Recent Advancements in Water Quality Monitoring - the use of miniaturized sensors and novel analytical measuring techniques for in-situ and on-line real time measurements

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Abstract: The European Union Water Framework Directive (WFD -2000) has created a demand among Government monitoring agencies and legislative bodies throughout Europe for water quality monitoring systems that are able to monitor reliably a larger number of water quality parameters at regular intervals. This requires trained personnel, reliable instrumentation and in the long run high laboratory costs to achieve the expected monitoring goals. To achieve the WFD-targets, there is a need for development of cost-effective instrumentation using advanced technology and shifting to automation to reduce overall analytical costs. The actual growing demand is requesting more and more that water quality is to be measured continuously and in real time. **WA**ter **R**isk **M**anagement in **E**u**R**ope (**WARMER**) is a research project funded by the EC 6th Framework Programme, under the IST-Environmental Risk Management program aiming to fill-up some of these existing gaps in automated water quality control and also to fulfil the growing demands in real-time monitoring to minimize effects from accidental spills. The project is being carried out by nine partners from seven European countries.

Keywords: water pollution, remote sensing, early warning, data handling, environmental risk management, on-line sensors.

Introduction

The current European Water Framework Directive, implemented in the European Union (EU) is a structured programme for management of water resources through Integrated River Basin Management (IRBM), with the aim to achieve overall good quality of water by 2015. This is accomplished through careful monitoring of surface water and groundwater habitats in Europe and implementation of stepwise improvements gradually to attain a 'good water status' which is the ultimate goal. ´The development of WFD was a long process where 'river basin' was considered as a basic unit for improvements of both surface and groundwater quality as well as quantity. A large number of specialists from different fields were brought together, including both scientists and legislators and they worked together with International River Basin Commissions and other stakeholders to develop strategic WFD-documents and guidelines required for comprehensive water resources management (EU-WFD, 2003; also http://forum.europa.eu.int/Public/irc/env/wfd/library.)

Water Pollution in Europe

Historically, pollution of the aquatic environment was recognized far back in human history. By 312 B.C the Romans decided that River Tiber was too polluted to use as drinking water supply and constructed their first aqueduct. In England, river pollution was considered as an environmental problem as early as the 13th century, when laws were passed prohibiting the charcoal burners in Middlesex, from washing their charcoal in the River Thames for fear of polluting the river downstream. The pollution of the rivers really began at the time of the Industrial Revolution, in the early 19th century. Many of the other major Rivers of Europe, such as the Elbe, Rhine and Danube, experienced marked pollution problems in the late 19th and early 20th centuries. The Rhine, which is used by the Dutch as a source of drinking water, is polluted by the discharges from the German industrial region of the Rhur and sewage from several upstream urban centres. High organic suspended solids and high ammonia levels, with high biological oxygen demand were characteristic of such problems. Reduction in fish species, invertebrate and aquatic plant species was followed by a total disappearance of fish. Water quality problems of the Rhine were recognized far back as the 15th century and up to 1970s the river was referred to as the 'sewer of Europe'. To overcome this situation, among other measures regular river water quality monitoring programmes were introduced in European rivers and several international commissions were formed to manage specific tasks. The continuous chemical and biological monitoring in Europe dates back to sixties and seventies (Kramer and Botterweg, 1991) and these monitoring-systems have been continuously improved, resulting in the emergence of some reliable, robust chemical and biological sensors during the nineties and they are reviewed in detail in Butterworth et al. (2001).

The need for cheap and generally accessible system for pollution control and early warning was perceived in the EU with the joining of new members. The task of the former SEWING project (**S**ystems of **E**uropean **W**ater monitoring), successfully completed in 2005 was to develop cheap and reliable micro-systems for this purpose (SEWING, 2005). The main goal of SEWING project was to produce a relatively cheap and generally accessible system for in-situ and in real-time monitoring and early warning of water pollution with inorganic ions. Both surface water and groundwater were selected for monitoring, particular in agricultural and mining areas and ammonia, nitrate, calcium, potassium and sodium were selected as parameters to be measured (Brzozka et al., 2004), and a prototype was developed under SEWING project using solid state chemical sensors (i.e. ISFETs / CHEMFETs). This objective is measurable in the following respect by producing large number of cheap, user-specified micro-sensors; to monitor different water pollutants in high risk regions should have the possibility of early warning which could prevent disastrous pollution events (Filipkowski et al., 2005).

WARMER Project – General System Architecture

WARMER project was launched in September 2006 as the successor of the SEWING project aims to create an extended system for real-time water quality monitoring with the main objective of Environmental Risk Management. To accomplish this objective, the project integrates different technologies in the areas of chemical sensors, analytical chemistry, micro-mechanical fluidic systems, Information Communication Technology (ICT), remote sensing and extensive networking of environmental water monitoring data in space and time. This new type of water quality monitoring system will integrate the following components to create an intelligent device comprising of: (i) miniaturised chemical and biological sensors for different pollutants (both organic/inorganic) in water; (ii) micro-mechanical systems for micro-fluidic sample handling; (iii) modular data processing software for optimum data fusion from different sensors; (iv) integration of all new elements in an easily field-deployable monitoring system. In addition there will be possibilities for integrating remote sensing data collected from near real-time satellite, and/or real-time light aircraft, and finally all these components put together would form a Web-based integrated water risk management system. The system developed will be tested in laboratory as well as in field prior to preparations are made for commercial production.

Sensors to be used in the water monitoring system

Four partners are responsible for production of different sensors to measure chemical (include nutrients and heavy metals) and biological parameters. So far the following results are obtained, and also the plans for future development are included below.

Planar ion-selective microelectrodes

Determination of inorganic charged pollutants (NO_3^-, NH_4^+, K^+, Na^+, Cl^-) is being performed using new miniaturised solid-state potentiometric sensors as planar ion-selective electrodes with polymeric membranes. Two structures of back-side contact miniaturised transducers are being developed: electrodes developed using silicon technology (Institute of Electron Technology, Poland) and solid-state Au and Ag/AgCl fabricated on epoxy-glass laminate support (Politechnika Warszawska, Poland). The all-solid-state microelectrodes (squares 5 × 5 mm, 0.5 mm in thickness) sensitive to inorganic ions are obtained by the deposition of polymeric membranes on the transducer surfaces. The ion-sensitive layers are based on commercially available ionophores and plasticised PVC. The method of membrane deposition, involving an automated dispensing unit, will enable the fabrication of cheap industrial based microsensors.

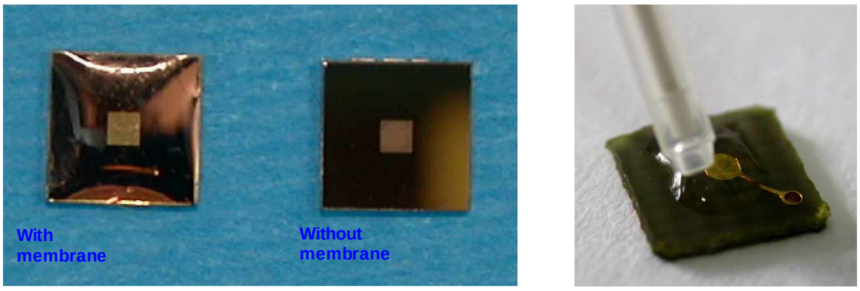

Figure 1. (Left) planar Au microelectrodes developed in silicon technology,
(Right) planar Au or Ag/AgCl microelectrodes fabricated on epoxy-glass laminate support
(double-sided printed circuit board).

The reliability and measurement parameters of the solid-state electrodes developed will be studied in detail during the project. However, a wide measurement ranges (at least 1-4 pX), high selectivity towards primary ions and favourable durability (2-3 months) of the microelectrodes are expected. Each microelectrode will be packed in an easily mountable modular flow-cell made in ABS material in a specific designed multiparametric assembly coupled with a miniaturized Ag/AgCl reference electrode (Medbryt, Poland).

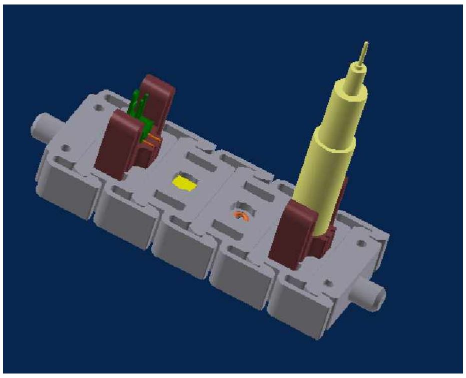

Figure 2. Multiparametric flow-cell assembly using planar potentiometric microelectrodes

Stripping voltammetry sensors

At present, the most common methods used for the analysis of heavy metals are flame atomic absorption spectrometry, graphite furnace-atomic absorption spectrometry, inductively coupled plasma-atomic emission spectroscopy and inductively coupled plasma-mass spectrometry. These techniques, commonly used for measuring trace metals in an advanced laboratory are not suitable for the task of on-site assays. By contrast with these techniques, electrochemical methods offer several advantages related to cost and simplicity. The most widely used electrochemical methods for heavy metals analysis, are stripping techniques. These techniques enhance selectivity and sensitivity by combining separation, pre-concentration and determination, all in one process. New sensors for stripping analysis of heavy metals based on screen-printed technology and integrated in an automated microfluidic hydraulic system are in process of development (Universitat Autonoma de Barcelona & Institut Català de Nanotecnologia, Spain). Improving the lifetime of these sensors by using novel composites and nanocomposite inks (based on carbon nanotubes and other nanomaterials) and specific analytical procedures to run the automatic analysis is one of the main objectives. The screen-printed electrodes will be managed by as specific multichannel hardware interface able to generate in a precise way low currents to manage the voltammetric analytical measuring process (Palmsens, The Netherlands).

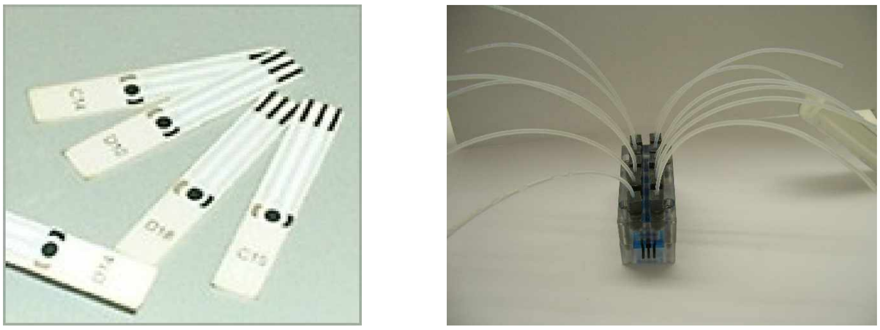

Figure 3. (Left): Typical screen printed electrodes
(Right): Cartridge chip prototype for screen-printed sensors.

Heavy metals - detection with chalcogenide glass potentiometric sensors

Along with the stripping voltammetry technique, the electrochemical analysis of liquid media using potentiometric sensors (ion-selective electrodes) and sensor arrays (multisensor systems) is a widely used analytical method and is highly prospective for the analysis of complex multicomponent solutions. The sensors to be used in the present project are based on chalcogenide glasses (St Petersburg University, Russia), which are chemically highly stable materials ensuring the highest possible durability and stability of the sensors based on such materials (Fig. 4). These materials are based on some typical glass-forming compounds such as arsenic sulphide or arsenic selenide and usually include some compounds of different transition metals. Finally, such composites are sensitive and selective to copper, lead, cadmium, silver, chromium(VI), iron(III) and some other ions in solutions. In recent years, efforts have been made to develop continuous modalities of analysis using chalcogenide glass sensors. Of particular importance is the possibility to detect heavy metal free ions in low concentrations (at nanomolar level), which is typical for most natural water contaminations (Legin et al., 2004). These sensors are going to be integrated in the same type of modular “plug-in” flow cell described above for the planar potentiometric sensors.

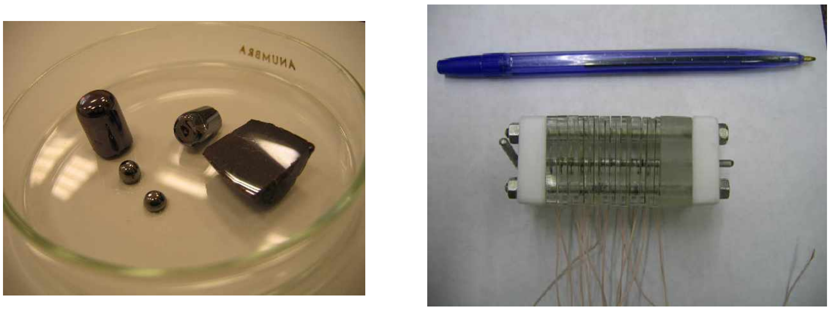

Figure 4. (Left): Typical examples of chalcogenide glasses bulk pieces and sensor membranes (Right): Chalcogenide sensors mounted in flow-through cell

Colorimetric and fluorimetric on-line measurements

The main aim of the research is to develop and run a flexible miniaturized and fully automated analytical cartridge, base on the micro **L**oop **F**low **A**nalysis (μ**LFA**) technology (SYSTEA, Italy), which will be designed in different versions to run in a conditioned and long-term mode for using with wide range of chemical sensors developed by project partners. Additionally, μLFA-analytical cartridge forms the central nucleus of the instrument as it is used for all standard colorimetric or fluorimetric procedures which are capable of measuring very low concentrations of an array of common chemical constituents in water and wastewater. (Due to the highly successful μLFA- technology, Systea SpA, Italy, is one of the few companies globally marketing in-situ probes to measure chemical parameters in water, using well-known and internationally tested standard colorimetric methods; see www.systea.it for details).

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Figure 5. (Left): μLFA hydraulic manifold
(Right): Miniaturized colorimetric flow-cell with fiber optics couplings.

Sensors integration within in situ monitoring probes

According to the requirements, three type of in-situ multiparametric water monitoring probes will be designed and tested:

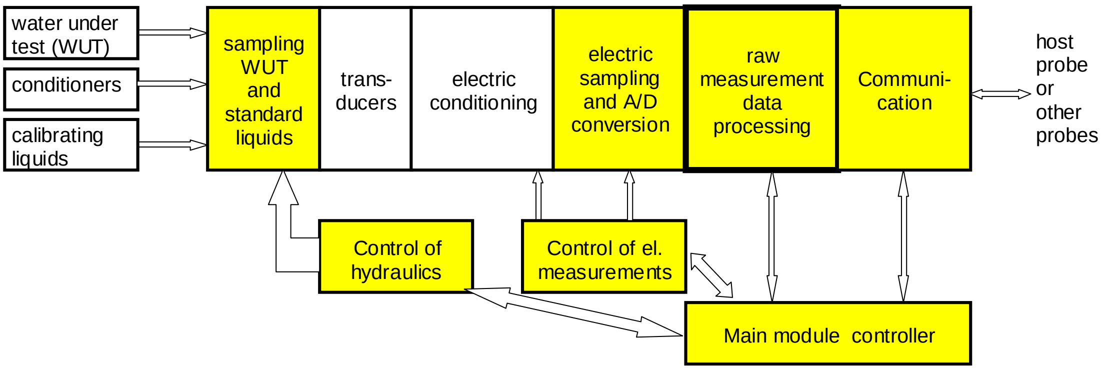
- *potentiometric sensor probe*, mounting in one or more multiparametric flow-cells the potentiometric sensors developed by partners, mainly inorganic ions and heavy metals; in case of heavy metals, a specific preliminary digestion phase will be included (for dissolved and total metals).
- *voltammetric sensor probe*, working with screen printed electrodes for heavy metals and, in the near future, even to integrate biosensors working with the same detection system; phenol measurements will bet tested using a specific selective sensor.
- *colorimetric/fluorimetric probe*, to run standard analytical methods (according to requirements).

The main common technical specification of these devices will be the following:

- external dimensions: height=550 mm, external diameter=140 mm
- external container made in PVC
- autonomous internal lithium rechargeable battery, 15 Ah, it will allow at least 250 unattended measurements
- automatic sleeping function after the end of the measurement, the probe will wake up automatically after any RS-232 command
- two part probe: analytical and reagents/calibrants compartment; most probably it will need an external DI water reservoir, a few liters to be placed on the buoy near the probe
- multiparametric capability, 4-8 parameters to be measured in a single device
- RS-232 protocol.

Particular attention will be given to data fusion; the design architecture to be applied is shown in Fig.6.

Figure 6: In-situ monitoring probe architecture layout.



To avoid cross-interferences on potentiometric sensors, three type of algorithms are going to be improved and tested integrated within the microcontroller of the probe:

- the first one based on the recursive calculation of the Nickolski equation (Brzozka et al., 2004)
- the second using a Fast Fourier Transform algorithm coupled with a neural network approach (Calvo et. al, 2007)
- Partial Least Squares method.

Field deployable water quality monitoring system

The above mentioned in-situ probes will be coupled together in an easy deployable water quality monitoring buoy with commercial multiparametric in-situ probes (by YSI-Hydrodata UK; project partner). The whole water quality monitoring system will be able to measure at required sensitivity the following main paprameters:

Table l. Main parameters to be measured by the integrated water monitoring system*

Physical-chemical	Chemical
Temp / conductivity	NH_4^+ / NO_3^-
pH / redox	Ca / Cl^-
Dissolved oxygen	Pb / Cd / Cu
Turbidity/colour	Hg / Fe^{3+} / Cr^{6+}
Chlorophyll/phyto pigments	NH_3 / PO_4
Water direction and flow	Phenols

*(according to requirements, other parameters will be included in the system)

Water monitoring data will be collected by a local remote programmable data-logger (Sysmedia, Italy); a GPS device will spatially identify any collected data with time. Data will be stored and then transmitted using GPRS to a sophisticated Web server system (www.zetaced.com, Sysmedia, Italy), which will allow not only data visualization in alphanumerical and graphic format but also manage the validation data process and remote configuration upgrades.

Integration of field and remote sensing data

Remote sensing data from satellites and aircraft play an important supplementary role to in-situ measurements of water quality parameters. Remote sensing images, which can be obtained from several instruments such as infrared radiometers, spectrometers, and imaging radars, can deliver simultaneous images over large areas. These images can be used to detect the location of polluting substances at the water surface and to map the extent of the polluted area. It is primarily in coastal regions that remote sensing is useful and practical, because large water areas can be surveyed. The most important water quality parameters that are monitored by remote sensing are oil spills, high density of algae concentrations, including mucilage and other substances that are reflected in the colour of the water surface. Monitoring systems for detecting oils spills and other water pollutions is presently under development under GMES (Global Monitoring for Environment and Security), where the use of satellite data is a major component. At present, the satellite images can be delivered a few hours after the satellites have passed over the target area. There is ongoing developments to improve the important real-time delivery of satellite data for pollution monitoring.

In WARMER project we aim to calibrate remote sensing data using real-time point measurements collected by our field monitoring system. The following key parameters will be used for the surveys: temperature, turbidity, water color and chlorophyll. Using the Web based infrastructure made available by Zetaced Web based system (www.zetaced.com) and the Web infrastructure developed during the former DISMAR project by NERSC (Norway; project partner), we intend to improve new interactive functions for near real time calibration of remote sensing images using point measurement data collected by the automated water monitoring stations, in order to develop spatial and short term temporal forecast of pollution coming from accidental spills in natural water bodies.

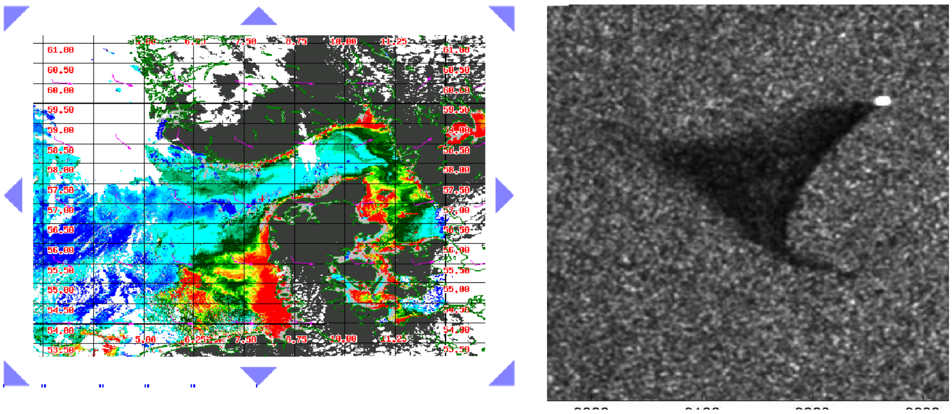


Figure 8. (Left) DISMAR map viewer [Sandven et al., (2005)]
(Right) ENVISAT ASAR image showing oil spill from a ship in the Black Sea [Malinovsky, et al., (2007)].

Conclusions

The experience gained in formulating and implementing WFD in Europe with the focus on Environmental Risk Management problems, could be used gainfully in Asia for improvement of river basins and to achieve ‘good water status’ step-wise in Asian rivers. With this intention European Union is going to help China in improving two of her major rivers, the Yellow River and the upper reaches of the Yangtze River by implementation of a WFD this year, based on same principles but with modifications to suit the Chinese situation. If it is successful, WFD could be extended to other major river basins in Asia.

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