

Are Member States ready for compliance checking monitoring ? A JRC initiative within the WFD Chemical Monitoring Activity

Georg Hanke, Jan Wollgast, Robert Loos, J. Castro Jiménez, Gunther Umlauf, Giulio Mariani, Anne Müller, Tania Huber, Eugen Christoph, Giovanni Locoro, Bernd Gawlik, José Manuel Zaldívar and Giovanni Bidoglio

EU legislation for control of chemical pollutants

JRC IES has been accompanying the preparation of the upcoming WFD Daughter Directive COM(2006)398 on Environmental Quality Standards EQS through chairing the workgroup on Analysis and Monitoring of Priority Substances AMPS (2003-2004), co-chairing the drafting of the CMA guidance document for surface waters within the Chemical Monitoring Activity CMA (2005-2006) and co-chairing the Chemical Monitoring Activity in 2007-2009. The assessment of available methods for WFD compliance checking is among the prime objectives of the chemical monitoring activity.

CMA on-site exercise

In order to assess the current state of monitoring methodologies, an exercise has been conducted in which invited laboratories sampled simultaneously river water and analysed according to their protocols, in view of the upcoming Directive and the available draft guidance document. In accordance with the participating laboratories a selection of challenging parameters included in the upcoming EQS directive was made (cited proposed EQS values are for Inland waters):

WFD Polycyclic aromatic hydrocarbons and proposed EQS

Anthracene	100 ng/L
Fluoranthene	100 ng/L
Benzo(a)pyrene	50 ng/L
Benzo(b)fluoranthene +	
Benzo(k)fluoranthene	Σ 30 ng/L
Benzo(g,h,i)perylene +	
Indeno(1,2,3-cd)pyrene	Σ 2 ng/L

WFD Polybrominated biphenyls, sum of

BDE-28	
BDE-47	
BDE-99	
BDE-100	
BDE-153	
BDE-154	
Proposed EQS Σ	0.5 ng/L

WFD Alkylphenols

Nonylphenol	
Proposed EQS	300 ng/L
Octylphenol	
Proposed EQS	100 ng/L

Participants

Invited laboratories from 7 EU Member States (Austria, Italy, Germany, Spain, Netherlands, Bulgaria, Denmark) participated. For the result presentation codes from CMA00 to CMA08 were attributed to the participants. Water was sampled from the Po river near Ferrara, Italy on 11. October 2006. In addition ampoules with standard solutions and with prepared river water extracts where distributed for evaluation of variability derived from sample preparation and measurement.

Sampling approach

The river water was measured continuously for basic water quality parameters and in high frequency for selected analytes, in order to assess the homogeneity of the river water. Participants sampled simultaneously at 11:00, while large volume sampling was continuous from 10:00 to 15:00. (see Fig. 1, red bars indicate sampling events).

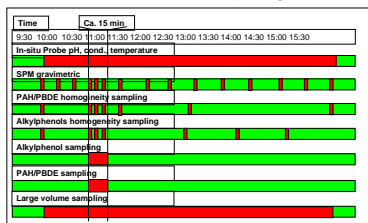


Fig. 1 Sampling plan scheme for the CMA on-site exercise

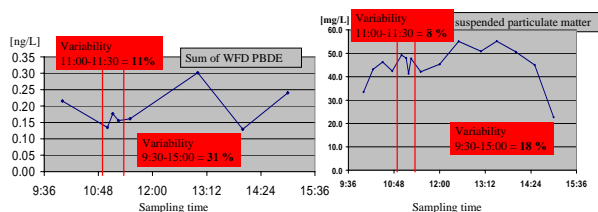


Fig. 2 Homogeneity test for PBDE and SPM during exercise

The differences in variability during the main sampling time 11:00 to 11:30 (11 % for PBDE and 8% for SPM) and the large volume sampling 10:00 to 15:00 (31% for PBDE and 18% for SPM) confirmed homogeneity of the river for these parameters during the sampling period and showed the advantage of time integrating approaches in assessing average values of concentrations in river water (see Fig. 2). Determination of SPM was done with a confidence interval < 5%, for PBDE < ± 20 %.

Approaches for water monitoring

A wide range of approaches has been applied by the participants: Samples where taken directly with a bottle, a bucket, with pumping systems and a flow-through centrifuge. Sample volumes ranged from 0.2 L to 4150 L. Sample preparation was done with liquid-liquid solvent extraction, solid phase extraction with extraction columns or extraction disks and by accelerated solvent extraction. Measurements where done by GC/high or low-resolution MS and LC/MS only for Alkylphenols.

Results

Only few laboratories have reported complete datasets. For PBDE, Alkylphenols and PAH only half of the participants obtained results, while for the PAH standard solution ca. 6 of 8 participants delivered data. Also the measurement of standard solutions and homogenised river water extracts appeared to be difficult for most substances and laboratories. Statistical evaluations have not been possible due to the low number of reported results. Octylphenol was not present in the environmental samples at concentrations relevant for WFD. Reported limits of detection are shown with grey columns and red numbers.

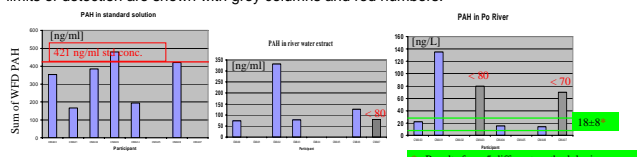


Fig. 3 Result comparison for Σ WFD PAHs

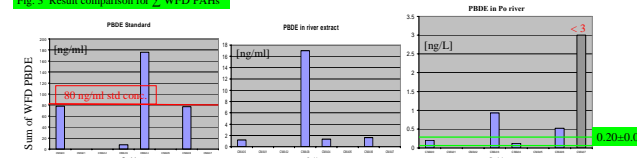


Fig. 4 Result comparison for Σ WFD PBDE

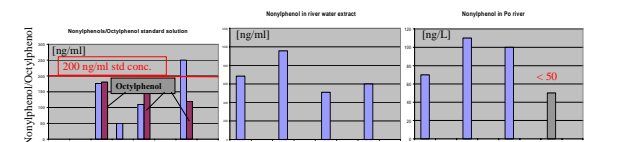


Fig. 5 Result comparison for Alkylphenols

Conditions for the on-site exercise have been very challenging due to the low concentration of target analytes in the Po river at the time of the exercise. Concentrations of target pollutants where still in the range of 0.3 EQS (COM(2006)398), as being proposed to be the required limit of quantification for compliance checking (WFD QA/QC Commission decision draft, February 2007). For PAH (Fig. 3) the result from 5 different methodologies (*Filtration + 20 L liquid-liquid extraction, 45 L filtration+ 100g XAD extraction, * and ** 2 L liquid-liquid extraction, 226 L cartridge filtration + 500 g XAD extraction and 2 L filtration + solid phase extraction disk) agreed well (18 ± 8 ng/L) and are shown as area limited by green bars in the result graph. The same approach has been used for evaluation of the obtained PBDE results (Fig. 4), comparing 3 methods (0.2 ± 0.07 ng/L). Comparison of these assigned values with the participant results shows that only few laboratories have delivered results within that margin. The results obtained by the participants show also that high data quality is important for compliance checking at low environmental concentrations.

Conclusions

It was shown that even some of the most challenging WFD priority substances, selected on purpose for this exercise, can be measured at WFD relevant concentrations (0.3 x EQS) with methods currently applied in Member States. Obtained results were not within proposed data quality limits for most participants and therefore further development of methods and harmonisations of efforts is suggested.

Acknowledgements

We like to thank the Servizio Risorse Idriche e Tutela Ambientale della Provincia di Ferrara, the participants and supporters of the exercise: Silvano Bencivelli, Susanne Boutrup, Daria Barceló, Ronald de Boer, Ivanka Dimitrova, Philipp Hohenblum, Peter Lepom, Paola Magri, Alicia Navarro Ortega, Lars Håkanson, Alain Hildebrandt, Wolfgang Moche, Olga Nitcheva, Stefano Polesello, Harald Schmid, Franz Leindecker, Ole Sortkjaer, Joan Staeb, Thomas Ternes, Graziella Leroy and Madeleine Rizzi.

Contacts

Georg Hanke, Jan Wollgast, Giovanni Bidoglio
European Commission • DG Joint Research Centre
Institute for Environment and Sustainability
Rural, Water and Ecosystem Resources Unit
Tel. +39 0332 785586 • Fax +39 0332 786351
E-mail: georg.hanke@irc.it