Integration of on-line and off-line methodologies for the assessment of river water quality


Context: stringent regulatory issues

WFD  Good ecological status of water bodies  Good chemical status  Priority substances  2009

Good biological status  Biological indicators  2015

Environmental Risk Assessment (ERA) based tool is needed

ELD  Certain professional activities that present danger to human health (e.g. WWTP)  Engage responsibility even if no fault is committed  Strict civil liability

Biological indicators needed (effects on ecosystems)

SCARCE 2nd Annual Conference 28-29 November 2011 - Madrid
Limitations of legislation

- **Chemical status**
  - Priority pollutants concentration (33 compounds)
  - Not representative of all the possible existing compounds present in water bodies.

- **Biological measurements**
  - River Basin Authorities oriented (intercalibration studies)
  - Not useful for water utilities

Emerging bio-chemically based tools

- Rapid
- Easy to use
- Overall measures
- Cost Effective
- Measure bioavailability

Context:

- Rapid
- Easy to use
- Overall measures
- Cost Effective
- Measure bioavailability

Toxcontrol:

Main characteristics:

- Detection of global toxicity (priority pollutants: metals, pesticides, …)
- Uses luminescent bacteria *Vibrio fisheri*
- Real time continuous monitoring (every 30 min). Alert system
- Low maintenance (once a week)
- On-line version of the standardized EU-EN ISO 11348 (EU, 2007) to be fully automated
Toxcontrol:

Main difficulties to overcome:

- High turbidity can alter measurement (false positive results)
- Sensitivity. Regulation limits are very low. SPE has been added to concentrate samples (x 50)
- Reagents cost (bacteria, solvents for SPE)

High values (10 o 20% inhibition) >> high turbidity
Low values (~ 5% o -10% inhibition) >> content of nutrients

Online UV-VIS spectrophotometer:

Main characteristics:

- Several parameters (Turbidity, TOC, Nitrates, SAC254) in the same measurement with one technology (less cost for purchase and maintenance)
- Real time continuous monitoring. Alert system
- All spectra 200-750 nm recorded. New parameters / compounds can be added in the future
Online UV-VIS spectrophotometer

Main difficulties to overcome:

- Water matrix changes fast in Mediterranean rivers (e.g. turbidity can change from 30 NTU to 1000 NTU in a few hours)
- Need to operate with one single calibration for “different waters”
- If we calibrate for “clean” water, data out of range for “dirty” episodes
- If we calibrate for “dirty” water, not sensitive enough for “clean episodes”

Fish scales

- Working principle
  - Pollutant ➔ Stress signal ➔ Changes in mRNA ➔ Changes in protein content and enzymatic activities ➔ Physiological adaptation to stress
  
  The magnitude of the stress signal can be evaluated by measuring changes in the abundance of mRNA coding for stress-responsive genes

- Protocol
  - Sampling of target tissue (scales) ➔ Extraction of mRNA ➔ Retrotranscription to cDNA ➔ qRT–PCR ➔ Quantification (amount of cDNA) (fluorescence)
Passive samplers

- Allow in situ determination of contamination problems associated with conventional water collection and filtration procedures are eliminated.
- Measure of time-weighted average (TWA)

**METALS: DGT (Diffusive Gradient in Thin Films)**
- In situ determinations of labile metal species in aquatic systems
- Analysis by IPC-MS

**ORGANICS: POCI (Polar Organic Chemical Integrative Sampler)**
- In situ determinations of pharmaceuticals, pesticides and alkylphenols
- Analysis by UPLC-MS-MS

**SCARCE 2nd Annual Conference 28-29 November 2011 – Madrid**

Area of study

- LA MINA. Impact urban WWTP and industrial discharges
- ST JOAN DESPI. Drinking water treatment plant raw water intake to supply Barcelona and surrounding area
- Existing on-line monitoring station
- TUBO DEL GOBERNADOR. Impact of by-passes done in the river to enhance the water quality in the drinking water intake

**2 monitoring campaigns in 7th - 18th June & 21st September – 4th October 2010 (6 samples/point/campaign)**

**1st monitoring campaign**

**2nd monitoring campaign**
Comparison of UV probe and lab measures

Turbidity (NTUeq) vs Sonda vs Laboratorio

TOC (mg C/L) vs Sonda vs Laboratorio

Nitrates (mg NO3-Neq) vs Sonda vs Laboratorio

UV-254 (Abs/100cm) vs Sonda vs Laboratorio

Validation for nitrates

VIP scores análisis
Main parameter = 225 nm
Validation for nitrates

Linear regression model using PLS plus cross validation for error calculation

<table>
<thead>
<tr>
<th>Components</th>
<th>LV's</th>
<th>Captured Variability</th>
<th>r²</th>
<th>RMSECV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrolyser</td>
<td>2</td>
<td>97.47%</td>
<td>0.848</td>
<td>6.7602</td>
</tr>
<tr>
<td>Milli-Q water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hach Lange</td>
<td>2</td>
<td>99.49%</td>
<td>0.940</td>
<td>4.8344</td>
</tr>
<tr>
<td>Milli-Q water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Spectrolyser</td>
<td>2</td>
<td>99.47%</td>
<td>0.968</td>
<td>3.8884</td>
</tr>
<tr>
<td>Surface water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hach Lange</td>
<td>2</td>
<td>99.34%</td>
<td>0.927</td>
<td>5.3425</td>
</tr>
<tr>
<td>Surface water</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fish scales: Exposure protocol

• 10 fish (1 year old *Danio rerio* males)
• 5000 mL, aired samples
• 24 hours at 25°C exposition.
• Positive control: A subset of fish was also exposed to β-naphthoflavone (1μM) as representatives of dioxin-like pollution using Dimetil Sulfoxide (DMSO) as solvent.
• Negative control: Aquarium water with the same quantity of DMSO
Fish scales: Results

Site 1: Mina Pública de Terrassa
Site 2: Sant Joan Despí
Site 3: Tubo del Gobernador

Pelayo et al. 2011, 401: 1861-1869  ABC

Presence of micropollutants
Fish scale assay was able to detect changes in the quality of the waters.

Passive samplers: POCIS

- Measured amounts were higher in the downstream sampling point in both water and POCIS samples.
- Decrease in the velocity of accumulation during the last period. As spot samples don't indicate a drop caused by environmental conditions.
- POCIS showed a higher detection capacity in front of the analysis of water.
Passive samplers: DGT

- Al, Fe and Mn were the metals detected at higher levels in the sampling points.
- Mn is mainly present in labile fraction.
- Al and Fe have tendency to form colloidal forms in neutral conditions.
- The point « tubo del gobernador » has higher concentration more relevant for environmental risk studies, and reflecting the higher toxicity of this sampling point.

Conclusions

- Toxcontrol represent an good biological early warning systems but the LOD must be improved (using a preconcentrator?)
- UV-Vis measures permits the on-line (an in-situ) detection of several parameter, but a new calibration must be performed.
- The analysis of cyp1a mRNA levels in scales of zebrafish represent a valid alternative method to detect dioxine-like contamination in water without implying the animal killing and only need 24 h exposure.
- Passive sampler provide with a measure of time-weighted average (TWA) concentrations of pollutants that complements the results obtained with spot sampling, that provide only a snapshot of the pollutant levels at the time of sampling, failing to detect and account temporal variation in pollutant concentrations.
Acknowledgements

This work has been financially supported by R+ i Alliance and by the Spanish Ministry of Environment through VIECO project (009/RN08/01.1)

Participants

R. López, S. González, J.L. Cortina
S. Pelayo, B. Piña
A. de la Cal, R. Céspedes, A. Díaz, M. R. Boleda, R. Devesa

THANKS FOR YOUR ATTENTION!