} (sorption) - Log K_{ow} (solubility) - Ionisation (sorption and solubility)	-Affect of changing flow on process performance and enrichment or dilution of pesticide concentrations - Temperature dependence of biotic processes - Disparate nature of microbial communities between locations - Possible back transformation of metabolites.
Surface waters (days-months)	-Runoff from the built and natural environment. -Groundwater -Field drains and ditches - Direct discharges from WWTW	- Flow regime - Microbiome - Matrix composition - Temperature	- Photolysis - Microbial metabolism (planktonic and biofilms) - Sorption to sediment - Volatilisation	- Log K_{oc} (sorption) - Log K_{ow} (solubility) - Ionisation (sorption and solubility) - DT_{50} (Photolysis) - DT_{50} (hydrolysis) - K_{WA}(Volatility)	- The effect of climatic variation on attenuation and inputs, such as sunlight, temperature and precipitation - Usage variation because of differential pest stress and cropping patterns - Variation in the contribution of different inputs to flow - Variation in the flow regime due low/high flows and the presence of vegetation - Penetration of less sunlight under turbid conditions
Drinking water treatment works (hours)	-Ground water abstraction -Surface water abstraction	- Types of processes - Process operation	- Adsorption (activated carbon) - Conventional and advance oxidation processes (chlorination and ozonation) - Reverse osmosis	- Log K_{oc} (sorption) - Log K_{ow} (sorption solubility) - Ionisation (sorption and solubility) - Resistance to oxidation	- Mixing of abstraction from multiple sources - Activated carbons loses efficacy with time and following each regeneration - Certain processes are less efficient in the presence of dissolved organic matter or reduced contact times or under different loads

Table 3. Comparison of water sampling methods for polar pesticide monitoring.

Sampling method	Performance						Versatility				Proficiency and availability			
	SV per sample	SV per day	Flow*	Time*	Sensitivity	Selectivity	Advantages	Disadvantages	Scope to optimise	Restrictions	Equipment	Skill	Usage	Cost
Spot sampling	L	L	N	N	L	H	All analyte fractions present in sample	Stability of labile compounds	Pre-treatment to prevent degradation or sorption of analytes	Logistical	Bottle	L	H	$
							High accuracy	Snapshot only	Repeat sampling	Logistical				
							Sensitivity	-	Increase sample volume	Logistical				
Automated sampling	Op	Op	Op	Op	L-M	H	Stability of labile compounds (in sample)	Stability of labile compounds	Pre-treatment or refrigeration to prevent degradation or sorption of analytes	Logistical	In-situ - Automated sampler and power supply (portable and left on site), may be large and expensive	M	M	$$$
							Representativeness	Problems may occur undetected or only become apparent after the event	-	QA/QC				
							Programmable to take multiple discrete or composite samples	Site requirements (security and power)	-	Logistical				
							Sensitivity	Less freedom to alter sample volume	Increase sample volume (shorter deployment)	Logistical				
On-line monitoring	0	0	Op	Op	H	H	Method developed for analyte	Limited to developed method	Expand method	Analytical	Fixed equipment for sampling and analysis	vH	vL	100x $
							Real time data	-	-	Economical				
							Stability of sample is assured	No sample retained	-	Information				
Passive sampling	L	Op	N	Y	vH	L-M	Freely dissolved fraction sampled	Analyte speciation may affect sampling	-	Information	In-situ - PSD and deployment apparatus (left on site)	H	L	$$$
							Integrative of time	Length of exposure may influence accuracy	Device configuration and exposure time (10-30 days typical)	QA/QC				
							TWA Concentrations can be measured	Requires calibration, may be affected be ambient conditions	Device configuration, deployment apparatus	QA/QC				
							High enrichment of analytes	Limited analyte selectivity	Multiple devices	Logistical				
							Representativeness	Concentration fluctuation is not captured	-	Information				
Active sampling	L	Op	Op	Y	vH	H	Freely dissolved fraction sampled	Analyte speciation may affect sampling	-	Information	In-situ - Active sampling device with power supply (battery or fixed)	H	vL	$$$$
							Integrative of time	Length of exposure may influence accuracy	Device configuration and exposure time (10-30 days typical)	QA/QC				
							Representativeness	Concentration fluctuation is not captured	-	Information				
							TWA Concentrations can be measured	Requires calibration, may be affected be ambient conditions	Device configuration, exposure conditions	QA/QC				
							High enrichment of analytes	Limited analyte selectivity	Multiple receiving phases within the same device	Logistical				

*integrative. Key: high (H); low (L); optional (Op); medium (M); no (N); sampled volume (SV); very high (vH); very low (vL); yes (Y). Abbreviations: passive sampling device (PSD); quality assurance (QA); quality control (QC); time-weighted average (TWA).

Table 4. Practical aspects of the design, handling, performance and availability of passive samplers used to monitor polar pesticides.

Passive sampling device	Specification	Versatility	Preparation and extraction	Design	Selectivity (analyte type/ log K_{OW})	Sorbent	DM/L: (µm/mm)	LOQ (ng L⁻¹)	Linear days (R_S (L d⁻¹))	Commercial suppliers and approx. cost	Ref
POCIS	Two x steel rings securing two x DM, between which granular sorbent is sandwiched, sampling area = 45 cm².	Sorbent mass can be altered or multiple sorbents mixed in a single device. More vulnerable to damage during field exposure than other devices.	Conditioning and extraction solvents and procedures defined for sorbent. Sorbent must be weighted separately for each device. PEG present in PES DM must be removed to avoid matrix effects.	- Type and mass of sorbent - DM, type, thickness, porosity and tortuosity	Neutral: -1.9 - 5.3	Oasis™ HLB	PES: 0.1	< 1 - 50 *200	14 (~ 0.18)	Yes - constructed devices and component parts can be purchased from several suppliers (Affinisep, EHSS, EST). $$$	[12]
					~ -2 - 3.5	Oasis™ HLB	NL: 30	N/A	< 1 – 21 (0.03 - 3.29)		[63]
					0.57 – 5.2	Bond Elut Plexa	PES: 0.1	< 1 - 15	14 (0.09 - 0.22)		[42]
					-1.9 - 5.2	Isolute ENV+/ Ambersorb 1500	PES: 0.1	< 1 - 10 *83	14 (~ 0.22)		[12]
					-2 - 4	Chromabond HR-X	PES: 0.1	N/A	< 21 (0.006 - 0.125)		[111]
					2.6 - 3	Strata X-CW	PES: 0.1	< 5	12 (0.139 - 2.6)		[123]
					Acidic: -2 - 4	Oasis™ MAX	PES: 0.1	N/A	9-21 (0.038 - 0.302)		[111]
					N/A	Envi-Carb	PES: 0.2	< 1	7 (0.035 - 0.07)		[100]
					1.9 - 3.38	Strata X-CW	PES: 0.45	N/A	< 8 (0.047 - 0.076)		[58]
					Glyphosate: -	MIPs	PES: 0.1	N/A	> 14 (0.078)		
							PES: 0.2	N/A	17 (0.111)		
							NL: 30	N/A	< 13 (N/A)		[75]
o-DGT	Plastic housing, 0.75 mm diffusive and binding hydrogels, embedded granular sorbent (binding), sampling area = 3.1 cm².	Reusable (housing only). Preparation is difficult for non-experts. Gels used in construction are vulnerable to damage and may be eaten by biota.	Thickness of diffusive and binding layers and position of sorbent particles govern sampler performance and must be consistent between devices. Device preparation requires more expertise than POCIS or Chemcatcher®.	- Type and mass of sorbent - Type and thickness of diffusive and binding gels	Neutral: N/A (various)	Sepra™ ZT	Ag: 0.75	N/A	> 25	Yes – constructed devices and component parts can be purchased (DGT Research). $$	[101]
							PA: 0.75				
						Oasis™ HLB	Ag: 0.75				
							PA: 0.75				
					1.14 - 3.2	Amberlite XAD 18	Various	0.03 - 2.73 *1094	N/A		[81]
					~ 1.5 - 6	Strata-X	A = 45 cm² Ag: 0.2 - 2	2	> 21		[79]
					Acidic: N/A	Oasis™ MAX	PA: 0.77	3 – 13 (14 days)	43		[110]
						Oasis™ HLB					
					Glyphosate: -	TiO₂	A = 4.91 cm² PA: 0.8, PES: 0.45/ PA: 0.4	0.03	2 - 6		[78]
Chemcatcher®	PTFE housing 52 or 47 mm receiving disk overlain with DM, sampling area = 17 cm².	Reusable (housing only). Preparation and handling simpler than POCIS/o-DGT.	Conditioning and extraction solvents and procedures defined for commercially available receiving phases. PEG present in PES DM must be removed to avoid matrix effects.	- Type of sorbent - DM, type, thickness, porosity and tortuosity	Neutral: -1.9 - 5.3 (POCIS)	Atlantic™ HLB	PES: 0.2	< 1	> 14 (0.016, metaldehyde)	Yes – Housing, DM and receiving phases can be purchased (TelLab). $$$	[12,126]
					-1.2 - 4.7	Empore™ SDB-RPS	2 x PES: 0.1	< 1- 20 * 1300	> 14 (~0.05)		[12]
					1.3 - 5.3	Empore™ C₁₈	2 x PES: 0.1	< 1 – 10 *230	< 14 (~0.02)		[12]
					1.78 - 3.51	Empore™ SDB-XC	PES: 0.45	N/A	< 5 (0.03 - 0.07)		[58]
					Acidic: -2.6 - 4.6	Empore™ SAX	PES: 0.2	2	6 - 58 (0.044 - 0.113)		[21]
					1.9 - 3.38	Empore™ SDB-RPS	PES: 0.2	N/A	< 7 (0.01 - 0.018)		
					1.9 - 3.38	Empore™ SDB-XC	PES: 0.2	Poor affinity (1 detection)	4 (0.04, haloxyfop)		[58]
Silicone rubber based devices	Single phase PSD comprised of multiple sheets or rods used in SBSE	Can be re-used if cleaned. Multiple sheets can form one device.	Oligomers must be removed before use this takes time and solvent. Soxhlet extraction (solvents: methanol-acetonitrile, 1:2 v/v).	- Surface area, embedded sorbent	Neutral: 0.70 - 7.0	SR sheets	450 cm²	< 1 - 5 *2000	< 7 (~0.88)	Yes – SBSE (Gerstel). No – Sheets $$$	[12]
					2.18 - 5.11	SR SBSE twisters	-	< 2	< 4 (0.001 - 0.121)		[85]
Naked SPE disks	SPE disks exposed directly in sampled waters.	Must be deployed in appropriate apparatus. Fouling or damage of the disk possible.	Conditioning and extraction solvents and procedures defined for commercially available receiving phases.	- Type of sorbent	Anionic: -1.1 - 4.2	Empore™ SDB-RPS	-	< 2	1.5 (0.1 - 0.18)	Yes (Affinisep, Merck, Biotage). $	[92]
									1.5 (0.48 - 1.1)		
					Neutral: 0.78 - 4.21	Empore™ SDB-XC	-	< 2	14 (0.018 - 0.047)		[47]

*maximum outlier above the range typically for most analytes. Abbreviations: agarose (Ag); diffusion membrane (DM); diffusive layer (DL); limit of quantification (LOQ); molecularly imprinted polymer (MIPs); *n*-octanol and water partition coefficient (K_{OW}); not available (N/A); nylon (NL); passive sampling device (PSD); polyacrylamide (PA); polyethersulphone (PES); polyethylene glycol (PEG); polytetrafluoroethylene (PTFE); sampling rate (R_S); silicone rubber (SR); solid-phase extraction (SPE); stir bar sorptive extraction (SBSE).

Table 5. Examples of applications of POCIS for monitoring polar pesticides.

Application	Analytes	Sampler design*1	Description	Ref
TWA concentrations	Acid herbicides, fungicides, herbicides, insecticides and molluscicides	- PES DM (0.132 mm thick, 0.1 μm pore)/ 200 mg Oasis™ HLB	- POCIS, o-DGT and MPTs were exposed (22-24 days) in 36 agricultural streams in New Zealand, alongside grab sampling, PFMs and temperature/light data loggers to characterize pesticide pollution, with quantitation through LC-MS/MS or LC-q-Trap, and evaluate sampling method performance.	[89]
TWA concentrations	Fungicides, herbicides and insecticides	- PES DM (N/A)/230 mg Oasis™ HLB	- 21 day exposures at 4 sites in the Bizerte lagoon catchment (Tunisia) alongside grab and sediment sampling to quantify (LC-MS/MS) 25 pesticides and 7 transformation products, to evaluate agricultural pollution.	[127]
Calibration and performance	Fungicides, herbicides and insecticides	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB	- Effects of suspended sediment (3600 ppm) on the extent of PSD fouling and uptake of 12 pesticides evaluated in laboratory 10 day exposures.	[108]
Calibration and performance	Neonicotinoids	-PES DM (0.1 μm pore)/220 mg Oasis™ HLB	- R_S determined in 21 batch sorption experiments before investigation of performance under non-steady state conditions typical of serious pollution event (1000, 100 or 10 μg L^{-1}) in 3, 14 day laboratory exposures.	[128]
Screening (target) / TWA concentrations	Fungicides, herbicides and insecticides	- (N/A) DM (N/A)/200 mg Oasis™ HLB	- 14 day exposures at 16 sites in the Tagus River catchment (Spain) alongside grab sampling to screen (LC-q-ToF) for pesticides and organic chemicals originating from point sources (430), to characterize site chemical profiles and prioritize chemicals for subsequent quantitative (LC-MS/MS) analysis. The suitability of each sampling method and uncertainty of results were also investigated.	[129]
TWA concentrations	Fungicides, herbicides, insecticides and metabolites	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB (30 μm particle size)	- 6 non-consecutive 14 day exposures over 1 year at 51 sites in the Adour-Garonne catchment alongside grab sampling to characterize profiles of 29 pesticides analysed through LC-MS/MS, in relation to land use and evaluate the temporal representativeness of each method.	[116]
TWA concentrations	Fungicides, herbicides and insecticides	- PES DM (N/A)/230 mg Oasis™ HLB	- 1 month exposures at 9 river, transition and coastal sites (Dublin and Cork regions of Ireland), representative of pollution sources and land use, alongside grab sampling to explore barriers to future inclusion of passive sampling in regulatory monitoring of Priority and Watch List CECs (e.g. WFD and MSFD). CECs were quantified by LC-q-Trap.	[120]
TWA concentrations	124 pesticides	- PES DM (0.1 μm pore)/220 mg Oasis™ HLB (30 μm particle size)	- The ability of monitoring methods (Chemcatcher®, POCIS, SR and composite sampling) to characterise concentrations and fluxes over 6 weeks at 2 river sites (Sweden). Pesticide concentrations (GC-MS or LC-MS/MS) and detection frequency for each method is compared. - An *in-situ* calibration is performed for each PSD was and PRC suitability was investigated and found suitable for SR PSDs (only).	[8]
Calibration and performance	Glyphosate and AMPA	- PES DM (0.1 and 0.2 μm pore) or nylon DM (0.2 μm pore)/220 mg Oasis™ HLB	- 31 day laboratory calibrations to investigate the performance of a novel MIP sorbent and three types of DM.	[75]
Calibration and performance	Fungicides, herbicides and insecticides	- DM (N/A)/200 mg Oasis™ HLB	- Effects of flow velocity (0-20.5 cm s^{-1}) and temperature (8-39 °C) on R_S (LC-MS/MS) investigated in lab exposures (21 days) and an Arrhenius model.	[109]
TWA concentrations (modelled)	Metolachlor	-	- Comparison of monthly passive sampling data from extant literature and 2-D modelling (MARS) at 5 coastal and 6 upstream river sites in Arcachon Bay (France) to develop a simulated proxy for metolachlor concentration in the bay.	[130]
-	Atrazine	-	- Review of passive sampling (POCIS and Chemcatcher®) of atrazine. Sampler configuration and geometry, uptake kinetics, calibration best practice, effects of flow and temperature and suitability of models describing mass transfer were discussed and developed (flow dependency R_S). - Measures to improve data quality were proposed: standardization of sampling area and sorbent mass (POCIS), and calibration conditions (WBL thickness). Recommendations for reporting PSD configuration included, DM material, pore size, tortuosity and thickness, and sorbent mass, exposed area and area: sorbent ratio.	[50]
TWA concentrations	Neonicotinoids and metabolites	- PES DM (N/A)/220 mg Oasis™ HLB	- 13-15 days exposures in raw and treated waters of 6 DWSWs in the Lake Erie region (Canada) alongside grab sampling (LC-q-Trap). - PRCs (DIA-d$_5$, propranolol-d$_7$ and metoprolol-d$_6$) were used to calculate *in-situ* R_S.	[24]
Calibration and performance	Acid herbicides, fungicides, herbicides and insecticides	- Miniaturized design (A= 9.8 cm^2) - PES DM (0.1 μm pore)/54.4 mg Oasis™ HLB (30 μm particle size): 180 cm^2 PES DM/(per) g Oasis™ HLB	- R_S and partitioning of organic compounds over a range of hydrophobicity (log K_{OW} -0.03 to 6.26) in miniaturised POCIS (sorbent and DM) and a mono-phasic mixed polymer sampler through batch experiments to investigate the performance of each PSD.	[88]
TWA	Fungicides, herbicides,	- PES DM (0.1 μm pore)/200 mg	- Consecutive 14 day exposures at 3 sites on both, the Auvézère (Jan 2012-Dec 2014), and Aixette (Jan 2014-Oct 2016), rivers (France),	[35]

concentrations	insecticides and metabolites	Oasis™ HLB/PRCs (DIA-d₅)	alongside grab sampling with quantitation by either LC- MS/MS or LC-q-ToF to characterize pesticide occurrence in agricultural catchments.	
M$_S$ (spiked samplers)	Herbicides and insecticides	- PES DM (N/A)/200 mg Oasis™ HLB	- Stability of analytes in POCIS stored at -20° C for 6 years showed +/- 14% mass variation (average LC-MS/MS), < o-DGT (+/- 9%) stored for 18 months.	[131]
-	-	-	- Review of POCIS, o-DGT and Chemcatcher® passive sampling devices in environmental monitoring.	[67]
TWA concentrations	Fungicides, herbicides, insecticides and metabolites	- PES DM (0.1 μm pore)/220 mg Bond Elut Plexa/PRC (DIA-d₅ and Caffeine-d₃)	- 2, 14 day exposures at 2 sites receiving mixed inputs on the Marque River (France), alongside composite sampling to evaluate the ability of each method to monitor compounds with differential temporal concentration flux and the reliability of using R_S reported previously in the literature and PRC correction (46 pesticides and 19 pharmaceuticals, quantitated by LC-MS/MS or LC-Orbitrap/MS).	[42]
Calibration and performance	Atrazine	- Diffusion cell separated by PES DM (Supor-200 145 μm thick, 0.2 μm pore)	- A method to adjust R_S for flow conditions during exposures using alabaster dissolution is developed and discussed.	[102]
Calibration and performance	Acid herbicides, fungicides and herbicides	- Oasis™ HLB (various mass) in spiked solutions	- Equilibrium partitioning to Oasis™ HLB is investigated in batch experiments, including the influence of sorbent concentration, temperature, pH and salinity.	[112]
TWA concentrations	Acid herbicides, fungicides, herbicides, insecticides and metabolites	- (N/A) DM (N/A)/Oasis™ HLB (N/A)	- Exposures (mean 37 days) at 97 river sites representative of different types of land use and river hydrology in the Midwest region (USA), alongside weekly grab and sediment sampling and ecological surveys to profile pesticide pollution, with quantitation through LC-MS/MS.	[115]
TWA concentrations	Acid herbicides, fungicides, herbicides and glyphosate	- PES DM (N/A)/200 mg Oasis™ HLB	- Exposures at 11 sites around Toronto (Canada) representative of pesticide sources in the built environment, agriculture (rivers) and downstream locations (lakes), to identify and quantify the contribution of sources of pollution (current use pesticides), with quantitation through LC-MS/MS.	[132]
TWA concentrations	Fungicides, herbicides and insecticides	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB	- 12 consecutive 1-month exposures at 3 sites, alongside monthly grab sampling at 10 sites in the River Ugie catchment to evaluate both methods, within the constraints of regulatory monitoring of pesticides and calculate flux and risk to aquatic organisms, with quantitation through GC-MS.	[32]
Screening (target and suspect)	Various pesticides	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB	- Multiples exposures (15 days or a month), alongside grab sampling at 2 groundwater sites dominated by agricultural, or agricultural and urban pollution to profile polar organic micro-pollutants, through screening (LC-q-ToF) and interpretation/identification using target and suspect databases and multidimensional data visualization.	[117]
Calibration and performance (modelled)	Acid herbicides, herbicides and insecticides	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB	- R_S is modelled for 73 compounds using artificial neutral networks by 2 methods, namely modelled chromatographic retention, or molecular descriptors such as topological, constitutional, geometrical and physiochemical properties, and validated through laboratory determined R_S.	[125]
Calibration and performance	Fungicides and herbicides	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB or Strata X-CW	- The performance of 7 candidate PRCs is evaluated through laboratory (17 days) and multiple field (12-21 days) exposures in 3 rivers with agricultural and WWTW inputs (Switzerland), including alongside automated sampling, with quantitation by LC-MS/MS.	[123]
Calibration and performance	Fungicides, herbicides and metabolites	- 3 POCIS configurations	- Inter-laboratory study to access sources of error in passive sampling (multiple devices) and causes of data variability within and between labs.	[119]
Calibration and performance	Fungicides, herbicides and insecticides	- PES DM (0.1 μm pore)/220 mg Oasis™ HLB	- Batch laboratory exposures (28 days) to determine the influence of temperature (18, 24 and 30 °C) on R_S of 48 pesticides, quantified through GC-MS/MS.	[98]
Calibration and performance	Fungicides, herbicides, insecticides and metabolites	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB/PRCs (DIA-d₅)	- Method to remove PEG from PES DMs and reduce matrix effects and improve quantitation (LC-q-ToF) of coeluting pesticides is developed and validated through 14 day field exposures at sites (2) on the La Pude and the Arnac rivers (France).	[122]
TWA concentrations	Fungicides, herbicides, insecticides and metabolites	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB	- Consecutive 14 day exposures over 9 months at 3 sites in the Auvézère River catchment to evaluate the performance (detection frequency and LOQ) of grab and passive sampling and suitability of each method to calculate concentration flux with quantitation by LC-MS/MS.	[9]
Calibration and performance	Acid herbicides, fungicides, herbicides, insecticides, molluscicides and metabolites	- PES DM (N/A)/220 mg Oasis™ HLB or 220 mg mixed sorbent (Isolute ENV+ (80%) and Ambersorb 1500 (20%))	- Characterization of 5 PSDs (2 types of POCIS and Chemcatcher® and SR) in laboratory exposures in river water spiked with 124 pesticides. - Analysis occurred by GC-MS or LC-MS/MS and R_S and K_{SW} were evaluated and 3 PSDs (1 x each device) deployed (6 x 7 days) in the River Halland.	[12]

Calibration and performance	Fungicides, herbicides, insecticides and metabolites	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB/PRCs (DIA-d₅)	- Analytical method (LC-q-ToF) developed for 46 polar pesticides and validated through analysis of POCIS exposed for 14 days at 2 river sites (France). - Full scan MS data enabled non target screening and identification of PEG compounds causing instrumental interference.	[65]
TWA concentrations	Fungicides, herbicides, insecticides and metabolites	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB	- Data from various 14 day exposures (extant literature) on the Trec River (France) is compared to regulatory monitoring data (Government Agency) to evaluate the limitation of POCIS in regulatory monitoring programmes. - A procedure to incorporate POCIS in regulatory monitoring (WFD) is proposed.	[11]
Calibration and performance	Herbicides, insecticides and metabolites	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB/PRCs (DIA-d₅)	- Consecutive 14 day exposures alongside automated sampling at 2 agricultural river sites (France) to investigate the influence of exposure conditions (e.g. flow velocity, pH and conductivity) on R_S and the suitability of PRC correction, with quantitation by LC-MS/MS.	[55]
Calibration and performance	Herbicides and metabolites	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB/PRCs (various)	- Performance of 21 candidate PRCs was evaluated in batch experiments and validated in 3 week field exposures alongside grab sampling (GC-MS or LC-MS/MS).	[52]
Calibration and performance	Fungicides, herbicides, insecticides and metabolites	- Nylon DM (65 μm thick, 30 μm pore) or PES DM (100 μm thickness, 0.1 μm pore)/200 mg Oasis™ HLB	- Accumulation kinetics of a novel POCIS with nylon DM is developed and evaluated alongside POCIS with PES DM in batch experiments (0-30 days) with quantitation by GC-MS/MS and LC-MS/MS. - A intraparticulate diffusion model considering multiple compartments (e.g. water, biofilm, DM and sorbent) is proposed and used to evaluate accumulation.	[63]
Calibration and performance	Acid herbicides, herbicides	- Miniaturized design (A= 16 cm²) - PES DM (0.45 μm pore)/Strata-X 600 mg	- Versions of Chemcatcher® and POCIS PSDs were exposed and removed at intervals (26 days) in spiked water to investigate the relationship between PSD configuration, analyte properties and analyte uptake (LC-MS/MS).	[58]
Calibration and performance	Acid herbicides, herbicides and metabolites	- Four designs - PES DM (A=16 or 45 cm², 0.1 μm pore)/200-600 mg Oasis™ HLB/PRCs (various)	- Batch exposures of 4 POCIS designs to compare performance and optimize PSD configuration for monitoring of neutral (LC-MS/MS) and acidic (HILIC-MS/MS) herbicides.	[77]
TWA concentrations	Atrazine	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB/PRCs (DIA-d₅)	- Two consecutive 28 days exposures at 24 sites in the South Nation River catchment (Canada) alongside *in-situ* calibration (PRCs) at 4 sites over 2 non-consecutive 2 month exposures to determine atrazine pollution throughout the catchment with quantitation through LC-q-Trap.	[105]
M_S (R_S unknown)	Fungicides, herbicides, insecticides and metabolites.	- PES DM (0.1 μm pore)/200 mg Oasis™ HLB.	- Deployments of 1 or 2 weeks, over 1 month, in 2 rivers in a French vineyard. Semi quantitative and qualitive results (LC-MS/MS analysis of 19 pesticides), obtained from Stir bar PSDs were compared to POCIS and automated grab sampling coupled to SBSE.	[84]
TWA concentration (estimated- R_S unknown)	Herbicides and metabolites	- Altered design (A= 95 cm²) - DM (N/A)/450 mg Oasis™ HLB	- Four consecutive exposures (14-21 day) in groundwater abstraction well at a DWSW (Paris, France) and 2 consecutive 7 day exposures in a well upstream of an abstraction well field (Troyes, France) alongside grab sampling to access the ability of each method with quantitation through LC-MS/MS.	[76]
Calibration and performance	Fungicides, herbicides and metabolites	- DM (N/A)/230 mg Oasis™ HLB	- 21 day laboratory calibration to determine the R_S of 17 polar pesticides (LC-MS/MS).	[133]
Calibration and performance	Fungicides, herbicides, insecticides and metabolites	- PES DM (N/A)/220 mg mixed sorbent (Isolute ENV+ (80%) and Ambersorb 1500 (20%))	- Transfer kinetics are modelled in POCIS and Chemcatcher® after laboratory exposures using a three compartment first order kinetic models.	[57]
Calibration and performance	Fungicides, herbicides and metabolites	- DM (N/A)/230 mg Oasis™ HLB	- In-situ calibration through 21 day exposure (samplers removed at days 3, 7, 10, 14, 17 and 21) in a water pumping station on the Rhone River (France) to determine the R_S of 10 polar pesticides and the influence of environmental factors on uptake, alongside grab sampling, with quantitation by LC-MS/MS.	[134]
Calibration and performance	Acid herbicides, fungicides, herbicides and metabolites	- PES DM (0.1 μm pore)/Oasis™ HLB or Oasis™ MAX or Chromabond HR-X (sorbent mass N/A)/PRCs (DIA-d₅, dicamba-d₃)	- The performance of 3 versions of POCIS are evaluated in 21 day batch exposures, including the influence of matrix composition (drinking water or river water) and the presence of nitrates on performance (acidic and neutral pesticides), with quantitation by LC-MS/MS.	[111]
-	-	-	- Critical reviews of the calibration and use of POCIS in environmental monitoring.	[49,135,136]
Calibration and performance	Chlorothalonil, hexazinone, phosmet and propiconazole	- DM (N/A)/Oasis™ HLB (sorbent mass N/A)	- Batch laboratory exposures (spiked river water) to determine the influence of flow velocity and the presence of natural organic matter on R_S, with quantitation by GC-MS.	[53]
Calibration and	Fungicides, herbicides,	- PES DM (0.1 μm pore)/200 mg	- A method (LC-MS/MS) for quantitation of multiple pesticide classes in water was validated through analysis of water samples (grab and	[44]

performance	insecticides and metabolites	Oasis™ HLB/PRCs (DIA-d$_5$)	automated extracted, SPE) and PSD extracts calibrated over 24 days (spike tap water) or exposed in a river for 14 days optimize the method and reduce matrix effects. The performance (e.g. LOQ, sample treatment/processing and representativeness of pesticide pollution) of monitoring methods was also evaluated.	
Calibration and performance	Herbicides and metabolites	- PES DM (0.1 µm pore)/200 mg Oasis™ HLB/PRCs (DIA-d$_5$)	- Laboratory calibration (7, 14, 21 and 28 days in spiked tap water) followed by in situ calibration (6, 13 and 22 days) and field trial alongside automated sampling (five consecutive 14 day exposures) in two French rivers, to investigate the performance of Oasis™ HLB sorbent and PRC correction (LC-MS/MS).	[61]
Calibration and performance	Herbicides and metabolites	- PES DM (0.1 µm pore)/200 mg Oasis™ HLB	- Batch exposures (9 days) in spiked river water to investigate performance under different concentration fluxes during 3 day 'events' (GC-MS).	[45]
Calibration and performance	Herbicides and metabolites	- PES DM (0.1 µm pore)/200 mg Isolute ENV+ and Ambersorb 572 (80:20) or 200 mg Oasis™ HLB	- Laboratory exposure (5 days) in spiked tap water of two versions of POCIS to evaluate PSD performance. PRC spiked POCIS (Oasis™ HLB) were then exposed (5, 10, 15 and 21 days) to determine the uptake kinetics of selected neutral and weakly acidic or basic herbicides and metabolites (HPLC-DAD).	[59]

*[1]Unless stated sampling area is 41 cm^2. DM is described as: "polymer" DM (thickness, pore size (if available)). DM is separated from sorbent by "/". Key: sampling area (A). Abbreviations: contaminants of emerging concern (CECs); diffusion membrane (DM); drinking water supply works (DWSW) ; gas chromatography-mass spectrometry (GC-MS); gas chromatography-tandem mass spectrometry (GC-MS/MS); high-performance liquid chromatography-diode array detector (HPLC-DAD); hydrophilic interaction liquid chromatography- tandem mass spectrometry (HILIC-MS/MS); limit of quantification (LOQ); liquid chromatography-Orbitrap/mass spectrometry (LC-Orbitrap/MS); liquid chromatography-quadrupole-time-of-flight (LC-q-ToF); liquid chromatography-quadrupole-Trap (LC-q-Trap); liquid chromatography-tandem mass spectrometry (LC-MS/MS); Marine Strategy Framework Directive (MSFD); microporous polyethylene tubes (MPTs); molecularly imprinted polymer (MIPs); n-octanol and water partition coefficient (K_{OW}); not available (N/A); passive flow monitors (PFMs); passive sampling device (PSD); performance reference compounds (PRC); polyethersulphone (PES); polyethylene glycol (PEG); sampled analyte mass (M_S); sampler and water partition coefficient (K_{SW}); sampling rate (R_S); silicone rubber (SR); solid-phase extraction (SPE); stir bar sorptive extraction (SBSE); time-weighted average (TWA); wastewater treatment works (WWTW); water boundary layer (WBL); Water Framework Directive (WFD); α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA).

Table 6. Examples of applications of Chemcatcher® for monitoring polar pesticides.

Application	Analytes	Sampler design*	Description	Ref
Targeted screening	Fungicides, herbicides and insecticides	- Atlantic design - PES DM (Supor® 200, 0.2 μm)/HLB-L (Atlantic™, 52 mm)	- PSDs exposed at 7 sites on two rivers impacted by wastewater in the Hartbeespoort Dam catchment (South Africa), over a 14 day deployments. - A method coupling passive sampling of ground water to semi quantitative analysis (LC-q-ToF) was used to perform a risk assessment based on hierarchical ranking of detection frequency and relative abundance.	[118]
TWA concentrations	Metaldehyde	- Atlantic design - PES DM (Supor® 200, 0.2 μm)/HLB-L (Atlantic™, 52 mm)	- The ability of four monitoring techniques (PSDs, spot and automated bottle sampling and online GC-MS) to monitor metaldehyde concentrations in a river and a DWSW (Herts, UK) was tested over five, 14 day PSD exposures. - Advantages (e.g. data resolution) and disadvantages (e.g. cost), and information provided by each method are discussed.	[43]
TWA concentrations	124 pesticides	- PES DM (0.1 μm pore)/C$_{18}$ disk (47 mm)	- The ability of monitoring methods (Chemcatcher®, POCIS, SR and composite sampling) to characterize concentrations and fluxes over 6 weeks at 2 river sites (Sweden). Pesticide concentrations (GC-MS or LC-MS/MS) and detection frequency for each method is compared. - An *in-situ* calibration was performed for each PSD was and PRC suitability was investigated and found suitable for SR PSDs (only).	[8]
TWA concentrations	Acid herbicides	- Empore design - PES DM (Supor® 200, 0.2 μm pore)/anion-exchange disk (Empore™, 47 mm)	- Novel PSD is developed and R_s determined in laboratory exposure, and tested in 2 field trials (12 sites, Exe Catchment, UK). - Concentrations obtained through high frequency spot sampling and passive sampling used to locate sources of pollution.	[21]
-	Atrazine	-	- Review of passive sampling (POCIS and Chemcatcher®) of atrazine, including sampler configuration and geometry, uptake kinetics, calibration best practice, effects of flow and temperature and suitability of models describing mass transfer were discussed and developed (flow dependency of R_S). - Measures to improve data quality were proposed: standardization of sampling area and sorbent mass (POCIS), and calibration conditions (WBL thickness). Recommendations for reporting PSD configuration included, DM material, pore size and thickness, and sorbent mass, exposed area and area: sorbent ratio.	[50]
TWA concentrations	Metaldehyde	- Atlantic design - PES DM (Supor® 200, 0.2 μm pore)/ HLB-L (Atlantic™, 52 mm)	- Metaldehyde R_S determined in laboratory exposures, and PSD performance evaluated in 5 x 14 day exposures at 3 river sites (UK). - Ability of passive sampling to monitor pollutants with stochastic inputs, locate sources and integrate concentration fluxes is discussed.	[126]
TWA concentrations	Metaldehyde	- Atlantic design - PES DM (Supor® 200, 0.2 μm pore)/ HLB-L (Atlantic™, 52 mm)	- 14 day exposures of PSDs and grab sampling (14 day intervals) at 14 sites throughout England and Wales over the course of a year are compared.	[33]
TWA concentrations	Acaricides, fungicides, herbicides, insecticides and metabolites	- Empore design - PES DM (Supor® 200, 0.2 μm pore)/SDB-RPS disk (Empore™, 47 mm)	- Exposures in 7 German rivers receiving wastewater effluent over 2 sampling campaigns of 2 and 3 weeks, alongside event driven samplers (peak concentrations) and passive flow monitors to access the impact of pesticide in effluent on invertebrates. Quantitation occurred through LC-MS/MS.	[137]
TWA concentrations	Herbicides	- Empore design - PES DM (Supor® 200, 0.2 μm pore)/SDB-RPS disk (Empore™, 47 mm)	- 2 months of overlapping exposures (average 28 days) before, during and after a flood event at a site in the Barratta Creek catchment (Australia) alongside grab sampling and a passive flow monitor, to monitor TWA concentrations and determine herbicide load with quantitation through LC-MS.	[37]
TWA concentrations	Fungicides, herbicides and insecticides	- Empore design - PES DM (Supor® 200, 0.2 μm pore)/SDB-RPS disk (Empore™, 47 mm)	- Chemcatcher® and SR PSDs and grab sampling monitoring were evaluated alongside PFMs through 1 month exposures (2 years) at four sites in the Barratta Creek catchment (Australia) to profile temporal and spatial trends in pesticides presence, concentration and fate, with quantitation by HPLC-MS/MS.	[36]
TWA concentrations	Fungicides, herbicides, insecticides and	- Empore design - PES DM (Supor® 200, 0.2 μm pore)/SDB-RPS disk	- Multiple 3 week exposures in 37 site/streams in an agricultural region of Germany with quantitation by LC-MS/MS, compared to compiled data 1998-2011 on pesticide concentration, physiochemical status, habitat and invertebrate community composition to access pesticide toxicity to invertebrates (SPEAR pesticides).	[138]

	molluscicides	(Empore™, 47 mm)		
Calibration and performance (in-situ)	Acid herbicides, fungicides, herbicides, insecticides and metabolites	- Improvised design - PES DM (0.45 µm pore)/SDB-RPS disk (Empore™, 47 mm)	- in-situ calibration through exposures (14 day over 4 months) alongside time proportional composite sampling in 5 rivers in varied catchments. - 322 compounds were analysed by LC-MS/MS, however, R_S could only be calculated for 88 which included pesticides and pharmaceuticals. Uncertainty of the results obtained and suitability of passive sampling for monitoring different organic pollutant are discussed.	[95]
Calibration and performance	Acid herbicides, fungicides, herbicides, insecticides, molluscicides and metabolites	- Improvised design with PES DM overlain on each side of either a SDB-RPS or C$_{18}$ disk (Empore™, 47 mm) in metal housing	- Characterization of 5 PSDs (2 types of POCIS and Chemcatcher® and SR) in laboratory exposures in river water spiked with 124 pesticides. - Analysis occurred by GC-MS or LC-MS/MS and R_S and K_{SW} were evaluated and 3 PSDs (1 x each device) deployed (6 x 7 days) in the River Halland.	[12]
Calibration and performance	Neonicotinoids	- Empore design - (naked)/SDB-RPS, SDB-XC or C$_{18}$ disk (Empore™, 47 mm)	- A multi-residue analytical method for neonicotinoids is developed and validated (UPLC-MS) using spiked and unspiked river water samples. - Receiving phase performance (retention and recovery) was investigated in batch experiments followed by laboratory exposures of selected PSDs (SDB-RPS) in spiked water with samplers removed and analysed at intervals for 21 days repeated to investigate uptake and desorption.	[139]
TWA concentrations (estimated)	Herbicides, insecticides and metabolites	- Empore design - PES DM (with and without DM) (Supor® 0.45 µm pore)/SDB-RPS disk (Empore™, 47 mm)	- Chemcatcher® were deployed for either 7 days (no DM) or 28 days (with DM), alongside SR, SPMD and XAD resin PSDs in 5 ground water wells located at distances from an aquifer recharge and recovery well to quantify (LC-MS/MS) pollutant transport and attenuation in a storm water recycling system.	[140]
Calibration and performance	Acid herbicides, herbicides	- Empore Design - PES DM (0.45 µm or 0.2 µm pore)/SDB-RPS or SDB-XC disk (Empore™, 47 mm)	- Four versions of Chemcatcher® and POCIS PSDs were exposed and removed at intervals (26 days) in spiked water to investigate the effect of PSD configuration on analyte uptake (LC-MS/MS).	[58]
Calibration and performance	Fungicides, herbicides, insecticides and metabolites	- Empore design - PES DM (0.1 µm pore)/SDB-RPS disk (Empore™, 47 mm)	- Transfer kinetics are modelled in POCIS and Chemcatcher® after laboratory exposures using a three compartment first order kinetic models.	[57]
TWA concentrations	Herbicides and metabolites	- Empore design - PES DM (with and without DM) (Z-bind™ 0.45 µm pore)/SDB-RPS disk (Empore™, 47 mm)	- 2 years of non-consecutive deployments (between 4-20 days), at 4 sites located at river mouth, near shore, mid shelf and outer reef portions of the great barrier reef (Australia), to investigate the influence of extreme wet weather on pesticide pollution as part of an wider ongoing long term monitoring programme, with quantitation through LC-MS/MS.	[38]
Calibration and performance	Fungicides, herbicides and insecticides	- Empore Design - (naked) SDB-XC disk (Empore™, 47 mm)	- 2, 14 day laboratory calibrations to determine R_S for 12 pesticides at 2 flow velocities (0.135 and 0.4 ms^{-1}) and investigated the performance of 2 PRCs to correct for the influence of flow on uptake.	[54]
Calibration and performance	Atrazine and prometryn	- Empore design - PES DM (with and without DM) (Z-bind™ 200 0.2 µm pore)/SDB-RPS disk (Empore™, 47 mm)	- 5 lab calibration experiments in an exposure cell to investigate the influence of flow velocity 0-24 cm s^{-1} on R_S and the accuracy of flow velocity inference with PFMs followed by field exposures (28 days) at 8 freshwater sites (Australia), with analyte quantitation by GC-MS.	[106]
TWA concentrations	Herbicides and metabolites	- Empore design - PES DM (with and without DM) (Z-bind™ 200 0.2 µm pore)/SDB-RPS disk (Empore™, 47 mm)	- Chemcatcher® with or without DM were exposed over 2 years in non-consecutive deployments (between 4-29 days), including alongside SPMD and SR, at 14 sites in the Princess Charlotte Bay area comprising river mouths and near shore, mid shelf, and outer, reefs, to investigate temporal and spatial variation in pesticide pollution, with quantitation through LC-MS/MS.	[141]
Calibration and performance	Atrazine, diuron and simazine	- Empore design - PES DM (with and without	- Overlapping (3-24 days) exposures of PSDs with and without DMs alongside grab and automated composite sampling to investigate analyte uptake during a flood 'event' at 4 sites on the Brisbane River (Australia), with comparison to precipitation and flow data and analyte quantitation by	[74]

		DM) (0.45 μm pore)/SDB-RPS disk (Empore™, 47 mm)	LC-MS/MS. - Equilibrium and kinetic parameters were calculated *in-situ* based on dynamic concentrations obtained through each method.	
(in-situ)				
Calibration and performance	Acid herbicides, fungicides, herbicides and metabolites	- Empore Design - PES DM (with and without DM) (N/A pore)/SDB-RPS (Empore™, 47 mm) -(naked)/SDB-XC disk (Empore™, 47 mm)	- Three variations of the Chemcatcher® were exposed in WWTW effluent in batch experiments to investigate the influence flow velocity and sampler response time (5 day exposures) and the period of linear uptake (overlapping exposures 3-21 days) to investigate any relationships between analyte uptake properties and log K_{OW}, with quantitation through LC-MS/MS and toxicity (PSII inhibition) determined in bioassays.	[46]
Calibration and performance	Thiacloprid	- Empore design - PES DM (with and without DM) (0.2 μm pore)/SDB-XC disk (Empore™, 47 mm)	- 1 or 10 day exposures in thiacloprid spiked artificial streams (3.2 or 100 μgL^{-1}) of (pre)fouled and unfouled devices, with and without DMs (4 variations total), to investigate the influence of fouling on DMs or naked disks on uptake at different concentrations and exposure times, with quantitation by LC-MS.	[99]
TWA concentrations	Fungicides, herbicides and insecticides	- Empore design, -(naked) SDB-XC disk (Empore™, 47 mm)	- 10-13 day exposures in 16 European rivers alongside event driven and suspended particle samplers to compare method performance (GC-MS).	[142]
Calibration and performance	Acid herbicides and herbicides	-Empore design - PSU or PES DM (0.2 μm pore)/SDB-RPS or SDB-XC disk (Empore™, 47 mm)	- 4 variations (2 x DM and 2 x receiving phase) of Chemcatcher® exposed (21 days removed 3 day intervals) in a flow through system containing spiked tap water to investigate the influence of DM and receiving phase selection on uptake and desorption (separate exposures), with quantitation through HPLC-UV.	[72]
TWA concentration and bioassays	Acid herbicides, herbicides, insecticides and metabolites	- Empore design - (polymer N/A) DM (0.45 μm pore)/SDB-RPS (Empore™, 47 mm)	- 27 day exposures at 8 sites in the treatment stream of a DWSW (Australia), with chemical (LC-MS/MS) and toxicological (Microtox, E-SCREEN and photosynthesis inhibition) analysis to quantifying and attribute MoA for various compounds, including selected pesticides, as treatment progressed.	[113]

*DM is described as: "polymer" DM (thickness, pore size (if available)). DM is separated from sorbent by "/". Abbreviations: diffusion membrane (DM); drinking water supply works (DWSW); gas chromatography-mass spectrometry (GC-MS); high performance liquid chromatography-tandem mass spectrometry (HPLC-MS/MS); high-performance liquid chromatography-ultraviolet (HPLC-UV); liquid chromatography-mass spectrometry (LC-MS); liquid chromatography-quadrupole-time-of-flight (LC-q-ToF); liquid chromatography-tandem mass spectrometry (LC-MS/MS); mode of action (MoA); *n*-octanol and water partition coefficient (K_{OW}); not available (N/A); passive flow monitors (PFMs); passive sampling device (PSD); performance reference compounds (PRC); polyethersulphone (PES); polysulphone (PSU); sampler and water partition coefficient (K_{SW}); sampling rate (R_S); semipermeable membrane device (SPMD); silicone rubber (SR); solid-phase extraction (SPE); time-weighted average (TWA); ultra-performance liquid chromatography- mass spectrometry (UPLC-MS); wastewater treatment works (WWTW); water boundary layer (WBL).

Table 7. Examples of applications of o-DGT for monitoring polar pesticides.

Application	Analytes	Sampler design*[1]	Description	Ref
TWA concentrations	Acid herbicides, fungicides, herbicides, insecticides and molluscicides	- 0.75 mm polyacrylamide/0.75 mm/0.35 mg Sepra™ ZT	- POCIS, o-DGT and MPTs were exposed (22-24 days) in 36 agricultural streams in New Zealand, alongside grab sampling, PFMs and temperature/light data loggers to characterize pesticide pollution, with quantitation through LC-MS/MS or LC-q-Trap, and evaluate sampling method performance. - > 2 pesticides and > 3 pesticides were detected at 78% and 69% of sites respectively. Pesticide and nutrient concentrations were not correlated. POCIS had the highest detection frequency of the evaluated methods.	[89]
Calibration and performance	Herbicides, fungicides, insecticides and metabolites	- 6 types of DM investigated*[2] - (i) 0.5-2 mm, polyacrylamide or agarose/1-10 mg L^{-1} Oasis™ HLB. - (ii) 0.5-2 mm polyacrylamide or agarose/1-10 mg L^{-1} Amberlite XAD 18	- Evaluation of numerous DM, diffusive gels, sorbents, including determination of diffusion coefficients, the influence of DM type, DL thickness, sorbent mass and environmental conditions on performance, and the accuracy of PRC correction (atrazine-d_5 or linuron-d_6), in comprehensive lab experiments and subsequent field exposures in several rivers and reservoirs (China).	[81]
TWA concentrations	Acid herbicides, herbicides and insecticides	- 0.75 mm/0.75 mm, 25 mg Oasis™ HLB	- Performance of PSDs (o-DGT and POCIS) and grab sampling evaluated through exposures of 2-3 weeks for 7 months at 14 sites in the Red River, Lake Winnipeg, and Nelson River watersheds, which are influenced by agriculture and wastewater. Deployments encompassed environmental conditions ranging from fast flowing river, lakes with surface ice.	[80]
TWA concentrations	Acid herbicides, herbicides and insecticides	- (i) 0.75mm, polyacrylamide gel/0.75 mm, 350 mg Sepra™ ZT - (ii) 0.75 mm/0.75 mm, 350 mg Oasis™ HLB	- Diffusion coefficients in polyacrylamide gel were determined experimentally, using a diffusion cell. - Sampler performance under varying pH was investigated during batch laboratory calibration experiments lasting 25 days.	[101]
TWA concentrations	Herbicides and flutolanil	- Novel geometry (A= 45 cm^2) - 0.2-2 mm/0.75 mm, 50-1000 mg Strata-X	- Sorbent sorption isotherms were determined through equilibration in spiked water and a modified sampler geometry developed. - Exposures (17-21 days) over four months in a river in an agricultural catchment alongside an automated bottle sampler to investigate the influence of flow, temperature, DL thickness and sorbent mass on sampler performance and uncertainty.	[79]
M_S (spiked samplers)	Herbicides and insecticides	- 1 mm/0.75 mm, 25 mg Oasis™ HLB	- Stability of analytes in o-DGTs stored at -20° C for 18 months and POCIS stored at -20° C for 6 years was investigated.	[131]
-	-	-	- Review of POCIS, o-DGT and Chemcatcher® passive sampling devices in environmental monitoring.	[67]
Calibration and performance	Acid herbicides	- (i) 0.77 mm, polyacrylamide or agarose/0.67 mm, polyacrylamide, 300 mg Oasis™ HLB. - (ii) 0.77 mm, polyacrylamide or agarose/0.67 mm, polyacrylamide, 300 mg Oasis™ MAX	- Method (preparation/elution) for o-DGT for anionic pesticides, four model compounds and two sorbents investigated (HPLC-ToF analysis). - Uptake and desorption by diffusive and binding gels, binding capacity of sampler configurations, diffusion coefficients and the effect of pH, temperature and flow rate determined in lab experiments and validated through exposures (7-14 days) in spiked Evian® water and two French rivers.	[110]
Calibration and performance	Glyphosate and AMPA	- Novel geometry (A= 4.91 cm^2) - PES, N/A, 0.45 μm/0.4 mm, polyacrylamide/0.4 mm, polyacrylamide, 2 g TiO_2	- Diffusion cell and calibration experiments evaluating DGT containing TiO_2 binding phase (typically used for inorganic ions) to monitor glyphosate, including the influence of pH, flow rate, temperature and the presence of naturally occurring ions (e.g. copper, iron and magnesium).	[78]
Review	-	-	- Comprehensive review of o-DGT in environmental monitoring of polar organic compounds (including polar pesticides) in water (35 papers).	[70]
Calibration and performance	- Acid herbicides, herbicides and insecticides	- 1 mm/0.75 mm, 25 mg Oasis™ HLB	- A novel o-DGT is developed and validated in comprehensive batch experiments and laboratory calibrations investigating the influence of temperature, flow and subsequent field exposures alongside POCIS.	[104]

*[1]Unless stated sampling area is 3.1 cm^2 and all layers are formed of 1.5% agarose gel, the customary configuration for o-DGT samplers. If more than one diffusive and binding layer configuration is used, each is prefixed with Latin numerals e.g. (i). If a diffusion membrane (DM) overlays the diffusive layer, DM properties are listed first in the form DM = (polymer type, thickness, porosity (if available)). Otherwise diffusive layer is listed before binding layer and thickness is listed before composition properties (gel type or binding agent), and the properties of the diffusive layer and the binding layer and separated by "/". Where a range of layer thicknesses or sorbent masses are used the range is represented by a hyphen For example if a agarose diffusive gel was investigated at thicknesses between 0 and 0.2 mm with a 0.75 mm binding gel containing 25 mg of Oasis™ HLB sorbent this would appear as: 0-0.1 mm/0.75 mm, 25 mg Oasis™ HLB. *[2]Polyethenesulfone DM, 0.14 mm, 0.45 μm; Nucleopore track-etch DM, 0.01 mm, 0.45 μm; Nylon DM, 0.125 mm, 0.45 μm; Cellulose acetate DM, 0.115 mm, 0.45 μm; Mixed cellulose ester DM, 0.15 mm, 0.45 μm; Hydrophilic polypropylene DM, 0.114 mm, 0.45 μm. Key: sampling area (A). Abbreviations: diffusion membrane (DM); diffusive layer (DL); high performance liquid chromatography-time-of-flight (HPLC-ToF); liquid chromatography-quadrupole-Trap (LC-q-Trap); liquid chromatography-tandem mass spectrometry (LC-MS/MS); microporous polyethylene tubes (MPTs); not available (N/A); passive flow monitors (PFMs); passive sampling device (PSD); performance reference compounds (PRC); polyethersulphone (PES); sampled analyte mass (M_S); time-weighted average (TWA); α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA).

Table 8. Examples of applications of other passive sampling devices for monitoring polar pesticides.

Application	Analytes	Sampler design	Description	Ref
Calibration / performance (semi-quant)	Herbicides, insecticides, fungicides and metabolites	- (naked) SDB-XC (Empore™ 47mm)	- Laboratory calibration of novel PSD for use in groundwater of three polar pesticides and one PPCPs in matrix, flow and temperature matched media over 14 days, followed by field trials at 12 groundwater wells (Lyon, France) over 10 days, with quantitative analysis (LC-q-ToF). - The four R_S from the calibration study were extrapolated to obtain semi-quantitative TWA concentrations for 16 polar pesticides during field exposures.	[47]
TWA concentrations	Acid herbicides, fungicides, herbicides, insecticides and molluscicides	- (MPT) external diameter 0.8 cm, 2 mm thick, 2.5 μm pore, 35% porosity, 4-cm length/400 mg Strata-X	- POCIS, o-DGT and MPTs were exposed (22-24 days) in 36 agricultural streams in New Zealand, alongside grab sampling, PFMs and temperature/light data loggers to characterize pesticide pollution, with quantitation through LC-MS/MS or LC-q-Trap, and evaluate sampling method performance.	[89]
Screening	Fungicides, herbicides and insecticides	- Novel deployment rig design - (naked) SDB-RPS and SDB-XC (Empore™ 47 mm)	- PSDs exposed at five storm water infiltration system sites (Lyon, France) in ground waters and collected runoff over 10 days during a storm event. - A method coupling passive sampling of ground water to HRMS analysis (LC-q-ToF) was tested.	[40]
TWA concentrations	Diuron and metolachlor	- Custom metal housing - SDB-RPS (Empore™ 47 mm)	- PSDs and automated bottle samplers were deployed in three sewers over 10 day deployments during high rainfall/flow 'events'. - Concentration patterns for sewer overflows and rivers in hypothetical 'events' were modelled and compared to monitoring results. - Ability of passive sampling to integrate TWA concentrations of 'events' is investigated, and uncertainty/sources of error discussed.	[73]
Target and non-target screening	Fungicides, herbicides and insecticides	- (naked) SDB-RPS (Empore™ 47 mm)	- Multiple field exposures (four months) at two costal sites receiving fluvial inputs and a marine site, (Great Barrier Reef region). Non-targeted and targeted screening with either a LC-MS/MS or LC-q-ToF as part of integrated chemical exposure assessment of green turtle foraging grounds.	[143]
TWA concentrations	Various pesticides	- Mobile dynamic passive sampler - (naked) SDB-RPS (Empore™ 47 mm)	- Dynamic passive sampler attached to a boat. Sampling occurred over a 2130 km stretch of the Danube as part of integrated toxicological and chemical monitoring using several methods. Extracts were analysed for 40 pesticides with LC-MS.	[144]
Calibration and performance	Acid herbicides, fungicides, herbicides and insecticides	- PDMS sheet sampler, A= 47.5 cm²/100 mg (embedded) Oasis™ HLB	- R_S and partitioning of organic compounds over a range of hydrophobicity (log K_{OW} -0.03 to 6.26) in miniaturised POCIS (sorbent and DM) and a monophasic mixed polymer sampler through batch experiments to investigate the performance of each PSD.	[88]
Screening	Herbicides, insecticides, fungicides and metabolites	- 1 mm steel mesh pouches containing 3 g activated carbon	- PSDs deployed in 15 bore holes over 2 deployments of 6 months, were screened (GC-MS) for various organic compounds. Compounds detected (passive sampling) and quantitative results from grab sampling were used to profile pollution sources and optimise future monitoring.	[93]
Calibration and performance	Glyphosate and AMPA	- MTP PSD, 2 mm thickness, 2.5 μm A= 17.6 cm²/216 mg TiO₂ embedded in agarose gel	- Six day laboratory calibration followed by 11 day *in-situ* calibration in a freshwater lake alongside grab sampling to test novel diffusive material.	[90]
Calibration and performance	Fungicides, herbicides and insecticides	- Novel composite polymer PSD - PDMS/SPE sorbents*	- Composite polymers containing one of several SPE sorbents embedded in a PDMS matrix were prepared. - The physical and sorption properties of each composite were tested in batch experiments.	[87]
Equilibrium concentrations	Atrazine, diazinon and metolachlor	- Novel thin-film PSD. - EVA (0.03 g) coated Ti plates	- The ability of a novel equilibrium PSD, grab and biota monitoring to monitor three polar pesticides and dieldrin were compared in batch experiments and 10-day field exposures at 5 sites in coastal waters (Long Island Sound, USA).	[91]
Calibration and performance	Fungicides, herbicides and insecticides	- Gerstel Twister, PDMS stir bars (SBSE) applied as a PSD	- Calibration (lag phase and R_S) in a flow through system for 18 pesticides (log K_{OW} 2.18-5.11). A PRC (fenitrothion-d6) is also investigated.	[85]
TWA concentrations	Fungicides and insecticides	- Custom metal housing - (naked) SDB-RPS (Empore™ 47mm)	- Suitability of passive sampling to integrate polar pesticide concentrations during four episodic rainfall driven 'events' evaluated alongside event driven water sampling in 17 streams in a German vineyard.	[145]
M_S (R_S unknown)	Fungicides, herbicides, insecticides and	- Gerstel Twister, PDMS stir bars (SBSE) applied as a PSD	- Deployments of 1 or 2 weeks, for 1 month, in 2 rivers in a French vineyard. Semi quantitative and qualitive results (LC-MS/MS analysis of 19 pesticides), obtained from Stir bar PSDs were compared to POCIS and automated grab sampling coupled to SBSE.	[84]

	metabolites			
M_S at equilibrium (unknown log K_{SW} and R_S)	Acid herbicides, fungicides, herbicides, insecticides and molluscicides	- PDMS strip, A= 600 cm^2	- 54-day exposures alongside automated grab sampling (3 h intervals) at 3 sites on the River Ythan (UK) to determine the suitability of each method to profile diffuse agricultural pollution. Quantitation was by either GC-MS/MS (neutral pesticides) or LC-MS/MS (acid herbicides).	[82]
Equilibrium concentrations	Herbicides and insecticides	- PDMS strip, 0.5 mm thickness, A= 100 cm^2	- New instrumental method (LC-Orbitrap-MS) developed and applied to extract from two exposures (2 months) at five sites in coastal waters (Belgium). - K_{SW} determined in batch experiments and TWA concentrations calculated, however linear uptake over the exposure period was not confirmed.	[83]
Calibration and performance	Triazines	- Silicone hollow fibre membranes, V= 1 mL/(internal) 0.5 M nitric acid	- Laboratory exposures of 2, 3, 5 and 7 days to investigate performance and the influence of humic substances and flow velocity on analyte accumulation. - 7-day field exposures at three sites in the Hartebesspoort Dam catchment (South Africa), alongside Chemcatcher® and grab sampling could not validate method applicability as no triazines were detected by any method.	[86]
Calibration and performance	Herbicides	- Custom metal housing - (naked) SDB-RPS (Empore™ 47mm)	- Empirically determined and modelled mass transfer coefficients of four herbicides through a WBL investigated in order to predict WBL limited uptake in a naked SPE disk type PSD.	[146]

*SPE sorbets: i) OASIS™ HLB ii) OASIS™ MAX iii) OASIS™ MCX iv) Evolute ABN v) HyperSep Hypercarb™. Key: sampling area (A); volume (V). Abbreviations: diffusion membrane (DM); ethylene-vinyl acetate (EVA); gas chromatography-mass spectrometry (GC-MS); gas chromatography-tandem mass spectrometry (GC-MS/MS); high-resolution mass spectrometry (HRMS); liquid chromatography-mass spectrometry (LC-MS); liquid chromatography-Orbitrap/mass spectrometry (LC-Orbitrap/MS); liquid chromatography-quadrupole-time-of-flight (LC-q-ToF); liquid chromatography-quadrupole-Trap (LC-q-Trap); liquid chromatography-tandem mass spectrometry (LC-MS/MS); microporous polyethylene tubes (MPTs); n-octanol and water partition coefficient (K_{OW}); passive flow monitors (PFMs); passive sampling device (PSD); performance reference compounds (PRC); pharmaceuticals and personal care products (PPCPs); polydimethylsiloxane (PDMS); sampled analyte mass (M_S); sampler and water partition coefficient (K_{SW}); sampling rate (R_S); solid-phase extraction (SPE); stir bar sorptive extraction (SBSE); time-weighted average (TWA); water boundary layer (WBL); α-amino-3-hydroxy-5-methyl-4-isoxazolepropionic acid (AMPA).