Sensors - Challenges associated with sampling and calibration

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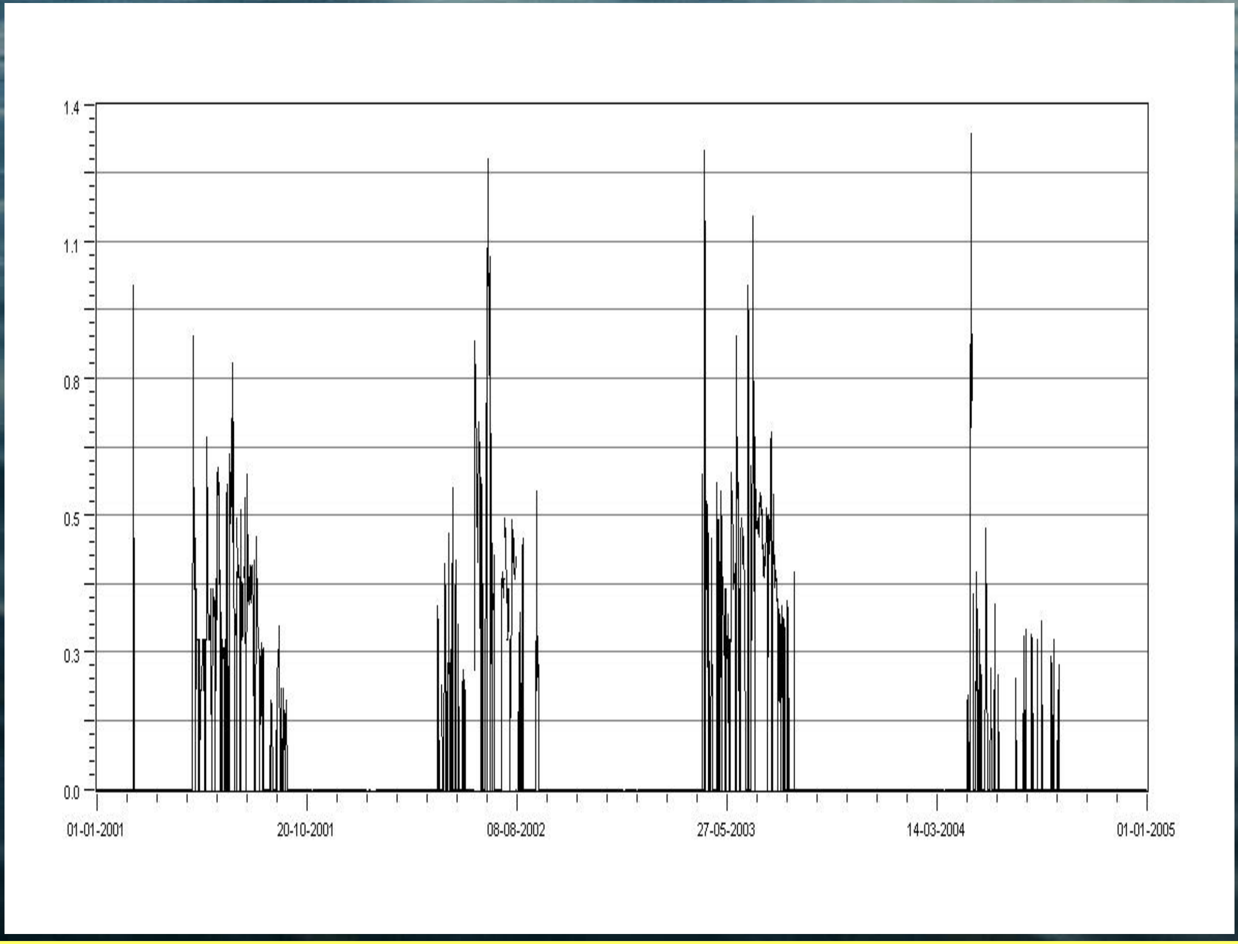
Monitoring of Chemical Quality of Environmental Waters

- Legislation is driving force for routine monitoring of environmental water
- In Europe, the fractions to be measured (whole water samples or filtered samples) are compared with Environmental Quality Standards (both maximum allowable (EQS MAC) and annual average (EQS AAC) concentrations) for individual pollutants
- Current practice is based on infrequent spot sampling

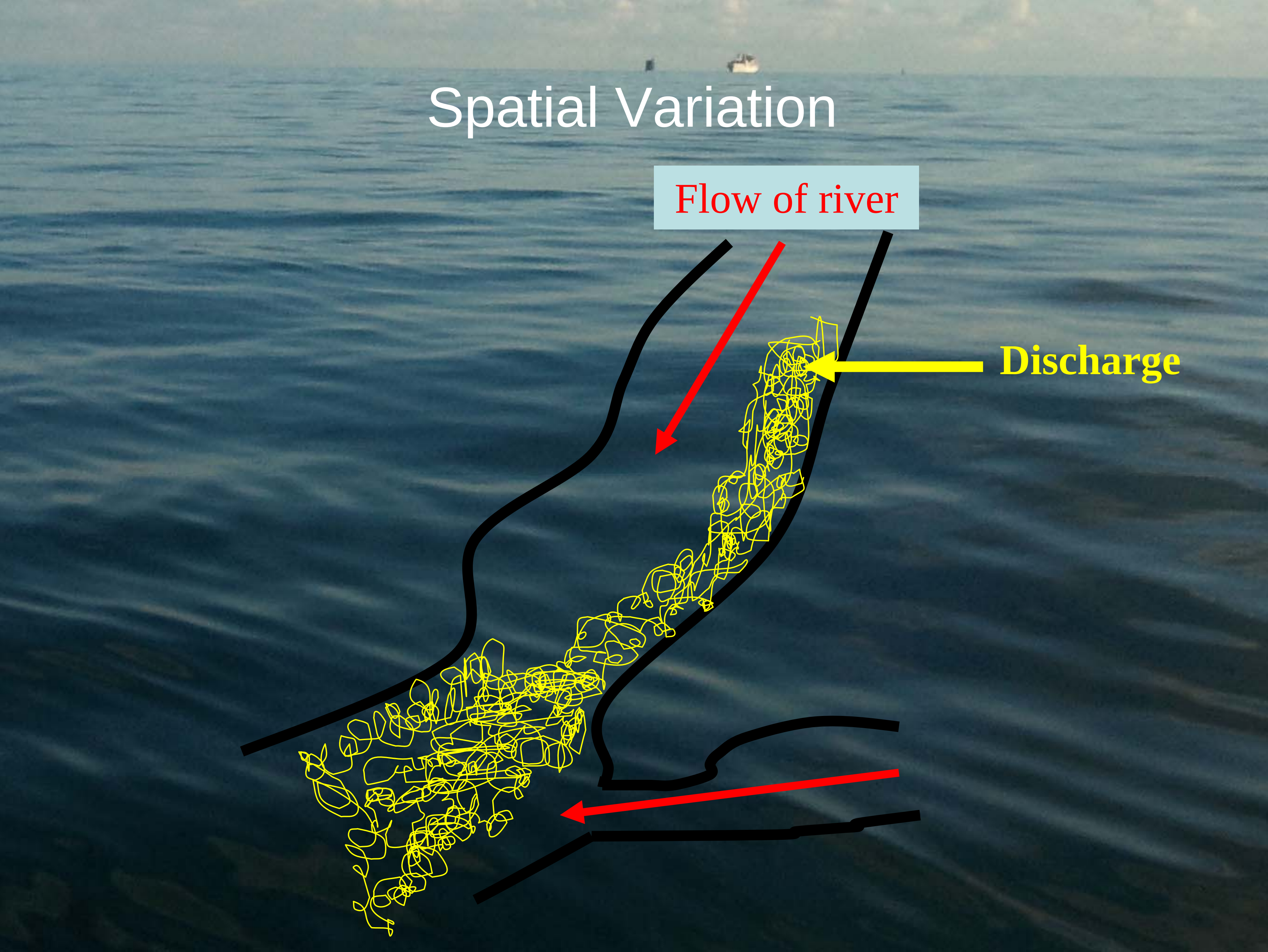
Monitoring of Chemical Quality of Environmental Waters

- The variable of interest is chemical quality of a body of water
- Estimates derived from infrequent spot sampling are associated with large uncertainties (despite low uncertainty associated with chemical analysis in accredited laboratories)
- The sampling process is not fit-for-purpose

Temporal Variation



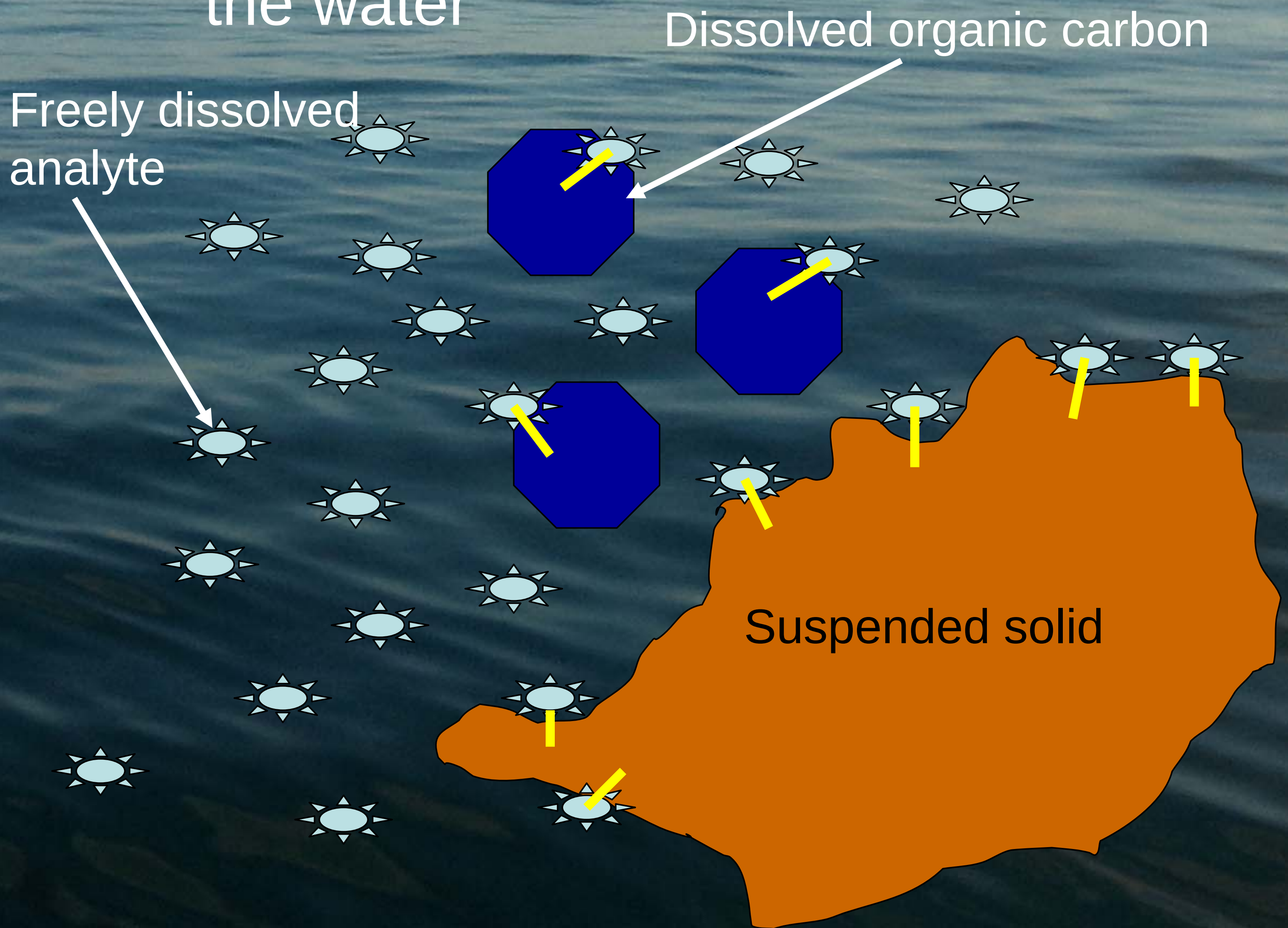
Diuron concentration (μg L^{-1}) continuously monitored in the Meuse River - RIZA's Eijsden station (2001-2005).


Spatial Variation
Flow of river
Discharge

Possible Solutions to the Sampling Problem

- Increased spot sampling
- Use of automatic sampling techniques
- Use of in-field methods
- Passive samplers
- The "Holy Grail" of environmental monitoring is the use of networks of remote field deployed sensors that transmit information on water quality in real time to the manager's desk top computer

Distribution of a pollutant in the water



What is Being Measured?

- For some metals, and for organic compounds that are very non-polar, concentrations measured in filtered samples will represent the freely dissolved fraction as well as that bound to dissolved organic matter

Operationally Defined Results

- In many cases the various methods of sampling, transport, storage, and sample preparation and analysis will give different estimates of concentrations of a chemical in the same sample
- The outcome of the analysis is operationally defined
- This is why standard operating procedures are important

Different Methods measure Different Fractions

- Passive samplers and most sensors will sample only the freely dissolved fraction, and that bound to DOM that dissociates in the time scale of diffusion across any diffusion limiting layer

Sensors for Physical Variables and Inorganic Analytes

- Well-developed, commercially available sensor systems available for a limited number of variables (e.g. temperature, pH, pO_2, pCO_2, turbidity, chlorophyll concentration)
- Robust sondes with long-life power supplies, rapid local data handling, and transmission are used to house sensors with self cleaning and *in situ* calibration capabilities

Sensors for Individual Analytes

- Many sensors including biosensors have been developed for a range of analytes
- Major commercial successes in biomedical area – glucose sensors 90% of this mature global market
- Environmental sensors not in the same league, but there are some mature technologies such as those for nutrients (nitrite and nitrate)

Sensors for Individual Analytes

- Some sensors developed to measure concentrations of legislatively relevant analytes - taken to proof of concept stage and no further - limited market compared with that for the sensors with biomedical applications
  - Organophosphate insecticides
  - Heavy metals
  - Organometallics
  - Industrial non-polar pollutants
  - Endocrine disruptors
  - Polar organic compounds of emerging importance
    - polar pesticides
    - components of personal and household care products

Opportunities

- In the UK, responsibility for routine monitoring of discharges of waste water lies with the discharger
- Increasingly production of drinking water is becoming automated and operated remotely
- Monitoring of wastewater treatment increasingly automated
- Investigative monitoring – forensic monitoring
- Screening

Evolution of Water Quality Legislation

- More to fulfilling legislative requirements than compliance in terms of sampling
- Need more representative sampling to
  - Understand sources, distribution and fate of environmentally significant analytes
  - Support risk analysis
  - Decide on possible remedial actions
  - Follow trends following remedial actions or changes of practice

Challenges to Application of Sensors in Legislative Framework

- Robust calibration
- Validation
- Quality Control and Quality Assurance Procedures
- Accreditation
- Commercialisation
- Roll out to end-users - marketing and training

Calibration

- Major problem What to use as the “gold standard” measurement of concentration in water?
  - Concentration in whole water sample
  - Concentration in filtered or ultrafiltered sample
  - Passive sampler available fraction (freely dissolved fraction)
- For non-polar compounds it is difficult to achieve a true solution at measurable concentrations
- Need for long term experiments to assess stability

Calibration

- Approaches to calibration
  - Static and semi-static systems most convenient, but not suitable where loss of analyte over time due instability or binding to system components
  - Through-flow systems ideal, but use large volumes of standard solutions
  - Well characterised field sites
- Need to measure performance under a range of conditions (temperature and turbulence) to generate a response surface

Calibration

- One potential way to reduce calibration work would be to house sensor in a controlled environment (in terms of temperature and turbulence) but this would increase cost of sensor and increase power requirements in the field

Validation

- Need to validate in field as well as laboratory because of impact of
  - Biofouling
  - Dissolved organic carbon
  - Other compounds in water (e.g. matrix effects, interference between closely related compounds)
- Need large volumes of standard reference materials for laboratory validation – expensive and not readily available- new approach needed (e.g. effervescent dispersible formulations)
- Same problem as for calibration and laboratory validation studies - selection of measures for assessing performance
- Need well defined reference sites
- Need for long term validation trials for some technologies

Availability to Potential End Users

- Several arrays of sensors (e.g., RIANA and AWACCS) for continuous monitoring developed using EU funds, but
  - not widely used
  - not commercially successful
- Possible explanations
  - Lack of commercialisation
  - Can be used by only a few experts
- Need appropriate marketing, and support and training for end-users who are not researchers

Needs

- Change of culture in funding bodies and industry to follow up successful research phase of sensor development with further support for the validation, and development phases
- Without this sensors will remain research tools

Challenges for the Monitoring Community

- EQS are defined in terms of whole or filtered water samples - the legislation would need to define EQS values in terms of the sensor available (freely dissolved) fraction
- Standards for calibration, and field application of sensors
- There is a need for a framework for QA and QC through accreditation of methods as for other analytical methods
- Need industrial standards to ensure compatibility of novel sensors with existing systems

Current Potential for Sensors

- Although passive samplers and sensors are not available to support the enforcement of legislation directly, they could be used in investigative mode to trace sources of pollution, and to increase the effectiveness of expensive spot sampling campaigns by focussing their use where necessary

Conclusions

- Current approach to sampling is not fit-for-purpose
- Sensors offer a potential alternative but there is a need for
  - Changes in legislation
  - Improved calibration
  - Development of sound QA and QC systems
  - Increased funding for development of sensors beyond proof of concept
  - Standardisation
- Currently most promising areas of application include
  - Investigative monitoring
  - Use in process monitoring in waste water and drinking water treatment plants
  - Screening to focus legislative sampling when and where needed