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Investigating the applicability of passive sampling devices to pesticide monitoring

Science Report – SC030189/SR2

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This report is the result of research commissioned and funded by the Environment Agency's Science Programme.

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Executive summary

Passive sampling is an emerging water quality monitoring technique, which may offer several advantages over conventional spot sampling. First, as a continuous monitoring technique, it should increase the chances of detecting transient contamination events. Second, passive sampling involves much larger volumes of water than are normally collected by spot samples, so lower levels of environmental contaminants can be detected. Thirdly, passive sampling devices only sample freely available contaminants; the results therefore provide a useful indication of contaminant bioavailability.

Despite these advantages we have found that currently, passive sampling is not a suitable quantitative technique for monitoring transient 'pulses' of contaminant exposure such as those that arise via spray drift following application of a pesticide to a crop.

The use of passive samplers for monitoring low level chronic pollution has been reported in peer-reviewed papers. A literature search identified two different passive samplers – the Polar Organic Chemical Integrative Sampler (POCIS) and SemiPermeable Membrane Device (SPMD) – for further investigation. In particular, it was necessary to conduct some field and laboratory trials to determine whether passive samplers were an appropriate sampling technique in shallow headwater streams that experience transient pesticide exposure and are at risk of impacts from pesticides.

A series of small scale field trials tested the practicalities of deploying passive samplers in shallow waters. The deployment cages put a lower bound on the water depth required, but results from the field trials indicated that, even in headwater streams, suitable sampling locations could be found.

The study considered the ability of passive sampling devices to provide quantitative results for short pulses of pesticide exposure such as spray drift following application of pesticides to a crop. This scenario is considered to be highest risk, in terms of causing ecological impacts. Laboratory trials demonstrated that whilst the passive samplers were able to accumulate contaminants after short exposures (less than 1 hour), not all the compounds tested would be quantifiable after such short durations. Furthermore, some of the contaminants were lost when the SPMD was placed in 'clean' water following accumulation, showing that compounds may depurate from the SPMD after exposure. These results suggest that passive samplers may not be suitable for monitoring the most high risk pesticide exposure scenarios.

In conclusion, the report found that passive samplers were not a suitable quantitative monitoring method for transient pesticide contamination caused by spray drift. This is because the short exposure times and the possibility that accumulated contaminants may be depurated from SPMDs lead to a risk of false negatives. Further research to examine how passive samplers accumulate pulsed exposures of contaminants such as pesticides would be beneficial. Passive samplers do offer advantages over spot sampling for the monitoring of continuous contamination by low level pollutants or where qualitative results are sufficient.

Acknowledgements

Contents

1   Introduction

Passive sampling is a continuous monitoring technique. It therefore increases the chances of detection of transient contamination that might otherwise be missed by spot sampling. In addition, because passive monitoring samples a larger volume of water than would normally be collected by spot sampling, much lower environmental levels of contaminants can be detected. As passive sampling devices (PSDs) only sample freely available contaminants, they also provide a useful indication of contaminant bioavailability.

These advantages over conventional spot sampling suggest that passive sampling would prove suitable for detecting transient pesticide contamination that may be missed by conventional spot sampling techniques.

A literature review was conducted to gather information on the types of PSDs available, and to collate data and information on their ability to detect and quantify pesticides in the aquatic environment. Small, shallow streams with little dilution are believed to be most at risk from impacts of pesticide contamination, so the search focused on the practicalities of deploying PSDs in these conditions. Pesticides may enter watercourses by spray drift, drainflow and run-off and be present for varying lengths of time at variable concentration. It was therefore also important to consider whether PSDs were a suitable way to monitor all these exposure scenarios.

Trials of PSDs have been conducted both in the laboratory and field. Laboratory trials investigated which compounds were accumulated by the different PSDs, the length of required exposure, and whether accumulated compounds were depurated if the PSD was returned to 'clean' water. Field trials were conducted to determine the practicalities of deployment, especially for shallow waters.

The results of the trials and the information from secondary sources were used to make recommendations on whether passive sampling was a suitable sampling methodology for use in a planned large scale pesticide monitoring programme (Environment Agency, 2006).

2   Literature review

2.1   Introduction

Passive sampling is an emerging water quality monitoring technique which has been extensively reported by researchers in Europe (Zhang and Davison, 1995; Booij, Sleiderink and Smedes, 1998; Kingston *et al*., 2000; Vrana *et al*., 2001), the USA (Huckins *et al*., 1993; Alvarez, 1999) and Australia (Shaw, Tibetts and Müller, 2004). The use of passive samplers and their potential application have been under investigation by the Environment Agency since 1997 (Goddard, Getting and James, 2004).

A range of Passive Sampling Devices (PSDs) has been developed and while there are design differences between devices, they function on the same basic principles. The PSD is deployed in the watercourse for a period of time, ranging from a few hours to several weeks. Waterborne contaminants diffuse through an outer membrane and accumulate by absorption onto an inner matrix. Only contaminants that are freely dissolved in the water are accumulated; those bound to particulates or present as precipitates cannot pass through the outer membrane. Once the PSD has been exposed for the required monitoring period, it is removed to the laboratory and the contaminants are extracted from the inner matrix and quantitatively analysed. Using knowledge of the contaminant sampling rate by the device, the total amount of each contaminant accumulated can then be converted to an environmental time-weighted average concentration (Booij *et al*., 1998; Huckins *et al*., 2000; Alvarez *et al*., 2004).

Passive sampling offers a clear advantage over conventional spot sampling: it is a continuous monitoring technique, so increases the chances of detection of transient contamination events that might otherwise be missed. As the process of contaminant accumulation is specific to freely available contaminants, the results also provide a useful indication of contaminant bioavailability. Furthermore, because passive monitoring samples a larger volume of water than would normally be collected by spot sampling, much lower environmental levels of contaminants can be detected. Limits of detection can be further improved by increasing the number of devices deployed or increasing the time of deployment.

Organisms, such as caged mussels, have also been used to monitor contaminant bioavailability. However, passive sampling may offer better reproducibility, because it avoids the natural variations in uptake by organisms. PSDs will also function in more toxic conditions whereas organisms may stop feeding or die (Herve *et al*., 1995). PSDs use a process of chemical diffusion; they require no power source or human intervention during deployment.

The main differences between different types of PSD are the contaminant species that each is designed to monitor for, their physical make up, and field handling and laboratory analysis procedures. Discussion on the different devices is provided in the following section (more detailed information is available in the cited references).

2.2   Passive sampling devices

Of the passive samplers currently available, the following are of direct relevance for use in monitoring pesticide contamination of water.

2.2.1 SemiPermeable Membrane Device (SPMD)

These samplers were first reported by Huckins, Tubergen and Manuweera (1990) and are now well developed (Huckins *et al*., 2000) and widely used (e.g. Petty *et al*., 1995; Rastall *et al*., 2004; Shaw *et al*., 2004). They consist of layflat, low-density polyethylene (LDPE) tubing (approximately 98cm x 3cm) containing triolein lipid (1ml) as the absorption matrix. The LDPE tubing used in SPMD is normally described as non-porous (Huckins *et al*., 2002b). However, random thermal motions of the polymer chains create small, transient cavities in the polymer. Hydrophobic compounds that have a cross sectional diameter smaller than these cavities will partition into the SPMD. In effect, this results in only dissolved (i.e. readily bioavailable) organic contaminants diffusing through the membrane and being concentrated over time. SPMDs are available commercially from Environmental Sampling Technologies, USA and Exposmeter, Sweden. The Environment Agency's National Laboratory Service (NLS) also has experience in manufacturing SPMDs 'in-house'.

SPMDs are used to monitor for non-polar organic compounds, defined as those with a log K_{ow}>3, with maximum cross sectional diameters of 1nm (Huckins *et al*., 2002b) and a molecular weight <600 Daltons (Rastall *et al*., 2004). Only non-ionic compounds are extracted because charged species lack membrane permeability (Huckins *et al*., 2002b).

2.2.2 Polar Organic Chemical Integrative Sampler (POCIS)

First reported by Alvarez (1999) these samplers are designed to monitor for the more polar organic compounds which are not accumulated by SPMDs, i.e. compounds with a log K_{ow}<3. Although less well established than SPMDs they have been produced by the same research group at the US Geological Survey Columbia Environmental Research Centre (USGS CERC), where research and development is continuing (Alvarez *et al*., 2004). The POCIS devices consist of solid phase extraction (SPE) resin sandwiched between two polyethersulphone membranes clamped together by steel or acetyl plastic rings (9cm outside diameter, 5cm inside diameter). Two alternative SPE resins are available, depending on the polarity of the compounds of interest, their chemical structure and functional groups. Either an admixture of Isolute ENV+ (80mg) with S-X3 dispersed Ambersorb 1500 (20mg) can be used or Oasis HLB (100mg) for highly polar compounds. Like SPMDs, POCIS devices are available commercially from Environmental Sampling Technologies, USA and Exposmeter, Sweden. The NLS have experience in manufacturing POCIS devices too.

POCIS devices sample for polar organic compounds, defined as those with a log K_{ow}<4, with maximum cross sectional diameters of ~0.1µm (Alverez *et al*., 2004).

2.2.3 Portsmouth Passive Sampler (PPS)

Developed at Portsmouth University (Kingston *et al*., 2000), these devices are designed to monitor for polar or non-polar organic contaminants, depending on the configuration selected during manufacture. The PPS consist of a C_{18} Empore disk (47mm diameter) with either a polyethylene (for non-polar organic compounds) or polyethersulphone (for polar organic compounds) outer membrane held in a specially designed assembly unit made of Teflon plastic. Although the PPS monitors for a similar range of contaminants as SPMD and POCIS devices, they have lower sampling rates because the membrane is one-sided and so has a much smaller surface area than the two-sided SPMD and POCIS models. The PPS is therefore less suitable for trace level contaminants. Presently, prototype PPS devices are available from Portsmouth

University, but a commercial version should be available in the future (Goddard *et al*., 2004).

Depending on the sorbant used in the PPS they are capable of accumulating contaminants with log K_{ow} 2-4 or >4 (Kingston *et al*., 2000).

2.2.4 TRIMethylPentane Sampler (TRIMPS)

This sampler has been designed as an alternative to the SPMD. The triolein lipid used as the absorption matrix in SPMDs is replaced with 2,2,4-trimethylpentane, whilst the diffusive membrane remains unchanged (Leonard, Hyne and Pablo, 2002). This change is reported to eliminate any fouling of the membranes by periphytic growth and simplifies analysis by reducing the extraction and clean-up procedures required. The TRIMPS also has different dimensions to the SPMD, with 10ml 2,2,4-trimethylpentane being contained in an LDPE bag (approximately 3cm x 10cm). The Environment Agency has not yet used these devices, but the advantages they offer over SPMDs – simplified preparation and analysis, and reduced potential for fouling – makes them of interest. However, the release of the adsorption matrix to the environment during deployment is a disadvantage (Leonard *et al*., 2002). TRIMPS are not available commercially and have not been manufactured previously by the NLS. However, due to the similarity in manufacture to SPMD they could be made if required.

TRIMPS sample for non-polar contaminants with log K_{ow}>3.5 (Leonard *et al*., 2002).

2.2.5 Other Passive Sampling Devices

In addition to the device detailed above, there are several PSDs that are designed to accumulate metals. As these devices are not directly relevant to this project they are only listed below and not discussed further. However, more information on these devices is available in Goddard *et al*. (2004) or from the cited references.

- Diffusive Gradient in Thin film device (DGT) (Zhang and Davison, 1995);

- Stabilised Liquid Membrane Device (SLMD) (Brumbaugh *et al*., 2002);

- Passive Integrative Mercury Sampler (PIMS) (Brumbaugh *et al*., 2000).

2.3 Suitability for pesticide detection

To date, studies have demonstrated the advantages of PSD over spot samples, and their suitability for use in monitoring for some pesticides (Huckins *et al*., 1995; Alvarez *et al*., 2002; Kingston *et al*., 2000; Leonard *et al*., 2002). However, the devices have only been shown to monitor for a limited number of pesticides to date. Appendix 1 lists the 99 pesticides identified as candidates for monitoring based on use in England and Wales (Garthwaite *et al*., 2003). Appendix 1 also identifies which of these have been detected by passive sampling methods thus far, and those which would be predicted to be accumulated by PSDs based on the chemical's log K_{ow}.

There are four PSDs that show potential for pesticide monitoring: SPMD, POCIS, TRIMPS and PPS. None of the PSD sample compounds across the whole range of polarity. Therefore, at least two must be selected to cover the whole range of compound polarities. As these are relatively novel devices it would be advantageous to select those PSDs on which most work has already been done i.e. the SPMD and POCIS. TRIMPS could offer advantages over SPMD due to the simplified preparation

for analysis, as the analytes are already in a solvent, rather than lipid. However, TRIMPS would require more developmental work initially as they have been used for only a small number of compounds. Alternatively, polar and non-polar PPS could be used. However, PPS sampling rates are low; several devices would have to be aggregated in order to detect trace contaminant levels.

Of the PSDs described, SPMD and POCIS have been shown to accumulate the broadest range pesticides (Appendix 1) and have had the most research into quantifying contaminant concentrations (Section 2.5). Furthermore, the NLS has increasing experience in manufacturing and analysing SPMD and POCIS. For SPMD, the NLS at Leeds is in the process of gaining UKAS accreditation for the extraction and analysis of SPMD. Work on POCIS has been based at the NLS at Llanelli, where extraction and analysis methods are available. The Environment Agency has only recently started to use PPS devices, with the extraction and analysis being carried out by the laboratory at Llanelli. The NLS has no experience with TRIMPS.

2.4   How are contaminants accumulated by PSD?

The rate at which contaminants are accumulated by PSDs is controlled by the rate of their diffusion through the membrane or boundary layer. For those contaminants which can be accumulated onto an individual PSD absorption matrix, the driving force for uptake, and therefore the sampling rate, is largely dependent on the contaminant's log K_{ow} (Booij et al., 1998; Leonard et al., 2002). More specifically, it is directly related to the contaminant's K_{PSD} (equilibrium PSD-water partition coefficient), which is approximated by their K_{ow} (Huckins et al., 2002b). The overall resistance to chemical uptake is inversely proportional to flow, and directly proportional to the thickness of the aqueous boundary layer and the membrane (only when uptake is controlled by the membrane). The effects of environmental variables on sampling rates are discussed further in the following section.

Sampling rate is defined as the daily volume of water cleared of chemical by the PSD (l/d) and is independent of contaminant concentration. This is a first order uptake rate constant. If the sampling rate of a PSD is 5l/d it can accumulate all the contaminant present in 5l of water, whatever the concentration. Therefore, the rate remains constant but the amount of contaminant accumulated is proportional to the environmental concentration.

Uptake by a PSD is represented by one of three phases (Figure 2.1):

- linear - no loss of accumulated contaminant, equilibrium not approached during the exposure

- curvilinear - equilibrium approached

- equilibrium - the amount of chemical accumulated is exactly equal to the amount of chemical lost, per unit time.
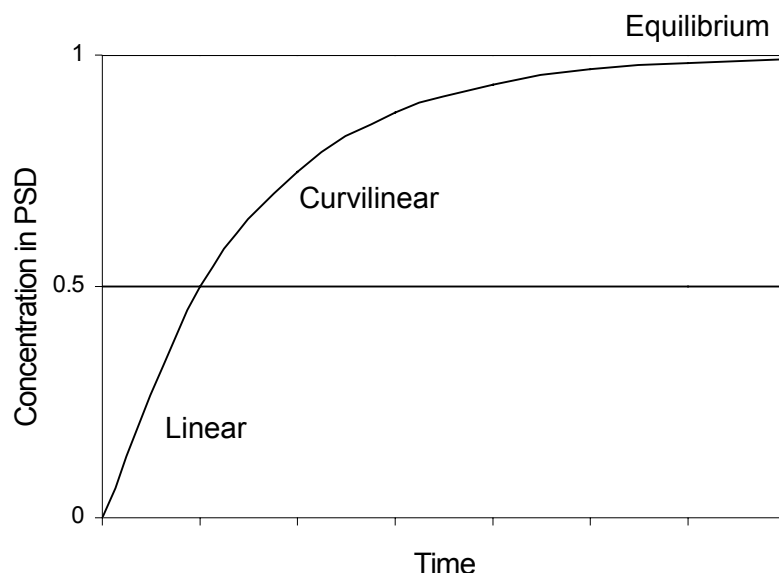
Figure 2.1 Theoretical uptake of a compound by a PSD

The uptake phase is dependent upon the contaminant's K_{ow} and the duration of exposure. Chemicals with higher K_{ow} have a greater affinity for the lipid layer, and therefore take a longer time to reach equilibrium.

When less than half the PSD capacity is reached during an exposure the PSD the environmental concentrations of the contaminant can be estimated from linear uptake models. It has been reported that in general the uptake by SPMDs of contaminants with log K_{ow}>4.9 is integrative or linear (i.e. equilibrium not approached) during exposures of 30 days, and SPMD concentrations are proportional to ambient environmental concentrations (Huckins *et al*., 2002b). For organic compounds with log K_{ow}<4.9, equilibrium concentrations of analytes may be reached or approached in $\leq$30 days. POCIS devices have only rarely been shown to reach equilibrium, even after deployments of 2 months (Alverez, D. A., pers. comm. 2005). It can therefore be generally assumed that POCIS remain in the linear phase for shorter deployments.

2.5 Quantification of contaminant concentrations

2.5.1 How do you quantify?

After the PSD has been deployed and retrieved, the initial analytical results will be in terms of mass of contaminant per device. Although this useful qualitative result reveals which contaminants were present at the site during the deployment period, quantification of ambient pesticide concentrations is vital to determine their environmental significance. Each contaminant will be accumulated by the PSD at different rates, and external environmental variables can also affect this uptake (see below). However, by knowing the rate at which a contaminant is taken up by the PSD, a time weighted average (TWA) concentration can be calculated. Data establishing the sampling rate is termed calibration data.

In order to establish the sampling rate for each contaminant a series of tests need to be carried out in which PSDs are deployed in a flow-through system where analyte concentrations and water temperature remain constant (e.g. Huckins *et al*., 1993;

Alvarez, 1999; Kingston et al., 2000; Leonard et al., 2002). Researchers at the USGS CERC, the University of Queensland and the University of Portsmouth are currently undertaking this type of work. In addition to the information on sampling rates provided by these research groups it is likely that further calibration work will need to be undertaken by the NLS if PSDs were to be used as sampling instruments by the Environment Agency.

The generation of calibration data in order to be able to calculate TWA concentrations can be time consuming and expensive. However, it is possible to generate this data after the sampling event, when it is known which pesticides were present. In this way resources can be focussed on those pesticides which are of interest.

Appendix 1 lists the pesticides of potential interest for monitoring based on high use and details those for which calibration data exist. Where the sampling rate for a pesticide/PSD combination is known, the TWA concentration can be calculated.

Different formula must be used to calculate the TWA depending on which phase of uptake the contaminant is in at the end of the exposure period. The calculation is most simple if the contaminant remains in the linear uptake phase. The TWA concentration can be calculated as:

$$TWA = C_S M_S / R_S t \qquad \text{(Alverez et al., 2004)}$$

where C_S is the analyte concentration in the sorbant, M_S is the mass of the sorbant, R_S is the sampling rate and t is time in days. R_S is dependent on the size of the PSD so the M_S term is used to correct for cases where a non-standard size PSD is used. Where standard PSDs are used, and standard PSDs have been used to derive the R_S, then the M_S term can be removed.

For example, to quantify the concentration of chlorpyrifos in a watercourse using a standard SPMD deployed for one day on which the typical minimum quantifiable mass of 10ng/l was accumulated:

$$R_S = 3.1 l/d$$

$$TWA = 10/(3.11 * 1)$$

$$TWA = 3.2 ng/l$$

TWA concentrations for TRIMPS and PPS have been calculated slightly differently in the literature. Instead of calculating a sampling rate that is independent of time and concentration a concentration factor (Hyne et al., 2004) or accumulation factor (Kingston et al., 2000) is calculated. This is the ratio of the concentration accumulated in the PSD to the concentration in the water. This factor varies with time. The TWA concentration is calculated as:

$$TWA = C_S(t)/AF(t) \qquad \text{(Kingston et al., 2000)}$$

where $C_S(t)$ is the concentration of analyte in the sorbant at time t and AF(t) is the accumulation factor at time t. Therefore, $AF(t) = R_S t$.

If equilibrium is reached during deployment then the following equation can be used to calculate the environmental concentration:

$$TWA = C_{SE}/K_{PSD} \qquad \text{(Huckins et al., 2002b)}$$

where C_{SE} is the concentration in the sorbant at equilibrium and K_{PSD} is the PSD-water partition coefficient, which can be approximated by K_{ow}. Although SPMDs may reach equilibrium during longer deployments, POCIS devices have only rarely been shown to reach equilibrium even after two-month deployments (Alverez, D. A., pers. comm. 2005).

2.5.2 How do environmental variables affect sampling rate?

The main concern with interpretation of data collected by passive monitoring is the difference in contaminant uptake in the environment compared to that in the laboratory. The three major factors that affect sampling rates are temperature, flow rate and degree of fouling (Kingston *et al*., 2000; Huckins *et al*., 2002a). Under some exposure conditions, the effects of environmental variables have been shown to alter sampling rates of SPMDs by close to an order of magnitude (Huckins *et al*., 2002a). Temperature affects sampling rate, regardless of which step in the uptake process is rate limiting or has the most resistance to mass transfer. Water flow will only affect sampling rates if uptake rates are dependent on the aqueous boundary layer (Huckins *et al*., 2002b).

Passive sampling is a diffusive technique. For a gradient to be maintained between the PSD and the sample media there must be mixing of the bulk solution and aqueous boundary layer. Increased flow does not increase the concentration of contaminant at the membrane surface, but it does ensure that the concentration in the aqueous boundary layer reflects that in the bulk solution. In low flow situations, or where there is little water movement (i.e. stagnant ditches or ponds) the concentration at the membrane surface may become depleted.

For exposure conditions of low to moderate flow, SPMD uptake is under membrane control for compounds with log K_{ow}<4.4 and under aqueous boundary layer control for compounds with log K_{ow}≥4.4 (Huckins *et al*., 2002b). Similarly, Booij *et al*. (1998) found that at water flow velocities <30cm/s SPMD uptake was governed by aqueous boundary control for compounds with log K_{ow}>4. Sampling rates are unaffected by aqueous flow only when a chemical is completely under membrane control. This is because transport across the membrane is the rate-limiting step. As long as sampling does not deplete the chemical concentration at the membrane surface then chemical uptake is independent of flow regime. For compounds under aqueous boundary layer control, flow induced changes in the sampling rates of chemicals can be as high as ten-fold (Huckins *et al*., 2002a).

Given the wide range of environmental exposure conditions which PSDs may experience, flow effects are generally expected to have a greater impact on the SPMD sampling rate than temperature or biofouling (Huckins *et al*., 2002b). Flow rates have been demonstrated to alter SPMD sampling rate by up to ten-fold, whilst temperature and biofouling can cause changes up to four-fold (Huckins *et al*., 2002a). Flow rate is also expected to have greater influence than temperature on POCIS sampling rates as analyte uptake is usually under boundary layer control. Four- to nine-fold differences in sampling rate have been observed between still and stirred conditions (Alverez *et al*., 2004).

Temperature of the water body and flow rate can be measured and corrected for in TWA calculations (Zhang and Davison, 1995). Ideally, both of these variables would be measured continually over the deployment period. However, this is not always practicable and so measurements taken at the time of deployment and when the PSD is retrieved can be averaged and used as a surrogate. For example, Shaw *et al*. (2004) adjusted for differences in temperature between sites by calculating the average temperature over the deployment. This was then used to select the appropriate

sampling rate from a range of laboratory studies carried out at different temperatures. When the sampling rate had not been determined for the temperature of interest, interpolation between other results was used (Shaw *et al.*, 2004).

The main environmental variable which cannot be corrected for easily is the degree of fouling experienced by the device. It has been observed that the TRIMPS and POCIS devices are less susceptible to biofouling (Leonard *et al.*, 2002 and Alverez *et al.*, 2004 respectively). However, SPMDs can become heavily fouled, depending on the environmental conditions at a site. Biofouling impedes, but does not stop, the uptake of chemicals by PSD (Ellis *et al.*, 1995). Therefore, biofouling causes a reduction in the sampling rate and leads to an underestimation of the environmental concentrations of the analytes of interest (Kingston *et al.*, 2000). One study using an SPMD demonstrated decreases in sampling rate of between 26.1% and 38.6% after 56 days exposure, when compared to a freshly prepared SPMD (Ellis *et al.*, 1995). In particular, compounds with high K_{ow} are impeded more than those with low K_{ow} (Alverez *et al.*, 2004).

Petty *et al.* (1995) attempted to adjust for biofouling by altering the sampling rate constant. This was done by correcting the sampling rate by using an estimate of the reduction in sampling rate due to biofouling.

$$R_{SC} = R_S F_1 \qquad \text{(Petty et al., 1995)}$$

where R_{SC} is the corrected sampling rate and F_1 is 1-the fractional reduction in sampling rate due to biofouling. For their study, Petty *et al.* (1995) used the average fouling impedance of 31% (i.e. $F_1 = 0.69$) calculated by Ellis *et al.* (1995). Although this does attempt to correct for biofouling it is a fairly crude approach as the amount of biofouling will vary between studies and individual SPMDs.

2.5.3   How can you correct for environmental variables?

Taking account of these varying environmental factors, and the difficulties in measuring temperature and flow rate continually for the entire deployment period, novel correction approaches were looked for. One approach has been to spike the PSD with a compound that is not present in the environment. This compound, known as a Permeability/Performance Reference Compound (PRC) desorbs into the water during deployment. The term 'permeability' refers to compounds under membrane control and 'performance' to compounds under external boundary layer control (Huckins *et al.*, 2002b). The difference between the expected and actual loss of the PRC can then be used to provide a correction factor for the other contaminant sampling rates (Huckins *et al.*, 2002b). This correction factor, termed an Exposure Adjustment Factor (EAF), will compensate for all potentially influencing environmental variables (Huckins *et al.*, 2002a). To date, the PRC technique has been used successfully with SPMDs (Huckins *et al.*, 2002a) and TRIMPS devices (Hyne *et al.*, 2004) and investigations into their potential use with PPS devices are ongoing (Kingston et al., 2000).

The EAF is calculated as:

$$EAF = R_{e\text{-field}}/R_{e\text{-lab}} \qquad \text{(Shaw et al., 2004)}$$

where, $R_{e\text{-lab}}$ is the elimination rate of the PRC calculated in the laboratory and $R_{e\text{-field}}$ is:

$$R_{e\text{-field}} = \ln(C_{PSD\text{-}0}/C_{PSD})/t$$

where, C_{PSD-0} is the concentration of PRC spiked into the PSD and C_{PSD} is the concentration of PRC in the PSD after deployment. The EAF is multiplied by the sampling rate to give the 'field adjusted' sampling rate.

Most investigative work has looked at the use of PRC with SPMDs and this will be discussed here to outline the principles of this approach. *In situ* SPMD calibration is based on the principle that the rate of residue loss is proportional to the rate of residue uptake. Thus, PRC loss rate data can be used to adjust SPMD-derived estimates of ambient concentrations to reflect site-specific environmental conditions of an exposure. A fundamental assumption of the PRC approach is that the EAF of a PRC with log $K_{ow} \leq 5.0$, can be used to predict the EAF of chemicals with much higher log K_{ow}. Based on a study by Huckins *et al.* (2002a), this assumption appears valid and the difference between directly measured concentrations of an analyte and the PRC derived estimates are within a factor of two.

The compound selected as the PRC is an analytically non-interfering compound, which has moderate to fairly high fugacity (Huckins *et al.*, 2002a). Selection of compounds to serve as a PRC must take into account the need to have measurable losses of PRC residues during the exposure and the ability to differentiate PRC residues from other quality control standards, target compounds and unknowns of potential interest to an investigator (Huckins *et al.*, 2002b). Information on the environmental conditions (e.g. flow rate and temperature) at sample sites and the duration of planned exposures should be used to help ensure that an acceptable range of PRC loss occurs. For example, PRC losses are enhanced under exposure conditions of warm turbulent waters (Huckins *et al.*, 2002a), and it would therefore be necessary to use a PRC with a moderately high K_{ow} (>4.5) in order to prevent total loss. In addition, larger quantities of PRC may have to be spiked into the SPMD.

Even when PRC loss or retention is too great to use for the derivation of EAF, information on the uptake phase of the analyte at the termination of the exposure is still gained (Booij, Zegers and Boon, 2000). For example, if a PRC with a log $K_{ow} <4.5$ is completely lost during an exposure, then all analytes with log $K_{ow} <4.5$ should have attained equilibrium. Alternatively, if no loss of a PRC with a log $K_{ow} \geq 5.0$ is observed then linear uptake can be assumed for all analytes with log $K_{ow} \geq 5.0$.

Several different compounds have been suggested for use as PRC. These include certain perdeuterated PAHs, ^{13}C labelled compounds, 2, 2'-dichlorobiphenyl and 2, 4, 5-trichlorobiphenyl (Huckins *et al.*, 2002b). The choice of which PRC to use is important, and more than one may be necessary in each SPMD. For example, depending on the K_{ow} of target contaminants, PRCs that are representative of both membrane and diffusion control may be needed. Shaw *et al.* (2004) found large differences in the loss of two PRC from the same SPMD. This was attributed to the different size and K_{ow} of the PRC. It was therefore suggested that a range of PRCs representing the range of contaminants of interest, should be used to further improve field calibration of sampling rates (Shaw *et al.*, 2004).

PRCs have not yet been successfully developed for use in POCIS devices because the sorbants used in these devices do not allow a measurable loss of the PRC (Alverez, D. A., pers. comm. 2004). However, work is continuing in this area. Until the PRC technique is available the information for adjusting the sampling rate in the field can be read-across from SPMDs that are deployed concurrently (Alverez, D. A., pers. comm. 2004). This information is qualitative but does give an indication of relative conditions between sampling sites or times.

2.5.4   How do you define the environmental limit of detection?

Environmental limits of detection (LOD) for PSDs are difficult to define. They depend upon the analytical limit of detection, the sampling rate and the exposure time. Taking the earlier example of chlorpyrifos detection using an SPMD, if the device were deployed for 28 days during which chlorpyrifos was present in the water for only one hour the actual environmental concentration would have to be at least 77ng/l for enough contaminant to accumulate and be quantifiable. This compares to an environmental concentration of 3ng/l if chlorpyrifos was present continuously, for the analytical LOD to be reached.

Therefore, environmental LOD are not reported for PSDs. Instead, the LOD of the analytical methods are reported so that the minimum quantifiable concentration on the PSD is known (e.g. Method Quantification Limits; Vrana *et al*., 2001).

An inability to define LOD may cause problems during the data analysis. For some statistical techniques 'non-detects' are replaced by the LOD because zero values may cause the statistical assumptions to be violated, or prevent the statistical transformation of data to fit a particular distribution. For data from PSDs it is not possible to replace non-detects with LOD, as the LOD are variable and unknown.

The subject of variable environmental LOD also highlights another issue with using PSDs: we can only calculate average concentrations over the deployment period. For the example given above, both samplers would have 10ng chlorpyrifos per device but they have sampled very different environmental conditions. The problems associated with TWA concentrations are discussed further in the following section.

2.5.5   How useful is a TWA concentration?

The initial results of the laboratory analysis of a PSD will give the mass of each contaminant accumulated. These results can then be used to generate TWA concentrations in the environment using the appropriate calculation and calibration data. As Vrana *et al*. (2001) emphasise, this value is an average concentration rather than the maximum concentration reached during deployment.

The use of TWA concentrations leads to a situation where a PSD deployed at a site which experiences a single high peak concentration could have the same mass per device as a PSD deployed at a site where there is continuous low exposure. These two situations could lead to very different effects on the biota and can lead to difficulties in interpreting results in relation to biological impacts. When investigating the impacts of pesticides it is vital that we are able to distinguish between these two situations.

Calculating the average concentration over the total deployment time may not be the correct approach when monitoring for pesticides, as in certain circumstances, such as spray drift events, contaminants will only be present for a short time. The calculation of TWA concentrations could be adjusted by using an exposure time based on knowledge of spraying and rainfall events. Therefore, instead of dividing the mass of contaminant on the PSD by total deployment time, it is divided by predicted exposure time. This approach may give a more realistic estimate of environmental concentration for transient pollutants, although the calculation of exposure time would need to be validated.

2.5.6 How much greater than the LOD must the environmental concentration be to be picked up?

There has been concern expressed that passive samplers may not accumulate contaminants quickly enough to reach analytical detection levels if the contaminants are only present in the water body for short periods of time, i.e. a pulsed exposure. For example, many pesticides would only be expected to be present in the watercourse as short 'pulse' events.

As previously discussed, if in the linear uptake phase, the TWA concentration can be calculated as:

$$TWA = C_S/R_St$$

where C_S is the analyte concentration in the sorbant, R_S is the sampling rate and t is time in days.

This equation can be rearranged to answer the question "What is the ratio of analyte concentration on the sorbant to the environmental concentration if the contaminant is present for x hours?"

$$R_S(x/24) = C_S/TWA$$

This ratio is more easily understood if it is expressed as "How much greater is the TWA concentration than the analyte concentration on the sorbant after x hours?"

$$TWA/C_S = 1/(C_S/TWA) = 1/(R_S(x/24))$$

As there is a lower cut-off to the level of analyte we can detect on the sorbant – the LOD – this can also be expressed as "How much greater must the TWA concentration be than the LOD to be detected if the contaminant is only present for x hours?"

$$TWA/LOD = 1/(R_S(x/24))$$

Theory and experimental data suggest that standard SPMD sampling rates for most compounds range from about 0.5 to 10l/d (Huckins *et al*., 2002b). POCIS sampling rates are much lower at between 200 to 500ml/d (Alverez, D. A., pers. comm. 2005). These values were used as lower and upper bounds in the calculations. The results of these calculations are shown in Table 2.1.

Table 2.1 Showing how much greater the TWA must be than the LOD for the contaminant to be detected over different time periods

R_S	Time (hours)						
	0.5	**1**	**2**	**3**	**6**	**12**	**24**
0.2	240	120	60	40	20	10	5
0.3	160	80	40	26.67	13.33	6.67	3.33
0.4	120	60	30	20	10	5	2.5
0.5	96	48	24	16	8	4	2
1	48	24	12	8	4	2	1
2	24	12	6	4	2	1	**0.5**
3	16	8	4	2.67	1.33	**0.67**	0.33
4	12	6	3	2	1	**0.5**	0.25
5	9.6	4.8	2.4	1.6	**0.8**	0.4	0.2
6	8	4	2	1.33	**0.67**	0.33	0.17
7	6.86	3.43	1.71	1.14	**0.57**	0.29	0.14
8	6	3	1.5	1	**0.5**	0.25	0.13
9	5.33	2.67	1.33	**0.89**	0.44	0.22	0.11
10	4.8	2.4	1.2	**0.8**	0.4	0.2	0.1

Notes: Bold type shows when the TWA can be less than the LOD but still detectable

Table 2.1 shows that for a pesticide to be detectable:

- as the time for which the pesticide is present increases, the ratio of TWA concentration to the LOD can decrease;

- as the sampling rate increases, the ratio of TWA concentration to the LOD can decrease;

- passive samplers permit the detection of pesticides that are at concentrations below the analytical LOD, due to accumulation, if the compound is present for sufficient time

If pesticides are entering the aquatic environment by a single application event such as spray drift, they may only be present in the water body at a specific sampling point for a short period of time (minutes, rather than hours) before washing downstream. Table 2.1 demonstrates that compounds accumulated by POCIS would have to be present at concentrations over fifty times greater than the LOD in order to be accumulated to quantifiable concentrations in less than 1 hour, or over one hundred time greater to be quantifiable after 30 minutes. Compounds picked up by SPMD would be quantifiable at much lower relative concentrations over the same time period.

If pesticides enter the waterbody by drain flow then they may be present for longer periods of time. Lower concentrations could therefore be accumulated and quantified on both POCIS devices and SPMDs.

However, it should be noted that sampling rates in the field may be lower than those calculated in the laboratory due to differences in temperature, flow and biofouling, as previously discussed. The calculations in Table 2.1 may therefore represent the lower limit of detection times.

2.5.7   How much variability between replicates is there when using PSD?

For a sampling technique to be useful the results must be repeatable. Several studies have compared the mass of analyte accumulated on replicate SPMDs to quantify the amount of variability between samplers (Table 2.2). Data from studies using POCIS are shown in Table 2.3.

Table 2.2   Results of studies comparing variability between replicate SPMDs

Chemical	Coefficient of variation	
'Typical' chemical	<20%	Huckins *et al*., 2002b
PAH	14-33%	Shaw *et al*., 2004
PAH except:	<29%	Vrana *et al*., 2001
Acenapthene	44%	Vrana *et al*., 2001
PAH except:	0-21.8%	Goddard *et al*., 2004
Benzo[ghi]perylene	0.4-59.7%	Goddard *et al*., 2004
Organochlorine pesticides except:	<24%	Vrana *et al*., 2001
p,p'-DDD	40%	Vrana *et al*., 2001
Organochlorine pesticides except:	10-35%	Petty *et al*., 1995
2,4'-DDE	28-72%	Petty *et al*., 1995
Endrin	16-67%	Petty *et al*., 1995
Dacthal	20-65%	Petty *et al*., 1995

Table 2.3   Results of studies comparing variability between replicate POCIS devices (Alverez, D. A., pers. comm. 2005).

Chemical	Coefficient of variation
Chlortetracycline	8%
Tetracycline	3%
17 beta estradiol	11-52%
Crotamiton	3%
Atrazine	6-40%
Acetochlor	20%
Alachlor	0-6%
Metolachlor	3-37%
Chlorpyrifos	1-8%

2.5.8   Do chemicals diffuse out of samplers?

SPMDs and POCIS devices reputedly act as infinite sinks for accumulated residues whilst in the linear uptake phase (Huckins *et al*., 2002b, Alverez *et al*., 2004). This means that contaminants accumulated into the PSD are not lost back to the environment, even if the environmental concentration drops. This reduces the probability of a false negative, as residues from episodic events are retained and can therefore be detected. This is particularly important for contaminants such as pesticides, for which exposure is likely to be transient.

However, as the use of PRCs indicates, chemicals are able to move out of SPMDs. It is possible that for some devices contaminants will diffuse back into the water once the concentration drops (Huckins, J. N., pers. comm. 2004). Rogers (1997) demonstrated that exposure to peak concentrations followed by reversion to background levels resulted in compounds being lost from SPMDs resulting in an underestimate of environmental concentrations. POCIS devices are less likely to experience loss of accumulated analytes, as evidenced by the lack of a measurable loss of PRC

compounds over time. Further work is required in this area to determine whether the potential for losses is an issue that would compromise the calculation of TWA concentrations from PSDs. This is investigated further in Section 4.

2.6 Deployment methods

Passive sampler casings were originally designed for use in water bodies deeper than 50cm. For example, their use has been demonstrated on the tidal Thames, where they are secured by attachment to solid structures on the bank (Goddard *et al*., 2004). However, many locations of interest are much shallower, especially watercourses most vulnerable to pesticide contamination, and PSDs will need to be deployed in waters ~10cm+. This situation raises several potential problems (Alverez, D. A., pers. comm. 2005):

- Samplers must remain submerged for the entire sampling period. In very shallow streams it may be necessary to find a deeper pool or dig a hole to set the samplers in to keep them submerged.

- If silting is a major concern, then the PSD should be raised off the streambed. This could be achieved by driving posts/rods into the streambed and hanging the PSD from them. Alternatively, a deployment method using floats could be devised. If the streambed is rocky, then the PSD should work well sitting on the substrate.

- If there is a very fast flow, then the deployment canisters may be damaged by crashing against any rocks, or may be swept downstream if not securely anchored. Increased flow can increase the sampling rate (see previous section), but too much flow may cause damage to the PSD, jeopardising the experiment. When deploying the PSD, the flow at the site should be considered. If the river is particularly fast flowing it may be best to deploy out of the main flow to limit this risk.

- If the water is clear, photodegradation of some chemicals (e.g. PAHs in SPMDs) can be a problem. The PSD should be kept shaded as much as possible, especially in shallow depths, although the deployment canisters themselves will provide some shade. This is also an important consideration if the substance used as the PRC is photodegradable. It was suggested that some PAHs may be suitable PRCs (Section 2.5.3). Estimated photolysis half-lives of PAHs in direct sunlight range from 0.1 to 5h (Huckins *et al*., 2002b). To counter this, the use of a photolysis stability standard has been suggested (Huckins, J. N., pers. comm. 2005). This could be spiked into the SPMD with the PRC, but would be chosen as a compound that would not be lost from the SPMD even during extended exposures but which is susceptible to photolysis. Deuterated dibenz[a,h]anthracene has been suggested; any appreciable loss during deployment would indicate that the PSD had been affected by photolysis.

- The PSD must be anchored to the site. The deployment canisters can be attached to a solid support on the bank such as a tree, fence post, or some type of post that is driven into the ground. The use of steel woven cable and cable locks has been demonstrated to be a very good means of securing the PSD.

- Vandalism can pose the greatest threat to the samplers, especially in shallow streams where they can be easily seen. Anchoring the devices securely will prevent their removal from the site. However, this doesn't

> prevent the vandal from pulling the devices out of the water and leaving them on the bank.

A small scale field study will be carried out to examine ease of deployment and recovery of PSD and to investigate the potential for damage or fouling. Where compounds are detected during this trial, a comparison of the results from different PSD deployment configurations can be made, which will enable reproducibility to be assessed. The results of these trials are presented in the following chapter.

2.7   Summary

Several different types of PSD have been demonstrated to accumulate various pesticides. Based on the current state of knowledge and NLS experience, we would recommend that SPMDs and POCIS devices are taken forward for use in laboratory and field testing.

PSDs provide a means to monitor continuously over an extended period of time. This provides a clear advantage over spot sampling, which may miss transient pollutants such as pesticides. In addition, as PSDs are accumulative, concentrations below normal LOD can be quantified if contaminants are present in the watercourse for a sufficiently long period of time.

However, passive sampling does have some drawbacks. As it is a relatively new technology, only a few compounds have been tested to see if they are picked up, and even fewer have had calibration data generated so that a TWA concentration can be calculated. It will be necessary to demonstrate that the compounds of interest are accumulated on PSDs before using the devices for environmental monitoring. Calibration data will be required for the compounds detected, but can be generated retrospectively.

A TWA concentration is the average concentration of a contaminant over the deployment period. When trying to link contamination with adverse biological effects, the maximum concentration may be of more relevance than the average. With knowledge of the local pesticide applications and likely exposure routes it may be possible to model the maximum concentration, although this approach will require further development and validation.

Most previous studies with PSDs have investigated low level, chronic exposures. However, the highest risk exposures of pesticides are predicted to result from spray drift events (Environment Agency, 2006), and therefore short term exposures are of most interest. It is unclear how quickly contaminants are picked up by PSDs, but the shorter the exposure period the greater the concentration must be for a quantifiable amount of the compound to be accumulated. In addition, it is unclear whether, or to what extent, contaminants are lost from PSDs if the environmental concentration drops. Both the effects of short term exposure and possible loss of compounds will need to be investigated in the laboratory before a decision can be made on whether PSDs are a suitable chemical monitoring technique for transient pesticide contamination.

Monitoring for pesticides in the highest risk scenarios is also likely to test the limits of PSDs. The highest risk sites are likely to be small streams with little dilution. These shallow waterbodies may pose new problems as PSDs have not usually been deployed in these situations. Field trials will therefore be necessary to test the PSD *in situ*.

Sections 3 and 4 report the results of the field and laboratory trials respectively.

3   Field trials of PSD

3.1   Introduction

PSDs were trialled in a number of watercourses. These field trials were designed to provide information necessary to determine:

- which of the passive monitoring deployment devices were suitable for use in shallow waters;

- how much variability exists between deployment devices;

- how much variability exists within the same deployment model;

- the comparability of commercial and 'in-house' PSDs;

- the equipment needed to successfully deploy and retrieve the PSD.

Two of the trials were carried out jointly with the Science-2-Ops Project (Environment Agency, 2006b). The Science-2-Ops project was set up to improve the implementation of new techniques and technologies and to explore different approaches to environmental monitoring. The project team has been assessing various new techniques on the Ribble catchment. The Ribble is a pilot catchment for the Water Framework Directive (WFD), and is being used to test new monitoring tools.

3.2   Field trial outline

As noted in Section 2.6, passive samplers have been successfully deployed in deep water. However, it is likely that in many situations they would need to be deployed in shallow waters, as these are likely to be at most risk from pesticide impacts. The sites that were selected for the field trials were generally shallow (<20cm). In addition to the standard deployment cages for POCIS (Figure 3.1) and SPMD Figure 3.2), a prototype 'shallow water cage' was also used (Figure 3.3). This shallow water cage was designed to house SPMDs, POCIS and DGT (a passive sampler for metals) devices and provide a means to deploy these devices in a shallower water depth. One of the aims of these trials was to determine which of the deployment cages was most suitable for deployment in shallow waters.
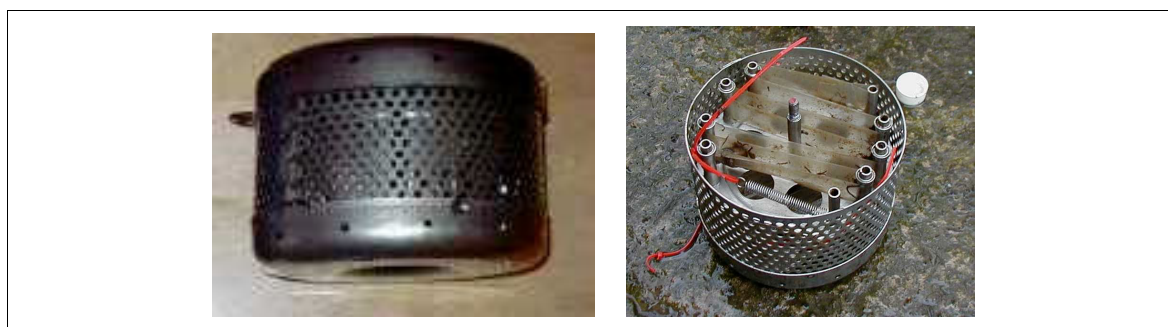
Figure 3.1   SPMD cage (left) and cage with SPMD after deployment (right)
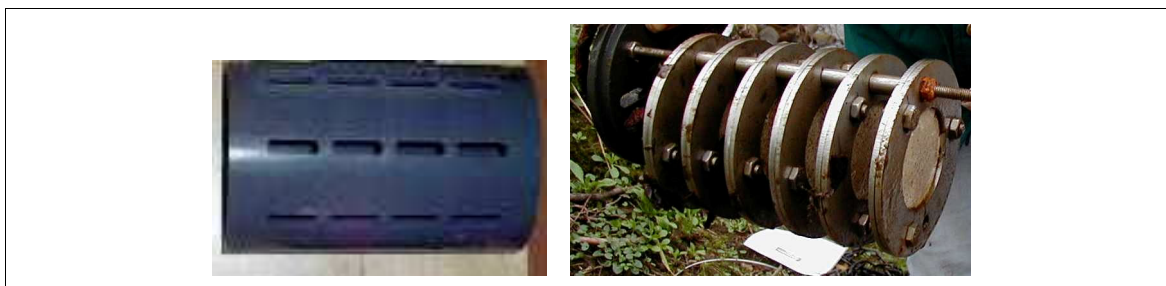
Figure 3.2 POCIS cage (left) and POCIS discs after deployment (right)
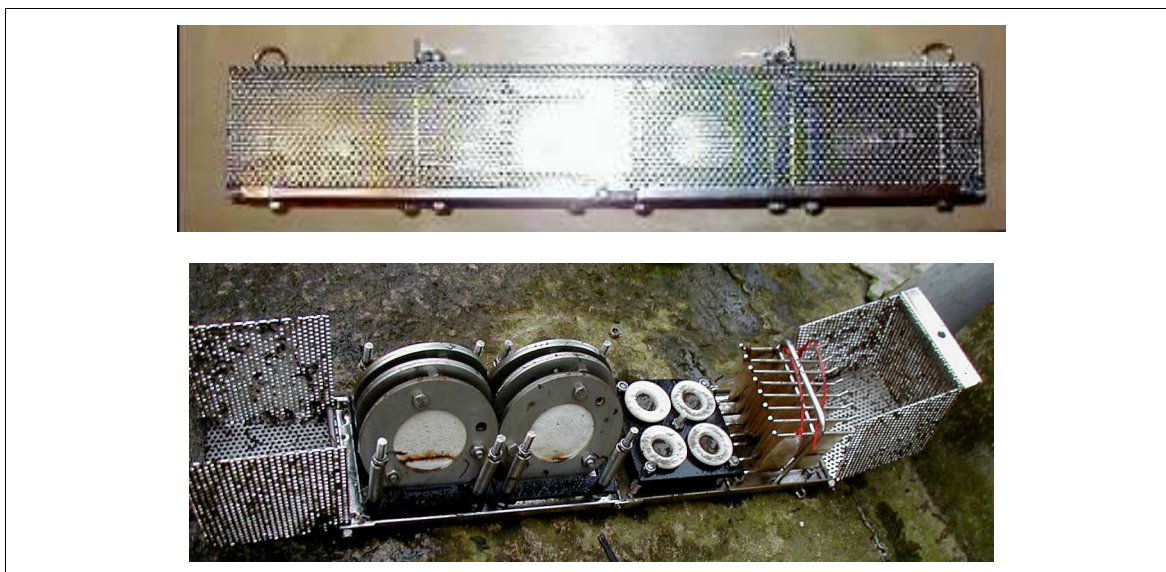
Figure 3.3 Shallow water cage (above) and cage with POCIS, DGT and SPMD after deployment (below)

3.2.1   Field Trial 1

Three sites in the Ribble catchment were selected to trial the passive samplers. The sites were not expected to have very high levels of pesticides, but were considered the most suitable for the needs of this trial. The main aim of this deployment was to test the different deployment cages to determine which were suitable for use in shallow water.

Site 1 (Samlesbury) was at the site of an Environment Agency continuous monitoring station on the River Ribble. The site was very wide, but shallow (~20cm) and slow flowing, with a fairly silty substrate with areas of bedrock (Figure 3.4). There was no shade and the water was very clear. The catchment was rural with some urban/industrial input.

Figure 3.4 Samlesbury sampling site

Site 2 (Jumbles Rock) was also at the site of an Environment Agency continuous monitoring point on the River Ribble. This site had very similar characteristics to Site 1 but was deeper (~40cm) and further upstream with less urban/industrial input (Figure 3.5).

Figure 3.5 Jumbles rock sampling site

The final site was on a tributary of the River Lune. This was a shallow (15cm), narrow (~1.5m) waterbody with a pebbly substrate and very clear water (Figure 3.6). This site

was shaded. This much smaller catchment was predominantly rural with some urban inputs.

Figure 3.6 Tributary of the River Lune sampling site

At each site, one of each of the three deployment devices were deployed from the 10th March 2005 to the 30th March 2005. Therefore, each site had:

- 1 SPMD cage containing 2 SPMDs;

- 1 POCIS cage containing 6 POCIS discs and;

- 1 shallow water cage containing 6 POCIS discs, 2 SPMDs and 4 DGT devices.

Results from the previous year's spot monitoring were used to guide which compounds were analysed for at the sites. In addition, the compound analysis included a number of priority substances from the WFD which were known to accumulate on PSDs. The selected determinands are detailed in Table 3.1. Although DGT devices were deployed in this field trial the results are not reported here.

Table 3.1   List of compounds analysed for in Field Trials 1 and 2, with the reason for their inclusion and whether they were looked for on POCIS or SPMD

Compound	Reason	POCIS	SPMD
Anthracene	WFD		Yes
Atrazine	WFD	Yes	
Azinphos methyl	Detected previously	Yes	
Benzo-a-pyrene	Detected previously		Yes
Chlorfenvinphos	WFD	Yes	Yes
Chlorotoluron	Detected previously	Yes	
Chlorpyrifos	WFD	Yes	Yes
Chrysene	Detected previously		Yes
Cypermethrin	Detected previously		Yes
Diazinon	Detected previously	Yes	Yes
Dicamba	Detected previously		Yes
Diuron	WFD	Yes	
Endosulfan	WFD		Yes
Fluoranthene	WFD		Yes
Hexachlorobenzene	WFD		Yes
Hexachlorohexane	WFD		Yes
Isoproturon	WFD	Yes	
Mecoprop	Detected previously		Yes
Naphthalene	WFD		Yes
Pentachlorobenzene	WFD		Yes
Pentachlorophenol	WFD		Yes
Phenanthrene	Detected previously		Yes
Pyrene	Detected previously		Yes
Simazine	WFD	Yes	
Trifluralin	WFD	Yes	Yes

3.2.2   Field Trial 2

Sites 1 and 2 described in the previous section were used in this field trial. The main aims of this trial were to compare sampler variability and to compare commercial and in-house samplers. At each site several of the same deployment devices were deployed from 30th March 2005 to the 20th April 2005. Each site either had:

- 8 SPMD cages each containing 2 SPMD or;

- 4 POCIS cages each containing 6 POCIS discs

The POCIS discs and SPMDs used in the first trial were bought from a commercial supplier. However, the Environment Agency's NLS is planning to manufacture both POCIS discs and SPMDs in-house. It is therefore necessary to compare the results obtained from commericial and NLS-manufactured samplers. To do this, half the cages at each site were stocked with bought samplers, whilst the other half were stocked with Environment Agency 'in-house' samplers.

Analyses were carried out for the same compounds analysed for in Field Trial 1 (Table 3.1).

3.2.3　Field Trial 3

The main aim of Field Trial 3 was to deploy the devices in situations likely to be representative of the sites at high risk of pesticide contamination.

Two sites being studied as part of the SOWAP project (http://www.sowap.org) were used to trial the passive monitors. Both sites were very shallow (<15cm), spring fed ditches running through arable agricultural land (Figure 3.7). POCIS devices and SPMDs were deployed at both sites from the 27th May to the 24th June 2005.

Figure 3.7　One of the SOWAP sites used in Field Trial 3. Photo shows SPMD and POCIS deployed in field edge ditch.

3.3　Field trial results

3.3.1　Field Trial 1

Three different deployment cages were used at each site in this trial. The SPMD cage and the POCIS cage were both easy and quick to use. The shallow water cage was very difficult to use. Its compact design made it very fiddly to attach the SPMD and POCIS and the large number of nuts and bolts were time consuming to fasten. Due to the slow preparation of the cage, the first samplers placed into it were exposed to the air for a long period of time before all samplers were installed and the cage placed in the water. Exposure to air should be minimised, as PSDs can accumulate compounds from the air as well as water. Although only a prototype, it was agreed that the height gain offered by the shallow water cage was outweighed by the negatives, and that the two other cages, although larger, were suitable for use in shallow waters.

None of the selected determinands were detected on the POCIS field blanks. The six discs from each deployment cage were combined prior to analysis, to increase the chances of detection. The results of the analyses from the deployed discs showed that atrazine, simazine, diazinon, diuron and carbendazim were detected (Table 3.2). Carbendazim, although not specifically requested, was also quantified as it was part of a pesticide analysis suite. At Sites 1 and 2, atrazine, simazine and diazinon were detected at very low levels by both replicates. Diuron and carbendazim were detected at higher concentrations. At Site 3, the much smaller tributary, only atrazine and simazine were detected, each by the pooled POCIS discs from one deployment cage.

Table 3.2   Results of POCIS analyses for POCIS cage (A) and shallow water cage (B) at each site in ng per device. Only those determinands which were detected are listed

Site		Atrazine	Simazine	Diazinon	Diuron	Carbendazim
1	A	[1]	[1]	[1]	86.8	22.4
	B	[1]	[1]	[1]	100.0	2.2
2	A	[1]	[1]	[1]	34.7	4.4
	B	[1]	[1]	[1]	40.4	4.1
3	A	[1]				
	B		[1]			

Notes: [1] The compound was detected at the LOD (0.01ng/disc) and should be treated as indicative only i.e. the compound was present but not quantifiable.

Phenanthrene and trifluralin were detected on SPMD field blanks from Site 3. The results from this site were adjusted for this control result. All results are presented in Table 3.3. As well as the determinands requested for analysis, DDT and its breakdown products were also reported as they were part of the analysis suite.

It was noted when deploying the SPMD that the SPMD cages had an oily residue that floated on the surface of the water when the cages were deployed. This may have contaminated the sampling devices and be the source of the PAHs detected. It is recommended that all cages should be cleaned thoroughly prior to use to avoid contamination of the PSD.

Table 3.3 Results of SPMD analyses for SPMD cage (A) and shallow water cage (B) at each site in ng per device. Only those determinands which were detected are listed

Site	1[1]				2				3			
	A		B		A		B		A		B	
	1	2[2]	1	2[2]	1	2	1	2	1	2	1	2
Anthracene[4]	26.9		27.0		22.5	24.5	19.7	26.5	35.7	37.4	38.8	41.3
Benzo-a-pyrene[4]	36.7		25.0		22.9	22.0	16.2	22.6	20.5	26.3	22.1	24.0
Chrysene[4]	108		87.9		67.1	69.5	57.4	68.2	81.3	100	92.9	101
Cypermethrin[3]												
p,p'-DDT	3.5		3.7		3.7	<0.4	2.5	<0.4	<0.4	<0.4	<0.4	2.6
o,p'-DDD	4.4		3.9		4.2	<0.4	<0.4	2.7	2.5	<0.4	2.8	2.0
p,p'-DDD	10.0		8.6		<0.5	<0.5	3.9	<0.5	2.2	<0.5	<0.5	2.0
p,p'-DDE	2.2		2.3		<0.8	<0.8	1.3	<0.8	2.6	3.3	<0.8	3.6
Fluoranthene[4]	541		458		373	393	329	405	591	694	713	
Hexachlorobenzene	3.1		3.8		2.2	1.8	2.0	1.9	2.9	2.7	4.0	3.4
Phenanthrene[4,5]	318		352		257	293	240	309	288	330	347	358
Pyrene[4]	728		635		435	445	370	459	448	565	524	547
Trifluralin[5]	1850		1400		1460	1170	1560	1370	1130	1100	2190	2150

Notes: [1] Field blank was breached (torn or punctured) so could not be analysed. Results from Site 1 are therefore not corrected for a blank.
[2] Sample was breached so could not be analysed.
[3] Cypermethrin internal standard failed so cypermethrin could not be quantified.
[4] In all cases there was interference which may have been due to oil contamination (see main text). This may have affected the results quoted, especially for the PAHs. One SPMD (3B) had no fluoranthene result reported due to high levels of interference associated with the peak.
[5] Adjusted for field blank readings at Site 3

3.3.2   Field Trial 2

The results of the POCIS deployment are shown in Table 3.4. The six discs in each deployment cage were analysed as two groups of three pooled discs. The only determinand detected on the field blanks was diuron. This was quantified on the NLS-manufactured and commercial POCIS discs at 8.4 and 3.3ng/disc respectively.

Table 3.4   Results of POCIS analyses in ng per device for cages 1-4. Two sets (a and b) of three discs were pooled from each cage. Only those determinands which were detected are listed.

| | NLS made | | | | Commercial | | | |
| | 1 | | 2 | | 1 | | 2 | |
	a	b	a	b	a	b	a	b
Atrazine	0.3	0.3	0.3	0.2	0.5	0.5	0.3	0.3
Carbendazim	4.7	5.3	3.3	0	5.3	7.3	4.7	7.3
Diazinon	0.2	0.2	0.2	0.2	0.2	0.3	0.2	0.2
Diuron[1]	251.6	234.3	200.3	144.9	232.0	269.4	160.7	195.4
Isoproturon	27.3	24.7	19.3	12.7	30	39.3	20	30
Simazine	0.5	0.5	0.5	0.3	0.7	0.8	0.5	0.7

Notes: [1] Adjusted for field blank readings

Results from the SPMD deployment are shown in Table 3.5. Seven of the compounds detected were also present on either the commercial or NLS-made field blanks, and results were adjusted for these control analyses.

Table 3.5 Results of the SPMD analyses in ng per device for cages 1-8. Two SPMD from each cage were analysed (A and B). Only those determinands which were detected are listed

Determinand	NLS made								Commercial							
	1		**2**		**3**		**4**		**1**		**2**		**3**		**4**	
	A	B	A	B[1]	A	B	A	B	A[1]	B	A	B	A	B	A[1]	B[1]
Anthracene[4]	17.5	12.3	18.3		10.1	<8.1	14.7	14.0		8.7	10.6	9.5	<8.1	<8.1		
Benzo-a-pyrene[2,4]	14.9	12.2	<1.1		<1.1	<1.1	11.7	11.3		6.9	8.0	7.2	5.0	6.3		
Chrysene[4]	39.6	32.3	43.8		18.1	19.1	29.4	29.1		19.7	24.6	19.2	16.3	18		
Diazinon[3]	<50000	<50000	56050		59610	<50000	<50000	<50000		<50000	<50000	<50000	<50000	<50000		
Fluoranthene[2,4]	204	39.0	201		117	45.9	184	166		109	129	112	83.1	88		
Hexachlorobenzene	1.4	0.9	1.2		1.0	0.8	0.9	0.9		0.7	0.7	0.7	0.5	0.5		
Pentachlorobenzene[3]	<50	<50	<50		150	470	960	1850		1320	960	380	830	960		
Phenanthrene[2,4]	210	177	192		116	120	131	125		85.7	81.6	76.8	57.5	59.1		
Pyrene[3,4]	245	15.7	189		108	<1.56	193	180		124	135	125	90.4	100		
Trifluralin[3]	2040	1620	970		1930	970	2040	2090		1690	2190	1910	2110	2210		

Notes:

[1] Sample was breached so could not be analysed.

[2] Commercial SPMD adjusted for field blank readings.

[3] NLS SPMD adjusted for field blank readings.

[4] In all cases there was interference which may have been due to oil contamination (see main text). This may have affected the results quoted, especially for the PAHs.

3.3.3   Field Trial 3

The main aim of this trial was to deploy the PSDs in realistic conditions at sites representative of those at high risk from pesticide exposure. Both sites were small waterbodies adjacent to arable land. At each site it was necessary to survey a stretch of around 100m in order to find a deployment site with sufficient depth (~15cm). However, suitable locations were found at both sites. Both samplers were still submerged upon collection, and showed no evidence (tide marks, splits) that they had been out of the water during the deployment period.

3.4   Field trial discussion

It was decided not to pursue development of the prototype shallow water cage trialled alongside the conventional deployment cages in Field Trial 1. The shallow water cage was difficult and more time consuming to use. In addition, although it was designed to allow deployment in shallower waters, its height advantage was minimal. Traditional SPMD and POCIS cages were used for the rest of the trials. These cages required a deployment depth of around 15cm and so placed a lower bound to the depth of water body that could be monitored. Despite this enforced minimum depth we were able to identify sites of this depth in situations representing high risk of pesticide contamination in Field Trial 3.

Commercial and NLS-manufactured PSDs were deployed together in Field Trial 2. For the majority of the compounds under analysis there was no statistical difference between the results from the NLS and commercial PSD (t-test, $p>0.05$). Results for simazine (POCIS), hexachlorobenzene, pentachlorobenzene, phenanthrene and trifluralin (SPMD) did differ significantly ($p<0.05$). For these five compounds there was no consistent pattern in which samplers accumulated the greatest concentrations. The commercial samplers accumulated significantly more simazine, pentachlorobenzene and trifluralin than the NLS made samplers, while the opposite was true for hexachlorobenzene and phenanthrene. It should also be noted that for two of these compounds (simazine and hexachlorobenzene), although there was a statistically significant difference, the absolute concentrations quantified were extremely low (~1ng/device).

Coefficients of variation (CV) were calculated for in-house and commercial samplers from Field Trial 2 (Table 3.6). In general, results from POCIS devices appear less variable than those from SPMDs. CV greater than 70 are associated with samples where the compound was below the limit of detection on one or more samplers. Diazinon was quantified from both SPMDs and POCIS devices, although the results are not directly comparable as they were deployed at different sites. On SPMDs the CV for diazinon on both sampler types combined was 233.7. This was because diazinon was only detected on some of the NLS samplers, probably due to a high limit of detection (50000ng) caused by high levels of interference.

Table 3.6 CV for in-house and commercial samplers from Field Trial 2

Sampler	Compound	NLS-made	Commercial	Both
SPMD	Anthracene	63.3	73.5	67.8
	Benzo-a-pyrene	138.1	31.6	72.9
	Chrysene	38.2	24.0	35.5
	Diazinon	137.0	0.0	233.7
	Fluoranthene	66.0	30.6	45.4
	Hexachlorobenzene	22.4	24.3	30.8
	Pentachlorobenzene	164.5	43.7	89.9
	Phenanthrene	26.2	33.3	42.9
	Pyrene	95.6	28.3	56.8
	Trifluralin	34.1	8.9	23.9
POCIS	Atrazine	27.6	23.7	30.2
	Carbendazim	71.3	22.0	49.4
	Diazinon	0.0	38.1	29.8
	Diuron	22.6	21.8	20.7
	Isoproturon	30.8	26.4	32.2
	Simazine	18.6	20.2	27.2

Site 1 in Field Trials 1 and 2 is also a routine chemical monitoring point in the Environment Agency's sampling programme. Data from routine spot samples taken during the passive sampling trials were requested for comparison of results. The only spot sample taken during the passive sampling trial was taken on the 30th March, the last day of the first trial and the first day of the second trial. For the first trial both SPMDs and POCIS devices were present at Site 1. For the second field trial only POCIS devices were present.

Table 3.7 compares analytical results from the spot sample taken on the 30th March and the PSD deployed at the same time period. Twenty compounds were analysed for in samples (spot and PSD) at Site 1. Of these, seven compounds were not detected at all, while one was detected by both methods. Eleven were detected only by the passive samplers, although this may partly have been due to PAH contamination from the newly machined SPMD cages. Only one compound (chlorotoluron) was detected in the spot sample and not on the passive sampler. Chlorotoluron has not previously been shown to accumulate on SPMDs or POCIS devices.

Table 3.7   Chemicals analysed for in the spot sample taken on the 30th March and SPMD in Field Trial 1 or POCIS in Field Trials 1 and 2 and whether they were quantified

Compound	SPMD?	Detected on POCIS?	Spot sample?
Total HCH	N		N
Aldrin	N		N
o,p'DDT	N		N
o,p'DDE	N		N
Dieldrin	N		N
Endrin	N		N
Anthracene[1]	Y		N
Benzo-a-pyrene[1]	Y		N
Chrysene[1]	Y		N
p,p'DDT	Y		N
p,p'DDE	Y		N
Fluoranthene[1]	Y		N
Hexachlorobenzene	Y		N
Phenanthrene[1]	Y		N
Pyrene[1]	Y		N
Chlorfenvinphos		N	N
Diazinon		Y	N
Isoproturon		Y	N
Diuron		Y	Y
Chlorotoluron		N	Y

Notes: [1] The source of these PAH compounds may have been contamination on the SPMD cages.

3.5   Field trial conclusion

The main aim of the initial field trial was to investigate shallow water deployments of PSDs. The original SPMD cage and POCIS cage proved easy to use. Loading and retrieving the samplers from the cages were quick, minimising the time samplers were exposed to air. Both these cages require a water depth of around 15cm to remain submerged through the deployment period. In Field Trial 3, SPMDs and POCIS devices were deployed successfully in small, shallow ditches which were considered to be high risk sites for pesticide exposure.

The NLS-manufactured POCIS devices and SPMDs gave comparable results to the commercially bought samplers, both in terms of mass per device and variability.

The results from the passive samplers compare favourably with the results of a spot sample taken as part of the routine Environment Agency monitoring. Even when the detection of PAH compounds is discounted (these may have been caused by contamination of the SPMD cages), more compounds were detected from the passive samplers than from the spot sample. At present we do not have the calibration data required to convert from a mass per device to an environmental concentration. Therefore, it is not possible to compare the results from both methods quantitatively.

Overall, these field trials suggest that passive monitoring is a useful technique that is able to accumulate a wide range of contaminants over a continuous period.

4 Laboratory trials of PSD

4.1 Introduction

Many pesticides have been found to accumulate in passive samplers. However, the majority of the compounds identified as potentially high risk in a recent risk mapping exercise (Environment Agency, 2006) have not been assessed for accumulation. Prior to their use for field based pesticide monitoring, a number of laboratory studies were undertaken to ensure that the pesticides of interest would accumulate on PSDs.

If passive samplers are to be used successfully in the field and accurately monitor episodic events such as pesticide contamination from spray drift, two aspects of their use require investigation:

- is the uptake rate sufficiently quick to allow sampling of short pulses of exposure such as following a spray drift event, when exposure times may be half an hour or less?

- if a sampler experiences a short pulse of exposure followed by exposure to a long period of 'clean' water, is loss of accumulated contaminant likely to occur from the PSD?

A series of lab trials was carried out to try and answer these questions

4.2 Exposure time and depuration investigations

A risk mapping exercise (Environment Agency, 2006) identified the application of pesticides to top fruit as posing the greatest risk to aquatic organisms. Cereals were also identified as a crop of national importance. For both crops, exposure by spray drift, rather than drain flow, posed the greatest risk to waterbodies. The pesticides identified with the highest risk potential are shown in Table 4.1.

Table 4.1   Pesticides identified by the risk mapping as contributing more than 0.01 toxic units to the total risk of top fruit or cereals via spray drift

Pesticide	Top fruit	Cereals
Captan	Y	
Carbendazim	Y	
Chlorotoluron		Y
Chlorpyrifos	Y	Y
Copper oxychloride	Y	
Cypermethrin		Y
Diflubenzuron	Y	
Dithianon	Y	
Diuron	Y	
Dodine	Y	
Fenpropidin		Y
Flufenacet		Y
Isoproturon		Y
Kresoxim-methyl	Y	Y
Paraquat	Y	
Pendimethalin		Y
Pirimicarb	Y	
Tri-allate		Y

4.2.1   Exposure trial method

A risk mapping exercise (Environment Agency, 2006) has identified spray drift during pesticide application as the most significant exposure route for the pesticides used in the scenarios listed in Table 4.1. Spray drift results in a short pulse of pesticide entering the watercourse, potentially lasting less than one hour.

It was therefore necessary to conduct some trials to investigate whether pesticides were accumulated to quantifiable levels after short exposures. Pesticides were spiked into the water at the spray drift Predicted Environmental Concentration (PEC) and the water was constantly stirred. SPMDs and POCIS devices were exposed to the solution for 5, 15, 30 or 60 minutes before analysis to determine mass per device.

4.2.2   Depuration trial method

To investigate the possible loss of compound when exposed to 'clean' water following exposure to a pulse of contaminant, POCIS devices and SPMDs were exposed to the same pesticides (Table 4.1) for one hour at the spray drift PEC. After exposure, the samplers were transferred to clean water for periods of 0, 5, 10 or 30 days. Although this depuration step used a static system, the clean water was replaced regularly and the water was kept moving. This continuous agitation was designed to prevent the system reaching equilibrium if the pesticides were moving out of the samplers. Samplers were analysed for the spiked compounds to determine mass per device immediately after exposure, and mass per device after the depuration periods.

4.3　Laboratory trial results

4.3.1　Exposure trial results

Eight compounds (captan, carbendazim, chlorpyrifos, dithianon, isoproturon, kresoxim-methyl, pendimethalin and pirimicarb) were extracted from either the POCIS or SPMD in quantifiable amounts (Figure 4.1 and Figure 4.2). The compounds which were accumulated were all quantifiable after the minimum exposure period of five minutes. Analytical methods were not available for two of the compounds identified in Table 4.1. These were dodine and copper oxychloride. Copper oxychloride was not expected to accumulate on the PSD, as it is not an organic compound.
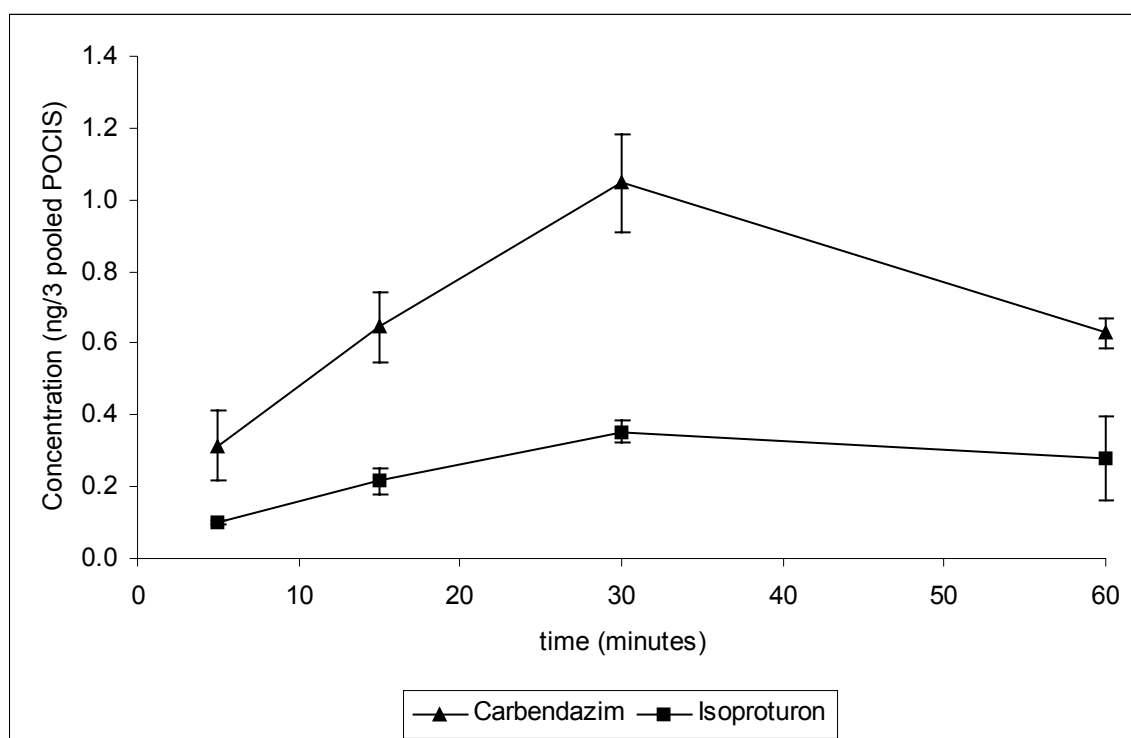

Figure 4.1　Compounds accumulated on POCIS after varying exposure periods. Error bars represent standard errors of two replicates
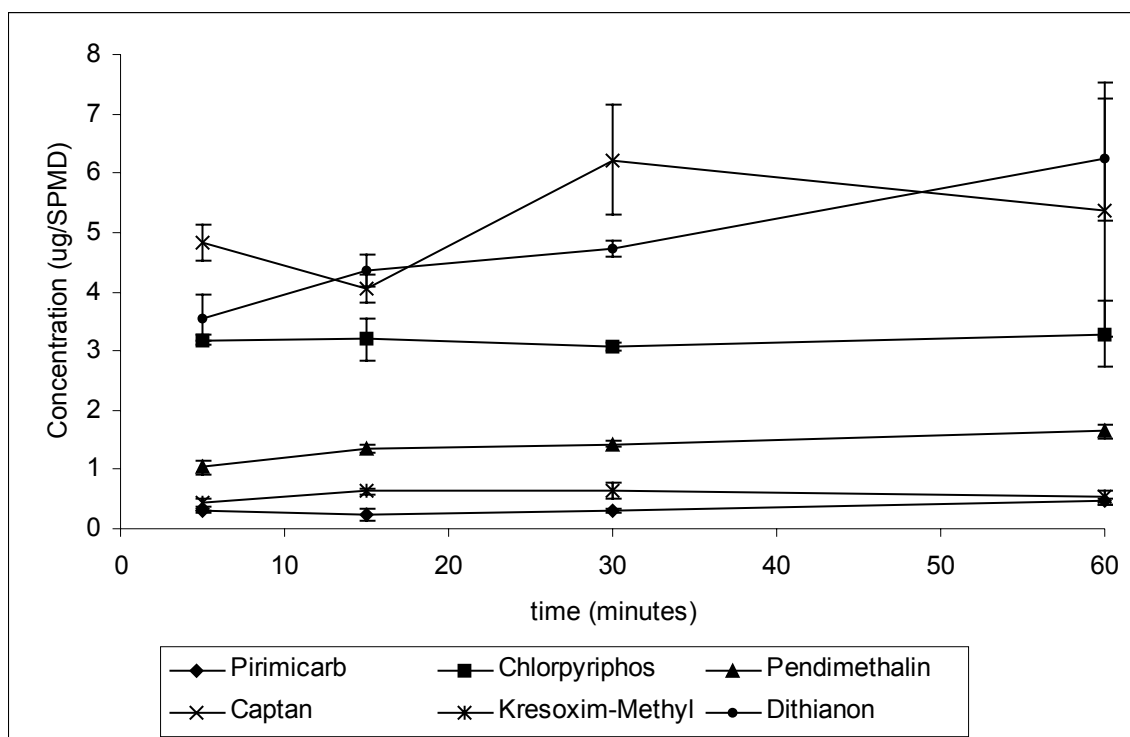
Figure 4.2 Compounds accumulated on SPMD after varying exposure periods. Error bars represent standard errors of two replicates

Carbendazim and isoproturon were extracted from the POCIS in quantifiable amounts. Pirimicarb, flufanacet and kresoxim-methyl were also present on the POCIS, though at concentrations below the minimum reporting values. Paraquat was also accumulated on the POCIS, but could not be extracted from the sorbant for analysis.

Six compounds (pirimicarb, chlorpyrifos, pendimethalin, captan, kresoxim-methyl and dithianon) were quantified on the SPMD. Cypermethrin, fenpropidin and flufenecat were also accumulated on the SPMD but were lost during the clean up and extraction process.

4.3.2   Depuration trial results

Compound uptake by POCIS was so low over the exposure period that it was decided not to proceed with the depuration trial.

The same six compounds (pirimicarb, chlorpyrifos, pendimethalin, captan, kresoxim-methyl and dithianon) quantified on SPMD after a one hour exposure period were again quantified in this trial. Figure 4.3 shows the change in concentrations of these compounds over time after normalisation to 100% on day zero. Although the results are variable there is a trend of decreasing concentration over time.
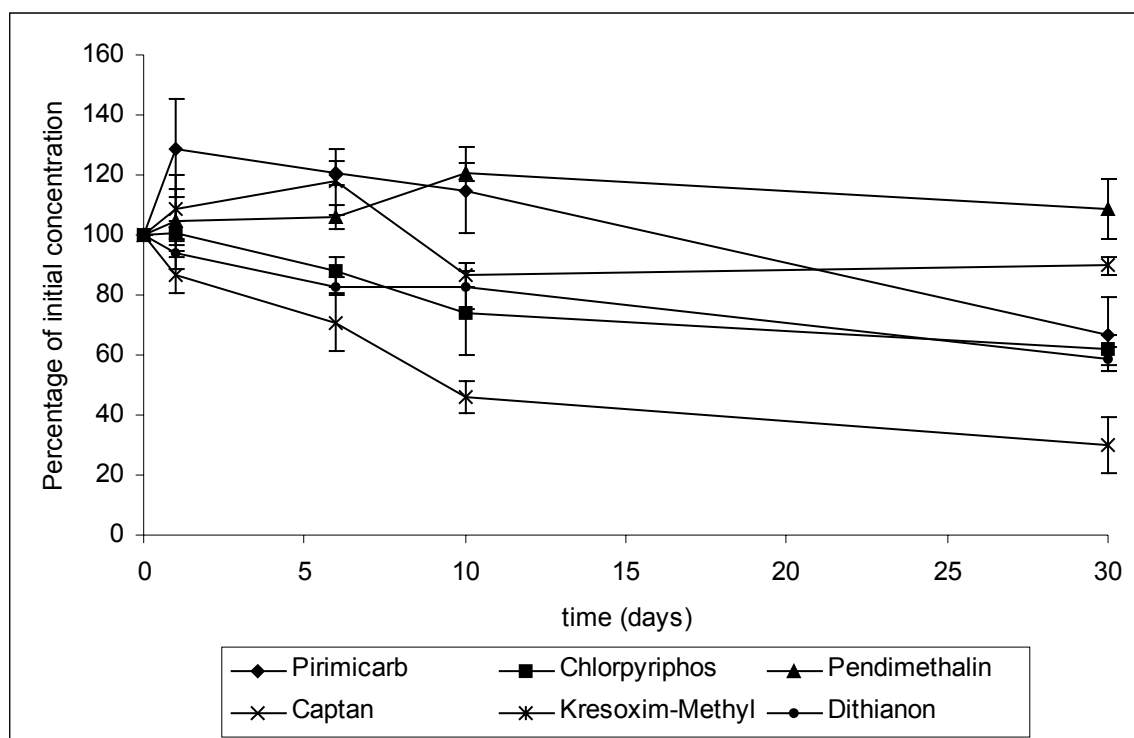
Figure 4.3 Change in concentration over time when exposed SPMD were placed in 'clean' water. Error bars represent standard errors of two replicates

4.4 Laboratory trial discussion

The results of the exposure time investigations indicated that compounds can be rapidly accumulated on both POCIS and SPMD. Realistic worst case PECs were used as test concentrations in the trials. In the field, concentrations are likely to be lower and sampling rates reduced due to lower temperatures and biofouling, so these results are likely to be best case scenarios for the ability of passive samplers to pick up pesticides in the field.

Diuron and pirimicarb have been shown to accumulate on a POCIS previously, but were not accumulated to quantifiable levels in this trial. The reason for this observation may be the sampling rates and low ambient water concentration. POCIS devices have a sampling rate of 200-500ml/d. This equates to sampling rates of 8.3ml/hour to 20.8ml/hour. If a compound is present at 1µg/l then after an exposure of one hour 8.3ng to 20.8ng would have accumulated on the POCIS. These are low concentrations to quantify from POCIS using available analytical methodologies. If the exposure time is less than an hour, or the environmental concentrations are lower, then it is unlikely that POCIS would detect water contamination from a spray drift event.

SPMDs have a faster uptake rate than POCIS, so a larger number of the compounds were quantifiable. SPMDs are therefore more likely to be able to monitor pesticides from a spray drift event.

Linear uptake was not seen for the two compounds accumulated by the POCIS. The spiked concentrations were far in excess of the masses accumulated so it is unlikely that the non-linear accumulation was due to equilibrium being reached. The trials were conducted in covered vessels that were protected from exposure to light. These measures should have minimised photolysis and volatilisation. The reason for reduced mass per sampler at 60 minutes is therefore unclear. Linear uptake was also not seen

for several of the compounds accumulated on the SPMD. However, this is likely due to equilibrium being reached as the mass per samplers for some compounds is approaching the mass spiked into the water.

The results of the SPMD depuration trial indicate that compounds may be lost from the sampler over time. Although the results were variable, up to 60% of the initial concentration was lost over 30 days. All compounds were still present at quantifiable concentrations after 30 days depuration, so presence/absence could still be detected, although calculation of a TWA concentration may be compromised. These trials represent a worst case scenario. After exposure the samplers were placed in clean water, which was regularly replaced. These conditions would therefore maximise diffusion rates out of the SPMD.

The POCIS was not tested for depuration, as the uptake rates had been so slow that their use to monitor spray drift events was effectively precluded. Furthermore, researchers have been unable to develop PRC for POCIS devices, as the compounds are not lost from the discs over time (Section 2.5.3). This observation suggests that once accumulated on the POCIS, compounds will not be lost over the deployment period.

4.5   Laboratory trial conclusion

SPMDs and POCIS devices have been demonstrated to accumulate a wide range of pesticides. Although the physico-chemical properties of a compound can provide an indication of which sampler is most suitable, this cannot be guaranteed. Laboratory work conducted at environmentally relevant concentrations is therefore required to ensure that the most appropriate PSDs are deployed for the compounds of interest and to avoid the possibility of false negatives in the field.

Initial results suggest that both SPMDs and POCIS devices have the ability to rapidly accumulate contaminants at environmentally relevant concentrations. This is particularly important for contaminants whose exposure is transient in nature. However, at the worst-case water concentrations used in these trials many compounds were not quantifiable after exposure of one hour. For the POCIS, this is likely due to the low water concentrations and low sampling rates. For the SPMD, low water concentration will also have an influence, although several compounds were accumulated but lost in the SPMD clean up process.

Contaminants are lost from the SPMD over time during exposure to 'clean water'. Over the 30 day deployment period up to 60% of an accumulated compound was lost. This should be considered when interpreting results. The SPMD works by diffusion. Compound loss is therefore unlikely to be linear, but tail off over time as an equilibrium is approached. This suggests that the contaminant may still be quantifiable, and therefore allow presence/absence to be determined. However, if a substance is lost over time this does complicate the calculations for assessing environmental concentration. Further work is required to determine the rate of loss for different compounds, and the variables that control this loss.

One of the major benefits of passive samplers is that they accumulative integratively over time. This phenomenon should prevent a transient presence of contaminants being missed, and also means that lower environmental concentrations can be quantified if compounds are accumulated to levels above the LOD. These qualities are excellent for detecting chronic, low level pollutants. However, pesticide exposure is likely to be as short pulses. There is a trade-off between exposure time and concentration, such that the shorter the exposure period the greater the water concentration must be to achieve a concentration on the PSD above the LOD.

Although both POCIS devices and SPMDs have demonstrated an ability to accumulate compounds after exposure periods of only five minutes, the quantification of compounds will depend on their ambient water concentration, exposure time, environmental conditions and available analytical method.

On the basis of the water concentrations used in this trial, many of the pesticides would not be accumulated sufficiently during short term exposures to allow quantification. As the water concentrations were based on realistic predicted environmental concentrations, we cannot be confident that these PSD would allow us to detect and quantify exposure of these pesticides in these scenarios. The use of POCIS devices and SPMDs does not appear to be suitable for the characterisation of pesticide exposure at sampling sites in England and Wales where risk to aquatic organisms is predicted to be highest. However, the PSDs have been proven to accumulate a wide range of pesticides and would be suitable, offering advantages over spot samples, in other situations. The limitations of the PSD, especially the risk of false negatives, should always be considered prior to the selection of the sampling technique and when interpreting data obtained using PSD.

5   Conclusions

The use of PSDs to monitor for pesticide exposure offers several attractive features. The ability to monitor over a continuous period means that transient exposures may not be missed, and that low level contamination could be accumulated over the deployment period to concentrations above the LOD. The literature review suggests that by deploying two PSDs (POCIS and SPMD) it would be possible to monitor for compounds with a wide range of K_{ow}. However, the review also highlighted several areas where further work was needed before PSD could be confidently deployed as a suitable monitoring technique for pesticides.

The field trials suggest that the currently available deployment cages are suitable for use in shallow waters, and that NLS-made samplers give comparable results to commercially bought samplers. In addition, when trialled in shallow headwater streams, suitable deployment locations were found. The results of the field trials are therefore encouraging, and suggest that passive samplers have the potential to be a useful monitoring technique.

However, laboratory trials based on the high risk scenario of pesticide spray drift from orchards (Environment Agency, 2006) demonstrate that around half of the compounds are not quantifiable after short term exposures at environmentally relevant water concentrations. In addition, the accumulated mass of a compound was shown to be lost from SPMDs once the sampler was placed in clean water. These results led to the conclusion that PSDs are not a suitable monitoring technique for spray drift events, with these particular compounds of interest, because of the high risk of false negatives.

Passive sampling is a monitoring technique that has been receiving greater interest as the need to monitor for diffuse, chronic pollutants has become apparent. A range of passive samplers is available, two of which were examined in this report. It was concluded that passive samplers were not a suitable monitoring method for transient pesticide contamination, although they do offer advantages over spot sampling for the monitoring of continuous contamination by low level pollutants. As with any sampling technique it is important to understand the limitations of the method before implementing a monitoring programme.

6   Recommendations

Listed here are the main recommendations from this report:

1. Although PSDs have benefits in terms of continuous monitoring over an extended period of time, the laboratory trials have raised concerns over two aspects of their use. Specifically, the ability to accumulate sufficient mass of a compound to be quantifiable in a short period of time, and the possibility that mass may be lost if the concentration of the compound drops in the waterbody. Passive samplers are therefore not recommended for the monitoring of transient pollutants if quantitative results are needed.

2. Passive samplers are a promising technique for other sampling requirements. The trials reported here and elsewhere have demonstrated that a large range of pesticides and other compounds can be accumulated on SPMDs and POCIS devices. However, we would recommend that laboratory trials are conducted to determine which passive sampler is most suitable for the compounds of interest before conducting field work. Passive samplers offer benefits when monitoring is designed to determine the presence or absence of low level pollutants or to provide estimates of the environmental concentrations of chronic contaminants.

3. It is vital that we are able to quantify the concentrations of contaminants at monitoring sites if we are to be able to link contamination with changes in biological communities or other evidence of impacts e.g. bioassays. At present, insufficient work has been done on generating calibration data and adjusting calibration data for the varying environmental parameters which can affect uptake rate.

4. When using passive samplers it is important to consider the data which will be produced. If calibration data are available, results from passive monitoring are expressed as Time Weighted Averages. You must consider whether this is suitable for your purposes or whether you need information on the peak contaminant concentration at the exposed site.

Appendix 1

Pesticide active ingredients identified as potentially of interest based on high use and summary of available calibration/detection data for each.

Active ingredient	SPMD	POCIS	PPS	TRIMPS
2,4-D		cal $_2$	det $_3$	
Aldicarb		pos	pos	
Alpha-cypermethrin	det $_5$		pos	pos
Amidosulfuron		pos	pos	
Amitrole		pos	pos	
Atrazine		cal $_{1,2}$	cal $_3$	
Azoxystrobin	pos		pos	pos
Benazolin		pos	pos	
Benomyl	pos	pos	pos	pos
Bentazone		cal $_2$	pos	
Bromoxynil		cal $_2$	pos	
Carbendazim		pos	pos	
Chloridazon		cal $_2$	pos	
Chlormequat		pos	pos	
Chlorothalonil	det $_5$	pos	pos	pos
Chlorotoluron		pos	pos	
Chlorpropham		pos	pos	
Chlorpyrifos	cal $_1$	cal $_1$	cal $_3$	det $_4$
Clodinafop-propargyl	pos	pos	pos	pos
Clopyralid	**cal $_2$**	pos	pos	pos
Copper oxychloride $_7$				
Cyanazine		**cal $_2$**	pos	
Cypermethrin	**det $_5$**		pos	pos
Cyprodinil	pos	pos	pos	pos
Deltamethrin	pos		pos	pos
Diazinon	**cal $_1$**	**cal $_1$**	pos	pos
Dichlobenil	**cal $_2$**	pos	pos	pos
Dichlorprop	pos	**cal $_2$**	pos	pos
Diclofop-methyl	pos		pos	pos
Difenoconazole	pos		pos	pos
Dimethoate		**cal $_2$**	pos	
Diquat		pos	pos	
Diuron		**cal $_{1,2}$**	**cal $_3$**	
Endosulfan	**det $_5$**		**cal $_3$**	**det $_4$**
Epoxiconazole	pos	pos	pos	pos
Esfenvalerate	**det $_5$**		pos	pos
Ethofumesate		**cal $_2$**	pos	
Fenarimol	pos	pos	pos	pos
Fenitrothion	**cal $_2$**	pos	pos	pos
Fenoxaprop-P-ethyl	pos		pos	pos
Fenpropidin	pos		pos	pos
Fenpropimorph	pos	**cal $_2$**	pos	pos
Fentin hydroxide	pos		pos	pos
Fluazifop-P-butyl	pos		pos	pos
Fluazinam	pos	pos	pos	pos
Flumethrin	pos		pos	pos
Flusilazole	pos	pos	pos	pos
Flutriafol		pos	pos	

Active ingredient	SPMD	POCIS	PPS	TRIMPS
Glyphosate		pos	pos	
Imazapyr		pos	pos	
Ioxynil	pos	**cal** 2	pos	pos
Iprodione	pos	pos	pos	pos
Isoproturon		**cal** 1,2	**cal** 3	
Kresoxim-methyl	pos	pos	pos	pos
Lambda-cyhalothrin	**det** 5		pos	**det** 4
Lenacil		**cal** 2	pos	
Linuron		pos	pos	
Malathion	**cal** 2	**cal** 1	pos	pos
Mancozeb 6				
Maneb 6				
MCPA		**cal** 2	**det** 3	
MCPB	pos	pos	**det** 3	pos
Mecoprop	pos	pos	**det** 3	pos
Mepiquat		pos	pos	
Metalaxyl		pos	pos	
Metamitron		**cal** 2	pos	
Metazachlor		**cal** 2	pos	
Methiocarb	pos	pos	pos	pos
Metsulfuron-methyl		**cal** 2	pos	
Paraquat		pos	pos	
Pendimethalin	**det** 5	**cal** 1,2	pos	pos
Pentachlorophenol	pos		**cal** 3	pos
Permethrin	**det** 5		pos	pos
Phenmedipham	pos	pos	pos	pos
Pirimicarb		**cal** 2	pos	
Prochloraz	pos	**cal** 2	pos	pos
Propachlor		**cal** 2	pos	
Propaquizafop	pos		pos	pos
Propiconazole	**det** 5	**cal** 2	pos	pos
Propyzamide	pos	**cal** 2	pos	pos
Pyrazophos	**det** 5	pos	pos	pos
Quinoxyfen	pos		pos	pos
Simazine		**cal** 1,2	**cal** 3	
Sulphur 7				
Sulphuric acid 7				
Tebuconazole	**cal** 2	pos	pos	pos
Terbuthylazine	**det** 5	**cal** 1,2	pos	pos
Terbutryn	**det** 5	**cal** 1	pos	pos
Thiabendazole		pos	pos	
Thifensulfuron-methyl		pos	pos	
Thiodicarb		pos	pos	
Thiophanate-methyl		pos	pos	
Tralkoxydim	pos		pos	pos
Tri-allate	**det** 5		pos	pos
Tridemorph	pos		pos	pos
Trifluralin	**det** 5	**cal** 1	**cal** 3	pos
Triflusulfuron-methyl		pos	pos	
Vinclozolin	pos	pos	pos	pos
Zineb 6				

Notes: cal = calibration data available,

det = detection confirmed,

pos = acumulation possible based on log Kow of active ingredient

[1] USGS Columbia Environmental Research Centre, MO, USA,

[2] COWI A/S, Denmark,

[3] University of Portsmouth, UK,

[4] Leonard *et al*, 2002,

[5] QHSS, Australia,

[6] Dithiocarbamate pesticide, normal method of analysis may not be suitable for use with passive samplers,

[7] Passive monitoring probably not suitable for these compounds

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List of abbreviations

CV	Coefficient of Variation
DGT	Diffusive Gradient in Thin film device
EAF	Exposure Adjustment Factor
K_{ow}	Octanol-water partition coefficient
K_{PSD}	Passive sampling device-water partition coefficient
K_{SPMD}	SPMD-water partition coefficient
LDPE	Low Density PolyEthylene
LOD	Limit Of Detection
NLS	National Laboratory Service
PEC	Predicted Environmental Concentration
PIMS	Passive Integrative Mercury Sampler
POCIS	Polar Organic Integrative Sampler
PPS	Portsmouth Passive Sampler
PRC	Performance/Permeability Reference Compound
PSD	Passive Sampling Device
SLMD	Stabilised Liquid Membrane Device
SOWAP	SOil and WAter Protection
SPE	Solid Phase Extraction
SPMD	SemiPermeable Membrane Device
TRIMPS	TRIMethylPentane Sampler
TWA	Time Weighted Average
USGS CERC	United States Geological Survey Columbia Environmental Research Centre
WFD	Water Framework Directive

Glossary

Passive sampler	A diffusion based monitoring technique that is used to sample continuously over a period of time.
Performance Reference Compound/ Permeability Reference Compound	A compound spiked into an SPMD which is lost from the sampler during deployment. The rate of loss is used to correct the rate of uptake of other compounds.
Pesticide	A compound used to control pests. In this report pesticide is used to refer to plant protection products e.g. herbicides, insecticides, fungicides.
Spot sample	A volume of water sampled at one point in time at one location which is collected for the purposes of chemical monitoring

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