

Chapter 4 – Water monitoring

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Recommendations

- Research and development is needed into biological contamination, including the pathogens, nutrients and other water quality indicators.
- Funding agencies should establish collaborative research efforts in areas of sensor development, communications technologies, data management and user group interface.
- The RSC to review the instruments, sensors and analytical approaches and techniques that may be best applied to meet the needs of WFD.
- The RSC to promote innovative research into appropriate sensor technologies to enable inexpensive flow and pressure measurements.
- The RSC to promote collaboration between water engineers and scientists and materials and sensor engineers and scientists, with a view to specifying and promoting combined sensor and materials research and development, and transferring the technologies into the water industry.
- The appropriate funding to develop the range of calibration data available for passive samplers particularly for polar organic pollutants, and to demonstrate the robustness of these samplers alongside current monitoring networks.
- Research and development is required to develop new analytical techniques to meet standards requiring detection of contaminants at lower concentrations.
- Research councils and other bodies must fund fundamental research to improve and further develop new sensors, materials and communication systems.
- Reference testing-sites need to be developed for novel technologies and continuous validation procedures that could be used by researchers, companies and agencies to test and validate technologies.
- A capability to scale-up technologies is needed so that they can be adequately tested before full-scale deployment.

Executive Summary

Investment in monitoring of European water bodies has been low, partly because of the high cost for such monitoring associated with the collection of samples, and their subsequent analysis at the laboratory.

Traditional spot sampling is suited for the collection of data on average water quality but does not normally allow the detection of transient events resulting from accidental discharges or storm overflows. This can be overcome to some extent by the use of passive sampling devices, which extract and concentrate pollutants from water by mimicking their uptake by living organisms using, for example, diffusion through a semi-permeable membrane and subsequent adsorption or reaction with reagent to capture and accumulate the contaminant over time. Various designs are available but more work is required to ensure their adoption as a routine monitoring tool.

Laboratory analysis is still the norm for the majority of parameters of environmental interest but, in the rapidly developing field of environmental monitoring, there is much published research in the area of sensor development. Although field-monitoring stations and sondes have been used for a limited range of parameters for several years, there is a need for the development of a wider range of low-cost but sensitive, specific, and reliable sensors, that can be deployed in the field to log and report data using wireless technology. Significant developments are underway, but many of these devices will never make it to the field for long-term measurements, or are deployed, but not tested, in parallel lab-based analyses for validation.

While the measurement and detection of environmental pollutants can be successful under laboratory-controlled conditions, continuous *in-situ* monitoring remains the most challenging aspect of environmental sensing. One of the visions of wireless sensor networks is that they enable remote monitoring of the environment. However, most current deployments use a laptop or PC to control the sensor network. There is limited evidence of the use of GPRS modems to remotely control sensor networks and enable real-time continuous monitoring.

Monitoring of water bodies will increase over the coming years, within Europe in response to the needs of the Water Framework Directive (WFD), and globally due to pressure from climate change, which will lead to resource scarcity in some areas as well as water quality changes, and increasing demand from population and manufacturing growth. Monitoring at river basin level for the WFD is a significant financial burden using conventional sampling and laboratory based techniques, but sensors offer the potential to reduce these costs considerably, as well as providing more useful, continuous monitoring capabilities.

Analytical Quality Assurance (AQA) will also form an essential component of the WFD and other monitoring programmes to ensure that methods are capable of measuring with the required level of accuracy and precision. There is a need for better coordination of programmes at national and EU level; in effect, a European-wide AQA scheme is needed that includes inter-laboratory testing to ensure that comparable data are produced by participating laboratories.

The ideal monitoring system of the near future might consist of a network of sensors deployed at key locations, capable of autonomous operation in the field for perhaps a year or more. In addition to basic water quality parameters such as dissolved oxygen, conductivity, pH and nutrient status, new developments will allow sensitive and specific monitoring for a range of organic contaminants such as pesticides or chlorinated hydrocarbons. In addition, toxicity monitoring will be used as a screening tool, albeit non-specific, for detecting the advent of unsatisfactory water quality.

The data from the monitors will be communicated by wireless technology for statistical processing and interpretation by expert systems. Rising trends for any constituent of interest or breaches of Environmental Quality Standards will alert scientific staff and lead to the collection of samples for laboratory analysis for the purpose of identifying the chemical of concern using the array of tools available to a modern laboratory.

Although some elements of this ideal system are in place, ongoing research and development is required in several areas relating to both sensor development and field-

testing. Funding agencies should establish collaborative research efforts in areas of sensor development and related areas of work and facilitate the field-testing of sensors over long periods of time. Funding is also needed for fundamental scientific aspects of novel devices for biological monitoring, priority pollutant detection, and nutrient analysis; and to develop prototype devices and laboratory/environmental trials, followed by scale-up of the devices for full-scale field trials and validation.

Technology transfer can follow the latter to involve relevant interested companies. The prospect for spin-offs of new technologies is greater where proper validation of the technologies has taken place, thus providing prospective investors with greater confidence in the technologies.

Introduction

It has long been recognised that the presence of chemical pollutants in water can affect its ability to support life and its suitability as a source of drinking water.

During the 19th and early 20th century, monitoring was mostly associated with reducing gross pollution of rivers and surface water from the discharge of untreated sewage and industrial wastes. This manifested itself by exerting a huge oxygen demand on the water during the process of natural purification by microbiological processes. This demand often exceeded the ability of the watercourse to re-oxygenate itself and resulted in foul-smelling rivers devoid of oxygen and incapable of supporting fish and other organisms. In the developed world, such gross pollution was largely eliminated by the middle of the 20th century but by then a growing awareness developed of the insidious nature of many man-made chemicals on the natural environment.

It was realised that many synthetic industrial chemicals were not 100% biodegradable in river or seawater and that many were in fact capable of bioaccumulation through the food chain due to their enhanced solubility in fats or oils. This was first recognised with several of the organochlorine pesticide family, such as DDT and dieldrin, that were found in fish and in animals that fed on fish, at concentrations thousands of times greater than in the water body itself. In some cases the body burden was so great that the breeding and survival of the fauna were affected. Similar effects were soon identified from polychlorinated biphenyls (PCBs), which were widely used by industry.

Much of the success in recognising these environmental problems was due to developments in analytical techniques and instrumentation that made the measurement of these contaminants possible for the first time.

Nowadays, anthropogenic pollution, eutrophication and human use & abstraction of water resources are still strongly affecting aquatic habitats. Pollution of water sources, aquifers and wetland systems caused by industry, agriculture, and municipally treated wastewater is a pan-European problem with extreme conditions existing in newly associated states. In

order to comply with the significant requirements of monitoring in Europe, a continuous sensor-based system is desirable.

Parameters of interest in this context include dissolved oxygen, nutrients (e.g. nitrates and phosphates) as well as commonly used heavy metals like cadmium and chromium, persistent organic pollutants including some industrial chemicals and pesticides, and increasingly, a range of pharmaceutical products.

By using sensing programmes for continuous monitoring, nitrate vulnerable zones might be protected, nutrient levels at coastal areas could be controlled, non point sources of pollution could be mapped and river basin districts might be better protected in general.

The present environmental monitoring programmes typically have a low resolution both in time and space. In order to monitor water quality and long-term changes, the use of a system of widely distributed monitoring platforms would be the most efficient, economic and reliable way to go as is discussed later in this section.

Priority Pollutants

In recognition of the dangers posed by certain types of synthetic chemicals, international legislation has developed to reduce the production and use of a range of chemicals that are known to be toxic, stable and bio-accumulative.

The Water Framework Directive (WFD) recognises this in the form of a list of Priority Pollutants that are known to be particularly harmful in this respect. In draft legislation tabled during 2006 the European commission proposed EU water quality standards for 33 chemicals on a water quality priority list. In addition, it judged that 12 of the list were priority hazardous substances and, under the framework law, emissions of these must end within 20 years.

There is also a contentious proposal that twenty-eight other substances, including widely used industrial chemicals such as the pesticide glyphosate and the flame retardant, TBBPA, should expand the priority list. This would require the commission to develop EU quality

standards for each pollutant. On top of this, a further eleven of the original thirty-three chemicals, including the plasticiser DEHP and lead, may be reclassified as priority hazardous substances subject to the 20-year phase-out. Twenty-two of the twenty-eight new chemicals should be classed as potential priority hazardous substances.

The monitoring of such priority substances in surface water, sediment and biota forms an important part of protecting the water environment to ensure that water is managed in a sustainable manner that ensures sufficient water of suitable quality for all users. The low concentrations of some of these priority pollutants, now known to have biological effect, requires the development of suitable analytical methodologies to allow cost-effective and rapid monitoring of the water environment.

Other pollutants

Besides the priority pollutants (concerning principally surface waters), the WFD establishes protection rules regarding a wide range of pollutants that are listed in its Annex VIII, and which concern surface and underground waters. In this respect, the new Groundwater Directive (daughter directive of the WFD) establishes complementary obligations for the Member States to establish Groundwater Quality Standards at the most appropriate level (national, river basin or groundwater body) for any pollutant representing a risk to groundwater at a defined scale. This imposes a new structured and systematic monitoring to be developed for chemical pollutants in groundwater, following the identification of pollution risks and related pollutants.

Legislative Background

This chapter deals with the monitoring of water quality, with particular reference to the European Water Framework Directive (WFD) (Directive 2000/60/EC) and its daughter directives. However, the developments described are equally applicable worldwide. Similar programmes are being implemented in other countries including the USA and Australia. The WFD sets ambitious targets and a tight time scale for improving the quality of water (inland, transitional, and coastal surface waters, and groundwater) and achieving sustainable use. This legislation came into force in 2000, and the target date for achieving good status in all European water is 2015. The first monitoring programmes for surface

waters came into operation in January 2007, with management on the river basin scale. This requires close cooperation between EU Member States where there are Trans-boundary Rivers. These programmes can be updated in 2009 in light of experience and technical developments.

A large part of compliance requirements to 'good chemical status of both surface and groundwater' is based on chemical monitoring data. This means in turn that the legal basis of the overall directive will be primarily linked to reporting of data, which should be of demonstrated and comparable quality throughout the European Union. (A1)¹

The WFD does not mandate any particular method of monitoring or chemical analysis, but requires that comparable methods, both of sampling and analysis, be used with good accuracy and precision so that differences between water bodies and trends can be detected reliably. The monitoring should support the establishment of a coherent and comprehensive overview of water status within each river basin district. Some of the emphasis has been on checking on compliance with environmental quality standards (EQSs) in surface water by means of spot or grab sampling combined with classical laboratory analysis for which well-established protocols are available. However, monthly (or less frequent) spot samples at a few fixed sampling stations may not provide an adequate picture of water quality where there are marked variations in space (for instance due to pressures such as discharges or run-off), or in time due to for instance seasonal agricultural applications of pesticides, or sporadic industrial discharges, or weather dependent run-off from roads or fields. High frequency spot sampling is very costly because of the labour and transport involved, and increasingly alternative methods of monitoring are being considered. This is also the case for groundwater, for which compliance checking to EU-wide standards (nitrates and pesticides) and nationally established standards will also be based on relevant monitoring data.

The Commission provides guidance through the WFD Common Implementation Strategy (WFD CIS) and this is updated as new technologies become available. This is complemented by the guidance documents produced as a result of the EU Mandate of

¹ P. Quevauviller, J. Environ. Monit., 2006, 8, 240-241

Chemical Monitoring Activity 2005-2006 (CMA). These documents are not legally binding but seek to provide information on best practices and international standards or procedures already in use. CIS Working Group C provides the equivalent guidance on ground water monitoring.

These documents aim to support Member States in their monitoring programmes, and cover priority pollutants and any other relevant pollutants, and other chemical parameters that impact on the ecological or chemical status of a water body, but exclude the monitoring of hydro-morphological elements (i.e. the physical characteristics of the shape, the boundaries and the contents of a water body). These guidance documents represent a consensus view of EU Member States on the most appropriate methods of monitoring chemical substances in the aquatic environment.

It should also be kept in mind that the monitoring of groundwater has much the same requirements in terms of analytical capability and must respond to problems that are unique to groundwater. For example, since groundwater moves slowly through the subsurface, the impact of anthropogenic activities may last for a relatively long time. The Directive 80/68/EEC on the protection of groundwater against pollution caused by dangerous substances provides a framework for groundwater protection by preventing the introduction of high priority pollutants into groundwater, which leads to monitoring requirements. (A2)²

This chapter will provide an overview of some of the current state of the art, and examine some of the problems faced by those responsible for regulating water quality. It will review quality assurance issues; particularly those surrounding the application of some of the methods that might provide a less costly alternative to frequent spot (grab) sampling. This is important when assessing the cost-benefit of implementing emerging technologies, while taking into account the cost of wrong decisions based on inadequate or flawed data. An overview of some of the emerging technologies will be provided with some indications of current trends in their development and application, and will attempt to identify developments necessary for their adoption.

² P. Podac et al, *Ecological Chemistry and Engineering*, 2005, 12, 1-17

Current state of the art

Sampling

Traditional sampling of the water environment relies on the collection of spot samples, which are then returned to a laboratory for analysis. Even this apparently simple exercise can give rise to significant errors at the trace concentrations of interest unless appropriate sample preservation procedures are used. Loss of material can occur due to a number of causes such as:

- *Adsorption on the walls of the container*
- *Volatility of the chemical of interest*
- *Degradation due to chemical and microbiological action*

The ways of minimising such effects are dependent on the nature of the chemical but include procedures like:

- *Addition of sterilising agents to kill off bacteria and stop biodegradation*
- *Addition of acid to reduce metal adsorption*
- *On-site chemical reaction to convert the chemical of interest to a more stable form*

These problems become more severe if auto-sampling equipment is used to collect samples at regular intervals, perhaps hourly, to give a more representative sample of the water body over one or more days. This introduces even more potential for contamination from the sampling hoses and the pumping system in addition to the problems described above.

Sampling presents a particular problem for the chemical priority substances identified by the WFD because of the low concentrations of chemical present in most water samples and the low EQS values for many of them. Any loss can represent a significant proportion of the chemical originally present and make monitoring for breaches of the EQS liable to large errors and reduced confidence.

Other sampling techniques have been developed to try to overcome the problem of spot sampling and to provide more continuous sampling of the water body and improve the chance of detecting sporadic pollution events. In addition to auto-sampling devices mentioned above that collect samples at predefined intervals, other techniques have been devised to try to mimic the uptake of pollutant by living organisms and thus provide more realistic data on exposure levels.

Passive sampling is one such technique . ³Passive sampler devices all depend on uptake of chemicals from the environment by passive diffusion and unlike active samplers do not require a forced flow of water through a receiving (collecting) phase, and therefore do not need a power supply. These devices consist of a receiving phase that accumulates contaminants, and has such a high affinity for them that the concentration remains close to zero at its surface. This is separated from the bulk water of the environment by a diffusion-limiting layer (Figure 1).

Under these conditions the mass of a contaminant accumulated during a given deployment period will depend on only its concentration in the water, and the sampling rate of the sampler. The latter is determined by the area of sampler available for diffusion, the properties of the diffusion-limiting layer, and the properties (e.g. size and polarity) of the chemical, and is independent of the concentration of the pollutant in the water. It can be interpreted as the volume of water cleared of pollutant per hour or per day. It is important to remember when interpreting data based on passive sampling that these devices measure concentrations of freely dissolved analytes and not total concentrations. Pollutant fractions that are bound to particulate matter or to dissolved organic carbon (DOC) are not measured due to their exclusion by the diffusion-limiting layer.

³ R. Greenwood, G. Mills, and B. Vrana (Eds.) *Passive sampling techniques in environmental monitoring*. Vol. 48 in Comprehensive Analytical Chemistry Series, Editor in Chief D. Barceló, Elsevier, Amsterdam, 2007

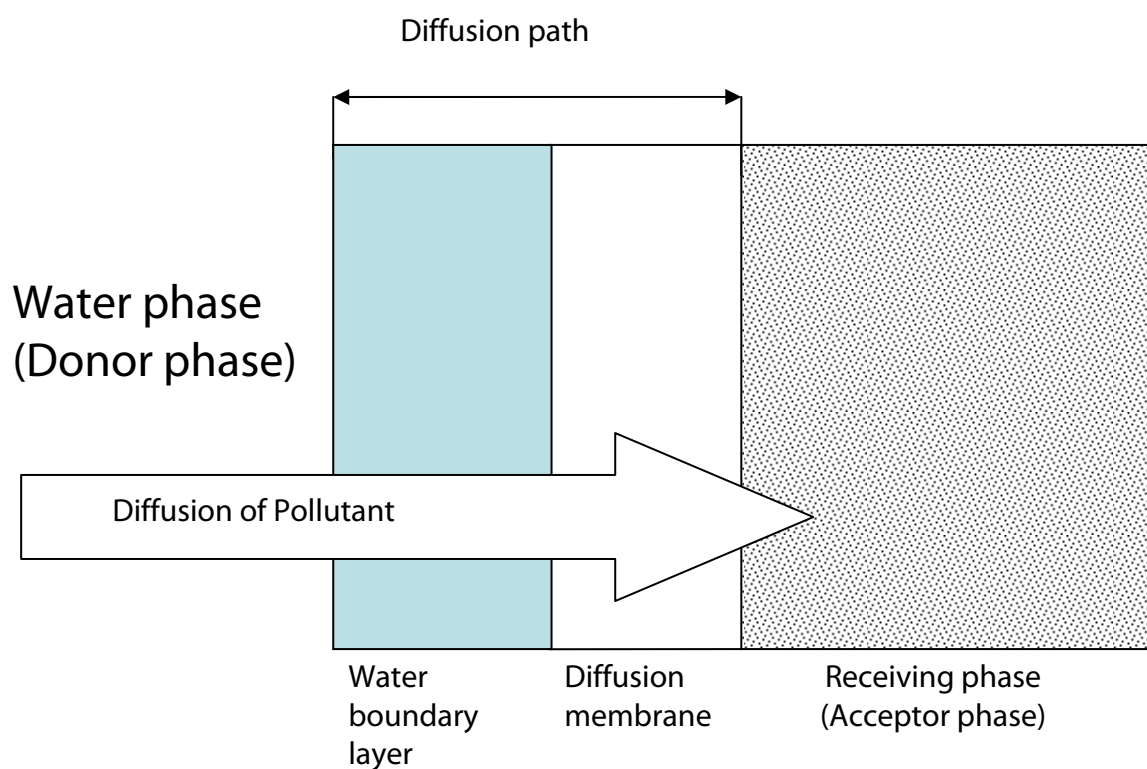


Figure 1: Passive samplers function by maintaining a very low concentration at the receiving phase surface so that pollutant molecules diffuse across the diffusion path from the higher concentration in the donor phase, and are accumulated. The amount accumulated in the receiving phase gives a measure of the time weighted average concentration of pollutant in the donor phase over the deployment period.

Passive sampling technology was developed to measure Time Weighted Average (TWA) concentrations of pollutants in air, and in water. It has the potential to mimic bio-monitoring where uptake by living organisms is measured and provides a good measure of the biologically relevant concentration of pollutants. Biomonitoring has been used in some countries such as the Netherlands as part of routine monitoring programmes in both freshwater and coastal waters, and will be discussed later.

Passive samplers can provide information similar to that obtained from biomonitoring, but have some advantages. Samplers can be placed in a wide range of conditions where organisms could not survive. Further, for most passive samplers the extraction and chemical analysis of accumulated pollutants is relatively simple. In comparison, because organisms contain large quantities of biochemical such as proteins and lipids, many steps are involved in the extraction and quantification of pollutants present in their tissues. This can result in significant losses during sample processing. Passive sampling has shown promise as a reliable, robust tool that can provide biologically relevant information on pollutant concentrations in a cost-effective manner in a wide range of aquatic environments. This technology could prove useful in monitoring programmes in support of the WFD.

The various designs of passive samplers work on similar principles. There are two classes, **Equilibrium Samplers** that are useful where concentrations of pollutants do not fluctuate markedly, and **Kinetic Samplers** that provide TWA concentrations even where levels of pollutants can change markedly over time.

Equilibrium samplers have been used to measure concentrations of pollutants in ground water and in sediment pore water. They have the same basic components as kinetic samplers but the receiving phase is typically water (or sometimes air for monitoring volatile organic compounds (VOCs)) that is free of the compounds of interest. Pollutant molecules diffuse into the sampler to come into equilibrium with the external environment without depleting the surrounding external medium. Passive diffusion bag samplers usually comprise a low density polyethylene (LDPE) bag filled with pure water, and protected by a metal mesh, or a glass tube filled with clean air and sealed at the ends by LDPE membranes. Such devices have been used successfully since the 1990s to monitor, map, and track changes in VOCs in ground water. They can provide information about concentrations at a range of depths in a well. This would be difficult to obtain reliably by pumping water since the sample becomes modified, and the local sampling environment is disturbed by this procedure. This type of sampler has been used to model

bioaccumulation and can be deployed where it would not be possible to deploy living organisms.



MESCO

POCIS

DGT



SPMD on deployment holder



Chemcatcher – exploded view

Figure 2: A range of passive sampling devices

A wide range of kinetic samplers has been developed and used in recent years (examples are presented in Fig. 2). Among the most widely used are the semi-permeable membrane devices (SPMDs) for non-polar organic pollutants and the diffusive gradients in thin films (DGTs) for metals and inorganic ions. Several novel passive sampling devices (polar Chemcatcher, and the polar organic integrative sampler (POCIS)) have also been developed to monitor a range of polar organic chemicals, including pesticides, pharmaceutical/veterinary drugs, and personal care products. The inorganic Chemcatcher, like the DGT, has been designed to monitor metals.

A range of sampler designs is available in addition to the SPMD for monitoring the TWA concentrations of non-polar organics, and includes Chemcatcher, LPDE strips and silicon strips, and MESCO.

The SPMD comprises a layflat low-density polyethylene (LDPE) tube (the diffusion limiting layer) containing some lipid (triolein) that provides the receiving phase. This sampler can have a large surface area and since the rate of diffusion is proportional to this, it can have very high sampling rates (the equivalent of extracting the pollutant from several litres per hour) for some compounds. This makes it particularly useful for monitoring substances present at only very low (trace) concentrations. However, the SPMD does have some disadvantages in that the several expensive extraction and purification steps involving large volumes of solvent are needed before pollutants can be analysed.

The non-polar Chemcatcher also has a LDPE diffusion limiting membrane, but has a chromatographic adsorbent as the receiving phase. This sampler has a smaller surface area than the SPMD, and hence a lower sampling rate, and lower sensitivity. However, it is very simple, and relatively quick and inexpensive, to extract pollutants from the receiving phase, and only small volumes of solvent are used.

The LDPE and silicon strips are similar to the SPMD but here there is no lipid phase and the plastic acts as the receiving phase, whilst a boundary layer of water provides the diffusion-limiting layer. These can have large surface areas, and associated high sensitivities, but require large volumes of solvent to extract the pollutants. The preparation of the extract for analysis is, however, simpler and less expensive than for the SPMD since steps to separate substances from lipid are eliminated.

The MESCO is a miniaturised sampler that comprises a small rod coated with an adsorbent (receiving phase) in a bag made of cellulose or LDPE (diffusion limiting membrane). The MESCO has a small surface area and sampling rates, but has the big advantage that it does not have to use a solvent extraction phase before analysis. Instead the pollutants on the sorbent coated bar can be desorbed by heating the bar in a special heated injector port of an analytical instrument. This increases analytical sensitivity since all of the accumulated

pollutant is available for analysis, and there is no interference from solvent. The disadvantage is that it is not possible to repeat the analysis to check repeatability, or if anything goes wrong.

One problem common to all passive samplers is that to a greater or lesser extent, depending on design, the uptake rates are dependent on temperature and turbulence of the water. The rate of uptake can be deleteriously affected by the growth of microorganisms (biofouling) on the surface of the diffusion limiting membrane. One solution to these problems for samplers for non-polar contaminants is the use of performance reference compounds (PRCs). These are compounds that are loaded onto the receiving phase of the sampler prior to deployment, and offload at a measurable rate. Since the offloading rates of the PRCs are affected by temperature, turbulence and biofouling in a manner similar to the uptake rates of pollutants, then the rates of loss of PRCs from the sampler can be used to correct the uptake rates of pollutants for the effects of those environmental variables. This approach shows great promise in increasing the reliability of field measurements where conditions can fluctuate over short periods of time.

The polar Chemcatcher and POCIS monitor concentrations of polar organic pollutants. Both use polyethersulphone diffusion limiting membranes and a range of adsorbent materials as receiving phase. Far less data is available for these samplers than for the non-polar samplers described above, but calibration work, and field-testing are currently underway, and the data and experience are beginning to be published. These may prove particularly useful in monitoring some of the pollutants such as pharmaceuticals that are becoming the cause of increasing concern. One limiting factor at the moment is the lack of suitable performance reference compounds for use in these systems.

The DGT comprises a hydrogel (diffusion limiting membrane) overlying a chelating agent receiving phase. The Chemcatcher uses a similar receiving phase but a cellulose acetate membrane provides the diffusion-limiting layer. Both have been used for the measurement of TWA concentrations of metals in water. The concentrations measured are close to the biologically available fractions of the metals. The DGT is available commercially and has a long track record in the monitoring of metals of concern such as cadmium,

chromium, copper, lead, and zinc in a wide range of aquatic environments from marine to freshwater. It can be used to provide information on the different forms in which the metal is present. This is important since some forms are far more toxic than others. These samplers have the advantage of ease of use and analysis, and the provision of biologically relevant information.

The information provided by passive samplers can be used for a number of purposes. One purpose is the detection of sources of pollution such as accidental or deliberate discharges into a sewer or catchment. This is done by deploying samplers at key points (e.g. above and below a junction) and comparing the masses of pollutant sequestered at the various sites over the deployment period. In addition they can be used in a more quantitative way to provide estimates of the TWA concentrations of freely dissolved fractions of pollutants to which the samplers were exposed. Since these devices provide average concentrations over periods of weeks, they can provide more representative information and greater confidence than is available with taking infrequent spot samples. They also overcome problems associated with changes in bottled water samples during transport, storage and preparation (e.g. filtration) prior to analysis. A further advantage is that since they accumulate compounds over a period of time, the masses accumulated may exceed the limits of detection and be quantitatively measured, even where the concentrations in the water are so low that the mass extracted from a standard bottle sample falls below the limit of detection.

Although passive samplers offer many advantages over infrequent spot sampling they have not been readily accepted by regulatory monitoring agencies. In order to enable their adoption in routine monitoring further work is needed to deploy samplers alongside conventional monitoring for period up to one or two years to demonstrate their robustness and ability to provide low cost, representative information on water quality. This technology is currently available and could be incorporated into monitoring programmes in support of the WFD when these are updated before the end of 2009.

Other solutions to some of the problems associated with spot bottle samples are available. These include various techniques for on-site measurement that avoid the need to collect,

transport and process samples but, as will be described later, suitable analytical techniques are not always available at the present time that can be used in the field. In the longer term the holy grail of environmental monitoring is represented by the development of suitable sensors capable of accurately measuring chemicals of interest in the field with a high degree of accuracy and specificity combined with the ability to transfer data by wireless technology for interpretation. This would reduce the need for frequent, expensive visits to sampling sites, and for expensive laboratory-based chemical analysis.

Analytical Quality Assurance

The ability to detect low concentrations reliably, accurately and precisely is important in relation to WFD monitoring because wrong decisions based on poor analysis can potentially lead to huge costs by taking remedial measures that are not in fact necessary, or failing to take them when they are necessary.

This leads to the requirement that all participating laboratories are able to demonstrate that the analytical methodologies employed are capable of accurately measuring the analytes of interest to the required level of precision so that breaches of environmental quality standards can be established with a high degree of confidence.

Analytical Quality Control is therefore a very important area of work within an environmental laboratory where very low concentrations are being monitored with the potential for contamination either at the time of sampling or at the laboratory. In many cases the concentration of analyte in the sample may only be in the range of only 10^{-6} – 10^{-12} grams/litre of water.

It is not necessary for all monitoring laboratories to use exactly the same method of analysis although standardising sampling, sample preservation and preparation can reduce errors from these sources. What is important is that the performance characteristic of the analytical method is defined at the start based on the use to be made of the results. In other words, the analytical procedure should be fit for purpose.

This requires the setting of performance targets based on requirements as regards:

- *Concentration range*
- *Trueness (closeness to 'true' value)*
- *Precision (scatter around the mean value, covering both repeatability and reproducibility)*
- *Specificity (ability to detect only the analyte of interest)*
- *Bias (tendency of method to err on low or high side)*

There exist well-established procedures for laboratories to test their own methods against the target performance. Once a laboratory has shown its ability to meet the target analytical requirements it becomes necessary to demonstrate that different analysts can meet these under routine monitoring conditions. This can be demonstrated in a variety of ways including the use of Control Charts, which make use of the precision data developed during method testing to check that a standard of known concentration can be measured within target values. Participation in inter-laboratory tests is one way of demonstrating capability whereby samples of unknown composition are distributed at national or international level and the results between laboratories compared. The use of reference materials is another way by which laboratories can test their analytical performance and assess the accuracy of their chosen technique.

If monitoring for the WFD is to be successful, it is important to ensure that participating laboratories throughout Europe adhere to an agreed analytical quality assurance protocol. This indicates the need for a coordinated approach at both a national and European level. One option may be the formation of an EU-AQC body to harmonise the testing of methods and the distribution of samples for inter-laboratory comparison as well as the maintenance of reference materials.

The AQC testing described above is more suited to a laboratory environment than to field measurements where the measuring process cannot be controlled in the same way. Sensors deployed in the natural environment are exposed to many factors that influence the quality of data obtained. For example, sensors with optical windows can become fouled by biological slimes so wipers may be required to reduce this interference. Many

sensors are prone to drift over time and must be recalibrated at regular intervals to correct and minimise errors.

Nevertheless, monitoring the water environment in future will depend more and more on the use of sensor technology to provide real-time monitoring of water quality for a much wider range of parameters than currently available. It is important that sensors are developed with enhanced stability compared with many current systems. A recent example of how a long-established measurement has been improved is that of dissolved oxygen, which relied for decades on an electrode system that employed a membrane to allow diffusion of oxygen from the water sample to the sensing electrode - a system very prone to drift and requiring frequent recalibration. In recent years a new optical technique has been developed that utilises luminescence and is factory calibrated, drift free, and substantially free from interferences.

Research and development is required to produce a range of sensors that can be deployed in the field for prolonged periods and still provide accurate and precise data. Developments in sensor technology that combine chemical and biological sensing elements, integrated with optical and electronic devices may allow this and are described in a later section of this review.

Laboratory Measurement

Monitoring the water environment still relies heavily on the collection of field samples and subsequent analysis within a laboratory. In part this is historic but another reason is the lack of available analytical technologies to allow accurate analysis for many chemical parameters of interest at the required concentrations of environmental interest. At very low concentrations, analysis by a skilled analyst using sophisticated equipment may be required to give results that are sufficiently accurate and reproducible to allow firm decisions as to whether a contaminant is changing in concentration with time or exceeds its environmentally quality standard.

The analysis of environmental contaminants can be complex from several points of view. The chemical of interest may have to be separated from a wide range of other natural

chemicals, which are present at concentrations several thousand times greater, to prevent interference with the measurement and to allow unequivocal identification. Also, the concentration of contaminant may be too low for direct measurement in the sample so some form of pre-concentration is required and this can lead to losses and loss of accuracy.

The work and time required for good quality environmental analysis leads to high costs due to skilled staff costs, the need for sophisticated and expensive equipment and the provision and maintenance of suitable laboratories where analysis can be carried out under conditions that minimise contamination of the samples.

Accurate analysis at low concentrations is not guaranteed simply by the use of skilled analysts, as many inter-laboratory tests have demonstrated over the years. Methodologies need to be developed to suit particular sample types and tested in a systematic manner to produce information on the accuracy, precision, detection limit of the procedure and its freedom from interferences due to the sample matrix. These factors are covered by the term 'Analytical Quality Control', which was discussed earlier.

The ability to reliably detect and measure trace contaminants in the environment has increased dramatically in the last twenty years with the introduction of microprocessors as an integral part of many analytical instruments. Mass spectrometers now form part of the detection systems of many laboratory instruments for analysing trace metals or organic compounds with powerful computers used to gather the data in real-time and search digital libraries so that identification of quantities as low as a few picograms (10^{-12} g) of analyte can be made with 99% certainty in many cases.

A range of techniques is now available for pre-concentrating the analyte to allow low detection limits in the sample, such as "purge and trap" for volatile chemicals (e.g. chloroform) whereby the analyte is purged by a stream of inert gas from the water sample then trapped at very low temperature prior to analysis. Other pre-concentration techniques, such as solid-phase extraction, rely on adsorption of the analyte onto beads prepared from silica, polymer or carbon based material, held in small columns, and

subsequent desorption prior to analysis. The use of such techniques can result in a concentration factor of a hundred or thousand times to give lower detection limits.

A description of the range of instrumentation available to a well-equipped modern laboratory is beyond the scope of this review but typically will include the following two examples:

- *Inductively Coupled Plasma Mass Spectroscopy, mainly for metal analysis. The water sample is sprayed into a plasma torch at high temperature to produce free atoms and ions. These ions are then directed to a mass spectrometer, which identifies the elements from the extent they are deflected by a magnetic field and measures their amount from the current produced at the detector.*
- *Gas Chromatography Mass Spectroscopy, for organic analysis. The organic chemicals of interest are removed from the sample using some form of pre-concentration and transferred to a solvent. A portion of this solvent-based concentrate is injected into a coated glass capillary column (perhaps 100 m long) at elevated temperature and carried through the column by a gas flow. The column coating preferentially adsorbs the sample constituents with the result that they separate from one another as they pass through the column and are then detected at the outlet. The time required to elute from the column combined with the mass spectrum produced by the detector allows a very high confidence in the identification of many chemical contaminants.*

This brief overview of a couple of techniques available to a well-equipped laboratory perhaps illustrates that techniques are available to allow the measurement of trace contaminants in water samples for a huge range of potential contaminants in the water environment. The majority, but not all, of the contaminants of environmental concern that require monitoring under the WFD can be measured within a laboratory with sufficient accuracy providing good sampling and sample preparation techniques are followed to avoid sample contamination and to ensure sample preservation.

However, the tests do take many days to perform in many cases and are not suitable for detecting contamination from sporadic events. The future will look towards developing and employing sensors in the field that can provide continuous monitoring capabilities with minimum maintenance and wireless transmission of data. Sensor technologies are available for the continuous monitoring of a relatively restricted range of analytes at the present time and are discussed briefly below. More exciting capabilities are in sight due to new technologies coming on-stream that promise to significantly enhance remote monitoring and these are discussed later.

Field measurement

Current situation

Pollutant concentrations in our waters are changing as a result of anthropogenic inputs and changes in the water flow. With monthly sampling and analysis, it is unlikely that the concentration maxima are detected. The establishment of networks using autonomous monitoring systems has generated great interest. Sensor & continuous monitoring research has gained interest due to the need to obtain a selective response for a particular analyte at concentrations of environmental importance. Further, a considerable research activity has grown in the area of integration of sensors with low power wireless networks (LPWNs),⁴ though there is a significant challenge in bridging the communications technology with the sensor technology. Future developments in sensing will see the convergence of the chemical and biological sensors with LPWNs. The latter will require the scale-up of devices that are reliable for long periods in the field.

Chemical Monitoring

Water quality monitoring systems have been available for several decades for some physical and chemical parameters such as pH, conductivity, and temperature. Various spectroscopic instruments are available that can operate in the field and measure the analyte of interest, e.g. nitrogen species, phosphate, and others, by reaction with a reagent to form a coloured compound that can be detected by optical means. To be suitable, the analysers must have the capability to run for weeks with a sufficient stock of reagents and calibration standards stored within the instrument. The advantage of such systems lies in the wide range of chemistries available from laboratory-based instruments that can be translated to many field applications.

More sophisticated monitoring capabilities have been developed to address the analysis of a group of chemicals in the environment and these often utilise a field version of the chromatographic instruments used in the laboratory. Examples are ion-exchange

⁴ Diamond D, *Anal Chem*, (2004) 75(15) 278A-286A

chromatographic instruments that can continuously separate, detect and measure ions of environmental interest like nitrate, sulphate and phosphate. Chromatographic systems have also been developed for the analysis of organic pollutants such as phenols or a range of volatile solvents to allow monitoring to very low concentrations and with a high degree of specificity.

The disadvantage of many of the currently available field-monitors lies in the cost of purchase, the need for regular maintenance ⁵and, in some cases, a fairly bulky footprint, which makes them expensive to install if protective enclosures or platforms are required.

Improvements in sensor technology have led to the development of instruments called sondes with multiple sensors, perhaps six or eight, and which can be left submerged in a watercourse to log data at regular intervals. The data is then downloaded at regular intervals by computer or can be transmitted using Wireless USB and other communication interfaces.

These types of instrument, allied to ongoing developments in sensor technology, hold the promise of a new generation of water quality monitoring instruments that will be cheaper to produce, have a hugely expanded range of capability, as well as requiring little maintenance due to self-calibration capabilities. This is an area of R&D that is worthy of financial support to give a national competitive lead as well as supporting the maintenance of sustainable water in future years.

Biological Monitoring

Some biological monitoring techniques have been available for a long time but have only relatively recently been considered for use in support of legislation. Interest has been heightened because of the monitoring requirements of the WFD. Some of the alternative biological methods are laboratory based (off-site) and depend on the use of spot sampling. Others can be used in the field (on-site), for instance on the riverbank. A further set (*in situ* methods) can be used directly in the water. The latter methods have the advantage that they avoid the potential problems associated with taking samples, and with their

⁵ Whelan, A and Regan F, J. Environ. Monitor. 8 (2006) (9): 880-886

transport, storage, and preparation for analysis. Biological methods provide mainly qualitative data, and are not able to give information on the levels of individual contaminants, which must generally be measured by chemical analysis.

One solution to the problem of detecting water pollution events that has been used for many years is to deploy living organisms (usually sessile animals such as bivalve molluscs, but fish have been used) in the environment to be monitored, and to measure the concentrations of pollutants accumulated in their tissues. This bioaccumulation gives a qualitative indication of levels of pollutants to which the organisms were exposed during deployment, and can be used in a comparative way between sites and between times to measure spatial and temporal variation respectively. The most commonly used organisms are zebra mussels (*Dreissena polymorpha*) in freshwater or the blue mussel (*Mytilus edulis*) in marine or transitional waters.

There are some drawbacks to the use of this method. It is not possible to expose organisms in harsh conditions or where there are toxic levels of pollutants such as exist in some industrial and domestic discharges. The animals often contain measurable levels of some pollutants before deployment and there is a need to deplete them prior to use, and to take large control samples at the start of the monitoring campaign. The analysis of tissues from the organisms is difficult, and involves expensive and time-consuming sample preparation steps. Some pollutants are apparently not bioaccumulated not because they are not present in the water, or are not taken up, but because the animals can eliminate them at a rates that match the uptake rates. The advantages, however, are that the information generated is of direct biological and toxicological significance.

Immunoassay (IA) methods use antibodies (special forms of protein) with a highly specific recognition site that allows the recognition and specific binding of antigens (shorthand for antibody generators) that are foreign substances that can generate a specific antibody. For the development of an immunoassay, an animal produces antibodies in response to an injection of the target compound (that serves as the antigen). The antibodies are then isolated and tested and if one is found which can bind the antigen and thus serve as a basis of an assay, the antibody is produced in mass culture. Immunoassay tests can

therefore be useful additions to water quality screening, the primary function of the tests being to provide a qualitative to semi-quantitative screening to detect the presence or absence of a targeted chemical or chemical family.

Generally, the IA methods were developed to recognise antigens that were large molecules, and in particular proteins. However, recent developments have led to the production of antibodies against small organic molecules such as pesticides, and certain metals such as cadmium and mercury that normally would be unable to produce an immune response.

The basic principle of most IAs is the binding of an antigen by antibodies (usually immobilised on a surface/support), and that this event is coupled with mechanisms that transduce and amplify that event into a measurable signal. The measurement generally reflects the availability of binding sites after contact with the sample containing the antigen/analyte. Labels based on fluorescence, chemiluminescence, enzymes or radioisotopes are used in order to produce a measurable signal that quantifies the available sites. This is therefore an indirect measure of analyte concentration, and the results are expressed in terms of analyte equivalents.

As discussed above, the labels used in IAs can be radiochemical or fluorescent tags, or commonly enzymes. If an enzyme is used as a label it provides amplification of the signal since one molecule of enzyme can turnover many molecules of substrate, usually to produce a coloured product that can be measured by spectrophotometry. Such enzyme-linked immunosorbent assays (ELISAs) are widely available in various formats including coated-tubes, magnetic particles, or 96-well plates, enabling simultaneous processing of a large number of samples (high throughput).

These methods can be very sensitive with limits of detection in the ng/l range, and upper limits in the range of 10 to 100 µg/l. They can be very specific, but some may suffer from cross reactivity with compounds similar to the target analyte. An example of this is provided by assays for the triazine herbicide atrazine, where there is a high cross-reactivity

with closely related analogues (ametryn, propazine or the atrazine degradation product de-ethylatrazine).

Environmental quality standards (EQSs) for some priority pollutants fall within the working range of these assays. This and the potential for the application of robotics and high throughput technology make these methods particularly promising for screening purposes. The major advantage of IA test kits is that they are often produce results comparable with those obtained with chromatographic methods, but are relatively easy to use.

Generally they require minimal sample manipulation but may be affected by sample matrix effects (e.g. DOC, pH, and ionic strength of the water). In order to minimise these effects calibration standards must be prepared using water with characteristics equivalent to that of the sample. Since some IAs can be used on-site, they are potentially useful for rapid mapping of contaminants in an aquatic environment.

Sensors

Sensors can provide a valuable resource for monitoring the aquatic environment. Sensors provide a link between the world in which we live and the world of modern communications systems.⁶ Sensor systems make it possible for us to obtain real time or near real-time information about things we can and cannot detect – that could be harmful or beneficial to us. There are many different types of sensors that are characterised based on the mechanism of measurement. The most common types are chemical and biological sensors.

While much of the chemical monitoring to date has been focused on chemical sensors for chemical and physical parameters much work is underway on the development of biosensors for monitoring the chemical status of the environment.

A chemical sensor is a device that consists of a transducer and a chemically sensitive material that generates a signal related to the concentration of a particular species in a sample. In a similar way a biological sensor or biosensor, is a device that consists of a transducer and a membrane that contains biological material such as an enzyme or

antibody that generates a signal related to the concentration of a particular species. Biosensors have been developed for use as continuous water monitoring systems that can provide on-site measurements of both inorganic and organic priority pollutants.⁷ Gu and co workers applied an early warning system for monitoring toxicity of effluents.⁸

The aquatic environment contains a vast mixture of chemical and biological species that provides a challenge for the analyst. An ideal sensor is a device that will only detect a specific target analyte present in a particular sample. However, the complex nature of many samples hinders the sensors ability to detect the target analyte. As a result it becomes necessary to design sensors with a degree of specificity while discriminating against some interfering species.

The developments in sensor technologies have been assisted by the growth in the area of device and platform fabrication techniques, miniaturisation and integration of many components in a single device. In the past decade, fibre optic sensors have reached much attention with many examples of laboratory concepts evolving into field prototype⁹ and eventually product. Recent advances in fibre optic capabilities¹⁰ i.e. novel optical platforms, has meant a greater versatility in developments of sensors in this area. The underlying science continues to grow with novel concepts in measurement techniques and new fibre optic sensor components emerging from the international research community. The driving force behind the development of sensor technology includes general health monitoring, environmental monitoring requirements (e.g. under WFD), food regulations, the wireless communications advances, workplace health & safety and new trends in technologies e.g. "SmartCoast, Smart Bay, smart garments" etc.

Exciting developments have taken place in recent years using a variety of optical, biometrics and other technologies, sometimes with integrated data processing and reporting capabilities. If these can be realised at a commercial scale they will form the

⁶ Shepherd, R, Beirne, S, Lau, K, Corcoran, B, Diamond, D, Sensors and actuators – B Chemical, 121 (2007) (1): 142-149

⁷ Bhattacharyya J, Read D, Amos S, Dooley S, Killham K, Paton GI, (2005) Environ Pollut 134:485-492

⁸ Gu MB, Kim EJ, Cho J, Hansen PD, (2001) Environ Monit Assess 70: 71-81

⁹ Kraft M, Jakusch M, Karlowatz M, Katzir A, **Mizaikoff B**, Applied Spectroscopy 57(2003) (6): 591-599

¹⁰ McCue RP, Walsh JE, Walsh F, **Regan F** Sensors and Actuators B – Chemical, 114 (2006) (1): 438-444

launch pad to other developments that will enlarge the range of environmental contaminants that can be monitored. One factor that is facilitating such capabilities is the advent of wireless telecommunications technology, which allows signals to be detected and transferred using mobile phone systems from field to laboratory to give warning of significant pollution or to allow trend analysis. This communication capability can be integrated with physical transducers and chemical and biological sensors to give what is essentially an autonomous sensing instrument that can exist in the field and communicate its data with little or no intervention required. The benefit of such devices is that they could be deployed at key points of a monitoring network or at high-risk locations to provide continual monitoring of the water network with the signals transmitted, collected, processed, interpreted and displayed on a real-time basis so that rapid intervention could take place as the need arose.

Specific sensors are available for use with hand-held instruments or with remote autonomous systems using a variety of data transmission approaches, as detailed on their environmental products website. Companies currently can provide multi-sensor modules covering, for example, DO, temperature, conductivity (salinity), pH, oxidation-reduction potential (ORP) and pressure. Key water quality parameters worthy of study and development of technologies are for dissolved oxygen (DO) and nutrients.

Recent advances in electrochemical sensors for dissolved oxygen have included the use of thick film (screen-printing) fabrication and photolithographic technologies for preparation of low-cost or micromachined devices.^{11, 12, 13} Some microelectrode devices that have been prepared manually in the research laboratory, and have been reported to offer fast response, low turbulence effects and incorporation of solid-phase materials¹⁴ also sensitivity over the range of concentrations has been noted.¹⁵ Photolithographically microfabricated microelectrodes and microelectrode arrays have been investigated by a number of researchers. Wittkampf *et al.*¹⁶ developed a three-electrode Clarke-type oxygen sensor compatible with CMOS technology. A gel electrolyte within a calcium alginate layer

¹¹ W Glasspool, JK Atkinson, *Sens Actuat B* (1998) 48, 308.

¹² JK Atkinson *et al*, *Sens. Actuat*, (1999) 54, 215.

¹³ A. Gac *et al*, *Meas. Sci. Tech*, (2002) 13, 2062.

¹⁴ TRS Wilson *et al*, *Sci Total Env*, (1993) 135, 115.

¹⁵ D Pletcher, S Sotiropoulos, *Anal Chim Acta*, (1996) 322, 83.

¹⁶ M Wittkampf *et al*, *Sens Actuat B* (1997) 43, 40.

was constructed and the oxygen-permeable membrane was then fabricated on top of the microfabricated electrodes. This system is reported to operate with no signal decay for 12 h. Other microfabricated Clarke systems include those by Lee *et al.*¹⁷, and Gobel *et al.*¹⁸ Yang *et al.*¹⁹ used thin-film arrays of silver cathodes for oxygen sensing. The sensor company YSI (USA)²⁰ has been active in getting sensor devices in the field, using a patented microelectrode array (MEATM) device.

In view of trying to prevent *in situ* sensors from being fouled by components of the waters, a floating ball dissolved oxygen system is available.²¹ This consists of a flat-ended sensor mounted into a relatively large diameter spherical flotation collar. This is situated in the water under investigation and due to the design solids do not readily lodge. Problems like membranes fouling, and reference electrode drift, associated with electrochemical sensors are well known, and as such a number of research groups have sought to develop optical oxygen sensors. The latter are based on oxygen's ability to modulate the optical (luminescent) properties of certain dye substances. These devices incorporate a dye into a substrate. The optical properties of the dye are then read. However, the dye molecule must of course be in contact with the liquid being measured so the transduction is not in contact but the molecular recognition is.

The Hach DO sensor has reported promise in monitoring DO in the brewing industry. Based on Luminescent dissolved oxygen technology the Hach LDO™ reports greater stability than other devices on the market. There are many publications^{22,23,24,25,26,27,28,29} relating to chemical and physical development of such optical sensors, covering topics such as suitable dye materials, their incorporation into different inert matrices as well as optical transduction mode. Many such sensors have been studied in the lab and shown to be stable and to be operable in complex multicomponent liquids (wastewaters, biological

¹⁷ KH Lee *et al.*, *Electroanalysis*, (2000) 12, 1334.

¹⁸ J Gobel *et al.*, *Water Sci Tech*, (2003) 47, 127.

¹⁹ Z Yang *et al.*, *Anal Chim Acta*, (1997) 357, 41.

²⁰ YSI Inc, www.ysi.com

²¹ ABB, www.abb.com

²² MT Murtagh *et al.*, *Electron Letts*, (1996) 32, 477.

²³ AK McEvoy *et al.*, *Analyst*, (1996) 121, 785.

²⁴ C McDonagh *et al.*, *Analytical Chemistry*, (1998) 70, 45.

²⁵ FN Castellano, JR Lakowicz, *Photochem. Photobio.*, (1998) 67, 179.

²⁶ AN Watkins *et al.*, *Appl Spectr*, (1998) 52, 750.

²⁷ D Garcia-Fresnadillo *et al.*, *Langmuir*, (1999) 15, 6451.

²⁸ J. Diaz-Garcia *et al.*, *Anal. Chim. Acta*, (2001) 429, 55.

²⁹ C McDonagh *et al.*, *Sens Actuat B*, (2001) 74, 124.

cell growth media – latter especially popular as it paves way to monitoring of respirometry of cells and their responses to chemical challenges).

YSI Inc, in a proposal to the USA's Department of Energy Small Business Innovation Research (SBIR) programme, stated that it sought to develop the next generation of oxygen sensors – overcoming the problems associated with all currently available amperometric oxygen sensors.³⁰ A German analytical instrument company, Dr Lange GmbH,³¹ also markets an optical oxygen probe based on a calibration-free probe, without need for replacement of membrane and electrolyte and does not suffer electrode poisoning by sulphide species in the water.

Nutrient sensors have recently become the subject of great interest. A number of publications has shown the development and *in situ* evaluation of nitrate selective membrane electrodes.³² A non-submersible electrode support system was developed and a field instrument was constructed comprising the nitrate electrode, a reference electrode and a temperature probe connected through a pre-amplifier to a data-logger and battery supply. The nitrate-ISE was constructed using a commercially available electrode body, with a membrane incorporated into the tip. Unisense has reported an on-line nitrate sensor.³³ This is a biosensor employing nitrate-reducing bacteria to produce nitrogen oxide which is then detected amperometrically as the same sort of device as used for DO detection. The biological component of this device makes its use in long-term deployment impossible. The Southampton Oceanography Centre has developed an optical nitrate sensor,³⁴ this is an absorption spectrophotometer that measures the absorption of light by water in the ultraviolet spectrum, giving the concentration of nitrate and is offered in shallow or deepwater application formats.

Phosphate determinations by selective electrodes are also possible e.g. a cobalt-wire electrode was developed for monitoring of hydroponic solutions (i.e. for growing plants in absence of soil). Interference from chloride, nitrate and sulphate were negligible, and this

³⁰http://sbir.er.doe.gov/sbir/Awards_Abstracts/sbirsttr/cycle18/phase1/077.f.htm

³¹ www.drlange.com

³² Braven J, et al, Analyst 128: 1067 (2003); Le Goff T, et al, J Environ Monitor 5: 353 (2003); Le Goff T, et al, Analytical Chemistry 74: 2596 (2002); Le Goff T, et al, Analyst 127: 507 (2002).

³³ <http://www.unisense.com/products/nitratsensor.html>

³⁴ <http://www.soc.soton.ac.uk/OED/index.php?page=ns>

electrode device provided chemical data equivalent to that obtained by ion chromatography or spectrophotometry.³⁵

Diamond and co-workers³⁶ has investigated the determination of phosphate in rivers in an analytical micro fluidic system and sought to demonstrate stability of the chemical reagents needed over a 12-month period. This was part of his strategy on developing autonomous sensors for environmental monitoring.³⁷

While there are limited examples of operational sensor networks a number of studies have been reported for water quality monitoring in the literature, but also many interesting approaches have been reported for other applications – using wireless sensor networks.

The approaches in wireless technology may be developed as generic technologies having applications in many areas. In a study by A. Ailamaki *et al.*³⁸ an interdisciplinary research effort to couple large environmental databases with biological and chemical sensor networks to revolutionise drinking water quality and security decision-making is described. A distribution and operation protocol for the placement and utilisation of *in situ* environmental sensors by combining (1) new algorithms for spatial-temporal data mining, (2) new methods to model water quality and security dynamics, and (3) a sophisticated decision-analysis framework is described. The project was funded by the National Science Foundation (NSF) in a programme supporting safe and secure drinking waters to the population of the United States.

In a similar study by Lundquist³⁹ a comprehensive monitoring system across and within the Sierra Nevada is described. Because of the severe terrain and limited access, few measurements have been possible and therefore meteorological and hydrologic processes are not well understood at high altitudes. However, new sensor and wireless communication technologies are beginning to provide sensor packages designed for low maintenance operation, low power consumption and unobtrusive footprints. An aqueous

³⁵ R De Marco, C Phan, *Talanta*, 60, 1215 (2003).

³⁶ Bowden A, Diamond D, *Sens Actuat B*, 90: 170 (2003).

³⁷ Sequeira M, Bowden M, Minogue E, Diamond D, *Talanta*, 56: 355 (2002).

³⁸ Ailamaki A., *Sensors and Actuators B-Chemical* 102 (1): 27-34 SEP 1 2004

³⁹ [Lundquist JD](#), [Cayan DR](#), [Dettinger MD](#) Information processing in sensor networks, proceedings lecture notes in computer science, 2634: 518-528 2003

sensor network is described consisting of an array of sensor nodes that can be randomly distributed throughout a lake or drinking water reservoir.⁴⁰ The data of an individual node is transmitted to the host node via acoustic waves using intermediate nodes as relays. Each node of the sensor network is a data router, and contains sensors capable of measuring environmental parameters of interest. Depending upon the required application, each sensor node is equipped with different types of physical, biological or chemical sensors, enabling long-term, wide area, *in situ* multi-parameter monitoring. In this work an aqueous sensor network is described, with application to pH measurement using magneto-elastic sensors.

Beyond ensuring drinking water safety, possible applications for the aqueous sensor network include advanced industrial process control, monitoring of aquatic biological communities, and monitoring of waste-stream effluents. A miniaturised low-power wireless remote environmental monitoring system is described by Yun *et al.*⁴¹, the system described has been developed for on-site monitoring of water pollution by heavy-metal ions.

For the protection of wells and a groundwater recharge, Fleishman and co-workers developed an early warning system.⁴² The monitoring network design is based on sensor measurements only. For this purpose a submersible spectrometer has been tested for multi-parameter measurements directly *in situ*. It is reported that the developed system can easily be upgraded with other new sensors. Calibration and validation data are supplied by conventional grab sampling and laboratory analysis, which is a validation approach used by all researchers in the area of sensor technologies for water quality monitoring.

The SmartCoast⁴³ project endeavours to build components of a water monitoring system incorporating a series of multiple sensor units, wide area and local area network communications and a data handling system. This monitoring system uses off-the-shelf

⁴⁰ Yang XP, Ong KG, Dreschel WR, Zeng KE, Mungle CS, Grimes CA *Sensors* 2 (11): 455-472 NOV 2002

⁴¹ Yun KS, Gil J, Kim J, Kim HJ, Kim K, Park D, Kim MS, Shin H, Lee K, Kwak J, Yoon E *Sensors and Actuators B-Chemical* 102 (1): 27-34 SEP 1 2004

⁴² Fleischmann N, Staubmann K, Langergraber G *Water Science and Technology*, 46 (3): 33-40 2002

⁴³ <http://www.dcu.ie/~ncsr/about/SmartCoast.html>

sensors and novel sensors for dissolved oxygen and phosphate. Some of the sensors are autonomous consisting of power handling capability with solar panels and an internal modem for communication. The sensor networks tested in the field demonstrate the capability of the technology, while highlighting the need to view each monitoring site individually, and assess its need in terms of monitoring requirements. Similar studies are being carried out at the Ribble Catchment, ⁴⁴ where it is reported a grid of river sensors that monitor depth and flow enable the prediction of flooding.

The future

Ideal Monitoring System

European water bodies are still poorly monitored, and one reason is the high cost for such monitoring. In the rapidly developing field of environmental monitoring there is much published research in the area of sensor development for nitrates, phosphates, organics, and metals and dissolved species. However, many of these devices never make it to the field for long-term measurements. In addition, many of the devices that are deployed are not tested in relation to parallel lab-based analyses for validation and rely only on existing data. Because the need for environmental monitoring devices is generally driven by legislation, compliance with regulatory bodies' specifications and the standardised validation of new technologies is often mandatory. Simplicity, rapidity, robustness, as well as size and reliability are essential qualities that have become priorities when monitoring the environment.

The range of parameters that can be monitored in the field is relatively limited at the moment and more complex analysis requires samples to be returned to a laboratory for analysis. This is not only expensive from the point of view of sampling effort but involves a delay of hours or days before results become available from the laboratory. This is not a satisfactory situation when river systems are being monitored that may flow through several countries with many potential sources of pollution that can affect water quality use for water supply abstraction or the maintenance of fisheries. More rapid techniques are

⁴⁴ http://save-the-ribble.blogspot.com/2006_10_01_archive.html

required that can be used at monitoring stations to give continuous monitoring of water quality or can be deployed in the field in the form of inexpensive monitoring devices, preferably with report-back capabilities.

While the measurement and detection of environmental pollutants can be successful under laboratory-controlled conditions, continuous *in-situ* monitoring remains the most challenging aspect of environmental sensing. One of the visions of wireless sensor networks is that they enable remote monitoring of the environment. However, most current deployments use a laptop or PC to control the sensor network. There is not much evidence of the use of GPRS modems to remotely control sensor networks and enable real-time continuous monitoring.

Monitoring of water bodies will also increase over the coming years in the light of the development of WFD River Basin Management Planning (RBMP), which will require relevant monitoring data for better risk assessment of various pressures (including pressure from climate change, which will lead to resource scarcity in some areas as well as water quality changes, and increasing demand from population and manufacturing growth), identification and follow-up of the efficiency of programmes of measures, and compliance checking (based on EQS and Groundwater Quality Standards). Monitoring at river basin level is a significant financial burden using conventional sampling and laboratory based techniques but sensors offer the potential to reduce these costs considerably as well as providing more useful, continuous monitoring capabilities.

The ideal monitoring system of the near future might consist of a network of sensors deployed at key locations, capable of autonomous operation in the field for perhaps a year or more. In addition to basic water quality parameters such as dissolved oxygen, conductivity, pH and nutrient status, new developments will allow sensitive and specific monitoring for a range of organic contaminants such as pesticides or chlorinated hydrocarbons using some of the technologies described earlier. In addition, toxicity monitoring will be used as a screening tool, albeit non-specific, for detecting the advent of unsatisfactory water quality.

The data from the monitors will be communicated by wireless technology for statistical processing and interpretation by expert systems. Rising trends for any constituent of interest or breaches of EQS will alert scientific staff and lead to the collection of samples for laboratory analysis for the purpose of identifying the chemical of concern using the array of tools available to a modern laboratory.

Although some elements of this ideal system are in place others, ongoing research and development is required and some of these requirements are highlighted below.

1. Experts have highlighted the need for development of sensor technology for a number of key environmental parameters. Chemical sensors are needed for measurement of particulate and dissolved organic carbon, nitrogen, and phosphorus, phosphate and acetate, and sensors for speciation of elements would be desirable.
2. There is a need for robust, stable sensors that can operate at extreme temperatures and difficult environments.
3. The development of sensors for identification and detection of microbial activity is a high priority.
4. There is a clear need to ensure that the accuracy, precision, and interpretation of sensor data be improved.

The development of embedded networked sensing (ENS) systems has added huge advantages in sensor technology development and has been rapidly followed by successful deployment for investigations in environments ranging from forest ecosystems, to rivers and lakes, and to subsurface soil observations. As ENS systems have been deployed, many technology challenges have been successfully addressed. For example, the requirements for local and remote data access and long operating life have been encountered and solved with novel hierarchical network architecture and unique, low power platforms.

The coming decades will witness a rapid growth in moored, cabled, and autonomous observatories to investigate a spectrum of basic processes in aquatic environments. This technology will provide platforms for testing and validation of new sensor-based monitoring technologies.

Several technologies are under development that allow the production of suitable sensors that meet many of the characteristics summarised above such as:

- *Miniaturised membrane based sensors, essentially ion-selective electrodes with chemically sensitive membranes and internal reference electrodes*
- *Colorimetric analysers on a small scale that utilise micro-volumes of reagent to react with the parameters of interest and micro-optical cells with low power LED sources to measure the intensity of colour produced.*
- *Biosensors that use micro-array technology with biochips made of two components, a biological sensing element (tissue, enzyme etc) and a transducer (electrochemical, optical etc) to produce a detectable signal in response.*
- *Non-invasive sensors that irradiate a water surface then detects and analyses the fluorescent and scattered light to allow surrogate measurement of gross parameters like BOD and COD.*

Many of these developments rely not only on being able to devise a suitable optical-electronic integration but also need the development of software capable of processing signals using complex algorithms.

Development of such sensors needs a multidisciplinary approach and access to facilities where their fabrication can be accomplished at low cost and in a quality assured environment. For example, future development will require advances in several areas in parallel, including:

- *New molecular receptors of high selectivity to a wider range of species capable of remaining active under field conditions for a year or more*
- *Polymers and other materials for use in holding the receptor in place*
- *Developments in solid state based sensors to eliminate the need for internal electrolyte reference solutions*
- *Improvements in signal processing technologies especially to handle multi-component sensors generating large quantities of data*

- *Integration of biological sensing elements with transducers (electrochemical, optical, thermometric etc) will deliver sensors capable of detecting very low concentrations with a high degree of specificity.*

Such developments will allow biosensors and novel chemical sensors to make an increasing contribution to water quality monitoring allied to developments in nanotechnology.

The ideal water quality sensor would have a combination of several desirable properties, including:

- *Small size with the capability of dispersal within the water environment*
- *Use stable and renewable reagents to give long life in the field and reduce contamination problems*
- *Ability to utilise decay-time measurement techniques to reduce calibration requirements*
- *Non-contact to eliminate problems from fouling*
- *Communication capabilities as part of the sensor*

Some of these properties are being realised in the current generation of new sensors but serious funding is required to allow further research and to bring some of the instruments from the laboratory to the production line at reasonable cost. Research effort is also required to extend the range and complexity of analysis available.

Conclusions and recommendations

We are facing exciting challenges in the development of a water-monitoring programme in Europe. At a time when technological advances are providing new sensor capabilities, novel network capabilities, long-range communications technologies and data interpreting and delivery formats via the World Wide Web, we never before had such opportunities. However, the challenge is great. The success of a monitoring system that can provide real-time data on a variety of water quality parameters over long periods of time will rely on support of teams of researchers in the development of the building blocks of the systems, in working together to develop the internet scale sensing and in scaling that technology up, in order to validate its performance.

Currently passive sampling technologies provide an opportunity to obtain representative reliable information that could be used to support robust risk analyses, and avoid the potentially high costs of making inappropriate responses on the basis of flawed data collection. This approach will provide a means of supporting the legislation in the period necessary for the development of the necessary range of field validated sensors, and indeed could be used in assessing the field performance of sensors for a wide range of metals, and organic compounds of environmental concern.

Currently we have the capability i.e. the building blocks, to achieve our ideal scenario of measurement of multiple water quality parameters simultaneously in real-time. We need to improve the quality of some of our more sophisticated sensors for nutrients and biological contaminants while using the simpler devices cleverly in embedded networks.

We are heading toward the type of capability where the public will be able to access the information of their desired holiday destination on-line for example - and not only investigate the local weather conditions – but also the bathing water quality.

We will have the capability where agencies can intercept serious pollution incidents by evaluating the change in a water quality parameter measured numerous times every day – as an alarm sent to their mobile phone or by e-mail.

We will be able to predict the occurrence of an algal bloom or identify the presence of faecal pollution before it contaminates a population's water supply.

However, in order to achieve these challenging objectives, researchers need support at a variety of levels:

- *Funding to develop the range of calibration data available for passive samplers particularly for polar organic pollutants, and to demonstrate the robustness of these samplers alongside current monitoring networks.*
- *Continuity of funding for fundamental research to improve and further develop new sensors, materials and communications systems. Greater emphasis is desirable in the development of sensor networks and in real-time sensors for water quality monitoring. There is a need for a hierarchy of devices where the simplest devices can find use in monitoring water quality, as well as very sophisticated real-time monitoring networks – that can operate intelligently providing continuous measurements, actuate responses or further measurements.*
- *Development of reference testing sites for novel technologies and continuous validation that could be used by researchers, companies and agencies as well as standardisation organisations to test and validate, and possibly standardise, technologies. There is a need for funding to carry out adequate field-testing over long periods of time. This testing would benefit from the development of test sites e.g. Smart Sites for water quality comparison studies and for testing under reference conditions. These SmartSites could act as reference test locations for agencies, academic researchers, and technology development companies to test their technologies.*
- *There is also an immediate need for research and development in the areas of biological contamination, including pathogens (faecal species and cryptosporidium), nutrients (responsible for algal blooms) and other water quality indicators (dissolved oxygen, conductivity, turbidity). Further to that resources are needed to develop prototype devices*

and laboratory / environmental trials – this should then be followed by scale-up of the devices for full-scale field trials and validation.

- *Not only is there a need for these devices, they must be robust, reliable and capable for use over long periods of time without loss of response and need for calibration. The latter is a huge challenge and thus needs further development and validation. There are many devices already developed in the laboratory that have not been tested in the field or fully validated and this is an area of immediate resource requirement.*
- *There is a real need for the funding agencies to establish collaborative research efforts in areas of sensor development, communications technologies, data management and user group interface. The need for interpretation of sensor-based data compared with spot sampling is great and while some studies have been undertaken to investigate this, it can only be done effectively when sensors are tested in the field over long periods of time.*
- *In order to ensure the integrity of the analytical data produced both by conventional laboratory analysis and the envisaged new sensors, there is a need for a EU-wide AQC facility to coordinate the performance testing of methodologies and the organisation of inter-laboratory comparison programmes.*

The challenge of water monitoring is compounded in some EU states where river basins extend across Country boundaries. Continuous monitoring networks would provide the intelligence required for investigation or observation of pollution incidents in a country that may impact the water quality of a neighbouring country.

Technology transfer can follow the latter to relevant interested companies. The scale-up phase is currently not funded in many funding mechanisms and therefore many of devices never get past the laboratory development phase. The prospect for spin-offs of new technologies is greater where proper validation of the technologies has taken place, thus providing prospective investors with greater confidence in the technologies.