Water Quality Monitoring

A 'TOOLBOX IN RESPONSE TO THE EU'S WATER FRAMEWORK DIRECTIVE REQUIREMENTS

WATER/
Wastewater

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The Water Framework Directive

The Water Framework Directive (WFD, 2000/60/EC) is one of the most important pieces of environmental legislation produced in recent years and is likely to transform the way water quality monitoring is undertaken across all European Union's member states. The objectives of the WFD are to improve, protect and prevent further deterioration of quality for most types of water body across Europe. The Directive aims to achieve and ensure "good quality" status of all water bodies throughout Europe by 2015, and this is to be achieved by implementing management plans at the river basin level.

Monitoring is required to cover a number of 'water quality elements' including biological, chemical (inorganic and organic priority pollutants), hydro-morphological, and physico-chemical parameters. Three modes of monitoring regime are specified in the Directive and will form part of the management plans that must be introduced by December 2006. These include:

(i) *surveillance* monitoring aimed at assessing long-term water quality changes and providing baseline data on river basins allowing the design and implementation of other types of monitoring,
(ii) *operational* monitoring aimed at providing additional and essential data on water bodies at risk or failing environmental objectives of the WFD,
(iii) *investigative* monitoring aimed at assessing causes of such failure when they are unknown.

Monitoring Pollutants with Spot Sampling

Water quality monitoring generally relies on spot sampling (collection of a known volume of water in a bottle at a specific place) at prescribed periods of time followed by instrumental analysis with a view to quantify "total" concentrations of pollutants. This methodology is well established and validated and is accepted for regulatory and law enforcement purposes. However, this approach is valid only if one assumes that it provides a truly representative picture of the chemical quality of water at a particular sampling site. As this procedure only gives a snapshot of the situation at the time of sampling, it has considerable temporal and spatial limitations when assessing contaminant concentrations and for predictions of pollutant bioavailability. A number of factors such as the speciation of metals, pollutant sorption to suspended particles, dissolved organic matter or colloids have been shown to affect pollutant bioavailability. Furthermore continuously varying hydro-morphological and hydrological conditions and intermittent chemical releases associated with industrial/urban wastewater effluents, bed-sediment re-suspension and diffuse pollution lead to spacio-temporal variations in a water body's physico-chemical characteristics (Fig. 1).

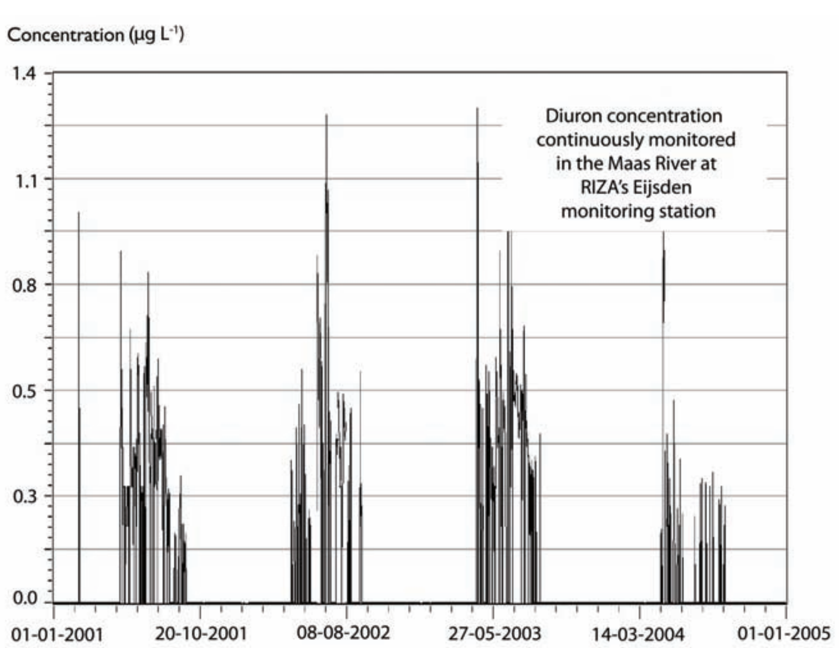

Fig. 1. Temporal variations in diuron concentration (µg L-1) continuously monitored in the Maas River water at RIZA's Eijsden (NL) monitoring station for the period 2001-2005.

A Directory of 'Emerging' Tools

Successful implementation of the WFD will require the development and use of alternative 'emerging' and low-cost monitoring methods. These methods may complement monitoring already in place by providing additional, more representative, information on the status of a water body. Each type of monitoring requires a set of fit-for-purpose 'tools' that can provide meaningful and reliable data. The choice of tools will depend on their deployment characteristics, cost, robustness, sensitivity, the type of measurand and the type of information required. The WFD does not mandate the use of a particular set of methods, but aims to ensure the establishment of adequate monitoring programmes based on the quality elements described above. Speciation and truly dissolved fractions will be crucial parameters in the WFD monitoring of metals. While polar organic compounds will be monitored in the water phase, for non-polar organics (log KOW>3) measurement of the fraction associated with suspended and bed-sediments will also be necessary.

In addition, since many large river basins encompass a number of countries, it is important to ensure that data collected by the different EU member states are comparable and of an appropriate quality.

This article is based on a directory of 'emerging tools' recently compiled for the European Union's 6th Framework Project, Screening Methods for Water Data Information in Support of the Implementation of the Water Framework Directive (SWIFT-WFD; www.swift-wfd.com). This project aims to provide materials and advice for QA/QC sectors, field and data demonstrations, and economic and policy analysis in support of the implementation of the WFD. In addition, several field trials for validation of these tools in European river basins are scheduled for 2005.

This directory aims to list techniques and tools that may be considered for use in the measurement of standard physico-chemical parameters and for the assessment of biological and chemical quality. The main types of biological and chemical monitoring tools discussed within the directory are presented in Fig. 2 (see next page bottom left).

Tools for Biological Monitoring

Biological monitoring can be conducted at a number of trophic or organisation levels. At the highest levels, ecological monitoring relies on the assessment of benthic algae, diatoms, macro-invertebrates, macrophyte and fish species and community structure and diversity (http://www.eu-star.at/). This community assessment is then combined to physico-chemical measurements at the sampling site and compared to community structure and assemblages that may be expected under pristine conditions. The outcome from such procedure is a measure of ecosystem health at the population level. Bioassays, biological early warning systems and biomarkers are amongst the other biological methods available for assessing water quality.

Bioassays: Whole-organism bioassays rely on measurement of the response of a test organism to a mixture of contaminants present in a water sample in a standardised test. The use of multiple test species and trophic levels may be crucial to obtaining meaningful results or for fingerprinting, since many assays exhibit differences in sensitivity to different compounds. Tests using microorganisms may make use of bioluminescence, metabolic status, growth or chlorophyll a fluorescence. Chronic toxicity testing using invertebrates is generally based on growth rate or survival of amphipods, chironomid larvae, daphnids, oysters and other higher organisms such as fish. Particularly applicable to investigative monitoring, chemical analysis and sample fractionation may be combined to toxicity assays in toxicity-directed analysis schemes, enabling the characterisation of toxic components of complex mixtures.

Within WFD monitoring programmes, bioassays may be used in the regulation of toxicity of wastewater treatment effluents, to detect changes in toxicity after accidental spills or to determine the source of a pollutant. Importantly, most of these tests also account for pollutant bioavailability and physical transfer (e.g. desorption from sediment particles and diffusion through cell membranes) to the test organism. These assays use spot samples of water taken back to the laboratory for analysis. Sample collection, preservation and assay time will, however, affect sample integrity. As part of an integrative risk assessment, in-situ bioassays such as the use of algal cells embedded into alginate beads for field deployment may provide an alternative to laboratory- and spot sample-based testing.

Biological early warning systems: Another approach to overcome problems associated with spot sampling is the use of in-situ or continuous biological early warning systems (BEWS). These generally consist of a living organism, a sensing element to detect changes in the test organism, and a processing element to translate the signal from the sensing element into a warning response system. An acute toxicity measurement based on physiological or behavioural changes is used to provide a rapid warning in response to deterioration in water quality. BEWS may based on the use of microorganisms (e.g. biological oxygen demand, bacterial growth rate or algal photosynthetic activity), invertebrates (e.g. daphnid swimming behaviour), bivalve molluscs (mussel respiration rates or valve closure movements), or fish (e.g. swimming behaviour or ventilation frequency). Applications of BEWS include monitoring of drinking water intakes, water distribution systems, monitoring of wastewater effluents, or effluents from contamination at remediation sites.

Successful exploitation relies on schemes for data handling and coordination of response measures to pollution events. BEWS may, however, suffer from the influence of environmental pathogens present in water, or remain unable to detect chronic toxicity due to long-term exposure to low-level of contaminants. Additionally, the use of higher organisms such as fish as bio-indicators may be constrained on legal and ethical grounds in some member states.

Biomarkers: These are defined as cellular, intra-cellular or physiological changes in a biological response within an organism, that can be related to pollutant exposure. According to the World Health Organisation, biomarkers can be of:

- *Exposure* covering measurement of an exogenous substance, its metabolites, or the product of an interaction between a xenobiotic agent and target molecules or cells within an organism (e.g. metallothionein synthesis).
- *Effect* including measurable biochemical, physiological or other alterations within an organism that can be associated with an impairment of health or disease (e.g. vitellogenin induction).
- *Susceptibility* indicating the ability of an organism to respond to the challenge of exposure to a specific pollutant.

Since pollutant effects may be shown at molecular and sub-cellular levels before whole-organism and population levels, biomarkers may be considered as early warning signals, and as such, are important tools for investigative and operational monitoring. Their use, however, needs to be accompanied by an understanding of the significance of these measurements to ensure the adequate interpretation of results by water quality managers.

Tools for Chemical Monitoring

Existing and emerging techniques for chemical monitoring mainly comprise passive samplers, immunoassays and sensors/biosensors.

Passive samplers: Some of the problems associated with spot sampling may be overcome by using passive sampling techniques (Fig. 3). The receiving phase (RP) of equilibrium and kinetic samplers is exposed to the water, and devices absorb/adsorb pollutants from water. Equilibrium samplers may be deployed in waters with relatively stable pollutant levels. Once thermodynamic RP/water equilibrium is achieved, pollutant concentrations in the water may be calculated from the accumulation in the RP. The rate of mass transfer to the RP of kinetic samplers is assumed to be proportional to the difference in chemical activity of the contaminant between the water phase and RP. When this sampling rate is known, time-weighted average (TWA) concentrations of a pollutant in the water phase can be calculated. The advantage of kinetic sampling is the detection of contaminants from episodic events commonly not observed with spot sampling. Thus, kinetic samplers are suited for use in water bodies with varying concentrations of pollutants.

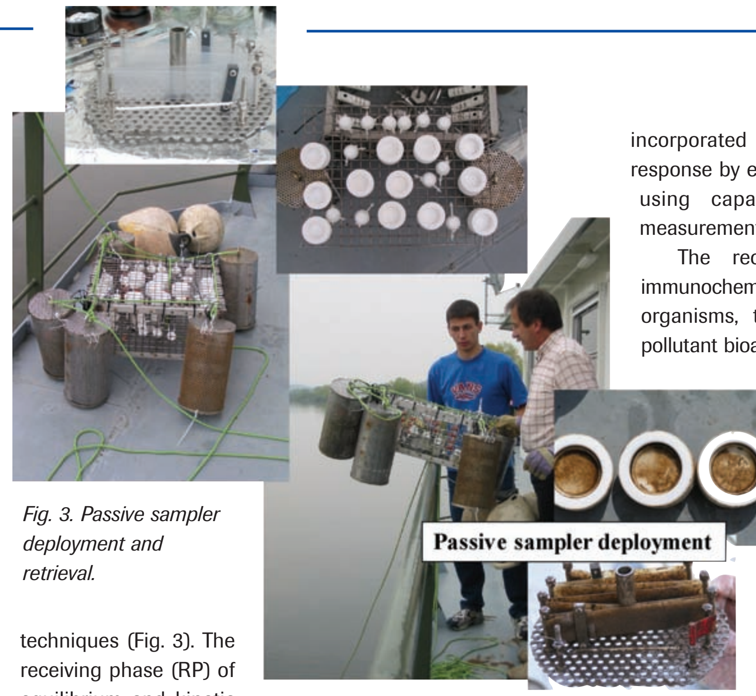

Fig. 3. Passive sampler deployment and retrieval.

Passive samplers may be used to relate patterns in pollutant concentrations in biota to TWA contaminant concentrations at one site or compare TWAs at different locations. Samplers can be applied to investigate temporal trends in levels of contaminants and to evaluate the location of contaminant sources. Extracts from passive sampling devices can be combined with in vitro bioassays. The marriage of passive samplers and bio-marker/bio-indicator tests offers many avenues of investigation to provide information concerning the relative toxicological significance of pollutants.

On-line, on-site and in-situ sensors and biosensors: Sensors generally rely on a chemical or physical receptor allowing specific recognition of the chemical under study connected to a transducing element transforming the signal from the receptor into a quantifiable output signal. For example, stripping voltammetry techniques have greatly evolved with the development of miniaturised screen-printed electrodes or molecularly-imprinted polymers incorporated in hand-held equipment. Detection of a response by electrochemical sensors may also be achieved using capacitance, conductance or potentiometric measurements.

The recognition event in biosensors may be immunochemical, enzymatic, or based on DNA and whole organisms, the latter providing useful information on pollutant bioavailability or on cyto-toxicity, geno-toxicity, and mutagenicity of water samples. Some immunoassay-based biosensors have been combined with optical sensing systems and flow injection analysis for the detection of pesticides. Bacterial or yeast-based biosensors developed for the quantification of toxicity may be immobilised onto screen-printed electrodes or in solution added to the sample and combined to fluorescence or luminescence measurement. Pollutant concentrations (bioavailable/bioaccessible fractions) may also be determined using certain whole-cell biosensors.

Many of these systems can provide easy, rapid, on-line, on-site or in-situ measurements. As such they can be used for monitoring drinking water intakes, effluent discharges, the efficiency of wastewater treatment works, and surface and ground waters. They may also be useful for mapping of contamination when it is important to obtain rapid in-field results.

Immunoassays (IAs): These kits use antibodies with a specific recognition site in their molecular structure allowing specific binding with respective antigens. IAs are based on the binding of antigen to antibodies usually immobilised on a surface. The measurement generally reflects the availability of binding sites after contact with the sample containing the antigen/analyte. A label/tracer (e.g. luminescence-based) is added to obtain a measurable signal and quantify available sites. Therefore, IAs do not provide a direct analyte concentration but results are expressed as analyte equivalents.

Many assays available as coated-tubes, magnetic particles, or 96-well plates, incorporate environmental quality standards within their working ranges, and are useful for screening purposes. However, it may remain difficult to use IAs for regulatory analysis owing to cross-reactivity and analyte-equivalency issues. IAs could be used to replace spot sampling campaigns providing a framework is in place to ensure the confirmation analysis of positive samples. Rapid mapping of contamination and the identification of contamination point sources are niche applications.

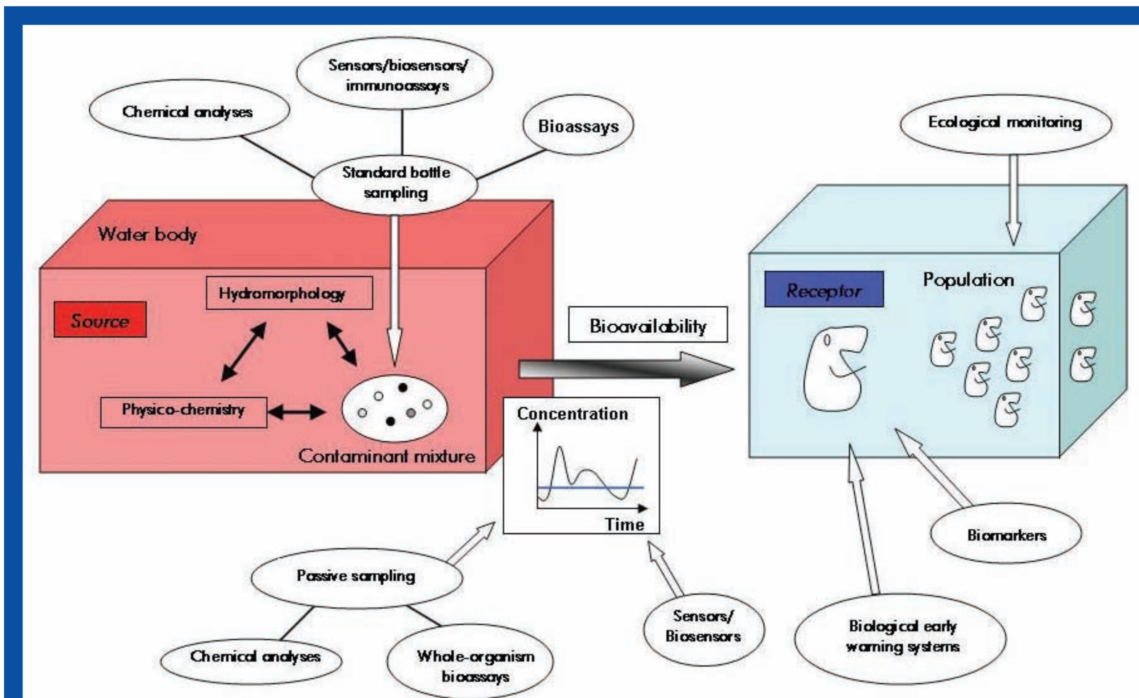

Fig. 2. Suitability of existing and emerging techniques and methods for water quality monitoring under Water Framework Directive.

Conclusion

Many of the emerging tools and techniques that have been developed in recent years provide alternatives for low cost and more representative monitoring of water quality. However, this is an expanding market with increasing opportunities for manufacturers and suppliers. Choice of a suite of tools for a specific monitoring task will be critical, and will depend on the type of information required and cost. Importantly, one needs to take into consideration that all these tools measure different fractions or have different endpoints/outputs (even within one class of tool). A clear understanding of the significance of the results obtained with these techniques is essential, particularly when comparing these with historical data that may have been gathered using other methods. While the cost of these tools will be a crucial factor affecting their implementation at the European scale, a further factor will be the development of appropriate quality assurance schemes in laboratories undertaking regulatory analysis will ensure data reliability and comparability. There is little doubt that the combination of these technologies, with associated ecological monitoring, should enable a more representative assessment of the health of an ecosystem, as required by the WFD.

This SWIFT directory is publicly available on the SWIFT-WFD project website (www.swift-wfd.com) and in the form of a live database that may be updated regularly. Any technologies omitted in this first edition will be added as we become aware of them. Authors welcome comments and suggestions on the directory.