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The use of field studies to establish the performance of a range of tools for monitoring water quality

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The aim of the Water Framework Directive (WFD) of the European Union (EU) to achieve good quality status for all European waters is ambitious and will succeed only if decisions concerning remedial action are based on sound information. Current regulatory practice based on spot samples of water and comparisons of measured levels of priority pollutants with environmental quality standards will not provide data of the required reliability.

Application of alternative methods (emerging methods) that can provide more representative data than infrequent spot samples can overcome some of the drawbacks of spot sampling linked with classical chemical analysis.

Some emerging methods replace the analytical step but still depend on bottle sampling; others can be used on-site or in situ. Another class, including passive samplers, provides more representative sampling. A further set of emerging tools is based on biological systems and provides information concerning water quality that is different from that provided by chemical analysis.

In order for these methods to be useful within the context of the WFD, they must provide cost-effective, reliable, representative information. The potential of a range of candidate methods has been investigated in field trials within the SWIFT-WFD EU Project (No. SSPI-CT-2003-502492). This article uses case studies to illustrate potential applications of some types of emerging monitoring tools, and indicates where research and development are needed to enable their adoption within the context of the WFD.

Keywords: Bioassay; Emerging tool; Field trial; Immunoassay; Passive sampler; Water monitoring; Water Framework Directive

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1. Introduction

The Water Framework Directive (WFD) of the European Union (EU) includes a wide range of measures aimed at achieving good quality status in all waters (surface waters and groundwaters).

Where waters meet this standard, then only surveillance monitoring is necessary, and this could readily be achieved using infrequent spot (bottle) samples analyzed by classical laboratory methods. However, where a water body is failing to achieve the necessary quality due to identified causes or where there are recognized pressures, then operational monitoring will be necessary.

Where the system is complex (e.g., tidal waters) or is subject to temporal fluctuations in levels of pollutants (e.g., due to seasonal use of pesticides or to weather patterns), then infrequent spot samples are

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unlikely to provide a representative picture of water quality.

Similar considerations apply where there are marked spatial variations in levels of pollutants due to the distribution of point or diffuse sources.

Under these circumstances, it will be necessary to have monitoring campaigns employing either frequent and/or widespread spot sampling, or alternative methods that can provide the equivalent information. Where operational monitoring is applied, the cost will be high because of the labor and transport costs involved in sampling, and the need for a large number of analyses. Some alternative methods may be able to deliver the necessary information at lower cost and or more quickly.

If a water system is failing to meet quality standards and the cause is not known, then investigative monitoring will be necessary. In this case, many of the “emerging” methods could provide the necessary information in a cost-effective manner. The thrust of the EU-funded SWIFT-WFD project was to identify available monitoring tools, evaluate their performance in the field, investigate quality-assurance issues, assess their potential for underpinning the monitoring requirements of the WFD, and research their potential socio-economic impact. This project aims to provide tools from which regulators and end users can select the most appropriate and cost effective to meet specific monitoring needs.

It is unlikely that all of the aims of the WFD will be achieved if regulators focus entirely on comparing concentrations of priority pollutants in infrequent spot samples with Environmental Quality Standards (EQSs). There is a need to consider what information will be necessary in order to measure progress towards achieving good water quality, and how the data can be obtained in a cost-effective way. The emerging methods provide information that may be similar to, or remarkably different from, that derived from the analysis of spot samples by classical analytical methods.

Some of the methods replace only the analytical stage and still depend on spot sampling. However, some can be less expensive, more rapid or portable, and can be used in the field (e.g., on a river bank or a survey boat). These methods include immunoassays, test kits, hand-held sensors, and some spectrophotometric methods. Some of these can be used in situ (e.g., by dipping a screen-printed electrode of a sensor directly into the water body under investigation, thus avoiding the sampling step).

A second set of emerging methods addresses the need for representative sampling and includes biomonitoring (the use accumulation by living organisms, usually bivalve mollusks) and passive sampling to provide time-weighted average (TWA) estimates of concentrations of pollutants to which the organisms or samplers were exposed. These sampling methods are linked to classical laboratory analytical methods.

A further set of methods provides completely different information on water quality: these are based on toxicological assessments, and they include direct toxicity assays (usually laboratory based and depending on spot samples of water) and biomarkers (ranging from changes at cellular levels to changes in behavior of whole organisms). Some biological monitoring systems can be used on-line or in situ, and they include biological early warning systems (BEWSs) (e.g., the mussel monitor, the *Daphnia* Toximeter, and the algal monitor [1]) that are deployed to provide warnings of changes in water quality in order to safeguard sensitive sites, such as drinking-water-intake points. The various methods provide data with a wide range of associated uncertainties, and, for some of them, the uncertainties are poorly defined.

There is a need to establish the performance criteria for the various emerging methods, to define the uncertainties associated with the data they yield, and to interpret the information that they provide within the context of the WFD. The SWIFT-WFD project addressed these areas for a range of emerging methods representing the categories identified in the previous paragraph. This article aims to provide some illustrative examples of how the information needed by regulators to allow them to assess the utility of the various emerging methods can be obtained in field trials. In order to provide a baseline against which the emerging methods can be compared, they were usually deployed alongside current regulatory methods. We have used the SWIFT-WFD trials to identify areas where further research and development work is necessary.

2. Case studies

2.1. Monitoring metals with passive sampling devices

The Aller river system is located in the Basin of the River Weser that is situated in central northern Germany, and is one of 10 German river-basin districts. Water management and monitoring in the Aller river system are the responsibility of the State Office for Water Management, Coast and Nature Protection (Niedersächsischer Landesbetrieb für Wasserwirtschaft, Küsten und Naturschutz, NLWKN). The frequency of measurements differs for the different groups of parameters, and ranges from monthly or every two months for chemical measurements in surface waters to every two to three years for organic pollutants in sediments. At a few key monitoring sites, automated on-line systems take continuous measurements of general water-quality parameters. NLWKN has substantial amounts of historical monitoring data based on the monitoring programmes described above and from the automated systems that deliver continuous information.

There are several considerable pressures on surface waters in this river system and these include both point

and diffuse sources. Municipal sewage plants, direct industrial discharges, rainwater run-off combined with wastewaters have been identified as significant point sources posing risk to water status in the Aller river system. Historical data indicate that contamination with metals can be expected in the Aller and Oker rivers, but generally at only low concentrations. Although metals are present at relatively low levels (within the average range, less than 1 µg/L) for European rivers, in the Aller river system, they are found in high concentrations upstream in the upper Oker. Higher levels of metals are found in sediments in the Oker than in those of the Aller, and there is the potential for these to be redistributed to the water column to produce sporadic high concentrations during high-flow events. This can lead to marked temporal variations in concentrations of metals in this river system.

Where there are fluctuations in concentrations of pollutants, such as those found in this river system, infrequent (monthly) spot samples may not provide a representative picture of overall water quality. In these circumstances, passive samplers offer an alternative tool that can provide (TWA) concentrations over deployment periods of weeks. Chemcatcher passive samplers fitted with an Empore chelating disk receiving phase and a cellulose acetate membrane as the diffusion-limiting membrane accumulate freely dissolved fractions of metals [2,3]. The standard Diffusion Gradient in Thin Films (DGT) sampler with an open pore (OP) gel (pore size >5 nm) [4–6] allows the diffusion of free ions and small inorganic complexes, and, in addition, those metal-organic complexes that dissociate during transit across the diffusion layer [7,8].

If used in long-term monitoring programmes, these samplers could give measures of background concentrations of metals in the Aller and the Oker, whilst incorporating any sporadic high concentrations into the

overall measure of metal contamination. This trial was designed to assess their utility in this role. DGTs and Chemcatchers were deployed over a period of 2 weeks to estimate the TWA concentrations of these metal pollutants at different selected locations. Some 18 DGTs were deployed at five sites (Börssum and Seershausen on the Oker, and Grafhorst, Brennecken Brück and Langlingen on the Aller, from up to downstream respectively), and there were 9 Chemcatchers at two sites (Langlingen and Borssum, from upstream and downstream, respectively). Triplicate spot samples were collected at the five sites at deployment and retrieval times of the samplers, and transported to the laboratory for analysis by inductively coupled plasma-mass spectrometry (ICP-MS). Filtration of the water samples (0.45 µm) was performed on site, and samples were acidified with nitric acid immediately after preparation to stabilize metal concentrations.

The concentrations of Cu, Pd and Zn tend to fall as the river flows from the Oker to the Aller. The concentration of Ni shows no such trend, and is higher in the Aller than the Oker (Tables 1 and 2). However, with the exception of Zn, all metals fell below the EQSs during the period of this trial. The relative concentrations found in the filtered and unfiltered spot samples give a measure of the proportion of bound to suspended particulate material (e.g., some 40% of the measured copper was removed by filtration). For Cu, the proportion of bound to particulates is reasonably constant from site to site. However, these data give no indication of the relative proportions that are either freely dissolved, or bound to colloidal organic components. The TWA concentrations measured using the Chemcatcher and DGT samplers represent the freely dissolved (bioavailable) metal [9–11], and the metal bound to the colloidal organic materials that can pass through the diffusion limiting

Table 1. Concentrations (µg/L) of metals measured by inductively-coupled plasma-mass spectrometry (ICP-MS) in spot samples of water from the Aller river system

Sampling site		Ni		Cu		Zn		Cd		Pb	
		U	F	U	F	U	F	U	F	U	F
Börssum	D	2.7	2.5	4.4	2.4	238	197	1.9	1.4	13.4	1.3
	R	2.3		3.7	2.3	213	181	1.5	1.1	5.5	1.5
Seershausen	D	2.4	2.3	1.9	1.0	80	62	0.7	0.3	2.7	0.4
	R	2.5	2.7	2.0	1.2	75	60	0.7	0.4	2.3	0.6
Grafhorst	D	4.4	3.8	0.7	0.4	4.1	3.1	<0.1	<0.1	3.1	0.2
	R	4.5	4.1	0.6	0.3	3.5	1.8	<0.1	<0.1	1.1	0.4
Brennecken Brück	D	3.2		1.2	0.6	7.8	5.1	<0.1	<0.1	0.7	0.3
	R	3.4	3.2	1.1	0.7	8.3	5.5	<0.1	<0.1	0.8	0.4
Langlinden	D	2.6		1.2	0.8	29	20	0.2	0.1	1.9	0.3
	R	3.1	3.1	1.3	0.9	36	27	0.3	0.2	0.9	0.1

D, Deployment day; R, Retrieval day; U, Unfiltered water sample; F, Filtered (0.45µm) water sample.

Table 2. Time-weighted average (TWA) concentration (mean and (standard deviation)) of metals measured by DGT and Chemcatcher passive samplers

Sampling site	TWA concentration ($\mu\text{g/L}$)				
	Ni	Cu	Zn	Cd	Pb
DGT					
Börssum	0.86 (0.13)	0.73 (0.07)	87.9 (12.28)	0.49 (0.08)	0.09 (0.03)
Seershausen	0.66 (0.13)	0.34 (0.04)	28.19 (2.73)	0.15 (0.02)	0.01 (0)
Grafhorst	1.63 (0.26)	0.1 (0.01)	1.47 (0.07)	0.01 (0)	0.01 (0)
Brennecken Brück	0.96 (0.05)	0.13 (0)	2.73 (0.08)	0.01 (0.01)	0 (0)
Langlinden	0.91 (0.1)	0.22 (0.02)	16.95 (0.26)	0.08 (0.01)	0.04 (0.05)
Chemcatcher					
Börssum	1.49 (0.12)	0.30 (0.14)	132.2 (3.9)	0.70 (0.02)	3.46 (2.52)
Langlinden	1.21 (0.18)	0.00 (0.12)	12.6 (4.0)	0.06 (0.02)	0.13 (0.13)

The sites on the Oker and Aller rivers appear in order from upstream to downstream.

layer and dissociate during the transit time [12–14]. The combination of these data and those obtained from spot samples can give an indication of the speciation, providing that sufficiently frequent spot samples are taken to provide a representative measure of the filtered and unfiltered TWA concentrations.

With the exception of Pb, for which Chemcatcher calibrations are associated with high uncertainties, there is a consistency between the TWA data for the two designs of passive sampler. It is difficult to compare classical spot sampling and passive sampling directly, because the two measure the concentrations of different fractions of metals. Further, unless frequent spot samples are taken to obtain a representative measure of TWA concentration over the deployment period, the estimates based on this method will have a large uncertainty associated with them, particularly where there is temporal variation in concentrations. This would be particularly marked where the river water is mixed locally with inputs from streams (that may be more or less polluted) and there is significant leaching from soils.

Although this trial was limited in time, it provides an example of the utility of passive samplers in providing robust maps of concentrations of pollutants where there is marked spatial variation. It also provides an indication of the potential of this method for providing

representative measures of pollutant levels in a river environment.

Passive sampling devices show potential for monitoring long-term changes in contaminant concentrations, as their use may help to reduce the error associated with environmental variability when compared with bottle sampling undertaken on a monthly basis.

In addition, it is possible to obtain information on speciation of metals, and this is pertinent to their bio-availability and potential toxicity.

However, in order for passive sampling to be useful in compliance applications, it would be necessary to reformulate EQSs in terms of concentrations of freely dissolved metals.

2.2. Mapping nitrate and atrazine in a river basin

The regulatory authorities in the River Hardt catchment area in France have had problems with contaminated groundwater for some years. The city of Mulhouse stopped using wells for drinking water in the Hardt catchment area because nitrates and pesticides were found in high concentrations, and, in some cases, exceeded EQSs. The hydrology of the catchment area is such that surface waters infiltrate groundwater through a series of gravel pits, and these may be an important route for the entry of pesticides used to protect corn in this region.

Remedial actions are currently planned to improve the quality of the groundwater in order to restore the use of wells in the region. However, the sources of the pesticides have not yet been fully identified, and the relative importance of potential inputs into groundwater is not known. Knowledge of the spatial variability of nitrate and atrazine in surface waters is necessary in order to select representative sampling sites.

The aim of this trial was to investigate the potential utility of a number of emerging methods for mapping levels of pollution across a large area to identify gradients, and optimize the design of monitoring networks. A set of portable instruments was evaluated. Nitrate was estimated using the PASTEL UV, YSI probe, and Merck test kits, and atrazine was determined in spot samples by immunoassays [15]. Some 36 sites, including Weiherbachgraben and Sauruntz surface waters, were selected within the Hardt catchment area, and total nitrate and atrazine concentrations were determined at each site. These sampling sites were selected on the basis of historical data describing nitrate and atrazine concentrations. In order to provide a measure of the performance of the emerging methods, spot samples were also collected for laboratory analysis (high-performance ion chromatography (HPIC) and high-performance liquid chromatography (HPLC)).

The PASTEL UV, YSI probe, and Merck test kits were used to measure nitrate directly in the field, and the samples used were then shipped to the laboratory for

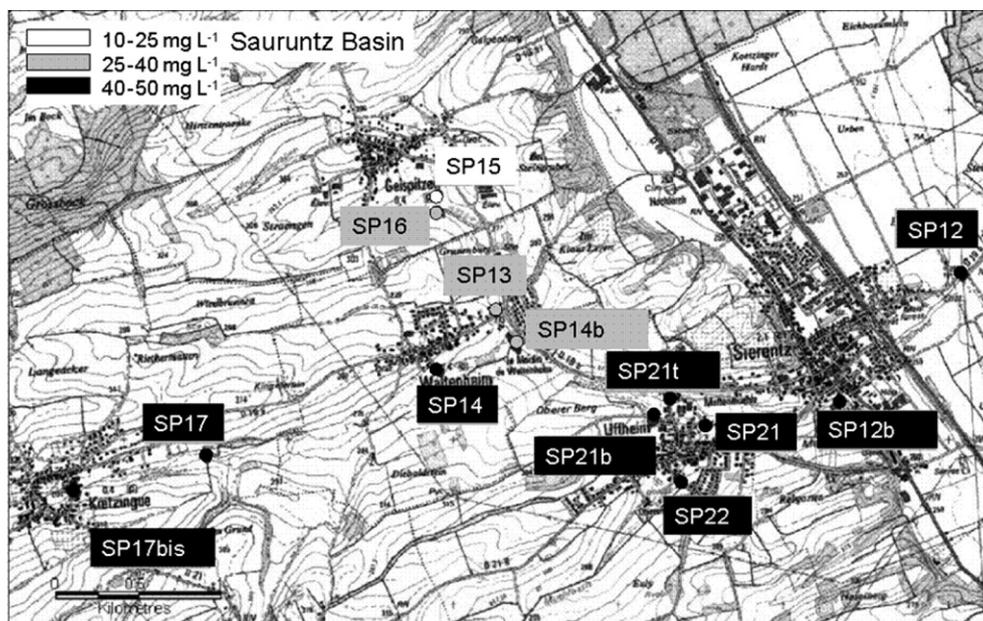


Figure 1. Nitrates measured by Pastel UV in Hardt (Alsace, France).

analysis by classical methods. The field data obtained by the first two methods were consistent with each other and with the standard laboratory-based analyses ($y = 0.95x + 1.97$, $R^2 = 0.85$, and $y = 0.97x + 1.39$, $R^2 = 0.78$, respectively) over the range of concentration of 3–15 mg/L. However, for the YSI probe, the data were not well correlated with those from the standard laboratory analyses over a range of concentration of 5–14 mg/L. This result may have been due to interferences caused by organic matter in the water. This illustrates the importance of assessing a wide range of matrix effects during validation studies for in situ methods, since, in the field, there is no control over the composition of the test medium.

On the basis of these preliminary field data, Pastel UV was selected for use in mapping nitrate contamination in the Hardt catchment area. The results demonstrated that most of nitrate concentrations in surface waters in the Weiherbachgraben and Sauruntz sub-basins were higher than 40 mg/L (Table 3).

This rapid (1 min/measurement) evaluation facilitated the mapping and the classification of the contaminated sites (30 sites in 1 to 2 days) (e.g., Fig. 1 shows the mapping carried out in the Sauruntz basin). This evaluation provides information that can make subsequent

investigative monitoring campaigns more efficient by indicating the location of representative sites. In this case, the emerging method showed that nitrate concentrations were above the quality standard defined by the EU Drinking Water Directive 98/83/CE [16].

Laboratory-based experiments indicated a good agreement ($y = 1.01x + 0.03$, $R^2 = 0.95$) between the results of the immunoassay and those from standard LC linked with a UV detector over the range 0.1–0.25 µg/L. The immunoassay kit was then used to map atrazine contamination in the Hardt catchment area. Atrazine concentrations were found to be below 0.1 µg/L in most of the tested surface waters in the Weiherbachgraben sub-basin, whereas, in the Sauruntz sub-basin (Fig. 2), most concentrations found were above 0.2 µg/L.

Table 4 presents a classification of sites according to concentration of atrazine, and shows that, at most sites, the concentrations exceeded the quality standard defined by the EU Drinking Water Directive [16].

These results indicate the potential for rapid, field-based measurements to provide cost-effective information on the distribution of contaminants across a wide geographical area. Emerging methods that can be used in the field (on-site or in situ) have some advantages over methods that rely on transport of samples to a distant laboratory for analysis. They allow simplification of the chain of measurement, and eliminate some steps (preservation, transport and storage) during which modification of the sample can occur. PASTEL UV, for example, requires no pre-treatment, addition of reagents, or on-site calibration. The analysis can be completed within 1 min from the time the sample is taken, minimizing any

Table 3. Distribution of sampling sites in the Weiherbachgraben and Sauruntz sub-basins on the basis of nitrate levels					
Concentration (mg/L)	2–10	10–25	25–40	20–50	>50
Number of site (%)	0	11	19.5	44.5	25

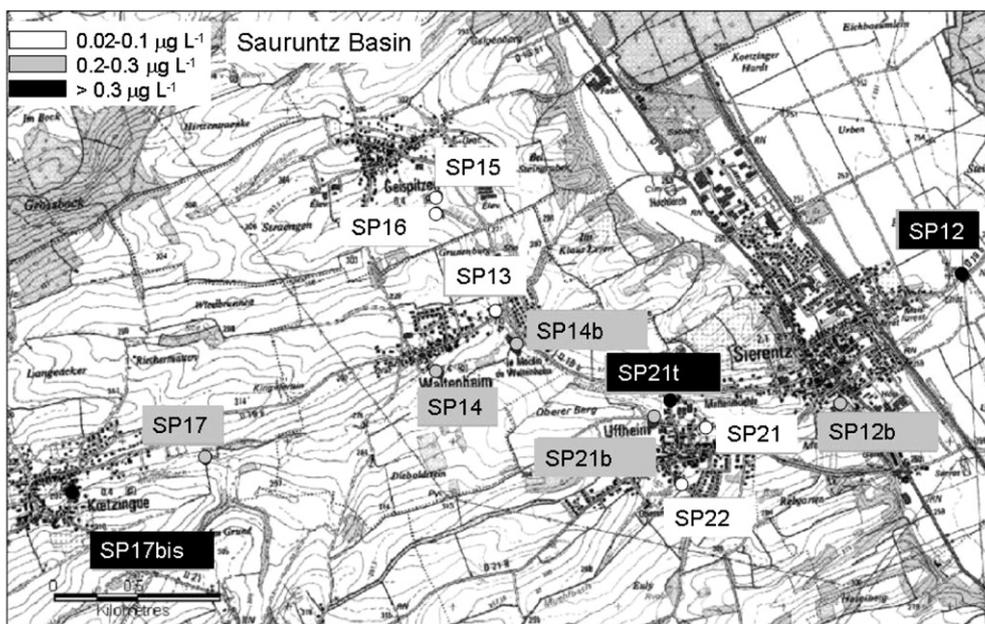


Figure 2. Atrazine measurements by immunoassays in Hardt (Alsace, France).

Table 4. Distribution of sampling sites in the Sauruntz sub-basin on the basis of atrazine levels

Concentration ($\mu\text{g/L}$)	0.02–0.1	0.1–0.2	0.2–0.3	>0.3
Number of site (%)	50	20.6	17.6	11.8

changes in the sample. The immunoassays for atrazine take 20 min to effect, so, with both of these methods that can be used in the field, many assays can be performed in one day. This enables replicate measurements at one site to increase confidence in the result, and representative sampling of a large area. This has potential use when tracking sources of pollution. In addition, these methods could, if fully validated, provide alternatives to current analytical procedures. The high specificity and sensitivity of immunoassays make them a useful complement to laboratory analysis. The rapidity with which mapping is obtained is advantageous in the selection of relevant sites in planning monitoring campaigns. However, for regulatory purposes, spot samples combined with classical laboratory analysis will continue to be necessary until the reliability of alternative methods has been established.

2.3. Monitoring toxicity in a tidal estuary

The Ribble Basin covers an area of 2024 km² in the north-west of England and includes the rivers Ribble, Hodder, Calder, Darwen, Douglas and Yarrow as well as the Crossens area in West Lancashire. The system drains via the Ribble estuary into the Irish Sea and is located on

the coast, between the towns of Lytham St. Anne's, Preston and Southport. The estuary is broadly funnel-shaped; near the mouth, it has a width of approximately 15 km, and its channel length is approximately 28 km. The estuary is subject to a macrotidal regime, with the tidal range decreasing landwards from the estuary mouth.

The Ribble Basin is a high-quality water environment. It is naturally beautiful and has good water quality throughout much of its waters, it provides an important source of drinking water for the region, and it is regarded as a valuable resource for industry, agriculture, fishing and recreation. However, in the tidal region, there are some identified pressures that pose a potential threat to water quality. These include agricultural run-off and sewage slurry, Preston docks (formerly a site of ship-building), sewage-works effluents, landfill run-off, and (depending on tides) the Lennox oil platform, just offshore from the estuary. The main EQS failures are associated with the industrial past of the region and have been mainly due to heavy metals (Cd, Cr, Fe, Pb, Cu, and Zn), and organometallic compounds (e.g., tributyltin. (TBT)). At present, monitoring is conducted monthly by the Environment Agency for England and Wales by collecting water samples, generally at one site in the estuary.

The estuary is a complex system, and it is difficult to monitor because of the diverse pressures, tidal flow, and fluctuations in the freshwater input depending on weather conditions. Pollutants can travel down the estuary as the tide falls, and return upstream as the tide rises. It would require a large number of spot samples to

map water quality in the estuary, and to obtain a representative picture over time. Methods that could be used to provide information on water quality rapidly and at relatively low cost could increase the efficiency of ongoing monitoring campaigns by focusing activity where there are identified problems.

In this case study, two commercially-available, laboratory-based toxicological assays (CheckLight Ltd) were used to monitor water quality at a range of sites down the estuary. ToxScreen is based on the inhibition of luminescence of *Photobacterium leiognathi* in the presence of toxic pollutants, and the Metal Detector on *Escherichia coli* that have been modified to express the luminescence system of *Vibrio fischeri*. Both assays use lyophilized bacteria and an appropriate buffer. For ToxScreen, two buffers are available, one (pro-organic) that enhances susceptibility to organic pollutants, and the other (pro-metal) that enhances susceptibility to heavy metals. If the two are used in parallel, they can discriminate between the presence of a wide range of organic and metallic toxicants at sub-mg/L concentrations. The assay uses reference samples of clean water. The test is carried out in cuvettes, and luminescence is measured directly using a luminometer after incubation (60 min at ambient temperature). This enables a large number of samples to be analyzed in a day, and the method could potentially be automated. In these assays, the result is expressed as the percentage of incubation medium made up by the original water sample that produces 50% inhibition of luminescence. Any result where the critical concentration of the original water sample is 50% or less of the total incubation medium is taken as an indication of noteworthy toxicity.

The aim was to investigate the utility of these assays in detecting poor water quality in order to focus classical sampling and analysis. Samples were taken at five points down the estuary between Preston and the estuary mouth. Site PL1 was just downstream of Preston Docks, and the others (PL2 to PL5) were roughly 2 km apart down the estuary. PL2 was just upstream of the landfill site, PL3 downstream of a large sewage works, PL4 just downstream of the input from the River Douglas, and PL5 near to Lytham St Anne's. Spot samples with the prefix PL were taken on the ebb tide, and those labeled LP were taken at the same points on the flood tide.

Significant toxicity was detected in samples LP1, LP2, LP3, PL4, PL3, PL5 using the ToxScreen test (with pro-organic buffer) (Table 5). The conclusion is that organic toxicants are present at these sites. No toxicity was detected with ToxScreen (pro-metal buffer). However, when samples were analyzed using the recombinant *E. coli* test (using Metal Detector) under conditions that favor the detection of heavy metals, the following samples exhibited significant activity: LP4, LP1, LP2, LP3, PL3, PL5. Hence, five samples (LP1, LP2, LP3, PL3, PL5) may contain both heavy metals and organic

Table 5. Distribution of toxicity (minimal concentration (% dilution) of water sample in which 50% light inhibition was detected) measured by ToxScreen and Metal Detector assays in spot samples of water collected in the estuary of the River Ribble

Sample ID	ToxScreen [Pro-organic buffer]	ToxScreen [Pro-metal buffer]	Metal Detector
PL1	80	NT	NT
PL2	65	NT	95
PL3	40*	NT	30*
PL4	35*	NT	80
PL5	35*	NT	30*
LP1	40*	NT	25*
LP2	20*	NT	10*
LP3	30*	NT	23*
LP4	65	NT	10*
LP5	70	NT	65

Sample identification (ID) as described in the text. NT = No toxicity detected; * = Significant toxicity detected.

toxicants; while, LP4 probably contains only heavy metals and PL4 only organic toxicants. It is noteworthy that no toxicity was detected in any of the samples using the standard Microtox test (based on inhibition of luminescence in the bacterium *Vibrio fischeri*).

These methods give information that is different from that obtained with passive sampling or chemical analytical methods. They provide semi-quantitative or qualitative data about the presence of one or more toxicants in the water, and can be used for screening to indicate where further investigation is necessary. The ToxScreen and Metal Detector assays are unusual in that they indicate whether the toxicants involved are metals or organic compounds, and this discrimination could reduce the costs of subsequent monitoring by limiting the number of samples to be taken, prepared and analyzed. The limitation to the utility of these bioassay systems is their sensitivity. Since there is such a large range of toxicants that might be present, it is possible that the bacteria might be tolerant to some that might harm organisms from different classes, and there is a possibility of false-negative results.

3. Conclusions

Some of the emerging tools (e.g., passive samplers, hand-held sensors, and field-test kits) can be used in monitoring programmes for a range of tasks, including mapping wide areas to identify where monitoring efforts should be concentrated. They can provide more representative measures of water quality through increased numbers of samples and frequency of sampling. This should give regulators more confidence in making decisions about frequency and spatial distribution of standard monitoring for compliance purposes, and about the

combination of water bodies for monitoring purposes. Since toxicological assays react to a wide range of toxicants and not only priority substances, they can provide information about the impacts of new (emerging) pollutants on water quality. There are potentially great advantages to be gained from deploying a number of tools simultaneously (e.g., the combination of passive samplers and bioassays as in toxic identification and evaluation) to obtain valuable data that would not be available from any one method.

The emerging tools used in the illustrative case studies described in this paper represent the three main areas where such methods might be applied in monitoring in support of the WFD. Passive samplers provide more representative measures of concentrations of pollutants than infrequent spot sampling (particularly where there are marked temporal fluctuations in the concentrations of pollutants), but they measure fractions different from those measured using laboratory analysis of spot samples (e.g., freely dissolved metals rather than total metals, including fractions bound to suspended solids).

For this technology to be adopted in the context of compliance monitoring, it will be necessary to rethink the definition of EQSs. On-site analytical methods that provide results in a short timescale (e.g., the PASTEL UV for measuring nitrate) reduce the opportunity for samples to be modified during handling, storage, transport and preparation for analysis; they also facilitate replicated measurements at one site and the sampling of many sites within a single day. This provides the potential for rapid, reliable mapping to facilitate remedial actions or measures to prevent the spread of contamination (e.g., after an accidental spillage). The toxicological assays exemplified in this article used bacteria as the test organism, and toxicity was measured as an inhibition of luminescence. These systems provide semi-quantitative or qualitative information and are designed to respond to wide range of chemical stressors. It is therefore impossible to link the data from these assays to individual quality elements, such as concentrations of priority substances. Their strength lies in their ability to provide information on the biological impact of substances in the water, even where these are not identified or are present in mixtures. They can therefore be used for screening purposes, but they are not suitable for checking compliance with EQSs for individual quality elements. The various emerging tools therefore exhibit a wide range of properties and can fulfill a number of roles within monitoring programmes, and there is a need to enable potential end users to make an educated selection of the most appropriate tool(s) for a particular job. This is one of the main aims of the SWIFT-WFD project.

Although the emerging methods could play a valuable role in monitoring used to support the WFD, it is important to understand their limitations as well as their strengths. Currently, few have standardized protocols for

their application, though standards are available for some toxicity tests (e.g., ISO 11348 for the Microtox assay, and BSI PAS61 for passive sampling). This is an area that must be addressed, if these methods are to become more widely accepted by the regulatory monitoring community. Work is also necessary to develop quality-assurance procedures for some of the emerging methods. The classical approach to this, as used in accrediting classical laboratory analytical procedures, is not universally applicable (e.g., in passive sampling where large volumes (hundreds of liters) of reference materials would be needed). This would be prohibitively expensive using available reference materials. A different approach is necessary, and this might involve the use of reference sites, or novel types of reference materials, such as pelletized reference compounds, that can be suspended to produce large volumes of homogeneous standard solutions. This would enable the use of proficiency-testing schemes to establish the uncertainties associated with these methods. It is only when this has been achieved that these methods will become acceptable in compliance monitoring. However, even without this, they have an important role to play, particularly in operational and investigative monitoring where some can provide information very quickly (e.g., in accidental spillages). Rapid, cost-effective mapping of an area is impossible where samples need to be transported to a distant laboratory for analysis. In addition, they have the potential to identify unknown causes or sources of pollutants where water quality has deteriorated due to an unknown cause. The cost effectiveness of some of the assay systems (e.g., immunoassays) could be further increased through automation in a way similar to that applied to achieve high-throughput screening in pharmaceutical and pesticide companies.

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References

- [1] K.J.M. Kramer, E.M. Foekema, in: F.M. Butterworth M.E. Gensebatt-Bonaparte, A. Gunatilaka (Editors), *Biomonitoring and biomarkers as indicators of environmental change: A handbook*, vol. II, Plenum, New York, 2000, pp. 59–87.
- [2] L.B. Persson, G.M. Morrison, J.U. Friemann, J. Kingston, G. Mills, R. Greenwood, *J. Environ. Monit.* 3 (2001) 639.

- [3] L.B. Blom, G.M. Morrison, J. Kingston, G.A. Mills, R. Greenwood, T.J.R. Pettersson, S. Rauch, *J. Environ. Monit.* 4 (2002) 258.
- [4] H. Zhang, W. Davison, B. Knight, S. McGrath, *Environ. Sci. Technol.* 32 (1998) 704.
- [5] W. Davison, H. Zhang, *Nature (London)* 367 (1994) 546.
- [6] H. Zhang, W. Davison, *Anal. Chem.* 67 (1995) 3391.
- [7] N.C. Munksgaard, D.L. Parry, *J. Environ. Monitor* 5 (2003) 145.
- [8] R.J.K. Dunn, P.R. Teasdale, J. Warnken, R.R. Schleich, *Environ. Sci. Technol* 37 (2003) 2794.
- [9] C.D. Luider, J. Crusius, R.C. Playle, P.J. Curtis, *Environ. Sci. Technol* 38 (2004) 2865.
- [10] M. Tusseau-Vuillemin, R. Gilbin, E. Bakkaus, J. Garric, *Environ. Toxicol. Chem* 23 (2004) 2154.
- [11] O. Royset, B.O. Rosseland, T. Kristensen, F. Kroglund, O.A. Garmo, E. Steinnes, *Environ. Sci. Technol* 39 (2005) 1167.
- [12] H. Ernstberger, H. Zhang, W. Davison, *Anal. Bioanal. Chem.* 373 (2002) 873.
- [13] E.R. Unsworth, H. Zhang, W. Davison, *Environ. Sci. Technol.* 39 (2005) 624.
- [14] H. Zhang, *Environ. Sci. Technol.* 38 (2004) 1421.
- [15] S.D. Comber, C.D. Watts, B. Young, *Analyst (Cambridge, U.K)* 121 (1996) 1485.
- [16] European Commission, *Off. J. Eur. Commun. L* 330 (1998) 32.