

New challenges for water quality monitoring: potential role of novel monitoring tools

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Abstract :

The European Union's Water Framework Directive (WFD) is one of the most important pieces of environmental legislation produced in recent years and is likely to transform the way that water quality monitoring is undertaken across all member states. The Directive aims to achieve and ensure "good quality" status of all water bodies throughout Europe by 2015, and this is to be achieved by implementing management plans at the river basin level. Monitoring is required to cover a number of 'water quality elements' including, physico-chemical, hydro-morphological, biological and chemical parameters. The successful implementation of the WFD will rely on the availability of low-cost tools and technologies able to deliver appropriate and reliable data. In addition, as many large river basins encompass a number of countries, it is important to ensure that the data collected by different EU member states are of comparable and appropriate quality. The WFD does not mandate the use of a particular set of monitoring methods/tools, but aims to ensure the establishment of an adequate monitoring programme (surveillance, operational or investigative monitoring).

The techniques currently available for the assessment of biological quality include biomarkers, whole-organisms bioassays, biological early warning systems (BEWS). For chemical monitoring the methods available are mainly, electrochemical sensors, biosensors, immunoassays and passive samplers.

Based on case studies investigated on several river basins across Europe, their potential role of these methods, their integration in water management strategy has been assessed.

Moreover, some of these methods/techniques are easy to use in field conditions and open interesting perspectives to water quality monitoring in developing countries.

Key words: water monitoring, field measurements, emerging tools, Water Framework Directive

WFD requirements

The Water Framework Directive aims to achieve good quality status for all surface, ground and coastal waters throughout Europe by 2015. In addition, it is expected to contribute to the protection, prevention of deterioration and improvement of all water bodies across the European Union (WFD 2000/60/CE).

As the WFD requires a River Basin Approach and many waters cross national boundaries, monitoring under the Water Framework Directive aims to harmonise the collection of water quality information to provide comparable, reliable and consistent data. The success of the implementation of the WFD will depend on the availability and quality of information available to those charged with managing water quality. Monitoring under the WFD is required to cover a number of biological, hydromorphological, physico-chemical and chemical (priority and/or emerging pollutants) quality elements.

The WFD does not mandate any particular monitoring methods, but requires Member States to ensure the establishment of programmes for the monitoring of water status in order to establish a coherent and comprehensive overview of water status within each River Basin District (Dworak 2005).

Three modes of monitoring are specified in the Directive:

- Surveillance monitoring will assess long-term water quality changes and help providing baseline data on river basins,
- Operational monitoring aims to provide additional and essential data on water bodies at risk or failing environmental objectives of the WFD,

- Finally, the objective of investigative monitoring is to determine causes of such failure when they are unknown.

According to the annex V of the WFD, the following table (Table 1) summarizes the quality elements (QE) required by the Directive for different water bodies.

	Rivers	Lakes	Transitional waters	Coastal waters	Ground waters
Biological					
Hydromorphological					
Physico-chemical					
T°					
Dissolved Ox					
Salinity (Conductivity)					
Acidification pH, alkalinity					
Nutrients					
Transparency					
Chemical					
Priority Hazardous pollutants					
Priority pollutants					

Table 1: Monitoring of ecological and chemical status according to types of water bodies

It can be noticed that most part of the physico-chemical parameters are required for all types of water. As well, priority hazardous pollutants and priority pollutants are in all cases monitored.

Moreover, the annex V of the Directive specifies the QE to be monitored according to the type of monitoring. The following table (Table 2) summarizes QE required for each kind of monitoring.

Quality elements	Surveillance monitoring	Operational monitoring	Investigate monitoring
Biological			
Hydromorphological			
Physico-chemical			
Priority Hazardous pollutants			
Priority pollutants			

Table 2: Quality elements required according to type of water monitoring

The Water Framework Directive requires a list of "priority substances selected amongst those which present a significant risk to, or via, the aquatic environment". This list is based on the toxicity, persistence, bioaccumulation potential, human health risk and the monitored and modelled concentration of each substance in the aquatic environment.

The frequency of monitoring will depend on the type of body of water (rivers, lakes, transitional, coastal or ground waters), on the quality element being monitored (i.e. biological, hydromorphological, physico-chemical or chemical) and of course for the type of monitoring undertaken.

Currently the most commonly used method for measuring levels of chemical pollutants for all three modes of monitoring is spot (bottle) sampling. This has a number of disadvantages, including cost and the fact that it provides only a snapshot of the situation at the instant of sampling. This is an important factor since levels of pollutants can vary with time even at a fixed location, and fluctuations associated with episodic events could be missed, or conclusions could be drawn on the basis of transitory high levels. There is therefore a need for improved screening methodologies that can provide a complementary approach to quality monitoring.

Indeed, screening methods could be proposed in order to improve water quality assessment. Currently these novel methods/tools for environmental assessment are under development and evaluation. They could be classified into three main types:

- Devices for measuring physico-chemical characteristics (e.g. DOC, pH, temperature, oxygen),
- Biological assessment techniques (e.g. biomarker analysis, bioassays/biosensors and biological early warning systems),
- Sampling and chemical analytical methods (e.g. sensors, passive sampling devices, test kits).

Techniques/tools towards water quality monitoring

In the frame of SWIFT-WFD project (Contract n° SSPI-CT-2003-502492-2007), an inventory of existing methods currently used or under development for supporting the Water Framework Directive (WFD) for the assessment of physico-chemical, biological and chemical quality elements and parameters (not including hydromorphological elements) has been published on a technical report (Greenwood, 2006) and on an international review (Allan, 2006). The table 3 summarizes the main techniques/tools available for water monitoring and details the sampling mode, the analysis/measurement procedure and finally the parameters or pollutants which could be investigated using those methods.

	Sampling				Analysis/measurement			Parameters		
	Spot sampling	Continuous (flow-through)	Passive sampling	No sampling	On site	Laboratory	In situ	Physico-chemical parameters*	Specific pollutants**	Toxicity
Chemical methods	✓				✓			✓	✓	
		✓			✓					
ELISA/Immuno assays	✓				✓				✓	
		✓			✓					
Sensors	✓				✓			✓	✓	
		✓			✓					
			✓			✓				
				✓			✓			
Biosensors	✓				✓			✓	✓	✓
		✓			✓					
			✓			✓				
				✓			✓			
Bioassays	✓				✓	✓			✓	✓
			✓			✓				
BEWS***		✓			✓				✓	
				✓			✓			
Biomarkers	✓					✓			✓	✓
Passive Samplers			✓			✓			✓	✓

Table 3: Screening methods actually available or under development

*Physico-chemical parameters : pH, COD, BOD, temperature, conductivity, nutrients - **Specific pollutants : organic compounds, metals

***BEWS: Biological early warning systems

This report gives a general overview of the methods frequently used for physico-chemical parameters measurements (NH₄, PO₄, DCO, DBO, COT, conductivity, turbidity, pH...), for priority pollutants monitoring and for biological assessment. A number of relevant information such as concentration levels generally observed in different water bodies (surface water, groundwater and marine water,...), physico-chemical properties of some targeted priority pollutants are available on this report. A section is in particular devoted to standards methods and to Quality Assurance procedures.

On the basis of this report, this article aims to highlight the most promising methods/tools that could be suitable for water monitoring as required by the WFD.

✓ Physico-chemical parameters monitoring

Different sort of devices are available based on a range of specific electrodes, optical sensors, UV, visible spectroscopy, colorimetry, chemiluminescence.

Table 4 summarizes the available techniques for physical-chemical parameters measurements.

	Specific electrode	Optical techniques
Ammonium	✓	UV, V, C, Ch
COD	✓	UV, V, Ch
Conductivity	✓	
Dissolved oxygen	✓	
Organic matter		UV
pH	✓	
Phosphate		V, C
Redox	✓	
TOC	✓	IR, UV
Total nitrogen		UV-V
Total phosphorus		V, C
Turbidity		N, UV, US, IR
UV=Ultraviolet V=Visible C=colorimetry Ch=Chemiluminescence IR=Infrared		

Table 4: Available technique (commercial or in development) for physico-chemical monitoring

✓ Priority pollutants monitoring

Priority pollutants mainly concern three categories:

- Non-polar organic compounds (e.g. some pesticides, and some industrial chemicals such as PCBs, and PAHs),
- Polar organics (some pesticides, and pharmaceuticals),
- Heavy metals (e.g. mercury and cadmium).

The methods for monitoring these pollutants are very different and depend on the level of concentration to be detected, their physico-chemical properties (polarity for example). The more common methods currently used for priority pollutants monitoring are chromatographic methods (gas chromatography, or liquid chromatography) linked to a sensitive detector (e.g. flame ionisation, electron capture, mass spectrometry, fluorescence spectrometry, UV spectrometry), and for metals methods such as inductively coupled plasma mass spectrometry, or graphite oven atomic absorption spectrometry. But these analytical techniques are not well fitted with field measurements and on-line water monitoring. However, the SAMOS (System for the Automated Monitoring of Organic Substances) flow-through system allows without interruptions, throughout an operation or for a predetermined time to monitor on-line specific pollutants (pesticides, PAH,...) . In this case, water is pumped from the river to a laboratory close to the intake site.

Some other alternative methods could be proposed to the currently used classical methods in order to provide more representative pictures of the chemical quality of water and to enhance the spatial and

temporal assessment of water bodies. New trends of current research are to develop miniaturised device with enough sensibility to detect priority pollutants generally present in water at low concentration. Electrochemical sensors are very promising in this case. Immunoassays, due to the interaction between pollutant and antibody, present a high sensibility.

- Electrochemical sensors

Voltamperometric probes and selective, or ion-specific, electrodes are particularly suited to *in situ* measurements because they require little or no sample treatment and enable continuous measurements to be performed. Electrochemical measurement systems have been miniaturised into screen-printed electrodes (SPEs) that are incorporated in hand-held equipment for on site monitoring of many heavy metals and certain pesticides (Laschi, 2006).

- Immunoassay test kits as screening tools

Immunoassays have been developed and proposed as screening tools in order to assess water quality and monitor some targeted pesticides (Candella, 1998). Immunoassay (IA) tests have been introduced in order to reduce the cost of water quality monitoring and enhance field measurements. Immunoassay test kits are now available for a wide range of organic pollutants such as PAHs, pesticides, PCBs, phenols.

Good selectivity, sensitivity, precision, and portability make immunoassays a cost-effective method for water monitoring. Due to their portability, immunoassay test kits show promise as screening methods in particular for mapping of pollutants. These immunoassays are also very useful in the case of known contaminant monitoring (Lesnik 2000, Hennion 1998, Bacigalupo 2005).

Enzyme-linked immunosorbent assays (ELISAs) based on the use of labelled enzyme conjugates are widely available in a range of formats such as coated-tubes, magnetic particles, or 96-well plates, enabling the simultaneous processing of a large number of samples. Enzyme conjugates are competitively displaced from binding sites by the free analytes. The tubes, magnetic particles or well-plates are rinsed and a chromogen is added to react with enzyme conjugates producing a coloured chemical. After a period of time the reaction is stopped, enabling spectrophotometric quantification of immobilised enzyme conjugates, and thus, from the difference, the concentration of analytes initially present in the sample (Pfeifer-Fukumura 1999, Ballesteros 2003).

- ✓ Biological assessment

The availability of powerful tools from biochemistry, molecular biology and genetics has contributed to development of sensitive and specialised biosensors. Research and development has stimulated the development of a series of novel on-line sensors that are promising and that are different from conventional sensors. As a result much effort has been made during recent years to develop and use different biosensors for toxicity evaluation of water samples (Castillo 2001, Rodriguez-Mozaz 2005). Whole organisms are used to measure the toxicity of a water or soil sample. For example, Cellsense, an amperometric sensor that incorporates *Escherichia coli* bacterial cells for rapid ecotoxicity analysis has been used within the direct toxicity assessment demonstration programme of the UK Environmental Agency. Biological tools have shown interest especially for toxicity assessment and identification of pressure points (Roig 2007). Moreover, in recent years biosensors have been shown to have great potential as analytical tools for effective monitoring of water and could be used as environmental quality monitoring tools in the assessment of biological/ecological quality elements or for the chemical monitoring of both inorganic and organic priority pollutants. They are intended for on-line or *in-situ* monitoring of some parameters including global pollution indicators and single or classes of compounds. The trends in RTD should be mainly focused on portability, on automated systems and on miniaturisation (Tschmelak 2005, Rodriguez-Mozaz 2004).

- Biosensors

Biosensors can be used for long-term monitoring of water. The main advantages are: quick analytical turnaround time, cost-effectiveness, portability, *in situ* measurement, high sensitivity and specificity. In general, biosensor devices combine a biological recognition element in contact with a transduction element, and have the potential to assess specific biological effects (e.g. toxicity, cytotoxicity, genotoxicity, endocrine-disrupting effects) due to contaminants. A very useful overview has been published recently describing an environmental application (Rodriguez-Mozaz 2006) involving monitoring both organic compounds (e.g. pesticides, PAHs, PCBs, and phenols) and inorganic compounds (e.g. heavy metals, nitrate, and phosphate).

- Whole organism bioassays

A whole-organism bioassay relies on the measurement of the biological response (acute or chronic toxicity) of a test organism to a mixture of contaminants present in water. Organisms commonly used include microorganisms, algae, amphipods, daphnids, oysters, and chironomid larvae. The test parameters usually measured include mortality, bioluminescence, metabolic status, and growth rate inhibition. Inhibition of bioluminescence in the bacterium *Vibrio fischeri* is the basis of the most common test. This type of assay is relatively simple to implement, and many commercial devices are available. A large toxicity database including many chemicals has been established for this assay, for which standard protocols exist (ISO 11348). These toxicity assays can be used for the rapid screening or mapping of contaminant levels (general toxicity, genotoxicity) in a water system.

- ✓ Passive samplers

Passive samplers provide alternatives to classical laboratory based analytical methods, and in some cases still depend on the collection of grab (spot) samples. In contrast, passive samplers replace spot sampling by accumulating pollutants over a prolonged deployment period to provide measurements of the average concentrations to which they have been exposed. The samplers are returned to the laboratory for extraction and analysis, and the latter is usually carried out using classical methods.

A range of integrative passive sampling devices has been developed and used in recent years. A comprehensive review of the currently available passive sampling devices has been published (Namiesnik 2005). Among the most widely used samplers are the semi-permeable membrane devices (SPMDs) for hydrophobic organic pollutants (Huckins 1993) and the diffusive gradients in thin films (DGTs) for metals and inorganic ions (Zhang 1998). Several novel passive sampling devices suitable for monitoring a range of polar organic chemicals, including pesticides pharmaceutical/veterinary drugs and other emerging pollutants of concern have recently been developed (Kingston 2000, Alvarez 2004). Passive samplers can be applied to investigate long-term temporal trends in water contaminants and to evaluate the location of point and diffusive contaminant sources (Vrana 2001, Blom 2002). These passive samplers are particularly relevant when the objective is to screen for the presence or absence of targeted pollutants (metals, pesticides). Due to their integrative function it is possible to quantify pollutants that are below the level of detection in bottle samples of water. Furthermore, they can provide a more representative picture of the level of freely dissolved contamination (but not material bound to particulate matter) since the mass accumulated will be indicated by the area under the concentration time profile to which they have been exposed. This is in contrast with spot sampling, which only provides an instantaneous measurement of concentrations of pollutants at the moment that the sample was taken. Passive samplers can thus reduce the uncertainties associated with the use of infrequent spot samples where contaminant concentrations fluctuate. Most passive samplers are suitable for deployment in surface waters, but only a few designs (e.g. the ceramic dosimeter) that has been used to monitor a range of organic pollutants including volatile organic compounds (Bopp 2005) have been developed for long term deployment in bore holes to monitor groundwater.

Performances evaluation of screening/emerging tools

In order to assess and evaluate in the field *in situ* methods and laboratory-based methods for screening pollutant levels in water bodies, field trials have been organised in several European sites. These sites have been selected based on the inventory of potential sites (River basins) given the main characteristics of water bodies; the Meuse River (NL), the Orlice River (CZ), the Upper Rhine (FR), the Ribble PRB (UK), the Daugava River (LV), the Aller River (D) and the Tevere PRB (IT).

The objectives of the testing activities were to compare current monitoring systems and screening methods (lab-based methods, passive samplers, sensors, biological methods, immunoassays) and to demonstrate the potential use of these tools in monitoring strategies (surveillance, operative and investigative monitoring).

The monitoring requirements for successfully implementing the WFD will directly depend upon available measurement techniques of demonstrated quality, which will be able to deliver reliable data. Due to the poor state of the art in the area of alternative/screening method validation, there is an obvious need to develop validation procedures in order to assess the performances of these methods for water monitoring under WFD requirements. The lack of an accepted validation process and performance evaluation plan is the main constraint on the acceptance of new technologies and their integration into water monitoring strategies.

The main concepts generally used for standard method (laboratory methods) should be adapted in particular for field measurement systems. In this context, the aim of SWIFT-WFD activities were to evaluate the performances of some selected screening methods (physico-chemical, biosensors, bioassays...) in laboratory and in field conditions and to compare to the specifications mentioned by the manufacture (C. Gonzalez 2007). The last field trial organized in Italy on Tevere river basin (near Perugia) focused on the validation procedure application.

The requirement for analytical quality control and analytical quality assurance is to ensure that data provided by new systems (on-site and/or in-situ methods) are of adequate accuracy for their intended use. A novel approach to validating some techniques for on-site measurement has been investigated (evaluation of method performance characteristics) and is summarizing in the Figure 1.

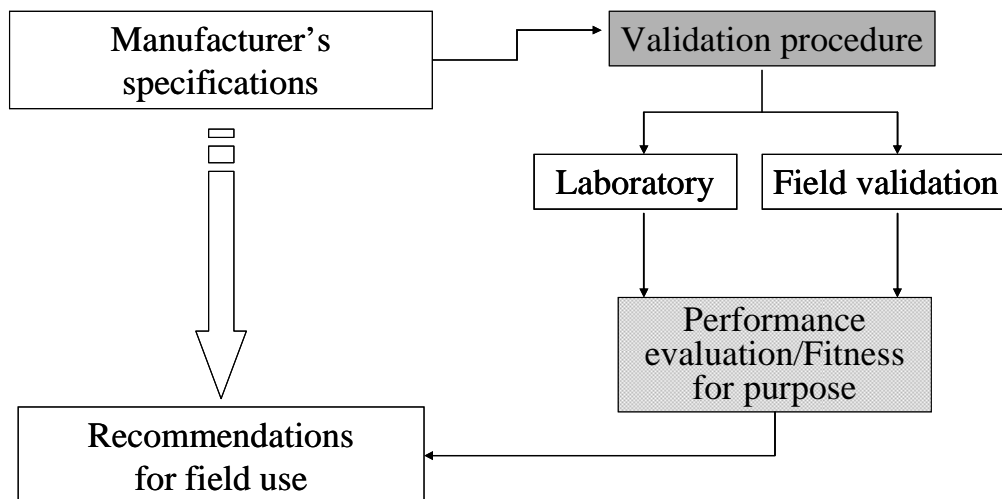


Figure 1: Proposed methodology for the evaluation of performances of screening methods

In accordance to objective, this methodology has been applied to selected tools and the results analysed on the basis of standard procedures (based on statistical tests):

- Portable UV instrument,
- Multiparameter probe,
- Chemical test kit,
- Palmsens (screen printed electrode),

- Immunoassays,
- Bioassays.

For the physico-chemical devices (Portable UV, multiparameter probe, chemical test kit, Palmsens device) and immunoassays, the classical validation procedure has been investigated and led to the evaluation of performance criteria (linearity, calibration line, repeatability, LoD, LoQ, selectivity and ruggedness). In general, the obtained results are in good agreement to manufacturer's specifications and performance criteria assessed in field conditions are not significantly different than those obtained in laboratory conditions (same measurement trends). Reference materials could be used as internal quality control tool in order to verify the methods performances as well in laboratory condition as field condition.

For bioassays, usually performed in laboratory conditions, two systems (Microtox and Toxscreen) have been deployed in field conditions in order to determine their portability despite practical constraints due to micro-organisms growth and storage. The performances have been evaluated according to the standard procedure NF ISO 11348-3. Results obtained in laboratory and field conditions are in good agreement. The two bioassays have been compared on the basis of raw samples. Finally, these bioassays have been used in order to monitor the toxicity in the tidal of the Ribble estuary.

Moreover, on the basis of field trials organized in several European sites (Aller in Germany, Daugava in Latvia, Orlice in the Czech Republic, Tevere in Italy, Rhine in France and Ribble in the United-Kingdom), the results obtained by screening methods/devices have been compared to classical methods in order to demonstrate their equivalence and to define their potential function/use for water quality monitoring.

Screening/emerging tools potential uses and their integration on water monitoring strategies

Some examples/case studies performed in the framework of SWIFT-WFD (European project n°SSPI-CT-2003-502492), illustrate the potential of screening methods for use in water monitoring programmes. Case studies (pilot river basins) were conducted in parallel with field trial activities in five different countries, i.e. the Ribble Estuary in the United-Kingdom (one of the pilot river basins of the EU Common Implementation Strategy developed by Member States and the European Commission for supporting the implementation of the WFD), the Aller River in Germany, the Daugava River in Latvia, the Alsace aquifer in France and the Orlice River in the Czech Republic. These activities built on: the analysis of technical and socio-economic information collected from the different sites; real-life testing and demonstration of screening methods and emerging tools; and interviews with various stakeholders (laboratory staff, experts from water management authorities, etc) and potential users of the screening/emerging tools. The selected sites illustrate different types of water that can be found in European river basins (surface water: rivers, lakes, estuaries) and groundwater. The other goals are to study spatial and temporal variability in water quality (using biological screening tools) and assess anthropogenic pressures (urban and agriculture activities).

On the basis of these case studies, the potential functions for screening methods and emerging tools in the development and implementation of WFD water quality monitoring are presented in the following table (Table 5). The function of screening/emerging tools is described and the more relevant methods proposed according to the monitoring requirements.

Monitoring requirements	Function of emerging tools	Relevant screening methods and emerging tools
Design future monitoring programmes efficiently and effectively	Account for natural variability and variability arising from anthropogenic activities (frequency of monitoring)	Biomarkers, passive samplers, sensors that can be used for continuous monitoring (e.g. multiparameter probe)
	Monitor a sufficient number of sites to adequately describe spatial effects (density and location)	Biomarkers, chemical/electro-chemical sensors
Surveillance monitoring: assessment of long-term changes in natural conditions as well as from widespread anthropogenic activities	Testing for long term trends	Bioassays, biosensors, passive samplers, Biological Early Warning Systems (BEWS)
	Monitor significant new/emerging pollutants	Bioassays, biosensors
Operational monitoring: assess impact and magnitude of pressures	Identify point and diffuse pollution and their dispersion/migration Select monitoring sites which give representative information on different impacts	Biomarkers, chemical/electro-chemical sensors, immunoassays
Investigative monitoring: assess causes of water bodies failing to achieve environmental objectives where reason is unknown	Analyse full range of potential impacts Identify locations of pressures/sources	BEWS, bioassays, biosensors, chemical/electro-chemical sensors, passive samplers

Table 5: Potential functions for screening methods and emerging tools in the development and implementation of WFD water quality monitoring

The integration of novel tools in water strategies is illustrating in the following process of decision making (Figure 2). According the objectives of water monitoring, the choice of the more relevant methods according the field measurement constraints is one of the most important step in the general procedure. Water monitoring is conducted based on specific parameters and targeted pollutants. The obtained data should then convert into information on water quality in order to define water status, to investigate quality trends. The third step is mainly dedicated, based on relevant models, to the prediction of deterioration of water bodies and to enhance the knowledge of aquatic ecosystem evolution.

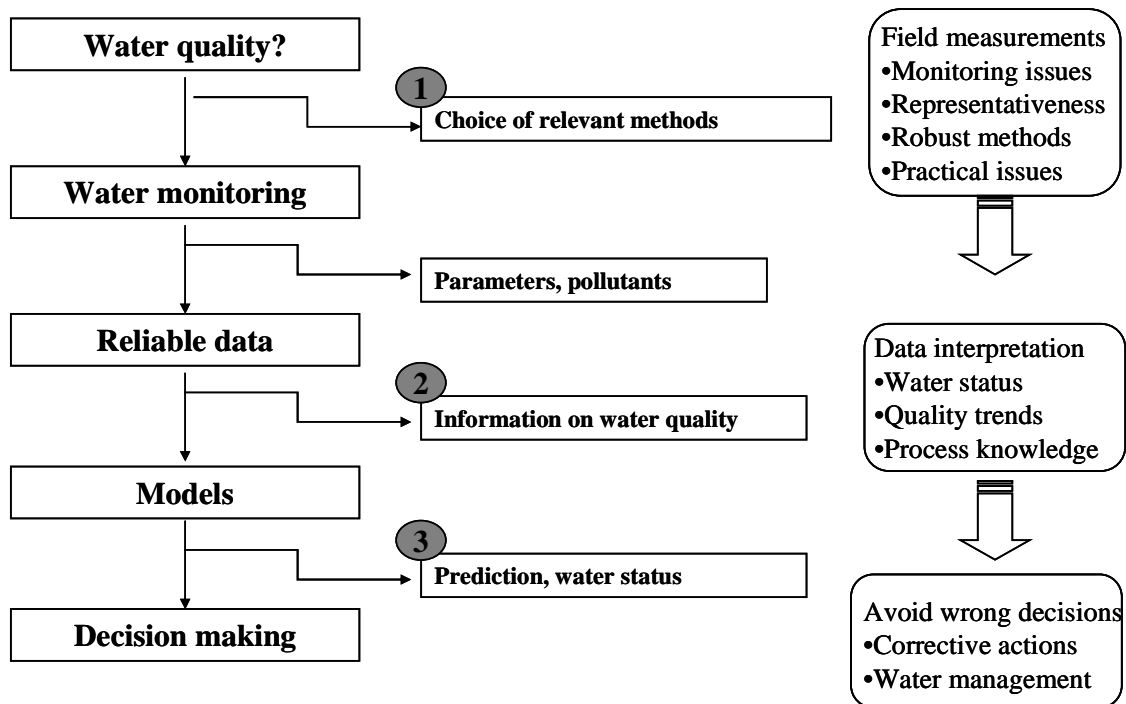


Figure 2: Integration of novel tools in water monitoring strategies

A socio-economic study of factors indicated that the main barriers to the acceptance of novel tools by water actors (regulatory authorities, water managers, stakeholders...) and the factors affecting the adoption of new technologies are:

- Limitation of change (continuity of historical data),
- Needs to provide protocols and training for the use of new tools/technologies,
- Comparability to existing methods (laboratory methods),
- Absence of Quality Assurance assessment and accreditation.

Moreover, the integration of novel tools in the water monitoring strategies could lead to cost saving but it depends on many parameters taking into account for the cost calculation (investment, personnel cost, consumable, transport, frequency of monitoring...).

Conclusion and perspectives

In order to assist in improving water monitoring programmes by providing new information concerning water status and monitoring through the selection and utilisation of screening methods, the SWIFT-WFD consortium published a Best Practice Guide (2007) enable stakeholders involved in water policy and management to decide how the field monitoring methods (existing and emerging) could be promoted, where and for which application, and at what approximate cost. Due to the diversity of water bodies across Europe, this Best Practice Guide proposes a general approach whilst still trying to provide a complete overview of the screening methods and a practical approach to their implementation.

The main conclusions that should be highlighted on the new challenges for water monitoring and the potential role of novel monitoring tools are:

- These methods/tools should be used are complementary approach to classical ones,
- The obtained information are complying the WFD requirements and are as relevant as the those got by classical methods,
- Finally, it should be noticed that all the studies investigated across Europe have shown real performances for investigative and operational monitoring.

Concerning the monitoring perspectives, there is a need for systems allowing timely warning and information on water pollution and on the total state of water system. For source water and environmental monitoring, as well as process control, instruments are needed that can be employed on location or in-situ and that can be monitored through remote control. In terms of new challenges for further research activities, the priority will be given to miniaturised sensing systems and wireless network technology for the deployment of essentially self-sustaining wireless sensor networks aimed at spatial and temporal water quality assessment.

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