Deltares

The use of passive sampling in WFD monitoring

The possibilities of silicon rubber as a passive sampler

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Abstract
This desk study examined the feasibility of passive sampling as an alternative monitoring method for the organic WFD-relevant substances in surface water (the priority substances and the specific pollutants). It specifically considered the possibilities of passive sampling with silicon rubber.
It emerged from the study that 'Brussels' will accept passive sampling as a supplementary method for WFD surveillance monitoring, on condition that the method is officially validated and documented. Although this is not yet the case for any of the existing sampling methods, it is nevertheless possible to deploy passive sampling as the 'best available technique'. An ongoing issue here is that the compliance checking of the water quality under the WFD with respect to organic compounds considers the total concentration in water and that passive sampling measures the freely dissolved concentration. However, this problem can be addressed by converting this freely dissolved concentration into a total concentration.
Passive sampling with silicon rubber appears to be an excellent approach to WFD monitoring and the time would appear to be ripe for the more extensive use of silicon rubber for this purpose. Silicon rubber can be potentially used for the measurement of 74% of the non-ionogenic organic priority substances. This is 31% for the specific pollutants and 81% for the possible future priority substances that were studied.
Passive sampling with silicon rubber is also suitable as a replacement for most bio-monitoring for water quality purposes. A major benefit of passive sampling compared with bio-monitoring is that no separate standards are required. It is possible to draw on the WFD standards in place for surface water (after conversion into freely dissolved concentrations).
It is difficult to say whether passive sampling increases or reduces costs. On the one hand, laboratory costs are higher because of the additional analysis of performance reference compounds required for the sampling rate. On the other hand, the sampling frequency for highly hydrophobic compounds can be reduced because of the time-integrated nature of passive sampling. The price-quality ratio is better with passive sampling.
The recommendation is to initiate passive sampling first at ten locations in the Netherlands and to start monitoring for those compounds that are difficult or impossible to measure using classical sampling methods because of the low concentrations in which they occur. On the basis of this first test, it will be possible to optimise the monitoring frequency and the number of samplers that have to be deployed in parallel.

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Contents

1 Introduction

The Centre for Water Management has asked Deltares to conduct a desk study as part of the Applied Research Programme (Normering en Chemie module) of the feasibility of passive sampling as an alternative monitoring method for organic compounds covered by chemical quality targets (the priority substances) or ecological quality targets (the 'specific pollutants') laid down by the Water Framework Directive (WFD).

The quality targets in the WFD for these two groups of substances are expressed as concentrations in 'total water', which means that these substances are monitored on the basis of water including the suspended matter.

However, toxicity for aquatic organisms is mainly determined by the freely dissolved concentrations of pollutants in water and not by the pollutants bonded to suspended matter.

'Total water' concentrations of hydrophobic compounds that actually adsorb to suspended particles are determined to a significant extent by the amount of suspended matter stirred up when sampling is taking place. The freely dissolved concentrations, on the other hand, are much less sensitive to these particles being stirred up either coincidentally and/or temporarily.

When there is little suspended matter in the sample, the concentrations of highly hydrophobic compounds in 'total water' can be so low that conventional methods cannot detect them. In these cases, the limit of detection is higher than the concentration to be measured. Furthermore (or indeed, precisely), when the freely dissolved concentration is measured, the limit of detection can be higher than the concentration to be measured. With some substances, it is even the case that the WFD quality target is so low that it is below the limit of detection.

Passive samplers could be a solution for these monitoring problems: they measure (i.e. sample) precisely the freely dissolved concentration and they generally have a lower limit of detection than a water sample taken in the classical way.

If passive sampling can actually be used for WFD monitoring of very low concentrations in the water compartment, separate standards do not need to be established for other compartments such as suspended matter, sediment or biota.

In this report, the opening chapters will describe how passive sampling works and what the pros and cons are with respect to conventional monitoring methods. An overview will then be provided of existing passive sampling materials and their pros and cons. This will be followed by a closer look at the possibilities associated with passive sampling using silicon rubber for measuring WFD-relevant nonpolar organic compounds. This will also include an examination of the relationship between passive sampling using silicon rubber and concentrations in biota that are measured for the purposes of determining environmental quality.

Finally, we will look at the costs of passive sampling with silicon rubber, comparing them to conventional monitoring techniques, and there will be an analysis of the 'legal' issues involved in the routine use of passive sampling for WFD monitoring (i.e. whether 'Brussels' allows this).

The report ends with a number of conclusions and recommendations.

2 The principles of passive sampling

2.1 Two types of passive sampler

There are two types of passive sampler: samplers in which target compounds for sampling dissolve (i.e. absorption) and samplers to which substances adsorb (i.e. surface bonding).

The first type of sampler is known as a partition sampler because the partition theory applies. If exposure remains constant for long enough, these samplers can achieve equilibrium. The material for the partition passive sampler is selected so that compounds dissolve in it much better than in water and are therefore highly concentrated and, as a result, easier to measure. Partition samplers are often called hydrophobic samplers because they are generally used for that type of compound.

The second type of sampler is known as the adsorption sampler. In this sampler, compounds bond very strongly to adsorption material. Because the bonding capacity of the adsorption material is so high, no equilibrium is reached. The adsorption materials used in these samplers often bond polar compounds very strongly as well and they are therefore frequently referred to as polar samplers.

The transport of the substances to be sampled from the water to both types of passive sampler is diffusion-controlled so that only freely dissolved substances are taken up or adsorbed. The variables in the uptake process for partition samplers are well known. The amount taken up by the partition sampler can therefore be used to calculate the freely dissolved concentration in the water phase. There are still a number of uncertain factors in the uptake process in adsorption samplers and so there are also more uncertainties involved in the calculation of the freely dissolved concentration.

2.2 Partition passive sampling

2.2.1 The uptake process

The most straightforward way of describing the uptake process in a partition passive sampler is to imagine this as a communicating vessel linked to the water system being studied (Figure 2.1). The volume V_w of the water system is infinite. The capacity of the sampler is defined as the mass of the sampler (m_p) multiplied by the sampler-water partition coefficient (K_{pw} in l/kg) where the capacity is expressed as litres of water.
The concentration in the water system can be seen vertically on the left of the figure (C_w) with the concentration in the sampler being shown vertically on the right (C_p) divided by K_{pw}, in other words the C_w in the fictive sampler water volume. The product of the base (volume = m_p K_{pw}) and right vertical (concentration = C_p / K_{pw}) is now m_p C_p and it therefore states the amount of the substance in the sampler after exposure (N_p) (eq. 1)

$$N_p = (C_p / K_{pw}) \times m_p K_{pw} = m_p C_p \qquad \text{(eq. 1)}$$

As with the statement of the sampler capacity as a fictive water volume, the sampling rate (R_s) can be stated as the number of litres of water per day that are sampled 'through' the sampler during the exposure time. The higher C_w is, the higher the amount of the substance from that volume of water that enters the sampler.

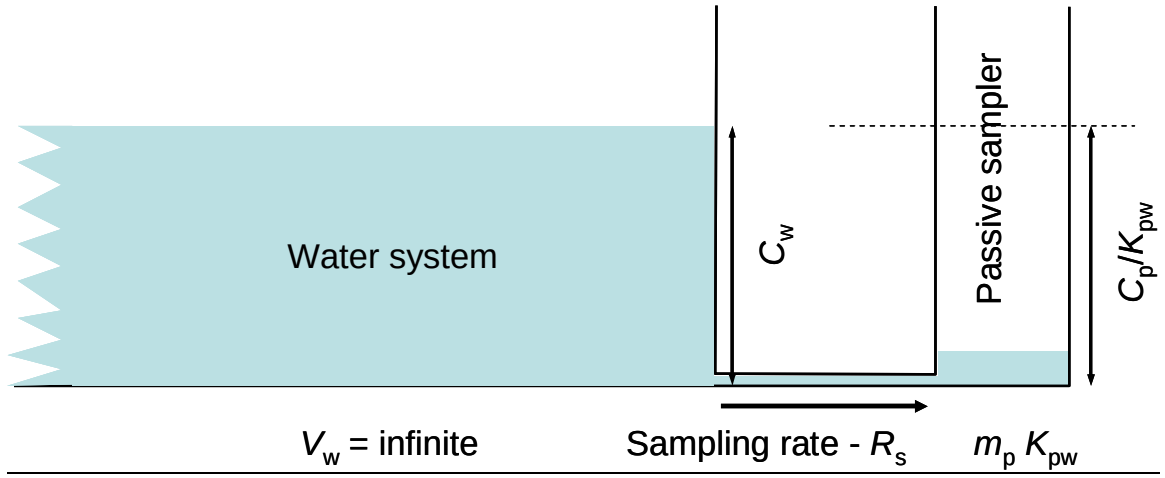

Figure 2.1 *Schematic diagram showing a passive sampler as a communicating vessel*

As when a communicating vessel fills, uptake in the passive sampler is based on an e-power that can be broken down into three stages (Figure 2.2):

1. In the first stage, uptake will be roughly linear over time and there is no tendency to flow back, in other words there will be no release.
2. In the next stage, the difference in the concentration between the water and the sampler falls and substances are again released into the water phase. In other words, net uptake declines.
3. Ultimately, uptake and release will be equal and equilibrium is then achieved.
4.

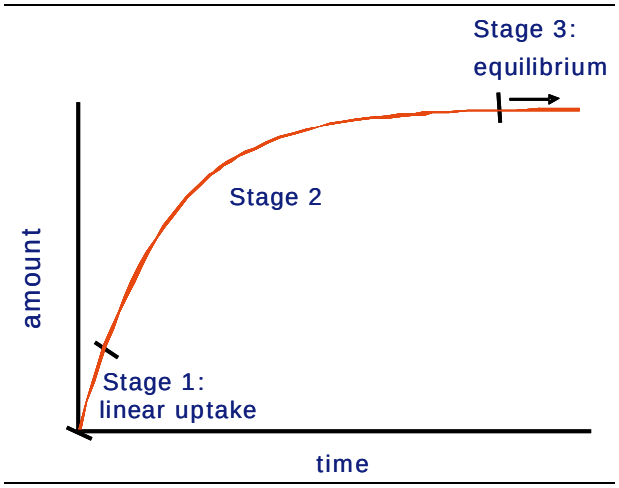

Figure 2.2 *The uptake kinetics in a partition passive sampler*

In the first stage, uptake is time-integrated and temporary higher or lower concentrations are 'registered'. The concentration measured is an average concentration during the exposure time. Here, there is 'one-way traffic' to the sampler. A higher uptake due to a temporarily higher concentration (a peak load) during the exposure time will therefore stay in the sampler. To calculate the concentration in the water phase during this first stage, only the sampling rate R_s is needed.

In the third stage, equilibrium is achieved so release and uptake are equal. In this case, a sampler will 'forget' (in part) a temporary increase or decrease in the water concentration from an earlier stage. The concentration in the water phase in stage 3 can be calculated with the partition coefficient K_{pw} alone.

In the second stage, which follows the linear phase, the release of the substance also starts to play a role. The rate of this release increases as stage 3 approaches. When a substance is released that has been accumulated earlier during a peak load, the sampler starts to 'forget' this peak load. To calculate the concentration in the water both R_s and K_{pw} are needed, as is the complete model with e-power.

Because hydrophobic compounds have a high K_{pw}, sampler capacity ($m_p K_{pw}$) for these compounds is high and uptake will generally remain in the linear stage. As a result, these compounds can be sampled on a time-integrated basis.
In the case of less hydrophobic compounds with $\log K_{ow} < 3$, such as naphthalene, the equilibrium time is often shorter than the exposure time and equilibrium will generally be achieved.

A partition sampler can sample several substances at the same time. Differences in the properties of the compounds means that one compound may, after a particular exposure time, still be in the linear phase while another compound will already have attained equilibrium. Competition between the different compounds does not play any role in the uptake of these mixtures of compounds.

2.2.2 The sampling rate

The sampling rate is determined by the transport resistances in the stagnant water boundary layer around the sampler and the resistances in the sampler itself. Which resistance dominates depends on:

1. The local water movement that determines the thickness of the water boundary layer;
2. The diffusion rate in the sampler.

In stagnant water, the water boundary layer is generally thick and so uptake is slow and the sampling rate is therefore low. When there is more water movement, the water boundary layer will not be as thick and so uptake will be faster, and the sampling rate will be higher.

If the diffusion rate in the sampler itself is low, the sampled substances will accumulate on the surface of the sampler and the uptake rate will be slowed down to the rate at which the substances diffuse deeper into the sampler. The sensitivity (limit of detection) of samplers of this kind is low.
The highest sampling rate is achieved with samplers in which the compounds being sampled have diffusion coefficients that are so high that the water boundary layer determines the sampling rate. The advantage of samplers of this kind is that the uptake model is relatively simple and that uptake can be modelled accurately. The sampling rate of the sampler can be accurately determined on the basis of the release of compounds with which the sampler is spiked beforehand (i.e. Performance Reference Compounds, PRCs) (Booij et al., 1998, Huckins et al., 2002). This is because the release rate is determined by the same resistances as the sampling rate. This means that, during the calculation of the concentration, the effect of water movement on the sampling rate is taken into account. The calculation model developed for this purpose in the course of time is described in Smedes (2010a).

In samplers where the uptake is determined by the water boundary layer, the uptake is higher when the flow rate (in a river) is higher. A peak in the flow reduces the size of the boundary layer and will result in more uptake, as will a peak in the concentration. An increase in the flow also leads to more release of PRCs and therefore to a higher sampling rate so that the flow will not affect the calculated concentration. The result is a time-integrated measurement in which time-integrated means both concentration-integrated and flow-integrated.

When the transport resistance in the sampler is of the same order or higher than in the water boundary layer, modelling is more problematic and the diffusion coefficient of the compound in the sampler is also needed (Booij et al., 2003). If the water movement changes, the resistances in the water boundary layer and in the sampler will determine uptake in turn so that both resistances have to be included in the model.

2.2.3 Required process constants

A number of process constants have to be known for every compound to be measured with passive sampling. To verify that the uptake process matches the assumed uptake model, it is important to know the diffusion coefficient of the compound to be measured in the sampling material. The value of the sampler-water partition coefficient K_{pw} is also needed to calculate the freely dissolved concentration.
Initially, when testing the possibilities for measuring a substance using passive sampling, estimated values are often used.
As a rule, each combination of sampler material and compound to be measured has a specific optimal exposure time at which sampling is still time-integrated. However, because sampling with a passive sampler usually involves several compounds at the same time, the exposure time is selected in a pragmatic way.

2.3 Adsorption passive sampling

2.3.1 The uptake process

Adsorption samplers are not based on dissolving the substance to be measured in the sampler but on bonding to the surface of an adsorbent behind a membrane or a filter. The material in the sampler (the adsorbent) is selected based on its strong bonding properties, including bonding of polar compounds. This strong bonding means that compounds are released by the sampler with great difficulty. Furthermore, the bonding capacity for compounds is so great that, at the concentrations in the sampling environments, equilibrium is usually not attained and uptake in these samplers is generally linear. Time-integrated measurements are therefore possible, in which temporary changes in the water concentration or the flow velocity are included, resulting in a time-averaged concentration. However, linear uptake will ultimately lead to the saturation of the sampler. So adsorption passive samplers can only be used if the concentration of the target compound is well below the equilibrium concentration.
Saturation of the sampler can also be caused in part by the fact that compounds other than the target compound, including dissolved organic material (DOC), may also be bonded. However, little is known about these possible competition effects.

The strong bonding means that the sampler effectively releases no substances to the water phase. This makes it impossible to use Performance Reference Compounds (PRCs) and to determine the sampling rate of an exposed sampler based on the release of the PRCs. In addition, sorption can be non-linear (for example, Freundlich) implying that PRCs cannot be used to determine the sampling rate of an adsorption sampler.
To express the amount of measured compound in terms of water concentrations, then, sampling rates are used that are measured in the laboratory. Here, then, no correction is made for the effect of the local flow on uptake.
The sampling rates of many compounds, which are slightly compound-dependent, have been measured for adsorption samplers in the laboratory. However, little is known about the link between the sampling rate and compound properties.

2.3.2 The sampling rate

The transport from the water phase to the adsorption sampler is, as in the partition samplers, determined by diffusion. However, the difference is that there are three, rather than two, different resistances:

1. The resistance in the water boundary layer;
2. The resistance in the filter or membrane;
3. The resistance between the parts of the adsorption material itself in the direction of deeper layers in the sampler.

Figure 2.3 depicts these resistances. Little is yet known about which of the three resistances dominates and whether that is the case in all circumstances. As a result, a quantitative calculation of the average water concentration is not yet possible and still more research is needed into in-situ calibration and conversion to concentrations in the water phase.

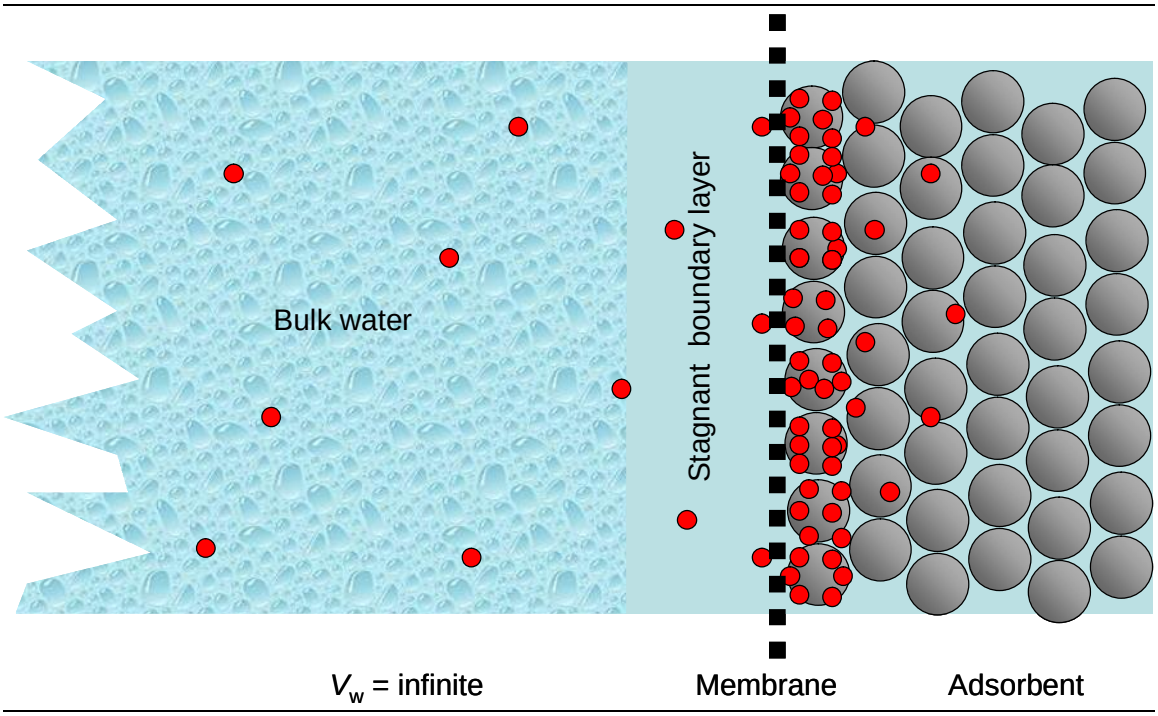

Figure 2.3 Schematic diagram showing the three resistances in an adsorption sampler

Despite these uncertainties, adsorption samplers are already in widespread use in research because they can also sample polar compounds. Furthermore, the time-integrated factor in particular justifies ignoring these uncertainties. This is because an average concentration obtained through the analysis of grab samples is also very uncertain. Furthermore, researchers try to calibrate the sampling rate of the adsorption sampler by taking grab samples in parallel. Research into passive sampling of more polar compounds is still in full swing.

3 The advantages of passive sampling

The advantages of passive sampling include higher sensitivity (lower limit of detection) and the possibility of measuring time-averaged concentrations. However, the main reason for using passive sampling is usually that it measures exactly what is needed for risk assessment, namely the freely dissolved concentration of a substance. This freely dissolved concentration is proportional to the chemical activity of the compound, which has been known to determine the risk for organisms for a long time (Ferguson, 1939; Reichenberg and Mayer, 2006).
This chapter looks at the various advantages of passive sampling.

3.1 The freely dissolved concentration

If the water, suspended matter, sediment and biota compartments are in equilibrium in a water system with respect to a particular substance, the chemical activity of this substance will be the same in all compartments, while the concentrations in the compartments will vary widely. This is because the various compartments have different affinities for different compounds and therefore a different uptake capacity. Hydrophobic compounds, for example, will bond mainly to the organic matter in suspended matter and sediment, and dissolve in the fat of aqueous organisms. As a result, concentrations in these compartments will be higher than in the water compartment (the freely dissolved phase).
In a passive sampler in equilibrium with the water system, a substance also has the same chemical activity as in the other compartments. The concentration C_p in the passive sampler, which is measured after extraction in the laboratory, can be converted to the freely dissolved concentration in the water compartment using the sampling rate R_s and/or the partition coefficient K_{pw} (see section 2.2).
This freely dissolved concentration is difficult or even impossible to measure directly in a water sample because, certainly with hydrophobic compounds, part of the substance will be bonded to dissolved organic carbon (DOC) from which it cannot be isolated. Adsorption to filters also presents a difficulty when it comes to measuring the freely dissolved fraction.
A major advantage of determining the freely dissolved concentrations in the water phase with passive sampling is that, by contrast with concentrations in total water, they no longer need to be corrected for local conditions such as concentrations of suspended matter and DOC. The results of passive sampling in different monitoring sites can therefore be compared directly without being corrected (Smedes et al., 2007a).

3.2 Low limit of detections

A partition passive sampler has a surface area of 400-600 cm^2. Provided that hydrophobic compounds are in the linear uptake stage throughout the entire exposure and there is enough water movement (at sea and in the large riversand sample volumes of 300-1500 litres of water can be obtained in six weeks. Given an analytical limit of detection of ca. 1 ng in the extract after extraction and concentration, a limit of detection for the freely dissolved concentration of approximately 1 pg/l (10^{-6} µg/l) is achieved. Less water movement will increase the limit of detection by up to a factor of five. This means that the limit of detection will be 200-1000 times lower than in case of a grab sample of one litre of water.

For less hydrophobic compounds, which reach equilibrium sooner, the volume of water sampled in the passive sampler is much less and so the limit of detection is higher. For example, for naphthalene (log $K_{ow} \approx 3$), the water volume sampled by the sampler after equilibrium has been reached is approximately twenty litres, which results in a limit of

detection of 50 pg/l. Here, the partition coefficient K_{pw} and the sampler size determine the maximum sampled volume in equilibrium.
Less hydrophobic compounds dissolve better in water and they are retained less effectively by the sampler. However, they also adsorb less to sediment and suspended matter and so the freely dissolved concentrations in the water are usually higher. The slightly higher limit of detection is no problem in that case in terms of measuring the concentration in surface water.

For groups of substances such as PAHs, PCBs, musks, lower PBDEs and a number of chlorinated pesticides, the limit of detection is low enough to allow them to be measured in Dutch surface waters. For dioxins and, for example, PBDE209, the limit of detection (LOD)is 1 pg/l, but the concentrations in surface water are probably even lower and so they are not detected. In the case of the LOD given above, we assume that several groups of substances are analysed in an extract from a single passive sampler. The limit of detections could be lowered, possibly by a factor of 10-100, by using the entire extract for the analysis of a single specific group of substances and using a specific clean-up and instrumental analysis (i.e. GC-HRMS). This will, incidentally, be necessary only for highly hydrophobic compounds. A longer exposure time, for example an entire year, can also contribute to a further lowering of the limit of detection.

For adsorption samplers, the uptake surface is often much smaller (30-100 cm^2) so that, depending on the filters used, a sampling rate of approximately 50-100 ml a day can be reached. With one month of exposure, that results in an uptake of a maximum of 3 litres. Unlike partition samplers, such as LDPE and silicon rubber, the usual adsorption samplers also adsorb dissolved organic material (DOC), whereas clean-up is often less simple than for the hydrophobic compounds sampled using partition samplers. This matrix can affect the analysis and a LOD of 10 ng is plausible in the extract for the analytical limit of detection. This results in a limit of detection for adsorption samplers of ca 3 ng/l (0.003 µg/l). Also with these samplers, the limit of detection for each substance or group of substances can vary greatly and depend on clean-up methods and the analytic instruments.

Finally, lowering the limit of detection is not a goal in itself. In principle, it is enough for a limit of detection to be below the (WFD) standard. However, the high sensitivity of passive sampling often makes it possible to determine how far below the standard concentrations are. Classical approaches to analysis can often only determine that a concentration is below the standard but not how far below. Once it has been determined several times with passive sampling that concentrations are well below the standard, the sampling frequency may be reduced, thereby saving costs. In addition, it is possible to detect an upward trend below the standard early so that timely steps can be taken to prevent standards being exceeded.

3.3 Time-integrated concentrations

The concept of 'equilibrium' was used several times in the description of passive sampling in preceding sections. However, it will be clear that there is a continuous trend towards equilibrium in water systems but that no equilibrium is ever achieved in most water systems for a range of reasons. Temperature fluctuations, variations in flow velocity, growth processes and human and animal activity may disturb the equilibrium to a greater or lesser extent.
For many substances measured with passive sampling, no equilibrium is reached during the exposure period and equilibrium is never achieved for any substance with adsorption samplers. This is a drawback to some extent because it makes the in-situ calibration of the uptake process necessary. However, the major advantage is that a time-integrated concentration is obtained that can be used for compliance checking with time-averaged standards such as the annual-averaged environmental quality standard (AA-EQS). All sorts of

fluctuations in the concentration during the exposure period are averaged. Of course, there is a downside to everything; although peak concentrations are included in the time-integrated result, the exact size and timing of this peak concentration cannot be specified with passive sampling. So passive sampling is less suitable for compliance checking with the MAC-EQS (the maximum acceptable concentration). Incidentally, classical monitoring requires a very high sampling frequency to detect a short peak concentration with a reasonable level of certainty. In many cases, then, classical monitoring techniques will also fail to detect a peak.

3.4 Other aspects of passive sampling

Relationship with concentrations in biota
The uptake of substances by lower aquatic organisms is largely partition-controlled and is very similar to uptake in partition passive samplers. That is why passive samplers give a good indication of the concentrations (i.e. the chemical activity) to which lower aquatic organisms are exposed. Because of metabolism processes, the concentration of a compound cannot always be measured accurately in the organism itself. Chapter 5 discusses this in greater detail.

Separation of matrix and substances to be measured
Passive sampling already separates the substances to be measured from the local matrix in the field, and this results in relatively clean extracts. In addition the targeted micro-contaminants, passive samplers also pick up other compounds. Because these other compounds are also concentrated strongly in the sampler, they may also be present in high concentrations in the extract and interfere with the analysis of the targeted micro-contaminants (i.e. the target compound(s)). Therefore, it should be borne in mind that clean-up procedures may be required prior to the analysis.

Contamination
The uptake and release of substances by passive samplers is not very fast and, after sampling, they contain substances from many litres of water. The concentration in the sampler can then easily exceed the concentration in the water by 1000 or even 100000 times. As a result, and because the sample compounds are safely contained in the samplers, passive samplers are less sensitive to contamination than water samples. Compounds that adsorb from the air are probably the largest (potential) source of contamination and evaporation from the sampler to the air can result in substances being lost. Diffusion-resistant sampling jars and short exposure to the air can be effective in limiting this problem.

Fouling
As soon as passive samplers are exposed in the environment, the sampler will come into contact with all sorts of aqueous organisms. Many organisms living in water settle on passive samplers and so the samplers can become completely overgrown when exposed for long periods of time. This fouling will affect the uptake of substances but not necessarily reduce uptake.
Algae and other fouling are in contact with the same water as the passive sampler and the chemical activity of a compound in this fouling is representative for the monitoring location.
The water boundary layer, which determines the sampling rate of the passive sampler, is re-allocated to the outside of the fouling due to the fouling process. The permeability of the fouling for the target compound is determined by the solubility and the diffusion coefficient of the compound in the fouling. And even though the diffusion coefficient in the fouling will not be as high as in water, the solubility of the target compounds in the fouling will be much higher than in water. These two factors roughly compensate for one another. As a result, the

impact of the fouling on the transport of the target compound through the fouling to the sampler is limited (Booij et al., 2006). When PRCs are also used, the release of PRCs is affected by the fouling to the same extent as the uptake of the target compound and any change in the exchange rate between the sampler and the water phase as a result of fouling is automatically seen in the sampling rate.

Sampler loss

Because passive samplers are usually mounted robustly, samplers are seldom lost.

It is important to realise that, when samplers are lost as a result of theft, damage, during transportation or in other ways, or when analysis in the laboratory is not successful, it is not possible to collect a new sample quickly the next day. This is due to the required exposure time of a number of days or weeks, depending on the target compound.

4 Existing passive sampling techniques

This report focuses on passive sampling with silicon rubber because extensive experience has already been acquired with many compounds using this technique and because Rijkswaterstaat Centre for Water Management is considering using this type of passive sampler for WFD monitoring. However, several types of passive sampler have been developed over the years. This chapter therefore provides a brief description of a number of widely used passive samplers.

The first sampler developed was the solvent-filled dialysis tubing, in which the tube is filled with an organic solvent, usually hexane, and closed off with a dialysis membrane. Hydrophobic organic compounds could diffuse from the water through the membrane to the solvent. However, highly hydrophobic compounds such as PCBs did not diffuse through the membrane adequately, and quantitative monitoring turned out to be very difficult (Stuer-Lauridsen, 2005). This type of sampler is hardly used any more and it is seen as a prototype for other samplers, of which many have been developed over the course of time. These are samplers with multiple phases, such as samplers in which the adsorption material is located between membranes. Examples are the SPMD (Huckins et al., 2006) and the POCIS (Alvarez et al., 2004). Single-phase samplers have also been developed and they usually contain polymers such as silicon rubber (Smedes, 2007b), low-density polyethylene (LDPE) (Adams et al., 2007) and polyoxymethylene (POM) (Cornelissen et al., 2008). Uptake with these materials involves diffusion. Not all samplers have been studied as extensively as others and nor are all of them suitable for monitoring dissolved substances in the environment. Section 4.1 describes a selection of samplers that have been studied or used extensively. The description in this chapter looks at the pros and cons of the samplers in question, mainly for field application in surface water. The chapter concludes with a table summarising the main features of the samplers discussed.

4.1 Widely used passive samplers

Semi-permeable membrane device (SPMD)

The SPMD sampler is a partition sampler in which a synthetic lipid, triolein, is positioned between two membranes of low-density polyethylene (LDPE). It is a two-phase sampler that has been widely studied and used (Huckins et al., 2006). Substances that normally accumulate in the fat of organisms do the same in hydrophobic passive samplers. This sampler is intended for compounds with a log K_{ow} > 3 and will achieve equilibrium, depending on the sampling rate, for compounds up to log K_{ow} ~ 4. The sampler can be spiked in a simple way with PRCs that are added to the triolein. The sampler is easy to use, even though there is a risk of the triolein leaking from the sampler. The application is standardised, and the samplers generate sensitive measurements (Huckins et al., 2002b). The drawback of the sampler is that the extraction method for removing the substances from the sampler is not very robust. The extract can be easily contaminated with the triolein and the procedure for correcting this problem is highly complex. Large quantities of solvents are needed for this purpose and extraction (dialysis) takes a number of days. The sampling rates for the target compounds must be determined in the laboratory first. A polynomial model has been developed that describes the relationship between the log K_{ow} and the sampling rate (Huckins et al., 2006). With this model, and a correction factor derived from the release of the PRCs, the sampling rates determined in the laboratory are converted to the field situation and ultimately used to calculate the concentration in the water phase. However, this model, which was developed empirically for the log K_{ow} sampling rate, does not match properly with the

chemical engineering theory relating to substance transport. As a result, Booij et al. (2003) have proposed a model for the relation between log K_{ow} and the sampling rate for SPMD. It takes into account the decline in the sampling rate for larger molecules and the limited diffusion of, in particular, the more hydrophilic compounds in the LDPE membrane, which slows down uptake. These hydrophilic compounds, for which the sampling rate is sometimes determined by the membrane, usually achieve equilibrium during exposure, and the sampling rate and diffusion are then no longer important for the calculation of the concentration in the water phase. The application of the model (Booij et al., 2003) is robust but diffusion coefficients in the LDPE are needed for the correct application of this model. For PCBs and PAHs, these have been calculated by Rusina et al. (2010a).

Low density polyethylene (LDPE)

The LDPE sampler consists only of an LDPE membrane and it is a single-phase partition sampler (Adams et al., 2007). It is suitable for compounds with a log K_{ow} > 3. Because the membrane, and therefore the sampler, are very thin, equilibrium is achieved for compounds with a log K_{ow} of up to 4 or 5. However, because the sampler is thin, it can tear or get entangled when long pieces are used. The advantage of this sampler compared to the SPMD is that the preparation and extraction procedures are simpler. The samplers can be spiked with PRCs (Booij et al., 2002). That makes it possible to determine the sampling rate and to quantify the concentrations in the water phase. With respect to the uptake model, the same considerations apply as with SPMD samplers.

Silicon rubber

Silicon rubber samplers consists of a single phase based on polydimethylsiloxane (PDMS) and, like other hydrophobic samplers, they are suitable for compounds with a log K_{ow} > 3. They are partition samplers that can be spiked with PRCs (Booij et al., 2002). For compounds with a log K_{ow} of up to 4 or 5, equilibrium is usually reached in practice. Silicon rubber is cheap and robust, and it can be used several times. The surface area and thickness of the sampler can be varied easily to adjust the sampling rate. However, the samplers must be thoroughly pre-extracted to remove oligomers before they can be used. If these oligomers are not properly removed, they can severely interfere with the analysis at a later stage. Extraction of the adsorbed substances after exposure is straightforward. The diffusion coefficient of compounds in the PDMS is such that the water boundary layer is always the determinant factor (Rusina et al., 2007). This simplifies the model for the calculation of the concentrations in the water phase, and the model agrees with the theory about the relation between the sampling rate and the diffusion coefficient in water (Rusina et al., 2010b).

Solid phase microextraction (SPME)

SPME consists of a silica fibre coated with a specific polymer that acts as a sorbent (Pawliszyn, 1997). The volume of the polymer varies between 10 and 150 nL. The type of sorbent can vary, so that different types of substances can be sampled. The coating could, for example, be made from PDMS and it is then suitable for the same substances as the silicon rubber samplers. After exposure, an SPME fibre is desorbed and analysed directly in the injector of a gas chromatograph. For HPLC applications, the fibre is generally extracted in the injection vial. As a result, no solvent is needed for extraction purposes. A clean-up procedure is not possible with this technique.

The small volume of the SPME means that only a small quantity of the target compound is absorbed, so the sampling is less sensitive and the achievable limit of detection is higher compared with other types of samplers (Vrana et al., 2005). Furthermore, the sample is lost after the analysis, and re-analysis or analysis for another group of compounds is impossible. In addition, the fibres can differ slightly from one another, which has an impact on the uptake

process. SPME is used almost only as an equilibrium sampler. However, there are no reports on the use of PRCs for confirmation purposes. The SPME method is mainly used in the laboratory and seldom in the field because the fibres break too easily.

Polyoxymethylene (POM)

POM consists of a single phase of the plastic polyoxymethylene and it is used for hydrophobic compounds with a log K_{ow} > 3 (Cornelissen et al., 2008). The material can cope with solvents and so extraction of the adsorbed compounds is straightforward. POM is difficult to spike with PRCs because the diffusion coefficients in the polymer are extremely low (Ahn et al., 2005, Rusina et al., 2007). Ter Laak et al. (2008) calculated that uptake by POM is membrane-controlled for most compounds, which results in much slower uptake in comparison with LDPE or PDMS. So there is no basis for achieving equilibrium quickly. Nevertheless, POM is still widely used as an equilibrium partition sampler.

Polar Organic Chemical Integrative Sampler (POCIS)

The POCIS consists of a sorbent material fixed between two microporous diffusion-limiting membranes of polyethersulphone (PES) (Alvarez et al., 2004). The advantage of PES is that there is little biofouling. The POCIS is an adsorption sampler and is primarily intended for sampling hydrophilic organic compounds. Hydrophobic organic compounds are also sampled but, because a lower volume is generally sampled than with partition samplers, they are not detected during the analysis. A range of sorbents can be used with a sampler, depending on the specific compounds or groups of compounds that have to be sampled. The most usual sorbent composition is a mixture of three sorbents (generic configuration) comprising Isolute ENV, polystyrene divinylbenzene (80% w/v) and Ambersorb 1500 carbon on S-X3 Biobeads (20% w/v). This mixture is used to monitor hydrophilic compounds such as pesticides, and natural and synthetic hormones. A single sorbent is used to sample pharmaceuticals: Oasis HLB (Vrana et al., 2005). The substances can be extracted easily using an organic solvent. When used in the field, the membranes are positioned between metal rings. However, at high flow velocities they might become detached or torn.
PRCs cannot be used and so quantifying water concentrations with this sampler is very problematic.

Empore® disk

The Empore® disk is a patented system with an inert filter made of polytetrafluoroethylene (PTFE) containing the sorbent particles. A widely used adsorption material is silica-bonded octadecyl (C18) or divinyl benzene copolymers, with or without functional groups. Empore disks are available commercially and are widely used for the extraction of hydrophobic compounds from water. Protocols for the extraction of various substances have been published and extraction is straightforward, with consistent recoveries. The surface area/volume ratio is high and so the sampler is highly sensitive. The sampler can sometimes be used as an equilibrium sampler (depending on the sorbent) and, in that case, PRCs can be used to estimate the sampling rate. A drawback of this sampler is that, for all compounds, the sampling rate has to be determined separately with all sorbents for every application (Stuer-Lauridsen, 2005). Empore disks are often used as sorbents in the Chemcatcher (see below).

Chemcatcher (for organic compounds)

The Chemcatcher consists of a diffusion-limiting membrane and a sorbent comprising a solid phase. The membrane and the sorbent are positioned in a re-usable housing of Teflon or a disposable housing of recyclable plastic, with the membrane on one side and the Teflon or plastic layer on the other side of the sorbent. Sampling rates and the selectivity of compounds

can be varied and depend on the selection of the type of membrane and the type of sorbent. For compounds with log K_{ow} > 4, a 47 mm C_{18} Empore disk is often used as the sorbent, with LDPE as the porous membrane. SDB-RPS and SDB-XC (both styrene divinyl benzene copolymer sorbents) are also frequently used as sorbents. SDB-RPS is particularly suitable for polar compounds such as herbicides and SDB-XC for moderately polar water-soluble compounds. Another design for more polar compounds consists of a Empore disk with a PES diffusion-limiting membrane (Vrana et al. 2005). Because the Empore disk is used as a sorbent, the sampling rate often has to be determined separately for all compounds when using the Chemcatcher. With the nonpolar Chemcatcher, PRCs can be used by filtering a aqueous standard solution through the C_{18} Empore disk. For the relationship between sampling rate and log K_{ow}, an empirical model has been developed that is analogous to the one for SPMDs (Vrana et al., 2007).

Table 4.1 Summary of the main characteristics of widely-used passive samplers in surface water

Sampler	Material	Type of sampler	Groups of substances	PRC	Advantage	Drawback
SPMD	Synthetic lipid between LPDE membranes	Partition	Hydrophobic organic compounds (log K_{ow}>3)	Yes	- Available commercially - Standardised - High sensitivity - Calibration data known for many compounds	- Extraction takes a lot of time and organic solvent - Sampling rate can be diffusion-limited. - Risk of triolein leakage
LDPE	Low-density polyethylene	Partition	Hydrophobic organic compounds (log K_{ow}>3)	Yes	- Simple construction - Cheap - Calibration data known for many compounds	- Sampling rate can be diffusion-limited
Silicone rubber	Polydimethyl siloxane	Partition	Hydrophobic organic compounds (log K_{ow}>3)	Yes	- Simple construction - Robust - Cheap - High diffusion coefficient - Modelling matches theory - Calibration data known for many compounds	- Oligomers from silicon rubber can severely disrupt analysis
SPME	Silica fibre with different types of coating such as PDMS or polyethlene glycol	Partition	Polar and non-polar compounds (depending on coating)	No	- Available commercially - Simple construction - Simple extraction directly in GC injector	- High limit of detection - Vulnerable in field
POM	Polyoxymeth ylene	Partition	Hydrophobic organic compounds (Log K_{ow}>3)	No	- Cheap - Robust	- Membrane-controlled uptake - Modelling unclear
POCIS	Fixed sorbent	Adsorptio	Log K_{ow} < 4	No	- High sensitivity	- Modelling is

Sampler	Material	Type of sampler	Groups of substances	PRC	Advantage	Drawback
	between membranes of polyethersulphone	n	(depending on sorbent)		- Little biofouling - Calibration data known for many compounds	complex - Risk of tearing or loss of sampler
Empore disk	Polytetrafluoroethylene (PTFE) with fixed sorbent material	Depending on sorbent	Polar and non-polar compounds (depending on sorbent)	Yes/ No	- Available commercially - Extraction protocols available - Extraction is simple	- Modelling still under development - Determination of sampling rate for all compounds separately
Chemcatcher with Empore disk	Diffusion-limiting membrane and a sorbent in Teflon or plastic housing	Depending on sorbent	Polar and non-polar compounds Depending on membrane and sorbent	Yes/ No	- Calibration data known for many compounds	- Modelling is complex - Determination of sampling rate for all compounds separately

5 Passive sampling and concentrations in biota

When concentrations of substances in the surface water are so low that they can no longer be detected with the classical monitoring methods, measuring concentrations in biota is used as an alternative. The concentrations in biota are higher than in water for hydrophobic compounds because bioconcentration or bioaccumulation occurs in the fat or tissue of the organism. The WFD permits the member states in certain cases to conduct monitoring with biota and to draw up standards in this area.

This chapter takes a closer look at the relationship between concentrations measured using passive samplers of silicon rubber and concentrations in biota.
The chapter concludes with a brief discussion of the question of which method is preferable for (WFD) water-quality monitoring: bio-monitoring or passive sampling.

5.1 Passive sampling and contents in mussels

Freely dissolved concentrations determined using passive sampling with silicon rubber and contents in mussels correlate closely. Figure 5.1 shows, for two PAHs and two PCBs, how the concentrations with silicon rubber samplers and the concentrations in mussels generate comparable patterns.

The RIKZ (now the Centre for Water Management) has been using passive sampling in marine waters since 2002 in parallel with monitoring using mussels in the Active Biological Monitoring Network (ABM). The results from the period up to 2005 have already been evaluated (Smedes, 2007b) and the period prior to 2009 is currently being used to make an appraisal of whether passive sampling can be used to replace monitoring with mussels.

The uptake process in partition passive sampling is largely the same as that in lower organisms such as mussels. A difference in chemical activity between the water and the mussel, or between the water and the passive sampler, results in the uptake of a substance; in both cases, equilibrium with the water phase may be achieved in time.

In addition to uptake through direct contact with water as determined by partition, organisms can also accumulate substances through food. Substances in food from the same water in which the organism itself is located will have the same chemical activity as in the water. This means that the food will contribute to the faster uptake of the substances by the organism than by the passive sampler. However, this means only that the mussel will be in equilibrium with the substances in the water phase faster, not that the chemical activity will be higher. The matching chemical activity in the food means that the growth of an organism does not result in 'dilution' and a lower concentration. Contents in mussels, that grew by up to a factor of two during exposure, and in mussels that did not grow or that even got lighter therefore all had the same ratio to the freely dissolved concentration based on passive sampling (Smedes, 2007b). This ratio (the bioaccumulation factor: BAF), expressed as a ratio between lipid-normalised contents in mussels and freely dissolved concentrations in water, can therefore be used satisfactorily to predict contents in mussels with passive sampling. The measured BAFs did vary to some extent but that is probably attributable to natural variation in the mussels themselves because the differences could not be linked to the monitoring location or monitoring season (autumn and winter).

Lipid-water BAFs are linked on the basis of the partition theory to the K_{ow}. For lower organisms, that primarily accumulate substances from the water phase, this relation is approximately 1:1.
At present, a second evaluation is being conducted of passive sampling results and contents in mussels during the period 2005-2009 (Smedes, 2010a).

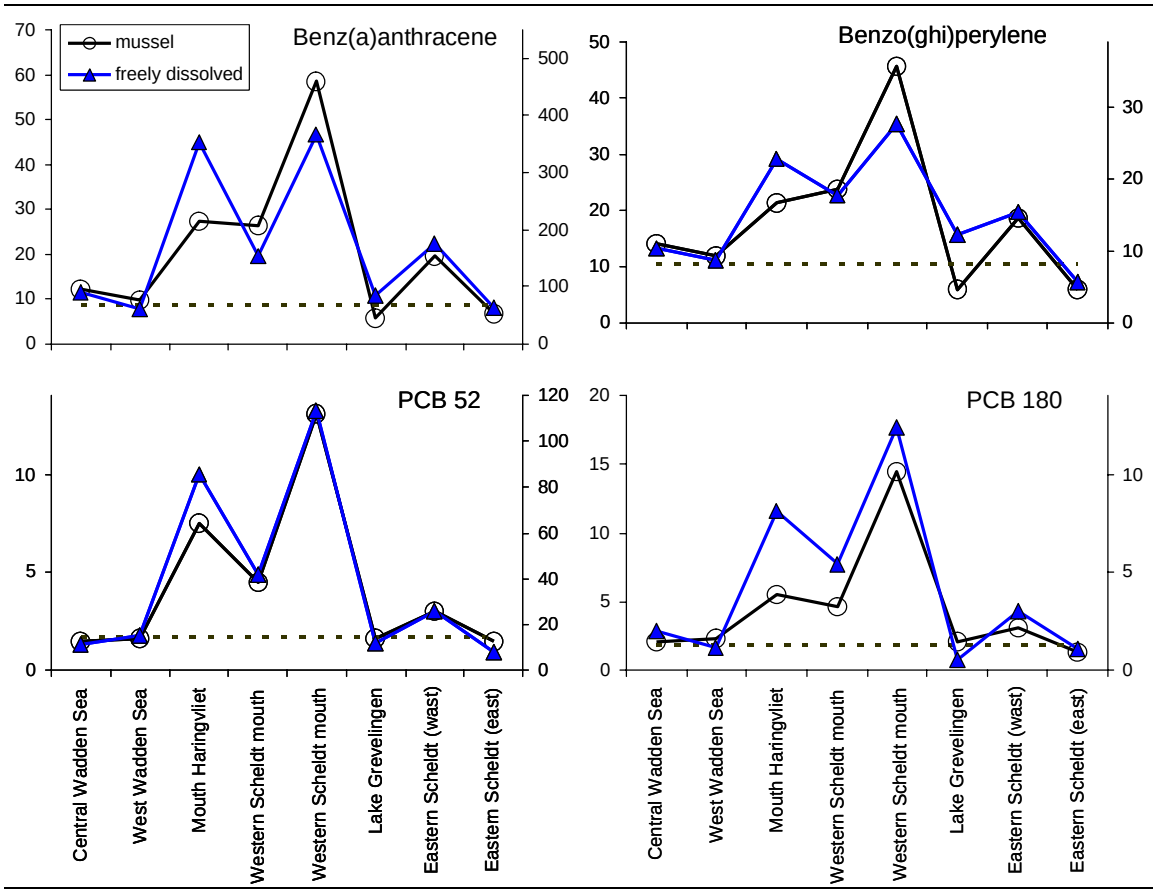

Figure 5.1.Freely dissolved concentrations (pg/l – right y axis) of benz(a)anthracene, benzo(ghi)perylene, PCB 52 and PCB180 determined by passive sampling with silicon rubber, compared to contents in mussels (µg/kg – left y axis). The monitoring period was winter 2005 and the exposure period was 6-7 weeks. The broken horizontal line shows the initial concentration in the exposed mussels. The lines joining the points have no significance; they are simply a visual indication of the profile. Data from Rijkswaterstaat Active Biological Monitoring Network programme..

5.2 Passive sampling and contents in higher organisms

Contaminants can accumulate in organisms that are higher in the food chain in a process known as biomagnification. As a result, contents in fat in higher organisms are often much higher and chemical activity is therefore also higher than in, for example, mussels.
Chemical activity is higher than in water and in lower organisms when food is intensively digested, as is the case in higher organisms. The digestion of food in the gastrointestinal tract results in the relative concentration of the contaminant because the uptake capacity of the food is lost through excretion so that chemical activity in the organism increases. Release is then possible only through gills or lungs and that process is much slower than uptake through food. Furthermore, release slows down as compounds become more hydrophobic. Release through gills or the lungs increases with the increasing difference in chemical activity inside and outside the organism. If the food is a constant source, the chemical activity will ultimately

attain a 'steady state' in which release matches uptake. Because the chemical activity in the higher organism is higher than in the environment, a lipid-water BAF for this organism will also be higher and exceed the 1:1 relation with the K_{ow}.

Given the above, it is reasonable to assume that passive sampling will only be useful for the quantification of the exposure of lower organisms, and not for higher organisms. However, a recent study (Smedes, 2010b) comparing passive sampling with biomonitoring data for zebra mussels, eels and the common roach in various Dutch waters found bioaccumulation factors (BAFs) that deviate only slightly from the K_{ow}. Good BAF values were not found for all compounds but this may possibly be attributed to the fact that the passive sampling and the biomonitoring did not take place in the same season and that the analyses were not conducted in a single laboratory.
The latter must certainly have played a role because the best correlation between the BAFs and the K_{ow} was also found for easily measurable substances such as PCBs. Relations with passive sampling were also found in eels and the common roach for PCBs, although contents in fat in these species were higher than in mussels. The results for the PCBs might imply that there is a correlation with passive sampling for certain substances in higher organisms too. Despite the increase in the concentration resulting from digestion, the steady-state concentration is still related to the freely dissolved concentration in the water phase, probably because the food comes from the same water as that to which the passive sampler is exposed.

5.3 Passive sampling or bio-monitoring

Despite the fact that sound correlations have been found between concentrations obtained using passive sampling with silicon rubber and contents in organisms, passive sampling will never be able to generate a precise prediction of a contents in an organism. Living organisms are dynamic and they respond to all sorts of factors that do not affect passive samplers. However, this can also be an advantage.

The benefits of passive sampling as compared to bio-monitoring include:

- Passive samplers remain in fixed positions and do not move into other areas;
- Passive samplers do not metabolise pollutants and so a measurement of the actual exposure is obtained;
- The same passive samplers can be used in fresh, marine, cold and warm water; with bio-monitoring, the selection of the organism depends on the matrix (fresh or marine) and the environmental conditions;
- Passive samplers also work in anoxic or even toxic water in which organisms cannot survive. In short, passive samplers do not die;
- Passive sampling results are comparable on the global scale, on condition that they are conducted in comparable ways;
- By contrast with organisms deployed as bio-monitors, passive samplers do not have initial concentrations;
- No organisms need to be sacrificed when passive sampling is used;
- No separate standards need to be set for passive sampling.

It is clear that passive sampling generates a large amount of monitoring information that is still being acquired at present by analysing organisms. Passive sampling can largely replace bio-monitoring for water quality purposes.

6 The potential use of passive sampling with silicon rubber in WFD monitoring

This chapter presents an overview of WFD-relevant substances that could (potentially) be sampled using silicon rubber. The WFD-relevant substances include the priority substances, the substances that have to be monitored for the purposes of ecological water quality (the specific pollutants) and a number of substances that may be added to the list of priority substances in the future (personal communication Hannie Maas).

Although it is theoretically possible to sample almost all organic compounds with passive sampling in one way or another, we will confine ourselves to the nonpolar compounds here. The samplers for these compounds are the only ones to have been developed to the extent that their introduction as a monitoring method makes sense.
SPMD is probably the most widely researched and applied of the hydrophobic passive sampler materials/methods. However, in recent years, it has emerged that samplers made from sheets of silicon rubber can also perform excellently as hydrophobic passive samplers. They are robust in use and modelling is relatively simple with them. Rijkswaterstaat has been successfully monitoring PCBs and PAHs since 2002 using passive samplers with silicon rubber. Comparing the results of these passive sampling activities with measured contents in biota shows that there is a good correlation between the two. This chapter therefore looks more specifically at the potential use of passive sampling using silicon-rubber samplers.
The assessment whether passive sampling of a substance using silicon rubber is possible will, incidentally, also largely apply to other hydrophobic samplers.

First of all, the log K_{ow} values, molecular weights and, when known, the silicon rubber-water partition coefficients (K_{pw}) have been collated for the substances in the lists referred to. Various sources were used for the log K_{ow} values. For the less well-known substances, they were taken from EPIsuite v4.0, which was developed by the US-EPA. All neutral compounds with a log $K_{ow} \geq 3.5$ can potentially be measured using passive sampling. Compounds with a lower log K_{ow} can often still be measured, possibly even with a lower limit of detection than in classical sampling and analysis. However, these compounds achieve equilibrium quickly so that the measured time-integrated concentration represents only a short period.

6.1 Substances that can be sampled using silicon rubber

Table 6.1 lists the substances from the WFD priority substance list (Bkmw 2009, 2010) for which passive sampling is possible. The column 'Applied' lists the substances for which passive sampling has already been applied; the column 'Potential' lists the substances that, on the basis of their properties, could be sampled using passive sampling; and the column 'Not probable' lists the substances for which passive sampling is improbable but which cannot be totally dismissed.

Table 6.2 does the same for the specific pollutants (MR Monitoring, 2010) and Table 6.3 lists the substances that might be added to the priority substance list in the future.
The figure listed in the tables alongside the substance refers to the WFD numbers in so far as a number has been allocated in the WFD. See Annex A for more details.

For all the listed substances, the limit of detection (estimated or actual) as a freely dissolved concentration is well below the Environmental Quality Standard (EQS). In the case of highly hydrophobic compounds, these freely dissolved concentrations cannot really be compared to

a standard for total water like the EQS. However, to establish an idea, the EQS has been converted into a freely dissolved concentration at 30 mg/l suspended matter that contains 10% organic C. The limit of detections for passive sampling have proven to be well below this converted EQS in all cases.
However, the extremely high log K_{ow} of PBDEs and dioxins means that the converted EQS values for these compounds are so low that the limit of detection for passive sampling with silicon rubber (and other sampler materials) is not low enough at the moment in standard conditions (600 cm^2 sampler surface area and 6 weeks of exposure) to measure the highly hydrophobic compounds. However, passive sampling, including passive sampling with silicon rubber, is still developing. Using a larger sampler surface area, a longer exposure time and an analysis method tailored to these compound calsses, it will probably be easy to achieve an even lower limit of detection.

Annex A lists the relevant parameters for all WFD-relevant substances.

Table 6.1 Passive sampling of priority substances (Bkmw 2009, 2010) with silicon rubber

no	Applied	no	Potential	no	Not probable
5	PBDE 28	1	Alachlor	3	Atrazine
5	PBDE 47	7	C10-13- chloroalkanes	19	Isoproturone
5	PBDE 99	8	Chlorfenvinphos		
5	PBDE 100	9	Chlorpyrifos (ethyl-chlorpyrifos)		
5	PBDE 153	9.1	Aldrin		
5	PBDE 154	9.2	Dieldrin		
9	ppDDT	9.3	Endrin		
9	opDDT	9.4	Isodrin		
9	ppDDD	14	Endosulphan		
9	ppDDE	24	Nonylphenols (4-(para)-nonylphenol)		
12	Di(2-ethyl-hexyl)phthalate (DEHP)	25	Octylphenols ((4-(1.1',3,3'-tetramethylbutyl)-phenol))		
18	Hexachlorocyclohexane	30	Tributyltin compounds (Tributyltin cation)		
22	Naphthalene	31	Trichlorobenzenes		
26	Pentachlorobenzene				
33	Trifluralin				
2	Anthracene				
15	Fluoranthene				
16	Hexachlorobenzene				
17	Hexachlorobutadiene				
28	Benzo(a)pyrene				
28	Benzo(b)fluoranthene				
28	Benzo(k)fluoranthene				
28	Benzo[ghi]perylene				
28	Indeno(1,2,3-cd)pyrene				

Table 6.2 Passive sampling of specific pollutants (MR Monitoring, 2010) with silicon rubber

no	Applied	no	Potential	no	Not probable
E 99	Benz(a)anthracene	E 5	Azinphos-ethyl	E 6	Azinphos-methyl
E 99	Phenanthrene	E 11	Biphenyl	E 9	Benzylchloride (alpha-chlorotoluene)
E 99	Chrysene	E 15	Chlordan	E 10	Benzylidene chloride (alpha,alpha-chlorotoluene)
E 101	PCB-101	E 25	1-Chloronaphthalene	E 24	4-Chloro-3-methylphenol
E 101	PCB-118	E 26	Chloronaphthalenes (technical mixture)	E 38	2-Chlorotoluene
E 101	PCB-138	E 43	Cumaphos	E 39	3-Chlorotoluene
E 101	PCB-153	E 47	Demeton	E 40	4-Chlorotoluene
E 101	PCB-180	E 75	Disulphoton	E 48	1,2-Dibromethane
E 101	PCB-28	E 81	Fenthion	E 49	Dibutyltin (cation)
E 101	PCB-52	E 82	Heptachlor	E 50	Dibutyltin (cation)
E 114	Tributylphosphate	E 82	Heptachlor epoxide	E 51	Dibutyltin (cation)
		E 86	Hexachloroethane	E 53	1,2-Dichlorobenzene
		E 87	Isopropylbenzene	E 54	1,3-Dichlorobenzene
		E 100	Parathion	E 55	1,4-Dichlorobenzene
		E 100	Parathion-methyl	E 56	Dichlorobenzidine
		E 103	Phoxim	E 63	Dichloronitrobenzenes (2,3-)
		E 108	Tetrabutyltin	E 79	Ethylbenzene
		E 109	1,2,4,5-Tetrachlorobenzene	E 80	Fenitrothion
		E 125	Triphenyltin acetate,	E 88	Linuron
		E 126	Triphenyltin chloride	E 104	Propanil
		E 127	Triphenyltin hydroxide	E 107	2,4,5-T (and salts and esters of 2,4,5-T)
		E 138	Octamethyltetrasiloxane	E 113	Triazophos
		E 139	**Abamectine**	E 122	2,4,5 trichlorophenol
		E 149	Deltamethrin	E 122	2,4,6 trichlorophenol
		E 150	Diazinon	E 129	m-xylene
		E 154	Esphenvalerate	E 130	o-xylene
		E 156	Fenoxycarb	E 131	p-xylene
		E 160	Lambda-cyhalothrin	E 146	Chloroprofam
		E 169	Pirimiphos-methyl	E 155	Fenamiphos
		E 171	Pyridaben	E 166	Metolachlor
		E 172	Pyriproxyfen		
		E 175	Terbutylazine		
		E 178	Tolclofos-methyl		
		E 179	Teflubenzuron		

Table 6.3 Passive sampling of possible future priority substances with silicon rubber

no	Applied	no	Potential	no	Not probable
		O 1	Bifenox	O6	Perfluorooctane sulphonic acid (PFOS)
		O 2	Cybutryne (Irgarol®)		
		O 3	Cypermethrin		
		O5	Dioxin (2,3,7,8 - Tetrachlorodibenzo-p dioxin,TCDD)		
		O7	perfluorooctane sulphonyl fluoride		
		O8	1,2,5,6,9,10-Hexabromocyclododecane (HBCDD)		
		O9	1,3,5,7,9,11-Hexabromocyclododecane (HBCDD)		
		O10	Quinoxyfen		
		O11	Dicofol		
		O13	Diclofenac		
		O14	Ibuprofen		
		O15	17alpha-ethinylestradiol		
		O16	17 beta-estradiol		

Table 6.1 and Annex A show that, of the 54 individual priority substances (four of which are ionogenic), 37 are measurable or potentially measurable with passive samplers of silicon rubber. This is 74% of all non-ionogenic individual priority substances.

Table 6.2 and Annex A show that, of the 167 individual specific pollutants (20 of which are ionogenic), 45 are measurable or potentially measurable with passive samplers of silicon rubber. This is 31% of all non-ionogenic individual specific pollutants.

Table 6.3 and Annex A show that, of the 16 individual possible future priority substances (two of which are ionogenic), 13 are measurable or potentially measurable with passive samplers of silicon rubber.

6.2 Interlaboratory tests

For the introduction and acceptance of passive sampling as a monitoring method, it is important for laboratories to be able to validate their work, for example by participating in interlaboratory tests. For classical analyses, samples are distributed. However, with interlaboratory tests for passive sampling, the sampling and the data processing also are important. This means that all participants need to expose their sampler at the same site and that the results should be compared after analysis and processing. The first interlaboratory test for passive sampling took place in 2006 (Smedes et al., 2007c and 2007d). This was a Europe-wide passive sampling survey with 13 participants, which also included laboratory inter-calibration. Laboratories exposed two centrally prepared samplers at a site they selected. The participating laboratories analysed one sampler and a central laboratory analysed the other. Comparison of the data provided an indication of the variation between laboratories.

At the moment, a number of initiatives are in place for interlaboratory tests. Cemagref in France has organised interlaboratory tests under the auspices of AQUAREF (www.aquaref.fr) for PAHs and several pesticides involving a number of foreign laboratories in addition to the French laboratories. The sampling was conducted in the Thau lagoon and the Rhone near Lyon. Each laboratory used its own sampler. The results have now been collected but there is no report yet.
In addition, interlaboratory tests are taking place for SPMDs in the Czech Republic (Ocelka, 2010). The results of this testing have not yet been published either.
NORMAN is organising interlaboratory tests in 2011 for metals, polar and nonpolar compounds. The preparations are now in progress.
Quasimem surveyed its participants two years ago to determine their interest in a 'proficiency testing scheme' for passive sampling but did not receive enough responses to justify launching the scheme. Encouraging interlaboratory tests by monitoring organisations is very important for widespread introduction.

6.3 Implementation

Laboratories that achieve good analytical results will, in principle, also do the same when analysing passive samplers. Some testing work will however be necessary to integrate the analysis of the passive samplers in existing laboratory procedures. It is also important for laboratory staff to undergo training so that they learn to work with passive samplers. More specific training is required in this area for staff who process and interpret the results. A consultation group in which people can discuss their experiences can be a useful support tool.

6.4 Further development of passive sampling with silicon rubber

Passive sampling with silicon rubber has been developed adequately for PCBs and PAHs. Coefficients for the partition between sampler and water (K_{pw}) are known for these compounds (Smedes et al., 2009). The relevant measurements were made in 2007 at what was then the RIKZ.
The K_{pw} values were measured again in 2009 in the Deltares/TNO laboratory for the performance reference compounds used for PCBs (Smedes and Beeltje, 2010).
The uptake process has also been studied intensively and the relationship between the sampling rate and the compound properties (K_{pw} or the molar weight) matches the theory of diffuse substance transport through water boundary layers (Rusina et al., 2010b). Furthermore, measurements of the diffusion coefficients in silicon rubber (Rusina et al., 2010a) have established that resistance to diffuse transport in the silicon rubber is negligible for all PCBs and PAHs. To calculate the in-situ sampling rate from PRC release, a fitting procedure has been developed that also allows for the calculation of uncertainty (Booij and Smedes, 2010). In scientific terms, this means that everything has been done to validate passive sampling for PCBs and PAHs.

K_{pw} values and/or diffusion coefficients are often lacking for other groups of substances. Deltares/TNO recently determined K_{pw} values for a larger number of groups of substances on behalf of CEFAS-UK (Smedes and Beeltje, 2010). The interpretation of the data from this study led to the assumption that the diffusion coefficients for compounds with polar groups are lower in silicon rubber than those for PCBs and PAHs. For substances such as chlorobenzenes and chlorinated pesticides that are closely related to PCBs it can be assumed that the diffusion coefficients are high enough.
Nevertheless, the absence of these data does not constitute a reason for not starting with passive sampling, because it is not the sampling, but only the processing of the final data,

that is dependent on the K_{pw} value and diffusion coefficient. An initial interpretation can always be done using estimated values.

It is possible to distinguish the following necessary and meaningful activities for the future:

- For substances to be sampled using passive sampling, it is necessary to know the sampler-water partition coefficients K_{pw}. The highly hydrophobic compounds (log $K_{ow} > 6$) are an exception to this. The associated K_{pw} is seldom required for the calculation of the concentration in the water phase because uptake is determined entirely by the sampling rate. The table in Annex A shows the compounds for which a K_{pw} is required for the silicon rubber sampler.
- For PCBs and PAHs, it is known that the diffusion coefficients in silicon rubber are high enough so that transport in the membrane does not slow down uptake (Rusina et al., 2007, 2010a and 2010b). For compounds with a completely different structure, it is sensible to verify whether the diffusion coefficients are high enough.
- It is useful to further study the model describing the relationship between compound properties and the sampling rate, as proposed by Rusina et al. (2010b), using as wide a variety of compounds as possible in order to establish a firmer foundation for the model (and therefore for passive sampling). This would appear to be indispensable to make the certification of passive sampling methods possible.
- The certification of passive sampling methods is still virgin territory. The analysis of a sampler is, in principle, no different from the analysis of a water or sediment sample. The problem is how to go about certifying sampling and the conversion into a freely dissolved concentration. Even though it is unclear how it will develop, this area requires attention and action. The certification of partition sampling, with a known sampling rate, would likely be much simpler than certification of passive sampling in which the results are dependent on an in-situ sampling rate.
  A first EN-ISO document (EN-ISO 2009) is already in the preparatory stage, but this document is a general guidance document and does not constitute an adequate basis for use as a standard.
- In order to respond to possible resistance to the use of PRCs (deliberate emission of anthropogenic compounds), it is advisable to think about an 'active' passive sampler. An active passive sampler moves, turns, pumps or shakes faster than the movement of the water being sampled. This movement determines the thickness of the water boundary layer instead of the local waves or currents. This means that the sampling rate is fixed and so PRCs are not required, or at most one for control purposes. An active passive sampler of this kind can even be desirable for sites where there is little water movement because in-situ sampling rates will be very low here. In addition to having a set sampling rate, a sampler of this kind will probably also minimise fouling. Wind or solar energy may be considered for the purpose of movement or rotation. This approach may also have advantages for adsorption samplers, for which checking the sampling rate is not straightforward.

7 The costs of passive sampling with silicon rubber

The description presented in this chapter of the costs of passive sampling for the purposes of WFD monitoring makes a distinction between investment costs, sampling costs, and pretreatment and analysis costs. The chapter concludes with a brief discussion of the price/quality ratio of passive sampling.
Some of the text below is generally applicable to passive sampling, whereas other sections specifically address passive sampling with silicon rubber.

7.1 Investment costs

Passive samplers need to be firmly mounted in the water to be sampled. At a number of existing monitoring sites, such as Lobith and Eijsden, facilities for positioning passive samplers can be installed simply and relatively inexpensively. In marine waters, buoys are usually used, and this is sometimes also possible in inland waters. At other sites, specific arrangements will be needed, resulting in the necessity for different designs depending on the individual locations. In many locations, it is important to take precautions against vandalism. The possibility of damage from ice also has to be taken into consideration. All this can vary according to the location and so it is not easy to make a generic estimate of costs. In local surface waters where there is no shipping, a stainless-steel pole with a mounting (including a lock) may be adequate. This will cost between two and five thousand euros. However, on routes where there is a lot of shipping traffic, a much more robust installation might be needed, and the costs will be correspondingly higher. We advise making the most of structures in place such as bridges, bollards, electricity pylons in the water, fish traps in lock complexes etc.

In addition to the investment costs for the physical installation, it is also important to take into account the time required to obtain permits to install the facilities.

7.2 Sampling costs

To obtain samples using the passive sampling method, two field visits are required; one to install the sampler and one to pick it up again. Furthermore, installing samplers in a frame takes a little bit more time than taking a water sample. And picking up the sampler also takes a little bit more time because the samplers have to be cleaned with local surface water after being retrieved in the field in order to remove fouling. This means it takes between about 10 and 20 min to pick up the samplers. The frame will also need cleaning at regular intervals. This can be done on-site with a high-pressure hose or, if the construction allows for this, in the washing machine in the laboratory.
In a properly planned monitoring programme, picking up one sampler can be combined with the installation of another so that only one trip per sampler is needed on average.

7.3 Pretreatment and analysis costs

To measure PCBs, PAHs and similar substances, passive sampling has already been adequately developed for some time now for the purposes of routine use. However, it has only been used on a small scale in practice yet. More widespread use requires start-up costs to be taken into consideration. For example, there is the purchase of materials, the setting up of facilities for large-scale pre-extraction of silicon rubber, a shaker and possibly the right glasswork or extractors for the extraction of the exposed passive samplers.

The material costs for the silicon rubber in the passive samplers are negligible (€1.50 per sampler) and the sampler can be used several times. Preparing passive samplers of silicon rubber does however involve more work than preparing sampling bottles for water samples. The silicon rubber has to be pre-extracted intensively before being used for the first time in order to remove oligomers because they may interfere with the chromatographic analysis later. In addition, the silicon rubber has to be spiked with the PRCs needed to determine the sampling rate before every sampling operation. This costs € 60 -100 per sampler but this could probably be halved with upscaling.
If only one substance group is being analysed, this will represent a substantial increase in costs. However, everything suggests that groups of hydrophobic compounds other than PCBs and PAHs involve the same uptake processes and that they can be easily added to the list of substances. If this is done efficiently, several groups of substances can be analysed in the same extract. Often separate extractions are performed for different groups of substances in water samples. Therefore, if several groups of substances need to be considered, passive sampling may nevertheless be cheaper despite the additional pre-treatment costs.

In addition, testing work will be necessary to integrate the analysis of the passive samplers in existing laboratory procedures. If passive sampling is initially used alongside the monitoring programme in place, the result will be a temporary doubling of the analysis costs. Finally, it is important for laboratory staff to undergo training so that they learn to work with passive samplers. More specific training is required in this area for staff who process and interpret the results. A consultation group in which people can discuss their experiences can be a useful support tool in this respect.

7.4 Price/quality

In broad terms, and assuming the same sampling frequency, the total monitoring costs for passive sampling will be higher than the costs for classical monitoring using water samples. In part, this is a result of the fact that an extra analysis will always be required for the purposes of measuring the PRCs in the passive samplers. Analyses are also required of a number of non-exposed reference samples in order to determine the initial concentrations of the PRCs.

For highly hydrophobic compounds, the silicon rubber sampler delivers a time-integrated result for a long period. To obtain an annual average concentration, the sampling frequency can be severely reduced in these cases, thereby cutting costs.

All in all, it is difficult to say whether passive sampling results in higher or lower costs on balance.

It is clear that the price/quality ratio of passive sampling is better. This is not only the result of the fact that passive sampling can achieve lower limit of detections and that it makes time-

integrated sampling possible, but also because the measured freely dissolved concentrations obtained with passive sampling produce a better picture of the actual environmental risks.

8 Passive sampling and Brussels

This chapter looks at the question of whether the Water Framework Directive allows the use of passive sampling as a monitoring method and, if so, whether the WFD imposes conditions or limitations in this respect. A number of relevant documents were therefore studied to determine what they have to say with respect to monitoring and sampling and whether they have anything to say about passive sampling and, if so, what. These were the following documents:

- The text of the Water Framework Directive itself (EC, 2000);
- The document 'Guidelines for monitoring surface water. European Water Framework Directive' (Van Splunder et al., 2006, in Dutch) which takes the first step towards establishing an approach to assessing the condition of water as set out in the text of the Water Framework Directive;
- Two documents drafted under the auspices of the European Committee for Standardization (CEN) about the chemical analysis of WFD priority substances (CEN, 2007a and 2007b);
- The guidance document for the monitoring of surface water under the Water Framework Directive (EC, 2009a), which was drafted by an informal working group acting under the CIS Chemical Monitoring Activity (CMA), made up of experts from various member states and stakeholders. This document was approved by the European Water Directors in November 2008;
- The guidance document for chemical monitoring in sediment and biota (EU, 2010) drafted by a working group made up of experts from various member states and stakeholders. This document was approved by the European Water Directors in May 2010;
- The Decree on Quality Objectives and Monitoring in ater 2009 (Bkmw 2009, 2010, in Dutch), which is a part of the implementation of the WFD in Dutch legislation and lists the WFD priority substances;
- The Ministerial Regulation on Monitoring Water Framework Directive (MR Monitoring, 2010, in Dutch), which is a part of the implementation of the WFD in Dutch legislation and regulations and which includes the WFD indicators of good ecological quality in surface waters (substances);

The Water Framework Directive (EC, 2000) distinguishes between three different types of monitoring:

- Surveillance monitoring: This monitoring approach provides an overall assessment of water bodies and establishes a long-term trend. The measurements related to priority substances, general physical/chemical quality, ecology (phytoplankton, phytobenthos, macrophytes, macrofauna and fish) and hydromorphology. In the Netherlands, there are 56 to 143 monitoring sites, depending on the selected parameters (Compendium voor de leefomgeving, 2009).
- Operational monitoring: This monitoring approach is intended for monitoring the condition of water bodies that do not comply with the chemical or ecological objectives . Here, not all parameters have to be measured. In the Netherlands, there are 190 to 438 monitoring sites, depending on the selected parameters (Compendium voor de leefomgeving, 2009).
- Investigative monitoring: This monitoring approach aims to determine the causes of failures to comply with chemical or ecological objectives.

Every type of monitoring requires the use of an appropriate set of monitoring techniques to collect meaningful and reliable data that are needed for the proper management of water bodies. Most techniques can be used for all three types of monitoring but some techniques are more suitable for, or specially adapted to, particular situations or locations (Allan et al., 2006). The choice of techniques depends upon the type of use, costs, robustness, sensitivity and the type of information required.

In the sections that follow, quotations are given from the documents studied that show what they have to say with respect to monitoring and sampling, and whether they have anything to say about passive sampling and, if so, what.

8.1 The Water Framework Directive

The Water Framework Directive (Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for community action in the field of water policy) (EC, 2000)) discusses monitoring in article 8 and Annex V.
In Article 8, 'Monitoring of surface water status, groundwater status and protected areas', sub-paragraph 3 states that 'Technical specifications and standardised methods for analysis and monitoring of water status shall be laid down in accordance with the procedure laid down in Article 21'. However, Article 21 looks only at the procedure for adoption, not the methods themselves.
Annex V, Section 1.3 'Monitoring of ecological status and chemical status for surface waters' discusses the establishment of a monitoring network and a monitoring programme. However, as in Article 8, no suggestions are made about the monitoring methods to be used or the methods that are permitted.
Consideration 49 of the Water Framework Directive states that: 'Technical specifications should be laid down to ensure a coherent approach in the Community as part of this Directive. The criteria stated in Annex V for evaluation of water status are an important step forward. Adaptation of certain technical elements to technical development and the standardisation of monitoring, sampling and analysis methods should be adopted by committee procedure. To promote a thorough understanding and consistent application of the criteria for characterisation of the river basin districts and evaluation of water status, the Commission may adopt guidelines on the application of these criteria'.

In short, it may be concluded that neither the text of the WFD nor the accompanying annex mention any specific monitoring methods.

8.2 Guidelines for monitoring surface water

In the Netherlands, the document 'Guidelines for monitoring surface water. European Water Framework Directive' (Van Splunder et al., 2006, in Dutch) took the first steps towards providing the guidelines referred to in the previous section. In version 1.3 of this document, Section 4.5. 'Sampling and analysis methods', sub-section 4.5.1 'Chemistry' and Annex 4a are important.

Sub-section 4.5.1 includes the following two relevant paragraphs:

Strategy with respect to analysis methods
'Laboratories are free to use their own methods to conduct measurements. The quality of applied analysis methods is safeguarded by monitoring the performance characteristics of the methods applied (particularly the reporting limit and measurement uncertainty). In this way, the laboratories involved maintain the possibility of applying innovative techniques that may produce more reliable results than

is possible at present using standardised methods. An overview of the possible analysis methods for the priority substances and a few other relevant substances can be found in Annex 4a'.

Choice of compartment
Organic compounds should be measured in "total water".
Metals should be measured as "dissolved metals in water". The operational definition formulated for "dissolved" corresponds to measurement practice (filtering through a 0.45 µm filter). As a rule, a maximum of one litre of water should be sampled. In the Netherlands, this recommendation is adhered to strictly and larger sampling amounts to attain the lower required reporting limits are consequently not used.
Note: This may sometimes result in inadequate information if the reporting limit for the analysis in water is too high for compliance checking. In the future, analysis techniques will continue to improve which might enable compliance checking. Information about sampling methods and chemical analysis methods can be found in Annex 4a.

In Annex 4a, the following paragraph is important:
'The following table lists the analysis methods for the priority substances and a few specific pollutants. There are no restrictions on the analysis methods, on condition that the performance characteristics of the methods (limit of detection, measurement uncertainty, selectivity) correspond to the current, best practicable means'.

In short, neither the body of the document nor Annex 4a discuss the use of passive sampling.

8.3 CEN Methods for WFD monitoring

The European Committee for Standardization (CEN) and the ad hoc working group 1 of the Technical Committee for Water Analysis (TC230) have, under the flag of the Chemical Monitoring Activity (CMA), drafted and described a list of ISO and EN standards for the chemical analysis of WFD priority substances (CEN, 2007a en 2007b). These documents state that 'The list will be considered for inclusion in Annex V 1.3.6 of the WFD'. It is unclear whether, and when, this has come about.

The CEN documents and annex contain no allusion to passive sampling methods.

8.4 Guidance on surface water chemical monitoring

A guidance document was written in 2009 covering the monitoring of surface water under the Water Framework Directive (EC, 2009a).

This guidance document was drafted after Member States, in the context of the Priority Substances Directive (2008/105/EC) developed under the Water Framework Directive, had stated that they required clarification relating to the monitoring of priority substances and other chemical compounds under the WFD. It supplements, among other things, guidance document no 7 Monitoring CIS Guidance. The document was drafted by an informal working group acting under the CIS Chemical Monitoring Activity (CMA) made up of experts from various member states and stakeholders. This document was approved by the European Water Directors in November 2008.

Chapter 7 'Complementary Methods' of this guidance document states that compliance checking with respect to WFD objectives may currently be based on the chemical analysis of spot samples taken at set intervals, but that it is desirable to introduce other techniques to improve the quality of the environmental assessment and to benefit from developments that save costs. Chapter 7 of the guidance document is based on Allan et al. (2006) (see section

8.8) and was drafted in collaboration with the EU project, SWIFT. Passive sampling is listed in Chapter 7 as one of the complementary methods that can be used for various purposes. The same text also states that supplementary 'performance criteria' might be required for passive sampling. The 'performance criteria' for the laboratory analysis of the extract from a passive sampler are largely the same as those for a water sample taken in the usual way. However, the uptake rates of the passive sampler required for the calculation of time-weighted averaged contaminant concentrations in the water and the fact that the use of passive samplers in the field is associated with relatively strict protocols require additional 'performance criteria'.

According to the guidance document, passive sampling can be used both in the monitoring network design and in the different types of monitoring. In the monitoring network design, passive samplers may play a role in the identification of both problem areas and non-problematic areas. For surveillance monitoring and operational monitoring, complementary methods, including passive sampling, may be used on condition that they comply with the requirements set out in the 'Commission Directive 2009/90/EC of 31 July 2009 laying down, pursuant to Directive 2000/60/EC of the European Parliament and of the Council, technical specifications for chemical analysis and monitoring of water status' (EC, 2009b).

Article 3 of this Directive states that all analysis methods, including laboratory, field and on-line methods, must be validated and documented in accordance with EN ISO/IEC-17025 or other equivalent standards accepted at international level. Furthermore, Article 4 of the same Directive states that the uncertainty of measurement of the method must be 50% or below estimated at the level of the relevant environmental quality standard and that the limit of quantification must be a maximum of 30% of the relevant environmental quality standard. This article also states that, in the absence of a method of analysis meeting these minimum performance criteria, Member States must use best available techniques not entailing excessive costs.

The guidance document also states that passive sampling can be used alongside spot sampling to confirm or refute the results of spot sampling. This would allow important evidence to be produced for water bodies in which contaminant concentrations fluctuate considerably over time because passive sampling is affected less by brief fluctuations than is spot sampling. Given the fact that determining annual average concentrations is one of the main objectives of the WFD, passive sampling would appear to be a highly promising method according to the criteria of the guidance document. Some passive samplers have already been validated and they can measure extremely low levels of contaminants in water, which is the first step towards establishing an internationally recognised standard.
'Biofouling', calibration and the back-calculation to concentrations in water are areas that can lead to difficulties in passive sampling. So further study and validation are required before passive sampling can be used for compliance checking.

Another area meriting attention according to the guidance document is the fact that passive sampling measures the freely dissolved (bio-available) concentration. This is the best measure for determining ecological risks. However, compliance checking of water quality in the WFD for organic compounds is based on the total concentration in water. The guidance document states that it is possible, using averaged measured DOC concentrations, concentrations of suspended matter and total organic matter levels in the suspended matter, to calculate the total concentration in water using equilibrium partitioning based on the freely dissolved concentration determined with passive sampling.

The guidance document also refers to passive sampling as a complementary method for Investigative Monitoring. Passive sampling may be of use in identifying sources of pollution in particular if extremely low levels have to be detected or when the source of pollution is not constant.

8.5 Guidance on chemical monitoring of sediment and biota

A guidance document was written in 2010 covering the monitoring of sediment and biota under the Water Framework Directive (EU, 2010).

The document links up to guidance document 19 (EC, 2009a) described in the previous section relating to the monitoring of surface water and also lists passive sampling as a 'complementary method' for monitoring in sediment and biota.
The guidance document states that passive sampling can be used to determine the freely dissolved concentration in the pore water of the sediment, which is a better measure for the impact on benthic organisms than a total concentration in sediment.
The guidance document also states that passive sampling can be used as an alternative to biomonitoring. Here, the same benefits and drawbacks are described as in Chapter 5 of the present report.

8.6 Decree on Quality Objectives and Monitoring in Water 2009

The following paragraphs from the Decree on Quality Objectives and Monitoring in Water 2009 (Bkmw 2009, 2010) are relevant to monitoring:

Next to the table with standards for priority substances (annual average environmental quality standard (AA-EQS) and the maximum acceptable concentration (MAC-EQS)):
'The calculation of the arithmetic mean and the analysis methods to be used will be in accordance with the provisions of article 20 of the Water Framework Directive, including the way in which an environmental quality standard is used in the absence of any appropriate analysis method that complies with the minimum performance characteristics'.

'Article 8 refers to Annex V of the WFD. This determines in detail how water status should be monitored. From section 1.3, it also emerges that the monitoring programme conducted for the purposes of drafting every new river basin management plan as referred to in article 13 of the WFD must be updated. Amendments of Annex V WFD relating to scientific and technical progress may be made on the basis of article 20(1) WFD in accordance with the procedure set out in article 21 WFD. An amendment of this kind comes into force in the Netherlands at the end of the implementation period in accordance with article 18 of this decree. Article 20(1) WFD also comprises the possibility of the European Commission drawing up guidelines for the application of Annex V WFD. Although guidelines of this kind are not binding in law, the member states may not simply disregard them when elaborating and implementing their monitoring programmes. Article 8 WFD also refers to technical specifications and standardised methods for the analysis and monitoring of water status which are also laid down in accordance with the procedure laid down in Article 21 WFD.'

The Decree on Quality Objectives and Monitoring in Water 2009 (Bkmw 2009, 2010) does not contain any other instructions relating to monitoring methods.

8.7 Ministerial Regulation on Monitoring Water Framework Directive

The following paragraph from the Ministerial Regulation on Monitoring Water Framework Directive (MR Monitoring, 2010) is relevant with respect to monitoring:

Next to the table with indicators of the good ecological quality in surface water (compounds) (JG-MKN and MAC-MKN):
'The calculation of the arithmetic mean and the analysis methods to be used will be in accordance with the provisions of article 20 of the Water Framework Directive, including the way in which an environmental quality standard is used in the absence of any appropriate analysis method that complies with the minimum performance characteristics'.

The regulation does not contain any provisions relating to monitoring methods.

8.8 Conclusion

It can be concluded from the preceding sections that passive sampling is not specifically mentioned as a monitoring method in the Water Framework Directive and the Dutch implementation of that directive (Bkmw 2009, 2001; MR Monitoring, 2010).
However, an important consideration is that the Guidance document on surface water chemical monitoring (EC, 2009a) does refer to passive sampling as one of the complementary methods that can be used for both monitoring network design and surveillance monitoring. Here, the precondition is that the method must be validated and documented in accordance with EN ISO/IEC-17025 or other equivalent standards accepted at international level.

Given the fact that the analysis of a passive sampler sample (the extract) is not very different from a water sample obtained in the traditional way, certification will not represent a major problem. However, more work will be required for the entire passive sampling process. Some passive samplers have been validated, but not yet documented in accordance with EN ISO/IEC-17025. As far as is known, there are not yet any known passive sampling methods that have been certified in full in accordance with the required standard.
A possible way of circumventing this difficulty is the fact that, when no analysis methods are available that fulfil the minimum 'performance criteria', the best available techniques not entailing excessive costs must be used. Passive sampling may be this best available technique for very low concentrations that are not detectable in water samples obtained in the traditional way.

In addition, passive sampling can also be used in parallel with spot sampling in order to confirm or refute the results for water samples taken in the traditional way, particularly in situations in which contaminant concentrations fluctuate considerably over time. Passive sampling can also play this role in Investigative Monitoring.

An ongoing issue is that the compliance checking of water quality under the WFD with respect to organic compounds is based on total water concentrations and that passive sampling measures the freely dissolved (bio-available) concentration. However, total concentrations in water can be calculated using averaged measured DOC concentrations, concentrations of suspended matter and total organic matter levels in the suspended matter with equilibrium partitioning on the basis of the freely dissolved concentration determined with passive sampling.

9 Conclusions and recommendations

9.1 Conclusions

Is it permissible to use passive sampling in WFD monitoring?

It can be concluded from studying a number of relevant documents that passive sampling is not specifically mentioned as a monitoring method in the Water Framework Directive and the Dutch implementation of that directive (Bkmw 2009, 2010; MR Monitoring, 2010).

However, an important consideration is that the Guidance document on surface water chemical monitoring does refer to passive sampling as one of the complementary methods that can be used for both monitoring network design and surveillance monitoring. This is conditional upon the method being validated and documented. Although we are not yet aware of any passive sampling methods that have been fully certified in accordance with this condition, there is a possibility of using passive sampling as the best available technique for compounds that cannot be detected in classical water samples but that can be detected with passive sampling.

An ongoing issue is that the compliance checking of water quality under the WFD with respect to organic compounds is based on the total concentration in water and that passive sampling measures the freely dissolved (bioavailable) concentration. However, this problem can be addressed by converting this freely dissolved concentration into a total concentration.

Can passive sampling with silicon rubber be used in WFD monitoring?

Passive sampling with silicon rubber has been found to perform excellently. Rijkswaterstaat has been successfully monitoring PCBs and PAHs since 2002 using passive samplers with silicon rubber. Comparing the results of these passive sampling activities with measured concentrations in biota shows that there is a good correlation between the two.

Sheets of silicon rubber are robust in use and modelling is relatively simple with them. Of the 54 individual priority substances, 74% are measurable or potentially measurable with silicon rubber. This figure is 31% for the 167 individual specific pollutants and 81% for the 16 individual possible future priority substances (see annex A for the compounds in question).

The time would therefore seem to be ripe to use silicon rubber more in WFD monitoring. An issue here is that passive sampling yields freely dissolved concentrations and that the WFD checks compliance with the environmental quality standards on the basis of concentrations in total water.

The higher sensitivity (lower limit of detection) and the possibility of measuring time-averaged concentrations are major advantages of passive sampling. However, the main advantage of passive sampling is that it measures exactly what is needed for risk assessment, which is the freely dissolved concentration. Another major advantage of the freely dissolved concentrations in the water phase is that, by contrast with concentrations in total water, they no longer need to be corrected for local conditions such as concentrations of suspended matter and DOC. The results of passive sampling can therefore be compared worldwide without correction.

Can passive sampling with silicon rubber replace measurements in biota?

Passive sampling has many advantages compared to biomonitoring: passive samplers stay in a single location, they do not metabolise contaminants, the same sampler can be used everywhere (in fresh, marine, cold, warm, anoxic and even toxic water), the results can be compared worldwide and no organisms need to be sacrificed when using passive sampling. Another important consideration is that passive sampling, by contrast with measuring in biota,

does not require any separate standards. It is possible to draw on the WFD standards in place for surface water (after conversion into freely dissolved concentrations).
Despite the fact that sound correlations have been found between concentrations obtained using silicon rubber and concentrations in biota, passive sampling will never be able to generate a precise prediction of a concentration in an organism. Living organisms are dynamic and they respond to all sorts of factors that do not affect passive samplers.
The limit of detection for passive sampling with silicon rubber is not low enough at present for highly hydrophobic compounds such as the higher PBDEs and dioxins, of which the freely dissolved concentrations are extremely low. However, passive sampling, including passive sampling with silicon rubber, is still developing and it may be possible to measure these compounds accurately in time as well.
Passive sampling can largely replace bio-monitoring for water quality purposes.

Is passive sampling more expensive than classical monitoring methods?
Assuming the same monitoring frequency, the total monitoring costs for passive sampling will be higher than the costs for classical monitoring using water samples. In part, this is a result of the fact that an extra analysis will always be required for the purposes of measuring the PRCs in the passive samplers.
For highly hydrophobic compounds, the silicon rubber sampler delivers a time-integrated result for a long period. To obtain an annual average concentration, the sampling frequency can be severely reduced in these cases, thereby cutting costs.

All in all, it is difficult to say whether passive sampling results in higher or lower costs on balance.

It is clear that the price/quality ratio of passive sampling is better. This is not only the result of the fact that passive sampling can achieve lower limit of detections and that it makes time-integrated sampling possible, but also because the measured freely dissolved concentrations obtained with passive sampling produce a better picture of the actual environmental risks.

9.2 Recommendations

Implementation strategy
It is not necessary to wait for all the additional studies before starting monitoring with passive sampling. We advise against the widespread abandonment of the current monitoring approach in favour of passive sampling, and recommend starting out with about ten sites spread around the Netherlands where passive sampling will be easy to implement. In the initial stages, the focus should be on those compounds that are difficult or impossible to measure using classical sampling techniques because of their low concentrations. Laboratories can then gradually make the transition and start the analyses. After the start-up phase, more compounds can be included and the diffusion coefficients and K_{pw} values for the compounds that are frequently detected can be determined. As things proceed, the results can be evaluated and consideration can be given to using passive sampling more widely.

Sampling strategy
For compliance checking with the WFD objectives, an annual average concentration is required (i.e. for compliance with the annual average-environmental quality standard, AA-EQS). In the case of hydrophobic compounds, passive sampling integrates the concentrations over a given period. The required measurement frequency depends on the target compound. With some compounds, such as higher PBDEs, exposure times of six months or even an entire year are possible without equilibrium being achieved and in which, therefore, sampling is time-averaged.

However, making one or two measurements a year constitutes a risk because of the possible loss of the sampler. Overlapping exposure of samplers over the course of time, for example by installing a single sampler every three months but exposing that same sampler for six months or an entire year, makes it possible to obtain more observations a year and also generates information about the variation of the concentrations. For compounds that attain equilibrium quickly, such as 2- and 3-ring PAHs, parallel samplers can be used with shorter exposure times of, for example, a single month. The frequency and the number of parallel samplers can be optimised in initial testing at about ten locations, as recommended above.

Suggestions for further research

Although passive sampling with silicon rubber is operational and can be used directly for water-quality monitoring for the purposes of the Water Framework Directive, there are a number of areas where further research is desirable. Possible avenues include:

- For every group of compounds to be sampled using passive sampling, it is necessary to know the diffusion coefficients in silicon rubber and the sampler-water partition coefficients K_{pw}. The highly hydrophobic compounds ($\log K_{ow} > 6$) are an exception.
  We propose further research looking at relevant compounds for which these data are not yet available. The table in Annex A shows for which substances for which the silicon rubber sampler is suitable;
- It is useful to further study the model describing the relationship between compound properties and the sampling rate, using as wide a variety of compounds as possible in order to establish a firmer foundation for the model (and therefore for passive sampling);
- In order to respond to possible resistance to the use of PRCs (deliberate emission of anthropogenic compounds), it is advisable to investigate the possibilities and development of an 'active' passive sampler;
- Passive sampling and certification is still completely virgin territory. It is therefore advisable to determine whether, and how, passive sampling can and should be certified.
- Samplers for polar compounds are already being used in a range of studies but they are still in full development. Virtually all new compounds are polar compounds and that is why it is important to invest in this development and acquire experience with this type of sampler.

10 Literature

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A Sampling WFD substances with silicon rubber

This annex includes a table stating whether it is possible to sample specific WFD-relevant substances with silicon rubber. The WFD-relevant substances include: the priority substances, the substances that have to be monitored for the purposes of ecological water quality (the specific pollutants) and a number of substances that may be added to the list of priority substances in the future (personal communication Hannie Maas).

The different columns of the table include parameters or results of calculations that are used to estimate which substances can (possibly) be sampled using silicon rubber. This estimate for silicon rubber will to a large extent also be applicable to other hydrophobic samplers.

In the **first** column, there is a number referring to the WFD list containing the substance in question. For the priority substances and specific pollutants, this is the number used in the WFD list, in so far as a number has been allocated. This numbering has been extended for the specific pollutants without a WFD number. The specific pollutants have been given the suffix E. The list of possible future priority substances has not yet been numbered. In the table, these substances are given the suffix O and a serial number.
The **second** column contains the name of the compound and the **third** column states the CAS number.
The environmental quality standard values ($\mu g.l^{-1}$) for inland waters and other waters can be found in columns **four** and **five** respectively**.** Columns **six**, **seven** and **eight** state the molecular weight (MW), the octanol-water partition coefficient (log K_{ow}), and the organic carbon-water partition coefficient (log K_{oc}). Different sources were used for the log K_{ow} and log K_{oc} values, such as Guchte et al. (2000), Lijzen et al. (2001) and various other literature sources. For the less familiar compounds, these data were obtained from EPIsuite v4.0.
The environmental quality standard is based on total water and that is why column **nine** states the value for the freely dissolved concentration ($\mu g.l^{-1}$) that is thought to be corresponding to the EQS based on total water concentrations. For this purpose, the lowest of the environmental quality standards for inland and other waters is converted to the freely dissolved concentration, assuming water with 30 mg/l of suspended matter [SPM in kg/l] that contains 10% of organic carbon (f_{oc}=0.1). The freely dissolved concentration associated with the environmental quality standard is therefore equal to:

$$EQS\ C_w = \frac{EQS\ \text{total water}}{1 + [SM]\, f_{oc}\, K_{oc}}$$

The K_{oc} values from column eight are used here. If they are not available, the K_{ow} is used. If there is no environmental quality standard known or available, the entry in column **nine** is “nd”.
The next step is to determine whether the limit of detection is low enough to be measured at the level of the standard. For this purpose, the possible limit of detection in the water phase is calculated assuming a limit of detection for the sampler ($LOD_{sampler}$) of 1 ng (0.001µg per sampler) (column **ten**). The calculation is based on a sampler weight (m_p) of 20 g (0.02 kg), an exposure time (t) of 42 days and a sampling rate of 10 litres a day. If the K_{pw} was known (not stated in table), it was used; in other cases, the K_{ow} was used. The limit of detection for passive sampling in water ($\mu g.l^{-1}$) can then be calculated with:

$$\text{Detection limit in water } (\mu g.l^{-1}) = \frac{DL_{sampler}}{K_{pw}\, m_p \left(1 - e^{-\frac{R_s\, t}{m_p\, K_{pw}}} \right)}$$

Of course, this is an estimate because the limit of detection for the sampler may be higher or lower and using the K_{ow} instead of a K_{pw} may together easily lead to a variation with a factor of 10. Column **eleven** then provides an estimate of the period (t_{LIN} in days) during which the sampler can conduct time-integrated sampling (i.e. the amount of time it is in the linear stage):

$$t_{LIN} = \frac{m_p\, K_{pw}}{R_s\, t}$$

Furthermore, column **twelve** lists the status with respect to the feasibility of passive sampling for the relevant compound. In principle, all neutral compounds with a log $K_{ow} \geq 3.5$ can potentially be measured using passive sampling. For these compounds, a “P” (Potential) is entered in column twelve, unless an application is known, in which case an “A” (Applied) is entered in column twelve. Furthermore, if good K_{pw} values and diffusion coefficients are known and passive sampling is used in monitoring, “Am” (Applied in monitoring) will be entered. The code “NP” (not probable) means that it is not probable that this compound can be sampled with passive sampling, but that the possibility is not being excluded either. Usually, the log K_{ow} is too low in these cases, but sometimes the compound is too volatile to get through pretreatment without losses. Application is perhaps possible using specific techniques.
Compounds with a lower log K_{ow} can often still be measured, possibly even with a lower limit of detection than in classical sampling. However, the length of time during which the sampler is sampling in a time-averaged way does get shorter and shorter. An example is naphthalene with a log K_{ow} of 3 and a t_{LIN} of 0.7 day but for which passive sampling has been used. The limit of detection will however be higher than the 0.00005 µg/l that has been calculated because this compound is common in air and the limit of detection of 1 ng on the sampler will not be achieved. Nevertheless, naphthalene can still be measured down to a factor of 1000 below the environmental quality standard.
In fact, all compounds accompanied by the codes P, A or Am can be measured well below the environmental quality standard (as converted to the freely dissolved concentration). Exceptions are the higher PBDEs (5) and Abamectine (E139). In the case of the PBDEs, longer sampling periods can lower the limit of detection but also the sensitivity of the instrument measurements might be enhanced.

Summary of the meanings of the codes in column twelve

P	Potential. On the basis of the compound properties, neutral and adequately high K_{ow}, it can be expected that this compound is amenable to passive sampling.
A	Applied. Simple or limited application known.
Am	Applied in monitoring. Widespread application or application in monitoring; partition coefficients and diffusion coefficients are known.
NP	Not probable. It is not probable that this compound is amenable to passive sampling but nor can the possibility be excluded.
N	Not. Sound measurement with hydrophobic passive sampling is as good as excluded.

1	2	3	4	5	6	7	8	9	10	11	12
No	**Name**	**CAS no**	**EQS-inland waters** ($\mu g.l^{-1}$)	**EQS-other waters** ($\mu g.l^{-1}$)	**MW** ($g.mol^{-1}$)	**LogK_{ow}**	**LogK_{oc}**	**EQS-Cw** ($\mu g.l^{-1}$)	**DL of PS** ($\mu g.l^{-1}$)	**T_{LIN}** (d)	**Applicability**
Priority substances											
1	Alachlor	15972-60-8	0.3	0.3	270	3.37		0.3	0.00002	2	P
2	Anthracene	120-12-7	0.1	0.1	178	4.45	4.30	0.09	0.000004	12	Am
3	Atrazine	1912-24-9	0.6	0.6	216	2.61	2.20	0.6	n.a.	n.a.	NP
4	Benzene	71-43-2	10	8	78	2.13	1.87	8	n.a.	n.a.	N
5	Total PBDE	32534-81-9	0.0005 b)	0.0002					n.a.	n.a.	
5.05	PBDE 28	041318-75-6	0.00008	0.00003	407	5.88		0.00001	0.000003	1800	A
5.10	PBDE 47	005436-43-1	0.00008	0.00003	486	6.77		0.0000018	0.000003	5000	A
5.15	PBDE 99	060348-60-9	0.00008	0.00003	565	7.66		0.0000002	0.000003	62000	A
5.20	PBDE 100	000006-01-5	0.00008	0.00003	565	7.66		0.0000002	0.000003	62000	A
5.25	PBDE 153	000006-01-7	0.00008	0.00003	644	8.55		0.00000003	0.000003	510000	A
5.30	PBDE 154	207122-15-4	0.00008	0.00003	644	8.55		0.00000003	0.000003	510000	A
6	Cadmium		0.08	0.2					n.a.	n.a.	
(6 bis)	Carbon tetrachloride	56-23-5	12	12					n.a.	n.a.	
7	C10-13-chloroalkanes	85535-84-8	0.4	0.4	300	5.00	5.00	0.3	a)	100	P
8	Chlorfenvinphos	470-90-6	0.1	0.1	360	4.15	3.10	0.1	0.000005	15	P
9	Chlorpyriphos (ethyl-chlorpyriphos)	2921-88-2	0.03	0.03	351	4.66	3.86	0.03	0.000003	49	P
9 (bis)	Total Cyclodiene pesticides:		0.01 b)	0.01					n.a.	n.a.	
9	Aldrin	309-00-2	0.003	0.003	365	6.50	3.94	0.003	0.000003	3500	P
9	Dieldrin	60-57-1	0.003	0.003	381	4.55	3.99	0.003	0.000003	40	P
9	Endrin	72-20-8	0.003	0.003	381	4.55	3.95	0.003	0.000003	40	P
9	Isodrin	465-73-6	0.003	0.003	365	6.75	5.60	0.0015	0.000003	6200	P
9 ter)	DDTs		0.025 b)	0.025					n.a.	n.a.	
9	ppDDT	50-29-3	0.006	0.006	355	6.91	5.58	0.003	0.000003	1360	A
9	opDDT	789-02-6	0.006	0.006	355	6.91	5.58	0.003	0.000003	2200	A
9	ppDDD	72-54-8	0.006	0.006	320	6.22	5.18	0.004	0.000003	260	A
9	ppDDE	72-55-9	0.006	0.006	318	6.96	5.35	0.004	0.000002	2100	A
10	1,2-Dichoroethane	107-06-2	10	10	99	1.83	1.60	10	n.a.	n.a.	N
11	Dichloromethane	75-09-2	20	20	85	1.34	1.34	20	n.a.	n.a.	N

1	2	3	4	5	6	7	8	9	10	11	12
No	**Name**	**CAS no**	**EQS-inland waters** ($\mu g.l^{-1}$)	**EQS-other waters** ($\mu g.l^{-1}$)	**MW** ($g.mol^{-1}$)	**LogK_{ow}**	**LogK_{oc}**	**EQS-Cw** ($\mu g.l^{-1}$)	**DL of PS** ($\mu g.l^{-1}$)	**T_{LIN}** (d)	**Applicability**
12	Di(2-ethyl-hexyl)phthalate (DEHP)	117-81-7	1.3	1.3	391	7.45	5.37	0.8	0.000003	45	A
13	Diuron	330-54-1	0.2	0.2	233	2.67	2.04	0.2	n.a.	n.a.	N
14	Endosulphan	115-29-7	0.005	0.0005	407	3.50	3.83	0.0005	0.00002	4	P
15	Fluoranthene	206-44-0	0.1	0.1	202	5.16	5.18	0.07	0.000003	33	Am
16	Hexachlorobenzene	118-74-1	0.01	0.01	285	5.73	4.06	0.01	0.000003	123	Am
17	Hexachlorobutadiene	87-68-3	0.1	0.1	261	4.72	2.93	0.1	0.000003	74	Am
18	Hexachlorocyclohexane	608-73-1	0.02	0.002	291	3.21	3.37	0.002	0.00003	2	A
19	Isoproturone	34123-59-6	0.3	0.3	206	2.84	2.30	0.3	n.a.	n.a.	NP
20	Lead and lead compounds	7439-92-1	7.2	7.2					n.a.	n.a.	?
21	Mercury and mercury compounds	7439-97-6	0.05	0.05					n.a.	n.a.	?
22	Naphthalene	91-20-3	2.4	1.2	128	3.30	2.98	1.2	0.00005	0.7	A
23	Nickel and nickel compounds	7440-02-0	20	20					n.a.	n.a.	N
24	Nonylphenols (4-(para)-nonylphenol)	104-40-5	0.3	0.3	220	5.99	4.58	0.3	0.000003	34	P
25	Octylphenols ((4-(1.1',3,3'-tetramethylbutyl)-phenol))	140-66-9	0.1	0.01	206	5.28	4.00	0.01	0.000002	160	P
26	Pentachlorobenzene	608-93-5	0.0007	0.0007	250	5.18	3.92	0.0007	0.000003	37	A
27	Pentachlorophenol	87-86-5	0.4	0.4	266	5.12	3.20	0.4	n.a.	n.a.	N
28	Polyaromatic hydrocarbons (PAHs)								n.a.	n.a.	
28	Benzo(a)pyrene	50-32-8	0.05	0.05	252	6.13	5.82	0.017	0.000002	460	Am
28	Total Benzo(b)- and Benzo(k)fluoranthene		0.03	0.03							Am
28	Benzo(b)fluoranthene	205-99-2	0.015	0.015	252	6.11	5.78	0.005	0.000002	460	Am
28	Benzo(k)fluoranthene	207-08-9	0.015	0.015	252	6.11	6.24	0.002	0.000002	460	Am
28	Total Benzo(ghi)-perylene and Indeno(1,2,3-cd)pyrene		0.002	0.002							Am
28	Benzo(ghi)perylene	191-24-2	0.001	0.001	276	6.22	6.43	0.00011	0.000002	960	Am
28	Indeno(1,2,3-cd)pyrene	193-39-5	0.001	0.001	276	6.87	6.02	0.0002	0.000002	1210	Am

1	2	3	4	5	6	7	8	9	10	11	12
No	**Name**	**CAS no**	**EQS-inland waters** ($\mu g.l^{-1}$)	**EQS-other waters** ($\mu g.l^{-1}$)	**MW** ($g.mol^{-1}$)	**LogK_{ow}**	**LogK_{oc}**	**EQS-Cw** ($\mu g.l^{-1}$)	**DL of PS** ($\mu g.l^{-1}$)	**T_{LIN}** (d)	**Applicability**
28	Simazine	122-34-9	1	1	202	2.40	2.17	1	n.a.	n.a.	N
(29 bis)	Tetrachloroethylene	127-18-4	10	10	166	3.40	2.42	10	n.a.	n.a.	N
(29 ter)	Trichloroethylene	79-01-6	10	10	131	2.61	2.06	10	n.a.	n.a.	N
30	Tributyltin compounds (Tributyltin cation)	36643-28-4	0.0002	0.0002	291	4.70	3.91	0.0002	0.000003	49	P
31	Trichlorobenzenes	12002-48-1	0.4	0.4	181	4.13	3.50	0.4	0.00001	4	P
32	Trichloromethane	67-66-3	2.5	2.5	119	1.97	1.66	2	n.a.	n.a.	N
33	Trifluralin	1582-09-8	0.03	0.03	335	5.31	4.22	0.03	0.000003	260	A
Specific pollutants											
E 2	2-amino-4-chlorophenol	95-85-2			144	1.24	2.17	Nd	n.a.	n.a.	N
E 4	Arsenic (and inorganic compounds of arsenic)	7440-38-2							n.a.	n.a.	
E 5	Azinphos-ethyl	2642-71-9	0.0011	0.0013	345	3.51	2.24	0.0011	0.000015	3	P
E 6	Azinphos-methyl	86-50-0	0.0065	0.0004	317	2.53	1.72	0.0004	n.a.	n.a.	NP
E 8	Benzidine	92-87-5			184	1.92	3.08	Nd	n.a.	n.a.	N
E 9	Benzylchloride (alpha-chlorotoluene)	100-44-7			127	2.79	2.65	Nd	n.a.	n.a.	NP
E 10	Benzylidene chloride (alpha,alpha-dichlorotoluene)	98-87-3			161	2.97	2.84	Nd	n.a.	n.a.	NP
E 11	Biphenyl	92-52-4			154	3.76	3.71	Nd	0.00001	4	P
E 14	Chloral hydrate	302-17-0			165	0.98	0.00	Nd	n.a.	n.a.	N
E 15	Chlordan	57-74-9			410	6.26	4.83	Nd	0.000003	180	P
E 16	Chloroacetic acid	79-11-8	0.58	0.058	95	0.34	0.16	0.06	n.a.	n.a.	N
E 17	2-chloroaniline	95-51-2	0.2	0.032	128	1.72	2.06	0.03	n.a.	n.a.	N
E 18	3-chloroaniline	108-42-9	0.41	0.065	128	1.72	2.05	0.06	n.a.	n.a.	N
E 19	4-chloroaniline	106-47-8	0.22	0.057	128	1.72	2.05	0.06	n.a.	n.a.	N
E 20	Chlorobenzene	108-90-7			113	2.64	2.37	Nd	n.a.	n.a.	N
E 21	1-Chloro-2,4-dinitrobenzene	97-00-7			203	2.27	2.76	Nd	n.a.	n.a.	N

1	2	3	4	5	6	7	8	9	10	11	12
No	**Name**	**CAS no**	**EQS-inland waters** ($\mu g.l^{-1}$)	**EQS-other waters** ($\mu g.l^{-1}$)	**MW** ($g.mol^{-1}$)	**LogK_{ow}**	**LogK_{oc}**	**EQS-Cw** ($\mu g.l^{-1}$)	**DL of PS** ($\mu g.l^{-1}$)	**T_{LIN}** (d)	**Applicability**
E 22	2-Chloroethanol	107-07-3			81	0.11	0.28	Nd	n.a.	n.a.	N
E 24	4-Chloro-3-methylphenol	59-50-7	6.4	0.64	143	2.70	2.69	0.6	n.a.	n.a.	NP
E 25	1-Chloronaphthalene	90-13-1			163	3.81	3.40	Nd	0.000008	5	P
E 26	Chloronaphthalenes (technical mixture)	025586-43-0			162	3.81	3.40	Nd	a)	5	P
E 27	4-Chloro-2-nitroaniline	89-63-4			173	2.66	2.52	Nd	n.a.	n.a.	N
E 28	1-Chloro-2-nitrobenzene	88-73-3			158	2.46	2.57	Nd	n.a.	n.a.	N
E 29	1-Chloro-3-nitrobenzene	121-73-3			158	2.46	2.56	Nd	n.a.	n.a.	N
E 30	1-Chloro-4-nitrobenzene	100-00-5			158	2.46	2.56	Nd	n.a.	n.a.	N
E 31	4-Chloro-2-nitrotoluene	89-59-8			172	3.00	2.77	Nd	n.a.	n.a.	N
E 32	Chlotonitrotoluenes (other than 4-Chloro-2-nitrotoluene)								n.a.	n.a.	
E 33	2-Chlorophenol	95-57-8	35	3.5	129	2.16	2.49	3	n.a.	n.a.	N
E 34	3-Chlorophenol	108-43-0	4	0.4	129	2.16	2.48	0.4	n.a.	n.a.	N
E 35	4-Chlorophenol	106-48-9	16	3	129	2.16	2.48	3	n.a.	n.a.	N
E 36	Chloroprene (2-Chloro-1,3-butadiene)	126-99-8	0.19	0.19	89	2.53	1.78	0.19	n.a.	n.a.	N
E 37	3-Chloropropene (allylchloride)	107-05-1	0.34	0.034	77	1.93	1.60	0.03	n.a.	n.a.	N
E 38	2-Chlorotoluene	95-49-8			127	3.18	2.58	Nd	n.a.	n.a.	NP
E 39	3-Chlorotoluene	108-41-8			127	3.18	2.57	Nd	n.a.	n.a.	NP
E 40	4-Chlorotoluene	106-43-4			127	3.18	2.57	Nd	n.a.	n.a.	NP
E 41	2-Chloro-p-toluidine	615-65-6			142	2.27	2.27	Nd	n.a.	n.a.	N
E 42	Chlorotoluidines (other than 2-Chloro-p-toluidine)								n.a.	n.a.	
E 43	Cumaphos	56-72-4	0.0034	0.00068	363	4.47	3.56	0.0007	0.000004	32	P
E 44	Cyanuric chloride (2,4,6-trichloro-1,3,5-triazine)	108-77-0			184	1.73	2.90	Nd	n.a.	n.a.	N
E 45	2,4-D (and salts and esters of 2,4-D)	94-75-7			221	2.62	1.47		n.a.	n.a.	N
E 47	Demeton	298-03-3			258	3.21	2.92	Nd	0.00003	1.5	P
E 48	1,2-Dibromethane	106-93-4	0.0033	0.4	188	2.01	1.60	0.003	n.a.	n.a.	NP

1	2	3	4	5	6	7	8	9	10	11	12
No	**Name**	**CAS no**	**EQS-inland waters** ($\mu g.l^{-1}$)	**EQS-other waters** ($\mu g.l^{-1}$)	**MW** ($g.mol^{-1}$)	**LogK_{ow}**	**LogK_{oc}**	**EQS-Cw** ($\mu g.l^{-1}$)	**DL of PS** ($\mu g.l^{-1}$)	**T_{LIN}** (d)	**Applicability**
E 49	Dibutyltin (cation)	683-18-1	0.09	0.09	304	1.89	3.27	0.09	n.a.	n.a.	NP
E 50	Dibutyltin (cation)	818-08-6	0.09	0.09	249	5.33	3.11	0.09	n.a.	n.a.	NP
E 51	Dibutyltin (cation)	1002-53-5	0.09	0.09	233	0.57	2.90	0.09	n.a.	n.a.	NP
E 52	Dichloroanilines	027134-27-6			162	2.37	3.10	Nd	n.a.	n.a.	N
E 53	1,2-Dichlorobenzene	95-50-1			147	3.28	2.58	Nd	n.a.	n.a.	NP
E 54	1,3-Dichlorobenzene	541-73-1			147	3.28	2.57	Nd	n.a.	n.a.	NP
E 55	1,4-Dichlorobenzene	106-46-7			147	3.28	2.57	Nd	n.a.	n.a.	NP
E 56	Dichlorobenzidine	91-94-1	5.2E-06	5.2E-06	253	3.21	3.50	0.000005	n.a.	n.a.	NP
E 57	Dichlorodiisopropylether	108-60-1			171	2.39	1.92	Nd	n.a.	n.a.	N
E 58	1,1-Dichloroethane	75-34-3			99	1.76	1.50	Nd	n.a.	n.a.	N
E 60	1.1-Dichloroethylene (vinylidene chloride)	75-35-4	9	0.9	97	2.12	1.50	0.9	n.a.	n.a.	N
E 61	1,2-Dichloroethylene	540-59-0	6.8	0.68	97	1.98	1.60	0.7	n.a.	n.a.	N
E 63	Dichloronitrobenzenes (2,3-)	027900-75-0			192	3.10	2.80	Nd	n.a.	n.a.	NP
E 64	2,4-Dichlorophenol	120-83-2	0.54	0.16	163	2.80	2.69	0.16	n.a.	n.a.	N
E 65	1,2-Dichloropropane	78-87-5	280	28	113	2.25	1.78	28	n.a.	n.a.	N
E 66	1,3-Dichloropropane-2-ol	96-23-1			129	0.78	0.75	Nd	n.a.	n.a.	N
E 67	1,3-Dichloropropene	542-75-6	0.18	0.018	111	2.29	1.86	0.018	n.a.	n.a.	N
E 68	2,3-Dichloropropene	78-88-6			111	2.42	1.78	Nd	n.a.	n.a.	N
E 69	Dichloroprop-P	15165-67-0	1	0.13	235	3.03	1.69	0.13	n.a.	n.a.	N
E 70	Dichlorvos	62-73-7	0.0006	0.00006	221	0.60	1.73	0.00006	n.a.	n.a.	N
E 72	Diethylamine	109-89-7			73	0.81	1.43	Nd	n.a.	n.a.	N
E 73	Dimethoate	60-51-5	0.07	0.07	229	0.28	1.11	0.07	n.a.	n.a.	N
E 74	Dimethylamine	124-40-3			45	-0.17	0.91	Nd	n.a.	n.a.	N
E 75	Disulphoton	298-04-4			274	3.86	2.92	Nd	0.000007	7	P
E 78	Epichlorohydrin	106-89-8	0.65	0.065	93	0.63	1.00	0.06	n.a.	n.a.	N
E 79	Ethylbenzene	100-41-4			106	3.03	2.65	Nd	n.a.	n.a.	NP
E 80	Fenitrothion	122-14-5			277	3.30	3.08	Nd	n.a.	n.a.	NP
E 81	Fenthion	55-38-9			278	4.08	3.37	Nd	0.000005	12	P
E 82	Heptachlor	76-44-8			373	5.86	4.61	Nd	0.000003	880	P

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E -82	Heptachlor epoxide	1024-57-3			389	4.56	4.01	Nd	0.000003	71	P
E 86	Hexachloroethane	67-72-1	0.44	0.067	237	4.03	2.29	0.07	0.000005	10	P
E 87	Isopropylbenzene	98-82-8			120	3.45	2.84	Nd	0.00002	2	P
E 88	Linuron	330-55-2			249	2.91	2.53	Nd	n.a.	n.a.	NP
E 89	Malathion	121-75-5			330	2.29	1.50	Nd	n.a.	n.a.	N
E 90	MCPA	94-74-6	1.4	0.14	201	2.52	1.47	0.14	n.a.	n.a.	N
E 91	Mecoprop-p	93-65-2	18	1.8	215	2.94	1.69	1.8	n.a.	n.a.	N
E 93	Methamidophos	10265-92-6			141	-0,93	0.73	Nd	n.a.	n.a.	N
E 94	Mevinphos	26718-65-0	0.00017	0.000017	224	-0.24	1.19	0.000017	n.a.	n.a.	N
E 95	Monolinuron	1746-81-2	0.15	n.a.	215	2.26	2.32	0.15	n.a.	n.a.	N
E 97	Omethoate	1113-02-6			213	-1.49	1.00	Nd	n.a.	n.a.	N
E 98	Oxydemeton-methyl	301-12-2			246	-1.03	1.09	Nd	n.a.	n.a.	N
99E-06	Benz(a)anthracene	56-55-3			228	5.52	5.25	Nd	0.000002	180	Am
E 99.02	Phenanthrene	85-01-8			178	4.35	4.22	Nd	0.000005	10	Am
E 99.03	Chrysene	218-01-9			228	5.52	5.26	Nd	0.000002	139	Am
E 100	Parathion	56-38-2			291	3.73	3.38	Nd	0.000009	5	P
100E-06	Parathion-methyl	298-00-0			263	2.75	2.86	Nd	0.00009	0.5	P
E 101	PCB (and PCT)								n.a.	n.a.	
E 101.01	PCB-101	37680-73-2			326	6.98	5.11	Nd	0.000002	2100	Am
E 101.02	PCB-118	31508-00-6			326	6.98	5.11	Nd	0.000002	2600	Am
E 101.03	PCB-138	35065-28-2			361	7.62	5.33	Nd	0.000003	6900	Am
E 101.04	PCB-153	35065-27-1			361	7.62	5.32	Nd	0.000003	5500	Am
E 101.05	PCB-180	35065-29-3			395	8.27	5.54	Nd	0.000003	11400	Am
E 101.06	PCB-28	7012-37-5			258	5.69	4.68	Nd	0.000002	290	Am
E 101.07	PCB-52	35693-99-3			292	6.34		Nd	0.000002	620	Am
E 103	Phoxim	14816-18-3			298	4.39	3.54	Nd	0.000004	24	P
E 104	Propanil	709-98-8			218	2.88	2.60	Nd	n.a.	n.a.	NP
E 105	Pyrazon (Chloridazon)	1698-60-8	27	-	222	0.76	2.59	27	n.a.	n.a.	N
E 107	2,4,5-T (and salts and esters of 2,4,5-T)	93-76-5			255	3.26	2.03	Nd	n.a.	n.a.	NP

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E 108	Tetrabutyltin	1461-25-2			347	9.37	4.90	Nd	0.000003	2500000	P
E 109	1,2,4,5-Tetrachlorobenzene	95-94-3			216	4.57	3.35	Nd	0.000005	11	P
E 110	1,1,2,2-Tetrachloroethane	79-34-5	8	0.8	166	2.19	1.98	0.8	n.a.	n.a.	N
E 112	Toluene	108-88-3	74	7.4	92	2.54	2.37	7	n.a.	n.a.	N
E 113	Triazophos	24017-47-8	0.001	0.0001	313	2.92	3.27	0.0001	n.a.	n.a.	NP
E 114	Tributylphosphate	126-73-8			266	3.82	3.37	Nd	0.000003	75	A
E 116	Trichlorofon	52-68-6			257	-0.28	1.00	Nd	n.a.	n.a.	
E 119	1,1,1-Trichloroethane	71-55-6	21	2.1	133	2.68	1.64	2	n.a.	n.a.	N
E 120	1,1,2-Trichloroethane	79-00-5	22	2.2	133	2.01	1.78	2	n.a.	n.a.	N
E 122	2,4,5 trichlorophenol	95-95-4	0.13	0.13	197	3.45	3.25	0.13	n.a.	n.a.	NP
E 122	2,4,6-trichlorophenol	88-06-2	0.26	0.26	197	3.45	3.25	0.3	n.a.	n.a.	NP
E 123	1,1,2-Trichlorotrifluorethane	76-13-1			187	3.09	2.29	Nd	n.a.	n.a.	N
E 125	Triphenyltin acetate	900-95-8			409	1.12	4.85	Nd	0.004	0.015	P
E 126	Triphenyltin chloride	639-58-7			385	3.93	5.72	Nd	0.000007	10	P
E 127	Triphenyltin hydroxide	76-87-9			367	3.47	5.72	Nd	0.00002	3	P
E 128	Vinyl chloride (chloroethylene)	75-01-4	0.09	0.09	63	1.62	1.34	0.09	n.a.	n.a.	N
E 129	m-xylene	108-38-3	2.44	0.24	106	3.09	2.57	0.2	n.a.	n.a.	NP
E 130	o-xylene	95-47-6			106	3.09	2.58	Nd	n.a.	n.a.	NP
E 131	p-xylene	106-42-3			106	3.09	2.57	Nd	n.a.	n.a.	NP
E 132	Bentazone	25057-89-0	73	7.3	240	1.67	1.00	7	n.a.	n.a.	N
E 133	Titanium	7440-32-6							n.a.	n.a.	N
E 134	Borium	7440-42-8							n.a.	n.a.	N
E 135	Uranium	7440-61-1							n.a.	n.a.	N
E 136	Tellurium	13494-80-9							n.a.	n.a.	N
E 137	Silver	7440-22-4							n.a.	n.a.	N
E 138	Octamethyltetrasiloxane	556-67-2			297	5.09	4.16	Nd	0.000003	122	P
E 139	Abamectine	71751-41-2	0.001	E 3.5	266	3.66	3.54	0.000003	0.000011	4	P
E 140	Ammonium-N	14798-03-9	0.30411	n.a.					n.a.	n.a.	N
E 141	Antimony	7440-36-0							n.a.	n.a.	N
E 142	Barium	7440-39-3	9.3	n.a.					n.a.	n.a.	N

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E 143	Beryllium	7440-41-7	0.0092	n.a.					n.a.	n.a.	N
E 144	Captan	133-06-2	0.34	n.a.	301	2.74	2.40	0.3	n.a.	n.a.	N
E 145	Carbendazim	10605-21-7	0.6	n.a.	191	1.55	2.58	0.6	n.a.	n.a.	N
E 146	Chloroprofam	101-21-3			214	3.30	2.55	Nd	n.a.	n.a.	NP
E 147	Chlorotoluron	15545-48-9	0.4	0.04	213	2.58	2.04	0.04	n.a.	n.a.	N
E 148	Chromium	7440-47-3	3.4	0.6					n.a.	n.a.	N
E 149	Deltamethrin	52918-63-5	3.1E-06	n.a.	505	6.18	4.90	0.000003	0.000003	1900	P
E 150	Diazinon	333-41-5			304	3.86	3.48	Nd	0.000007	7	P
E 151	Dimethanamid-P	87674-68-8	0.13	n.a.	276	2.57	2.00	0.13	n.a.	n.a.	N
E 152	Dithianon	3347-22-6	0.097	n.a.	296	2.98	3.35	0.1	n.a.	n.a.	N
E 153	Dodine	2439-10-3	0.44	n.a.	287	1.32	3.40	0.4	n.a.	n.a.	N
E 154	Esfenvalerate	66230-04-4	0.0001	n.a.	420	6.76	5.50	0.00005	0.000003	6700	P
E 155	Fenamiphos	22224-92-6	0.012	n.a.	303	3.29	2.60	0.012	n.a.	n.a.	NP
E 156	Fenoxycarb	72490-01-8	0.0003	n.a.	301	4.24	3.69	0.0003	0.000004	17	P
E 157	Fluorides	16984-48-8							n.a.	n.a.	N
E 158	Heptenophos	23560-59-0	0.002	0.0002	251	1.41	2.81	0.0002	n.a.	n.a.	N
E 159	Imidacloprid	138261-41-3	0.067	0.0036	256	0.56	2.99	0.004	n.a.	n.a.	N
E 160	Lambda-cyhalothrin	91465-08-6	0.00002	n.a.	450	6.85	5.53	0.00001	0.000003	8600	P
E 161	Metsulphuron methyl	74223-64-6	0.01	n.a.	381	2.00	1.97	0.01	n.a.	n.a.	N
E 162	Cobalt	7440-48-4	0.089	n.a.					n.a.	n.a.	N
E 163	Copper	7440-50-8							n.a.	n.a.	N
E 164	Metazachlor	67129-08-2			278	2.38	3.00	Nd	n.a.	n.a.	N
E 165	Methabenzthiazuron	18691-97-9			221	2.65	2.93	Nd	n.a.	n.a.	N
E 166	Metolachlor	51218-45-2			284	3.24	2.69	Nd	n.a.	n.a.	NP
E 167	Molybdenum	7439-98-7	7.2	n.a.					n.a.	n.a.	N
E 168	Pirimicarb	23103-98-2			238	1.40	1.75	Nd	n.a.	n.a.	N
E 169	Pirimiphos-methyl	29232-93-7	0.0005	n.a.	305	3.44	2.57	0.0005	0.00002	3	P
E 170	Propoxur	114-26-1			209	1.90	1.78	Nd	n.a.	n.a.	N
E 171	Pyridaben	96489-71-3	0.0017	0.00094	365	5.47	5.09	0.0007	0.000003	320	P
E 172	Pyriproxyfen	95737-68-1	0.00003	n.a.	321	5.55	5.08	0.00002	0.000003	370	P

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E 173	Selenium	7782-49-2	0.052	n.a.					n.a.	n.a.	N
E 174	Styrene	100-42-5			104	*2.89*	*2.65*	Nd	n.a.	n.a.	N
E 175	Terbutylazine	5915-41-3			230	3.27	2.50	Nd	0.00003	2	P
E 176	Thallium	7440-28-0	0.013	n.a.					n.a.	n.a.	N
E 177	Tin	7440-31-5	0.6	n.a.					n.a.	n.a.	N
E 178	Tolclofos-methyl	57018-04-9	1.2	n.a.	301	4.77	3.31	1.2	0.000003	59	P
E 179	Teflubenzuron	83121-18-0	0.0012	n.a.	381	4.64	3.32	0.0012	0.000003	49	P
E 180	Vanadium	7440-62-2							n.a.	n.a.	N
E 181	Zinc	7440-66-6	7.8	3					n.a.	n.a.	N
These compounds are on the list of possible future priority substances											
Possible future priority substances											
O1	Methyl 5-(2.4-dichlorophenoxy)-2-nitrobenzoate (Bifenox)	42576-02-3			342	4.15	3.57	Nd	0.000005	15	P
O2	Cybutryne (Irgarol®)	28159-98-0			253	4.07	2.40	Nd	0.000005	11	P
O3	Cypermethrin	52315-07-8			416	6.38	4.90	Nd	0.000003	2800	P
O4	Dichlorvos	62-73-7			221	0.60	1.73	Nd	n.a.	n.a.	N
O5	Dioxin (2,3,7,8 - Tetrachlorodibenzo-p dioxin, TCDD)	1746-01-6			322	6.92	5.40	Nd	0.000002	8600	P
O6	Perfluorooctane sulphonic acid (PFOS)	1763-23-1			500	6.28	4.86	Nd	n.a.	n.a.	NP
O7	perfluorooctane sulphonyl fluoride	307-35-7			502	9.62	5.56	Nd	0.000003	5300000	P
O8	1,2,5,6,9,10-Hexabromocyclododecane (HBCDD)	3194-55-6			642	7.74	4.99	Nd	0.000003	79000	P
O9	1,3,5,7,9,11-Hexabromocyclododecane (HBCDD)	25637-99-4			642	7.74	4.96	Nd	0.000003	79000	P

1	2	3	4	5	6	7	8	9	10	11	12
No	**Name**	**CAS no**	**EQS-inland waters** ($\mu g.l^{-1}$)	**EQS-other waters** ($\mu g.l^{-1}$)	**MW** ($g.mol^{-1}$)	**LogK_{ow}**	**LogK_{oc}**	**EQS-Cw** ($\mu g.l^{-1}$)	**DL of PS** ($\mu g.l^{-1}$)	**T_{LIN}** (d)	**Applicability**
O10	Quinoxyfen	124495-18-7			308	5.69	4.94	Nd	0.000002	500	P
O11	Dicofol	115-32-2			370	5.81	4.10	Nd	0.000003	710	P
O12	Cyanides – free (HCN and CN-)	1957-12-05							n.a.	n.a.	N
O13	Diclofenac	15307-86-5			296	4.02	2.66	Nd	0.000006	10	P
O14	Ibuprofen	15687-27-1			206	3.79	2.63	Nd	0.000008	5	P
O15	17alpha-ethinylestradiol	57-63-6			296	4.12	4.65	Nd	0.000005	13	P
O16	17 beta-estradiol	50-28-2			272	3.94	4.19	Nd	0.000006	8	P