Meeting reports

Monitoring and managing river pollutants

Report on the 3rd SWIFT-WFD Workshop, in collaboration with AQUATERRA, entitled ''Towards operational monitoring programmes and protocols for implementation of the Water Framework Directive; Chemical analysis and data interpretation of priority and emerging pollutants in the river basin'', Barcelona, Spain, 15–16 May 2006

Damià Barceló*, Rikke Brix, Marinella Farré

1. Introduction

This workshop was a combined effort of two projects funded by DG Research of the European Union (EU): *Screening methods for water data Information in support of the implementation of the Water Framework Directive* (SWIFT-WFD) [SSPI-CT-2003-502492]; and, *Integrated modelling of the river-sediment-soil-groundwater system; advanced tools for the management of catchment areas and river basins in the context of global change* (AQUATERRA). [Contract Number: 505428 (GOCE)].

In addition, this workshop also included reports on progress and recent results achieved within EU-funded project *Models for assessing and forecasting the impact of environmental key pollutants on marine and freshwater ecosystems and biodiversity*. (MODELKEY). [Contract Number: 511237 (GOCE)].

The focus of SWIFT-WFD is the evaluation of screening methods for the determination of pollutants of interest within the WFD. SWIFT-WFD is to provide the ''tools'' for an appropriate monitoring of pollutants. On the other hand, AQUATERRA is an integrated project that should provide management tools at the river-basin scale with particular relevance to the river-sediment-soil-groundwater system. Two sub-programmes of AQUATERRA are dealing with monitoring activities and also several case studies at various river basins, such as Ebro, Danube, Elbe and Meuse. Both projects, SWIFT-WFD and AQUATERRA, have a common interest in developing and using the best available screening and chemical analytical tools for monitoring pollutants at the river basin.

Based on these arguments, and in order to avoid duplication of work and reinforce expertise, a common workshop to exchange information on the results of both projects was organized. This workshop combined well the experiences gained in both projects very and was a unique platform for information exchange and dissemination.

In the course of the workshop, 25 lectures and 20 posters were presented, the main themes being:

- Progress on EU projects;
- Monitoring pollutants at river-sediment-soil-groundwater system;
- Immunochemical methods and biosensors;
- Biological effects and risk assessment; and,
- Data treatment and interpretation.

As chairman, Damià Barceló (CSIC, Barcelona, Spain) opened the workshop and was followed by Elena Domínguez, scientific officer working at DG Research, responsible for SWIFT-WFD, who outlined the projects funded under the EU's 6th Framework Programme on environmental chemical monitoring.

2. EU-funded projects

This session consisted of a brief overview of three EU-funded projects: AQUATERRA, SWIFT-WFD and MODELKEY.

Johannes Barth (University of Tübingen, Germany) described the progress of AQUATERRA, which is focused on aiding a better understanding of the behavior of environmental pollutants and their fluxes in the

Environmental Chemistry, IIQAB-CSIC, Jordi Girona, 18, E-08034 Barcelona, Spain.
*Corresponding author. Tel.: +34 93 400 61 70; Fax: +34 93 204 59 04;
E-mail: dbcqam@cid.csic.es

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soil-sediment-water system with the respect to climate and land-use changes.

Next, Werner Brack (UFZ, Leipzig, Germany) explained that the main aims of MODELKEY are to establish cause-effect relationships to link the chemical and the ecological statuses of a river basin and to identify, assess and prioritize the key chemical stressors.

Benoit Roig (Armines – Ecole des Mines d'Ales, France) presented progress on SWIFT-WFD, which included a guideline on the validation of screening methods, specific field trials and inter-laboratory exercises.

3. Monitoring pollutants

Monitoring of pollutant concentrations is an important tool in compliance with the WFD, so it is receiving marked attention. Philippe Quevauviller (DG Environment, Brussels, Belgium) started the session by describing the current status of the common implementation strategy of the WFD.

Richard Greenwood (University of Portsmouth, UK) continued by giving an overview of existing passive sampling devices and discussing pros and cons of this technique. One of the larger restrictions is the rather time-consuming laboratory calibration that is needed and the complications in applying this calibration to environmental samples. However, passive samplers are able to give a more representative assessment of the quality of water in a river basin with rapid fluctuations in pollutant concentrations.

A critical approach to the chemical-monitoring programme for water and sediments in Canada was taken by Olivier Thomas (University of Sherbrooke, Canada).

Thomas P. Knepper (Europa University of Applied Sciences Fresenius, Germany) explained that one of the major conclusions of the P-THREE project was that low removal efficiencies of P^3 (Persistent Polar Pollutants) were observed during activated sludge wastewater treatment (WWT). The results of this project indicate that these compounds occur throughout Europe and that, to ensure their removal, more effective WWT technologies are needed.

Further comments on the efficiency of WWT were made by Meritxell Gros (CSIC, Barcelona, Spain); a survey of pharmaceutical residues in influents and effluents from WWT plants (WWTPs) in the Ebro river (performed in the AQUATERRA project) and surface river water showed that anti-inflammatories and analgesics, lipid regulators, ß-blockers and some antibiotics are the major groups detected. Key compounds of the Ebro river basin are acetaminophen, ketoprofen, ibuprofen, diclofenac, mevastatin, atenolol, propranolol, sulfamethoxazole and trimetroprim, which were the most abundant, with concentrations in high ng/L or low μg/L levels. Carbamazepine and ranitidine were also frequently detected, but at lower concentration levels.

Two further presentations within the topic focused on the monitoring of brominated flame retardants (BFRs). Jana Hajšlová (Institute of Chemical Technology, Prague, Czech Republic) concluded from studies that fish is a good bioindicator of site pollution by bioavailable polybrominated diphenyl ethers (PBDEs) (and other BFRs); nevertheless, their pattern is species-dependent and perch has the contamination pattern of PBDEs most similar to sediments. Ethel Eljarrat (CSIC, Barcelona, Spain) presented additional monitoring data for BFRs at the Ebro river basin, as a part of the AQUATERRA project. Taking advantage of the high levels found in a hot spot of the Ebro river basin, two experiments with caged fish studied the bioavailability and bioaccumulation of HBCD and deca-BDE-209. At each point of contamination, 20 barbels were exposed to BFR contamination for 14 days. After the exposure, pools of 3 specimens were analyzed at each sampling point. In both cases, analysis of the barbels revealed bioaccumulation of HBCD and deca-BDE-209. In addition, five sewage-sludge samples collected at different WWTPs along the Ebro river basin were analyzed for their BFR content. The concentrations for the sum of PBDEs (from mono- to hepta-BDE congeners) were in the range 59–120 ng/g dw. However, the higher contamination came from the contribution of deca-BDE-209.

As part of the monitoring discussion, Julian Jones (Water 21, Cranfield Postgraduate Medical School, UK) underlined the need for microbial standards for freshwater systems.

Gert-Jan de Maagd (DG Water, Holland) presented the view of an end user and gave suggestions as how to make monitoring methods more user-friendly.

4. Immunochemical methods and biosensors

This session was initiated by Petra M. Krämer (GSB-GmbH, Neuherberg, Germany), who focused her presentation on the role of immunochemical techniques for implementing the WFD.

She also presented the results of an interlaboratory exercise organized by ENEA and QualityConsultant, Rome, Italy. In the inter-laboratory exercise, a sensitive Isoproturon ELISA was evaluated. The ELISA was based on monoclonal antibodies with a linear range (0.03–30 μg/L). The results of two other ELISAs for the analysis of atrazine and diuron were also analyzed. In addition, Krämer presented the results of the diuron immunoassay in a field trial organized at the Maas River at RIZA's Eijsden monitoring station (NL) within the SWIFT-WFD project.

The development, performance and precision of a highly-sensitive ELISA, with a limit of detection (LOD) of

17 ppt for the determination of PBDEs in environmental matrices was presented by Fernando M. Rubio (Abraxis LLC, Warminster, PA, USA). This presentation described the performance characteristics of a magnetic particle-based ELISA for the detection of PBDEs in environmental samples. The assay is fast, eliminates the need for expensive instrumentation and reduces solvent disposal. It exhibits good precision and accuracy, which can provide consistent, cost-effective monitoring of environmental and food samples. Using this ELISA, results from 50 water samples can be obtained in about 1 hour. The method was shown to be applicable to samples of milk, soil and fish with some clean-up, and the correlation studies comparing GC-MS with this ELISA demonstrated that this ELISA was very useful as a screening assay for these complex matrices.

Laura Lechuga (CSIC, Madrid, Spain) described the development and the application of a portable surface-plasmon resonance (β-SPR) biosensor commercially available from SENSIA S.L. (Spain) (Fig. 1). She showed the application of this new device with single and multiple immobilization approaches of monoclonal antibodies on gold-sensor chips for the determination of hazardous pesticides. This new β-SPR immunosensor enables on-site, real-time detection of DDT, chlorpyrifos and carbaryl with LODs at sub-ng/L levels.

M.-Carmen Estévez (IIQAB-CSIC, Barcelona, Spain) presented the immunochemical determination of anionic surfactants in natural and wastewater samples. A newly developed ELISA based on polyclonal antibodies allows the determination of linear alkylbenzene sulfonates (LASs) and their degradation products with LODs in the ng/L range.

A combined methodology involving immunochemical techniques (immuno-affinity chromatography (IAC) and ELISA) and chemical analysis (LC-MS), was presented by Ram Abuknesha (King's College London, UK) for the trace analysis of estrogens and progesterone in river samples. The ELISA assays presented in this lecture were based on polyclonal antibodies with LODs in the low ng/L range when the analyses were performed without a pre-concentration step. The main advantages and pitfalls of the different approaches were discussed.

In the last lecture of this session, Marinella Farré (IIQAB-CSIC, Barcelona, Spain) presented the immobilization of polyclonal antibodies on gold chips for their application to triazine analysis using the new *β*-SPR immunosensor (Fig. 1). This immunoassay showed LODs in the range of 10–30 ng/L without previous treatment of the samples. The immunoassay was applied for the analysis of different river-water and groundwater samples that were analyzed in parallel with SPE-GC-MS. A good correlation between the different techniques was shown.

5. Biological effects and risk assessment

As the WFD aims to improve and to protect the quality of all water bodies in order to achieve good chemical and good ecological status by 2015, great emphasis is placed on cause-effect relationships and biological effects.

Peter Hansen (Technische Universität Berlin, Germany) opened the session by describing new emerging, biochemical effect (biomarker)-related parameters in the field of immunotoxicity and endocrine effects. Environmental effects, such as genotoxicity and neurotoxicity, were detected in organisms from such ''hot spots''. Vital fluorescence tests are one way to allow us to unmask genetic alterations in field-collected

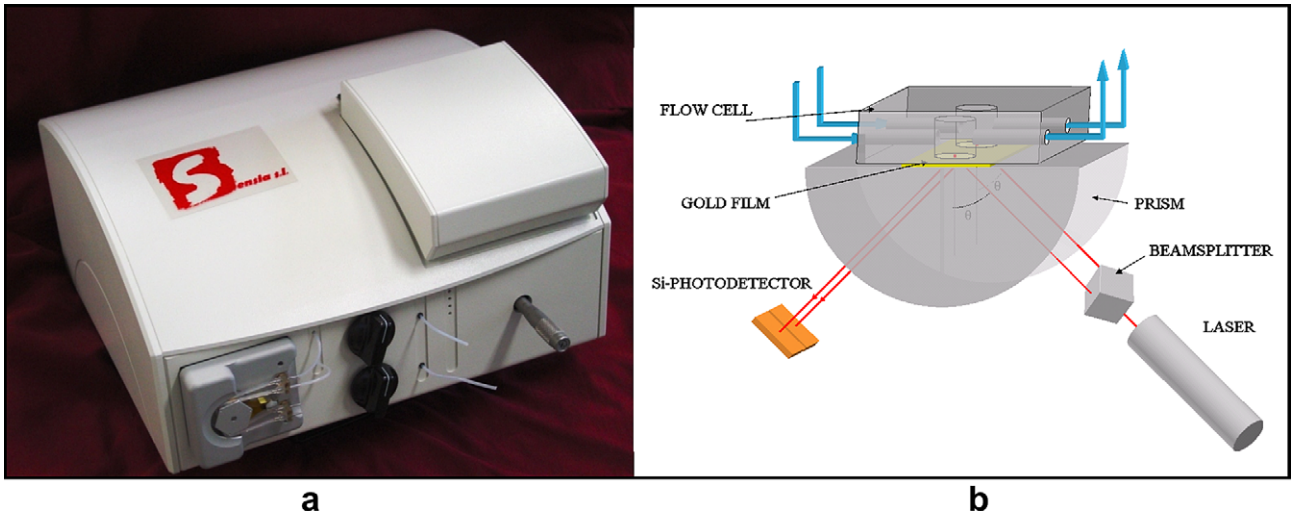

Figure 1. (a) commercial β-SPR sensor platform by SENSIA S.L. (Spain); and, (b) design of the SPR device. The applications of different immunosensors based on this β-SPR sensor platform were presented by Laura Lechuga and Marinella Farré.

animals or in situ-exposed organisms by a caging technique. The new emerging parameters for health of the ecosystem are linked closely to biomarkers of organisms exposed in the monitored areas. One problem is always to find the relevant interpretation and risk-assessment tools for the environment.

An evaluation of the toxicity effects of pesticides in aquatic invertebrate communities was presented by Carlos Barata (Intexter-UPC, Terrasa, Spain). The evaluation was performed in the Ebro delta with in situ bioassays using *Daphnia magna* and suggested a clear cause-effect relationship between biological responses and pesticide concentrations.

In rivers and streams, biofilms are the first to interact with dissolved substances and can therefore be used to detect early effects. To demonstrate this, Sergi Sabater (University of Girona, Spain) gave an overview of the existing methods of detecting toxicant effects with biofilms. He stressed that it was important to study a combination of short-term and long-term effects to reveal a cause-effect relationship adequately.

Continuing the focus on biofilms, Marina Coquery (CEMAGREF, France) described an analytical method (LC-tandem MS) for the measurement of diuron (and main metabolites) along with certain metals (As, Cu, Zn). It is planned to expand the method to include several other herbicides and fungicides.

Maria Fuerhacker (BOKU, Vienna, Austria) closed the session with an example of a risk-assessment process for cytostatic agents, which focused on a combination of modeled predictions, chemical-analytical monitoring and eco-toxicological evaluation.

6. Data treatment and interpretation

Romà Tauler (CSIC, Barcelona, Spain) explained that chemometric modelling (multivariate data analysis) of monitoring data, including geographical information system (GIS) data, is a powerful tool for environmental pattern recognition and for a better environmental understanding and assessment. The current knowledge base in Ebro river-basin management is not adequate to deal with the impact of contamination. In this work, chemometric methodologies currently used for identifying the more relevant contamination sources, especially for persistent and emerging contaminants, in the surface waters of the Ebro river basin and the description of their temporal and spatial (geographical) distributions were presented. For the Ebro basin, there are historical data since 1992 for water and sediments. Samples were analyzed by CHE (Confederación Hidrográfica del Ebro). Some recent results of application of these methodologies were given (Fig. 2).

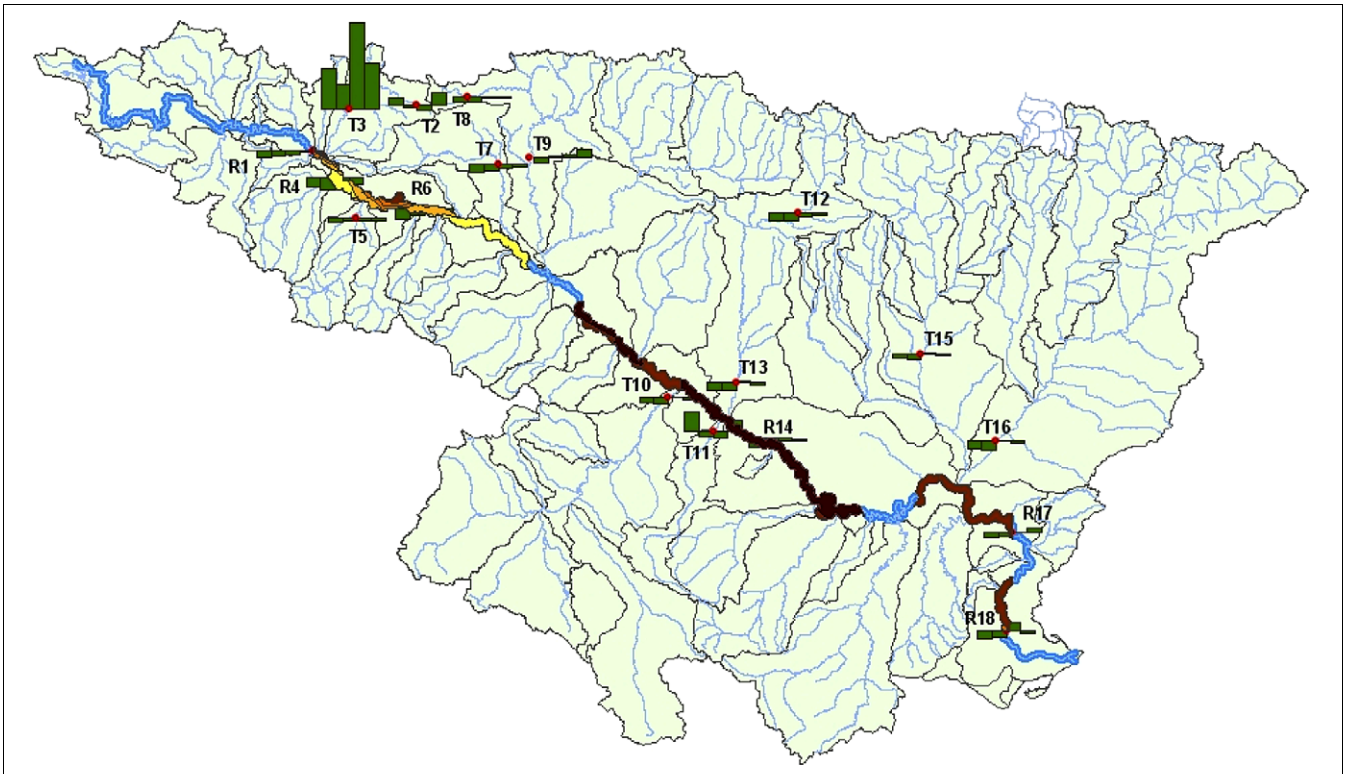

Figure 2. Geostatistical kriging interpolation of contamination source for metals in surface waters of the Ebro river. Graphical representation is of scores for each sampling site for the years 2000–03.

Rikke Brix (CSIC, Barcelona, Spain) described the technique of constructing uncertainty budgets and presented an example of their usefulness in method optimization.

Luisa Pasti (University of Ferrara, Italy) closed this session by giving an example of how chemometrics can be used to reduce the number of sampling points and to optimize the frequency of sampling.

7. Summary

We set out below some of the major conclusions reached during this workshop.

- Chemical monitoring activity (CMA) to comply with the WFD at the river-basin level is usually carried out using conventional analytical devices, generally involving some type of MS determination. In addition to the priority substances listed in the WFD, there is the need to investigate chemical substances of emerging concern that are usually discharged after their incomplete removal from sewage-treatment plants particular to each river basin (e.g., pharmaceuticals, estrogenic compounds and EDTA).
- Complementary monitoring devices, such as immunochemical methods and biosensors, have been demonstrated to be useful tools for the implementing the WFD. Biosensors, which generally incorporate a biological component (e.g., microorganisms, cell receptors, enzymes, antibodies, or nucleic acids) and an optical, electrochemical, thermometric, piezoelectric or magnetic physicochemical transducer system always need to be validated in order to be accepted as routine monitoring tools by the river-basin authorities.
- Biomarkers (biochemical responses) for environmental monitoring are complementary to chemical methods, since they can signal the presence of toxic compounds that require further instrumental analysis or ''bio-response-linked instrumental analysis''. There has been emphasis on the importance of considering specific (biomarkers) and more generalized and ecological related (grazing) in situ responses to identify and to evaluate biological effects of environmental contaminants in the field (e.g., using *Daphnia magna* for identifying ''hot spot'' areas).
- It was noted that monitoring sediments and/or suspended solids is needed for correct implementation of the WFD. Substances that tend to accumulate in the geo-sphere and are transported bound to particles may be better measured in suspended matter than in the water phase, which is particularly important for some new groups of compounds included in the WFD, such as BFRs (PBDEs). Examples from the Elbe and Ebro river basins were reported.
- Monitoring should include assessment of the bioavailable fraction of pollutants (metal speciation, organics), in both the laboratory and field situations. It has been recognized that there is a lack of knowledge in the fundamental processes constituting bio-availability. In this respect, there is a quest for chemical methodologies that can be used to mimic the biological availability of substances and this concept should be explored in detail using, for example, the vision of the Scientific Committee for Toxicity and Ecotoxicity and the Environment (CSTEE).
- Mathematical models, including chemometric models, coupled to GISs are useful tools for river-basin managers to assess pollution trends and to compare quality data from comprehensive monitoring of river basins in different years.

The great interest in this and similar workshops confirms that the continued sharing of knowledge between analytical chemists, environmental chemists, water-quality managers, biosensor-bioassay specialists and instrument manufacturers should help the development of common strategies to find out the optimum protocols for implementing the WFD.

Finally, following the workshop, the papers submitted will be published, after the usual refereeing procedure, in the journal *Analytical and Bioanalytical Chemistry*.

Acknowledgement

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