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Preface

This report has been prepared by H.A.G. Niederländer, J. Dogterom, P.H.L. Buijs and R. Hupkes (ICWS/International Centre of Water Studies, The Netherlands), in close cooperation with M. adriaanse (RIZA, The Netherlands). The guidance-committe on this report comprised of J. Botterweg, P.B.M. Stortelder, O. van de Velde (RIZA, The Netherlands) and C. Roos (Witteveen & Bos, The Netherlands.

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1. Introduction

1.1 General

The Convention on the Protection and Use of Transboundary Watercourses and International Lakes (hereinafter referred to as the Convention) was drawn up under the auspices the Economic Commission for Europe and adopted at Helsinki on 17 March 1992. The Convention was signed by 25 countries and by the European Community before the period of signature closed on 18 September 1992. It will enter into force 90 days after the date of deposit of the sixteenth instrument of ratification, acceptance, approval or accession. By the time of writing of this report, thirteen countries and the European Community had deposited their relevant instruments of ratification with the United Nations Secretary-General.

To comply with the obligations under the Helsinki Convention, the Parties will, inter alia, have to set emission limits for discharges of hazardous substances from point sources based on the best available technology. In addition, they will have to apply at least biological treatment or equivalent processes to municipal waste water. They shall also issue authorizations for the discharge of waste water and monitor compliance. Moreover, they have to adopt water quality criteria and define water quality objectives. To reduce the input of nutrients and hazardous substances from diffuse sources, in particular from agriculture, they shall develop and implement best environmental practices. Furthermore, environmental impact assessment procedures and the ecosystem approach shall be used to prevent any adverse impact on transboundary waters.

Consequently, the Helsinki Convention addresses such issues as monitoring, assessment, warning and alarm systems, and exchange and presentation of information. For example, the Parties bordering the same transboundary waters will have to set up joint or coordinated systems for monitoring and assessment of the conditions of transboundary waters, and set up coordinated or joint communication, warning and alarm systems. The clear objective of monitoring and assessment systems such as the Helsinki Convention is to prove that changes in the conditions of transboundary waters caused by human activity do not lead to significant adverse effects on flora and fauna, human health and safety, soil, air climate, landscape and historic monuments or other physical structures or the interaction among these factors.

The establishment of a system to furnish proof that these objectives are met is a challenging task. Moreover, monitoring compliance with the provisions of the Helsinki Convention demands reliable information on waters and factors influencing water quality and quantity. There is, for instance, a need for information related to in-stream quality, such as conditions of waters (water quantity and quality), aquatic and riparian flora and fauna, and sediment. Information related to extreme conditions in waters, caused by accidents, floods, drought or ice cover, is also needed. Emission sources also have to be monitored to obtain information on the concentration of pollutants in effluents, and to carry out pollution-load assessments.

Consequently, information on monitoring of surface waters and significant emission sources in catchment areas of transboundary waters is required. This includes information on the legal basis of emission monitoring, selection of variables, selection of sampling sites and frequencies and documentation and reporting of the results (both to authorities and to the public at large). Information on monitoring for early warning purposes, including biological warning systems, is required as well.

Following the adoption of the Convention, the Senior Advisers to ECE Governments on Environmental and Water Problems (now known as the ECE Committee on Environmental Policy) entrusted its Working Party on Water Problems with the implementation of the Convention, pending its entry into force. To implement the work plan, the Working Party has set up several task forces and groups of rapporteurs. The topics addressed are:

1. point sources;
2. diffuse sources;
3. legal and administrative aspects;
4. sustainable water management;
5. monitoring and assessment.

The present report has been prepared within the context of the Task Force on monitoring and assessment, which was led by the Netherlands.

This Task Force has been charged with the preparation of draft guidelines to ECE Governments on monitoring and assessment. During the first meeting of the Task Force, a phased approach towards this goal has been approved. During the first phase, the focus will be on 'running-water' transboundary water courses (i.e. rivers, streams, canals), while in later phases, the focus will be on lakes, estuaries and groundwaters.

The present report is one in a series of 5 background documents to be used for the drafting of guidelines on monitoring and assessment of running-water transboundary water courses. These reports deal with the following themes:

1. inventory of transboundary rivers and international lakes in Europe;
2. inventory of current monitoring and assessment practices in UN/ECE countries;
3. preparation of draft guidelines for biological assessment of rivers;
4. preparation of draft guidelines for quality assurance;
5. inventory of State of the Art practices in monitoring and assessment.

The present report is the result of the activities under item number 5: Inventory of State of the Art practices in monitoring and assessment.

1.2 Scope and definitions

This report provides an overview of State of the Art monitoring and assessment strategies and methodologies for running-water transboundary water courses. Primarily, this requires a proper definition of what exactly is meant with the terms monitoring and assessment. The terms monitoring and assessment are frequently confused and used synonymously [Meybeck and Helmer, 1992]. Here, the following definitions are used:

The process of water quality assessment is an evaluation of the physical, chemical and biological nature of water in relation to natural quality, human effects and intended uses, particularly uses which may affect human health and the health of the aquatic system itself. Water quality assessment includes the use of monitoring to determine the condition of the water, to provide the basis for detecting trends and to provide the information enabling the establishment of cause-effect relationships.

Water quality monitoring is the collection of information at set locations and at regular intervals in order to provide the data which may be used to define current conditions, establish trends etc.
In the context of this report, water quality monitoring is used in a broader sense, also including survey and surveillance (see also section 4.2):
- survey: a finite duration, intensive programme to measure, evaluate and report the quality of the aquatic environment for a specific purpose;
- surveillance: continuous, specific measurement, observation and reporting for the purpose of water quality management and operational activities.

1.3 Outline of the report

In Chapter 2, the strategy of water quality monitoring and assessment in general is dealt with. This chapter provides insight into the relevance of monitoring and assessment as tool for the provision of information required for management and control. Aspects covered include: the requirements of water resources (uses) which need to be sustained, the type of information needed for this purpose, the necessary framework for a monitoring and assessment programme to be able to provide this information (strategy and integration of elements), and finally methods for assuring the quality of the information produced.

In Chapter 3, consideration with respect to the definition and handling of criteria and objectives for the assessment of water quality are discussed. The chapter deals with the definition of criteria for the protection of the various uses of water resources and the setting of objectives for improving water quality. Furthermore, the setting of criteria for the protection of 'aquatic life', based on either chemicals or on ecosystem community structure and functioning, is considered.

Chapters 4, 5 and 6 deal with the more technical features of the design and operation of monitoring programmes. They address monitoring of running surface waters and effluents and monitoring for early warning purposes, respectively. Items discussed are: the selection of physical, chemical or biological variables, of sampling media, of sampling sites and of sampling frequencies. Furthermore, issues that should be considered when performing field activities (e.g. sampling and in-situ measurements), analysis and data validation, data storage, interpretation and presentation are also described. With respect to effluent monitoring, special attention is paid to the legal and organizational aspects. With respect to early warning monitoring, special attention is paid to the implications of the necessity for timely warning of 'downstream water users'.

2. Water quality management strategy and information needs

2.1 Multi-functional approach in water quality management

The need for information on water quality stems from the requirements of specific quality of water for specific uses. It can be stated that the human mind perceives water quality as being good if desired water uses are satisfied, and not good if they are not [McBride, 1986]. This means that a particular concentration of some chemical dissolved in water may reflect either good or bad quality water. For example, a concentration of 2 parts per million boron in a river may not affect any present uses of the river, and the river water might be considered to be of good quality. However, if the water is subsequently required for regular irrigation of certain horticultural crops, the boron concentration will be too high and the water may then be considered to be of poor quality (that will certainly be the irrigator's view) [McBride, 1986].

There is an increasing consensus that 'water quality' should be taken to mean the physical, chemical and biological characteristics of water necessary to sustain desired water uses. By defining 'water quality' as referring to the suitability of water for its desired uses, and by equating 'conservation' with promoting best uses of water, water resources management goals can be harmonized into a simple statement: to promote and protect desirable water uses [McBride, 1986]. This deliberately excludes notions of 'maintain or improve', as a monitoring goal, because a goal must be more clearly defined and quantifiable. Also, use of the word 'desirable' carries the implication that indicative water resource management plans should be formulated in the light of the public's desires for water use.

With the advent of industrialisation and increasing population, the range of demands for water has increased together with greater demands for higher water quality [Meybeck and Helmer, 1992]. Over time, water requirements for many end uses have emerged. These end uses include: drinking and personal hygiene, fisheries, agriculture (irrigation and livestock supply), industrial production, cooling in fossil fuel (and later also in nuclear) power plants, navigation for transport of goods, hydropower generation, and recreational activities such as bathing or fishing. The largest demands for water quantity, such as for agricultural irrigation and industrial cooling, generally have the lowest requirements in terms of water quality. Critical concentrations may only be set for a few variables. Drinking water supplies and specialised industrial manufacturers exert the most sophisticated demands on water quality but their quantitative needs are relatively moderate. In parallel with these uses, water has since ancient times been considered the most suitable medium to clean, disperse, transport and dispose of wastes (domestic and industrial wastes, mine drainage waters, irrigation returns etc.).

The uses of water can be defined to include the functioning of the aquatic ecosystem. However, it should be realized that it is not appropriate to interpret essentials for the functioning of the aquatic ecosystem in terms of a use of water resources.
The functioning of the aquatic ecosystem is rather an inherent

characteristic than a ‘use’ of water resources. The functioning of the ecosystem is not a commodity whose consumption can be weighed against negotiable benefits. Nevertheless, in (international) policy frameworks, ecosystem functioning is considered a use of water resources in order to provide principles and objectives for water resource management, based on a multi-functional approach [Agenda 21 (Chapter 18] [IRC, 1987]. Whenever reference is made in this report to the uses of water resources, the water quality requirements for ecosystem functioning are meant to be included.

Considering existing policy frameworks, including Agenda 21 (Chapter 18), international and regional conventions, and (strategic) action plans for river basins or seas, a total of 9 uses may be defined [Dogterom and Buijs, 1995]. Specific characteristics for the river basin and governing socio-economic sectors (with their demands) determine which uses are relevant to a certain river basin.

Table 1.2:
Uses of water resources

Category 1: Uses without quality standards	1. Transport system (water, waste water, shipping) 2. Mineral extraction (sand, gravel, natural gas, oil) 3. Power generation (hydropower dams)
Category 2: Uses with defined quality standards	4. Process/cooling water in industry 5. Irrigation in agriculture 6. Fisheries 7. Recreation and tourism 8. Domestic water supply
Category 3: ’Use’ with ‘undisturbed’ quality	9. Ecosystem functioning

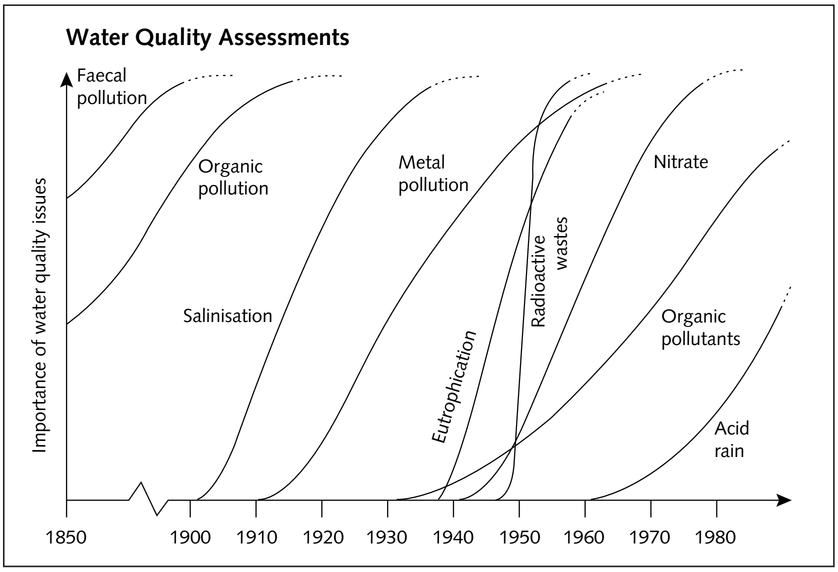
Knowledge on the relation of uses and the quantity and quality of the water resources is rapidly expanding [Dogterom and Buijs, 1995].
The category 1 uses do not require a specific quality of water resources: they can be met as long as there is sufficient water.
The category 2 uses need a defined minimum quality. They might come into conflict with each other and with category 1 uses in situations of water scarcity. Many countries have systems of ambient water quality standards in operation, sometimes internationally harmonized, as in the EU. For ecosystem functioning, an ‘undisturbed’ quality is required.
In practice, this means that ambient water quality standards are formulated for ‘no-effect’ levels (see also chapter 3).

The identified water uses may conflict with each other, in particular in situations of water scarcity and deteriorating quality. Chemical water quality issues, which have in the past or may presently lead to conflicts between water uses in industrialised countries, are summarized in figure 2.1.

A policy framework should formulate the objectives of a policy, based on clear choices for specific uses. An integrated approach, which is mostly chosen in recent policies and strongly recommended by Agenda 21 (Chapter 18), tries to find the balance between all uses desired, including the ecosystem functioning. A multi-functional approach allows the introduction of a hierarchy in uses, e.g. according to the categories presented in table 2.1.
It has the flexibility to be applied at different levels of development of

water resources management policies and for prioritization in time. This could be important for countries where basic needs like supply of healthy drinking water is so urgent that other uses will have lower priority, or for countries where water resources have already deteriorated to such an extent that 'higher' uses can only be gradually restored over a long time range and in priority order. It also allows for differentiation between different water resources. The political choice, however, is completely transparent to the consumer and is thus susceptible to correction, if the political system allows.

Figure 2.1:
The sequence of water quality issues arising in industrialised countries [Meybeck and Helmer, 1992]



2.2 Management strategy: an integrated approach

Modern water quality and water resources management is based on an integrated approach and the involvement of authorities at all levels and in all sectors. Information needs are thus not only determined by the national water authorities. Consumers' support is necessary for the acceptance of realistic user prices. The public at large should be aware of the competition among different water users for limited water resources. There should be a general awareness that water resources are scarce and have to serve many purposes simultaneously. The objective of integrated water quality and water resources management is to promote sustainability of all water uses, including the ecosystem functioning, by minimizing conflict between different water users. To accomplish this objective, involvement and commitment of all players is indispensable. Thus, integrated water management has an intrinsic institutional component, namely, conflict resolution and/or prevention by participation. This counts in particular, when an integrated management strategy for a transboundary water course has to be developed, negotiated and accepted.

If sustainability of water uses in an international river basin has to be promoted, certain principle approaches are an intrinsic part of an integrated management strategy:

- river basin approach;
- ecosystem approach;
- emission/water quality based approach.

These approaches each generate a specific type of information need, which should be tailored to the different players in the process as mentioned before.

2.2.1 River basin approach and information needs

A river basin approach implies that an information system has to be internationally harmonized and that communication structures have to be institutionalized. This means that there must be a consensus on choice of variables, sampling frequencies, comparability of analytical results, harmonization of legislation etc. A transnational monitoring network has to be established, based on national networks. In practice, this requires harmonized procedures for different types of monitoring and assessment. These procedures are discussed in chapters 3-6 of this report.

Historically, water resource management and therefore monitoring and assessment in river basins have been assigned to administratively defined programmes (i.e. confined to national or even local administrative units). However, there is now an increasing consensus that the best way to deal with water resources is to recognize the natural boundaries of the water systems, i.e. the river basins, rather than administrative boundaries [Van Dam and Wessel, 1993]. This approach recognizes that user conflicts will often extend outside administrative boundaries. Such problems can only be solved if there is a common agreement on the uses that should be protected within a river basin and an accepted to assess whether or not these uses are protected.

In some countries, e.g. New Zealand, the UK and France (Mc Bride et al. 1985 reference in [Meybeck et al., 1992]), national assessment programmes are undertaken using this river basin approach. On an international scale, such an approach is less common. New developments in the Elbe basin and the Danube Basin [EPDRB, 1994] are encouraging however. The cooperation of the riparian states of the Rhine River, amongst others, in the field of monitoring (including effluent monitoring and early warning), is probably one of the most illustrative examples [EC, 1977a] [Spreafico, 1992]. The 'Helsinki Convention' may provide a valuable impetus for further initiatives towards water resource assessment and management on a river basin level.

2.2.2 Ecosystem approach and information needs

The ecosystem approach to water quality and water resources management recognizes the importance of taking all ecological aspects of aquatic systems into account. Problems concerning ecosystem functioning require a specific type of information. The UN/ECE 'Guidelines on the ecosystem approach in water management' [UN/ECE, 1993a] provide some valuable directions to this end.

These guidelines state:
'Ecosystem assessments should be based on integrated criteria in terms of water quality and quantity as well as flora and fauna. Systematic analysis of water quality, flow regimes and water levels, assessment of habitats, biological communities, sources and fate of pollutants as well as mass balance derivations should be undertaken in order to provide reliable information'.

The guidelines further state:
'Such monitoring programmes allow for an integrated evaluation more capable of determining cause effect relations than other less comprehensive monitoring programmes currently under way'.

Special emphasis is placed on identifying and diagnosing a problem as early as possible so that remedial action can be taken before damage has occurred. Compliance, diagnostic and early warning indicators are required in order to determine whether or not ecosystem objectives are under pressure and to trace probable causes if they are. To this end, coordination of physical, chemical and biological measurements would improve understanding of the effect each variable has on the ecosystem. *'The ecosystem approach has to rely more than usual on continuous liaison between the disciplines involved in monitoring' [UN/ECE, 1993a].*

The number of chemicals that might affect water quality is nearly uncountable. In the European Inventory of Existing Chemical Substances (EINECS), about 100,000 chemicals have been identified. An unknown number of these chemicals has been discharged into surface waters. However, in chemical monitoring programmes, only a very limited number of chemicals – mostly about 30 to 40 substances – are monitored regularly in European aquatic systems [Adriaanse *et al.,* 1995]. Organisms studied in-situ can show the integrated effects of all impacts on the water body, and can be used to compare relative changes in water quality from site to site, or over a period of time. Disturbances, which cannot, or only with great difficulty be detected by physical or chemical monitoring, can sometimes better be followed by biological methods [Klapwijk *et al.,* 1994]. Biological methods, where appropriate, can also offer a cheaper option as compared to chemical analytical methods [Friedrich *et al.,* 1992]. The advantages of biological methods, however, do not eliminate the need for chemical analysis of water samples. In many cases, biological methods can provide a good indication of the existence of a pollution problem. However, chemical analysis will often be required for diagnostic purposes and to trace back the pollution source.

Monitoring only biological or chemical characteristics may even obscure the causes and the extent of the problem. For example, a low biodiversity may well be the result of toxic pollution, but it may also be caused by habitat disturbance. Similarly, a high concentration of for instance arsenic may or may not represent toxic pollution, depending on it's bioavailability.

Nowadays, for the quality assessment and monitoring of aquatic systems a triad of approaches is recommended [Chapman, 1986] [Van de Guchte, 1992], consisting of:

- chemical analysis of water, suspended matter, sediments and organisms;
- bio-assays and bio-alarming methods;
- biological survey.

Most of the arguments presented above promote the integration of chemical and biological methods, whereas hydrological methods are hardly mentioned. The necessity for integrating hydrological measurements with chemical (and biological) measurements as well, is illustrated by one of the most important findings within the project for evaluation of the monitoring, laboratory analysis and information capabilities of the riparian countries of the Danube basin [Lack *et al.,* 1994].

One of the most important findings on the missions which is further substantiated in the database concerns lack of coordination between water quality measurements and hydrological measurements. Although most of the countries make flow measurements, these are mostly done at the nearest hydrological station rather than at the water quality station itself. There are historical reasons for this division of tasks between the hydrological services and the laboratories and this is also reflected at ministerial level. In practice, this has resulted in the fact that the use of flow and concentration data to calculate loads, mass balances, import and export of major polluting substances is typically nonexistent.

This logically adds to the above made arguments for integrating chemical and biological monitoring. Hydrological causes may have biological effects.

2.2.3 Emission/water quality based approach and information needs

In this report surface water quality monitoring for running water courses ('water quality monitoring'), effluent monitoring ('waste water monitoring') and aspects with respect to the integration of these two types of monitoring will be considered. The interrelationship between these two categories of monitoring and assessment is governed to a large extent by the policy approach chosen. Two principal approaches can be recognized:

- the emission-based approach
- the water quality-based approach

The difference between these approaches is mainly characterized by the discharge limiting and charging systems applied. The differences are also reflected in the strategies taken towards hazard assessment and monitoring of discharges to water. Monitoring is either focused on effluent water (emission-based approach) or on receiving water, including the mixing zone (water-quality based approach).

In a pure emission-based (also called 'technology based') approach, it is essential that the discharge limits do not depend on the change in quality of the receiving water. Pollution prevention by a careful choice of raw materials, clean production processes, good-house-keeping and the application of the best practical or best technical treatment techniques is required. This requirement is generally referred to as necessitating BAT (Best Available Technology). The pollution reduction required is based on general (toxic) properties of the chemicals and properties like persistence and bioaccumulation potential.

Table 2.2:
Differences in the emission-based and the water-quality based approach [Stortelder and Van de Guchte, 1995]

	Emission-based	Water quality-based
Effluent limits	No site-specific load	Site-specific concentrations
Required treatment techniques	Based on intrinsic (toxic) properties of chemicals in effluent; or technology based	Based on water quality criteria or preventing toxic effects in the effluent receiving water
Data requirements	Basic chemical and ecotoxicological data	Basic chemical and ecotoxicological data. Physical, chemical and biological characteristics for the receiving water and the fate of discharged chemicals
Monitoring	Effluent	Receiving water
Competition	Equality for the law	Inequality
Practice	May tend to worst case approach in general, but may underestimate effects of discharges in specific situations	May tend to dilution as a solution in general, but stricter standards are possible when effects are intolerable in specific situations

In a pure water quality based approach, the resulting site-specific water quality (or ecological functioning of the receiving water body) is the focal point for the setting of discharge licenses. Prevention of pollution does not necessarily require BAT if integrity of the ecological functioning of the receiving water body can be warranted by other means. In other cases more stringent requirements than provided by BAT may be needed. In table 2.2 the most important differences between both approaches are presented.

It is obvious that the selected policy approach dictates the monitoring strategy to a large extent. Effluent monitoring is of primary interest in an emission-based approach while monitoring of the receiving water is of primary interest in a water quality-based approach.
But the monitoring strategy may also be determined by practical possibilities. If, for instance, diffuse pollution from agriculture or deposition (dry and wet) is considered, a water quality based approach will be more practicable, based on the fact that monitoring the quality of the receiving water is the only and most adequate method.

A pure emission based approach or a pure water quality based approach is hardly ever practised. In most countries, a combination of both approaches is generally used. Such a combined approach recognizes the fact that a practical approach to water pollution control should not endanger the economic viability of the dischargers (equality for law), by placing unrealistically high demands on effluent quality, and must protect important water uses (especially domestic water supply and ecosystem functioning) to a sufficiently high extent.

Such a combined approach is also reflected in the 'Helsinki Convention', which states [UN/ECE, 1992), Article 3, paragraph 1/b to d]:

1. To prevent, control and reduce transboundary impact, the parties shall develop, adapt, implement and, as far as possible, render compatible relevant legal, administrative, economic, financial and technical measures, in order to ensure,
   inter alia, that:

   (b) Transboundary waters are protected against pollution from point sources through the prior licensing of wastewater discharges by the competent national authorities, and that the authorized discharges are monitored and controlled;
   (c) Limits for wastewater discharges stated in permits are based on the best available technology for discharges of hazardous substances;

   (d) Stricter requirements, even leading to prohibition in individual cases, are imposed when the quality of the receiving water or the ecosystem so requires.

2.3 Customer-supplier relationships: translation of policy objectives to information needs

The policy objectives of water resource management, as formulated in international declarations, international and regional conventions and national policy plans and laws, reflect the choices for sustaining specific water uses. In order to define information needs, and to subsequently design water quality monitoring systems (the 'supply side') that support water quality management (the 'customer side'), a management strategy aimed at implementation of the policy objectives, must be clearly formulated.

Policy and legal documents generally are too generic to provide a sound basis for the definition of information needs, and for the subsequent design of a monitoring system [Cairns, 1985]). Examining the water quality objectives that have been included in policy and legal documents reveals the difficulty in developing a monitoring system design that will be able to provide the required information.

Ward et al. [Ward *et al.,* 1990] illustrate this difficulty based on the current US water quality 'working' objective of 'fishable and swimmable.' With this broad objective, it is not clear what information is needed in order to assess attainment of the objective. It appears that information on fish and swimmers is needed. First relevant (quality) criteria have to be derived before the design of a monitoring programme can start. Another illustration of a broad objective is the goal to bring 'the salmon back in the Rhine' (Rhine Action Plan, 1987). In this example, information is needed on breeding areas, migration routes, and physical constraints, rather then information on water quality.

A more specific definition of information needs can be extracted from the management functions and powers (management 'tools') that have been installed for implementation of policy and legal arrangements. Each of these tools requires specific information. The exact information needs of each tool are not usually spelled out in the legal and policy documents, but rather are defined by the staff charged with implementation. These water quality management professionals can provide guidance in defining exactly what information is needed to properly implement the available management tools. The management structure and strategies of a given organization will strongly influence information needs and expectations from monitoring [Ward *et al.*, 1990].

2.4 Information system design

In examining the various ways that a management agency's powers and functions are implemented, an information system designer has to carefully assess the regulations, water management policy plans and guidance documents being prepared as a part of the implementation strategy. Examining the various powers and functions in such an thorough manner will help define the information needs of management. The connection between the data collected by monitoring and their use within a management agency is an important element in the success of any water quality monitoring system design [Ward *et al.*, 1990]. The time and effort devoted to preparing a final report and developing a consensus on information goals will therefore be significant.

Apart from information needs, which are generally rather specific, some more general assessment objectives can be defined. Meeting the information needs will generally come down to a clarification of these assessment objectives for more specific purposes or situations as defined by water resource management strategies. In general, four types of assessment objectives can be distinguished:

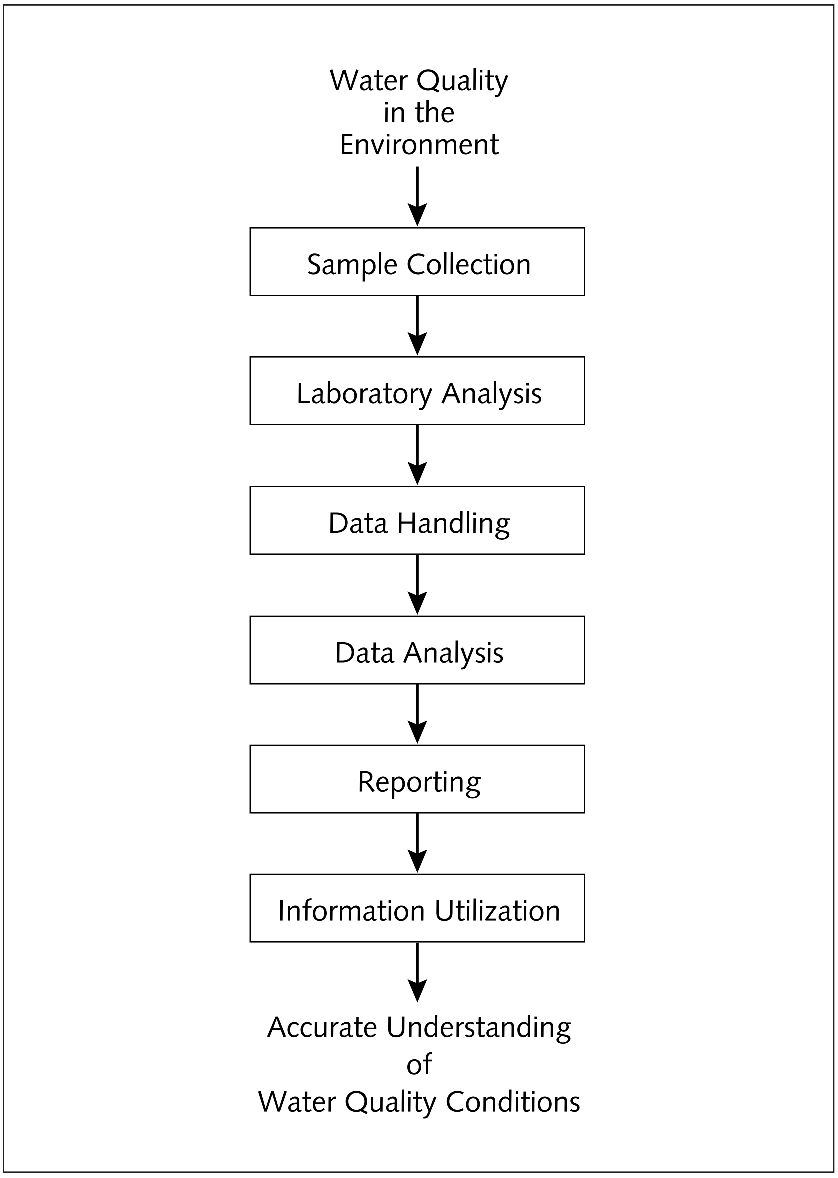
- checking of compliance with water quality criteria and objectives;
- estimation of mass flow and balances (loads);
- detection of trends (in concentration and load);
- timely recognition of (accidental) pollution (early warning).

From these general types of assessment objectives, specific assessment objectives can be formulated.

In section 2.3, the need for integrating different types of information needs in a monitoring and assessment programme, in order to get information that is mutually complementary and affirmative, was delineated. It is important that a monitoring programme is designed in such a way that an assessment actually meets the information needs. Designing a monitoring programme in this way requires insight into the general path from raw data to finally aggregated information.

There are certain standard elements that are common to all water quality monitoring programmes [Meybeck *et al.*, 1992]. These elements are developed depending on the type of assessment required. The collection of the water quality information as part of a monitoring programme departs from a situation where water quality is undefined and arrives at a definition of water quality that is sufficiently detailed to allow for a judgement in a comparison with specifically formulated standards. Along the way, information concerning the water quality is gradually made explicit. As such, a water quality monitoring system, following the flow of information, can be defined in a summary fashion as in figure 2.2 [Ward *et al.*, 1990].

Figure 2.2:
Flow of information through a monitoring system [Ward, 1994a]



The first three components of this 'information flowpath', i.e. sample collection, laboratory analysis and data handling, can be viewed as the data generation portion of the total system. The last three components in the figure, i.e. data analysis, reporting and information utilization, can be viewed as the information generation part of the total system. Each component imposes conditions on the type and quality of information flowing in from a previous component. It is therefore important that each component is designed so that it delivers the type and quality of information required in the next component. Especially the last three components (the information generation part) are rarely designed before the initiation of the actual monitoring (see also [Ward, 1986]).

Following from the need for input of a specific type and quality in the subsequent components in figure 2.2, it can be concluded that the design of a monitoring programme, aiming at water quality assessment, should address the various components in the opposite direction. The entire framework for designing a water quality monitoring system, can be summarized in the following [Ward *et al.*, 1990]:

Step 1: Define information needs of management
- identify information needs of each management tool
- summarize information needs of agency
- relate agency information needs to monitoring strategy
- define reporting and information utilization procedures desired by management
- determine appropriate statistical means for producing the desired information

Step 2. Define information that can be produced by monitoring
- statistically characterize water quality 'population' to be sampled
- review statistical methods applicable for generating the desired information, including their data requirements
- state what information can be produced
- compare information sought with information that can be produced

Step 3. Design monitoring network
- document sampling locations
- determine what to measure
- compute sampling frequency

Step 4. Document data collection procedures (data generation components)
- field sampling operations and procedures
- laboratory analysis methods and operations
- data storage and retrieval system

Step 5. document information generating and reporting procedures (information generation components)
- data analysis hardware and software
- reporting formats and frequency
- information utilization procedures

Not only should one question the design of the water quality monitoring system, but also the management structure that may be demanding more information than the monitoring system is capable of producing [Ward *et al.*, 1990]. In addition to quantifying the information required by the management in the first step of the design process, a later step is to quantify the information that the monitoring system can produce. If, after completion of these two steps, there are differences in the information expectations of management and the ability of monitoring to produce information, then the management strategy, the monitoring budget, the monitoring system design, and the law itself may have to be examined and reformulated. By identifying the information types that can be produced, it is less likely that naive and unrealistic information expectations will be placed on monitoring.

It can be concluded that considerable responsibility is placed on the designer of the monitoring system in deciding exactly what information will or will not be obtained, especially in the light of the economic constraints under which most monitoring systems must operate [Ward, 1986]. The generalized scheme for the design of a monitoring system, presented above, provides the lead for analysis of the various components of such a system. As such, it will serve as the framework in the succeeding chapters.

2.5 Reliability of information; the need for quality management

The reliability of information obtained through monitoring is of great importance for the preparation and evaluation of political decisions both on a national and international scale. The Helsinki Convention and various treaties on specific transboundary rivers [Danube, 1994] [IRC, 1987] as well as EC-legislation [EC, 1975] [EC, 1976] [EC, 1977] [EC, 1990] require information that is reliable and comparable on an international scale. The need for interchangeable information about water quality between different countries has given an incentive to system for exchange of the data as well as the procedures with which these data have been obtained. Apart from international standardization of specific methodologies, this includes the general approach in quality management (e.g. ISO 9000 [ISO, 1987]) and, more specifically, for testing of laboratories (e.g. ISO/IEC guide 25 [ISO, 1982] and the European Standard EN 45001 [CEN, 1989]).

The quality of information is considered high if the information meets the needs and is acquired in a cost effective manner [Cofino, 1994][1]. The only means of assuring that the data and information produced by monitoring satisfy this general quality goal is a well designed and functional quality management program, where it should be noted that cost-effectiveness is implicitly an important goal of quality management. Simply stated, quality management is 'nothing more' than monitoring of the monitoring system to insure that it is performing as designed [Ward *et al.,* 1990]. However, for a better understanding a more detailed investigation of (general) quality management is required.

Primarily, it must be realized that all the elements of a water quality assessment programme as presented in section 2.4. are an integral part of the process towards generating water quality information. Data are no better than the weakest link in this sequence [Clark and Whitfield, 1993]. Therefore, the scope of quality management should encompass all these elements.

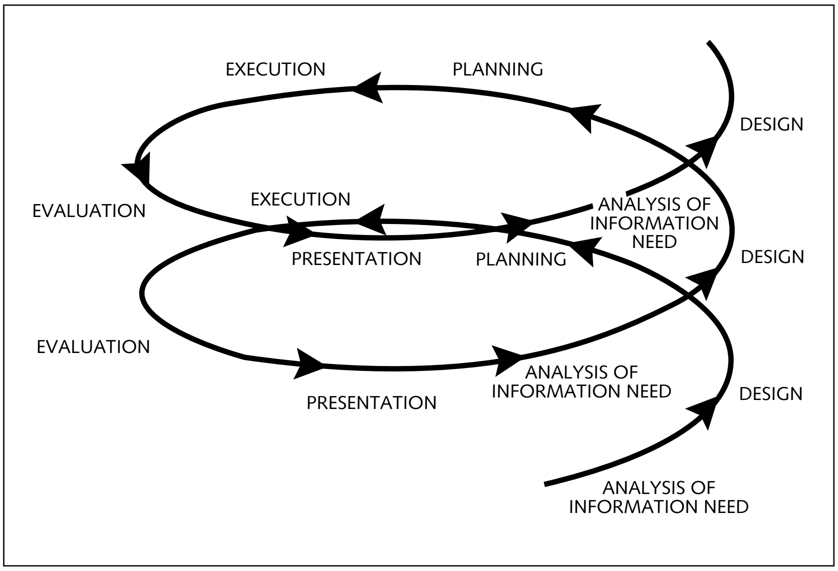
Secondly, monitoring is an ongoing activity with a dynamic nature. Several factors may cause re-assessment and modification of the water quality monitoring program. Targets may be reached, policies may change, or new methodologies may become available. Moreover, assessment of the final results may identify weak points that can be improved to increase the quality of future work, or reveal that the analysis or information was not sufficient.

The process for procurement of information, outlined in a spiral (figure 2.3), reflects all the elements, as well as the dynamic nature of monitoring. This quality spiral incorporates and uses feedback mechanisms to assure and control the level of quality required. The model ensures that the topics included are reviewed and optimized on a regular repeated basis at least once per study cycle. Each new cycle starts with a greater probability of solving the real problem [Broderick *et al.*, 1991].

Note

1) According to the International organization for standardization (SIO) quality is defined as follows: 'The totality of features and characteristics of a product or service that bear on its ability to satisfy stated or implied needs' [ISO (1986)].

Figure 2.3:
A quality spiral for the monitoring process [Cofino, 1994].



The major elements of quality management, contained in the quality spiral, have recently been reviewed by various authors [Cofino, 1994] [Broderick *et al.,* 1991] [Clark and Whitfield, 1993] [Cofino, 1993] [Taylor, 1988].

Primarily, quality management requires a *master plan* to be produced for the complete monitoring programme. Such a plan must deal with the procedures, facilities, personnel and management elements of the monitoring programme. It should include budgets, schedules, work force resources, people training requirements, safety programs, and vehicle and equipment requirements.

Secondly, up-to-date *protocols (Standard Operating Procedures* (SOPs)) have to be made available for every task included in the monitoring programme. Protocols are formal written procedures of all the methods to be followed during a project. Included in protocols are details as to how actions are performed and what records are to be kept. Furthermore, they should include procedures to verify that activities have been done in conformity with previously defined quality criteria. Protocols should be based on best available practices, should be safely archived and should correspond to genuine practices. Protocols for sample collection and preservation and on-site and laboratory analysis are already well known. However, data analysis protocols, for examples are also of major importance [Ward, 1994].

Thirdly, *documentation* of the actual operations undertaken and any additional remarkable observations (all exceptions-to-the-rule or nonconforming events), is required. Especially in those situations where deviations from predetermined procedures have occurred, documentation is indispensable for data validation.

A further major element of general importance concerns communication structures between those participants conducted related activities. These communication structures have to be good in order to secure timely provision of e.g. supplies, samples, and data.

If certain tasks are completely performed according to specific quality criteria, this can be expressed by means of an accreditation system.

Accreditation refers to the certification of specific tasks, or complete institutes, as to their compliance with specific standardized practices, such as Good Laboratory Practice (GLP). Accreditation of individual laboratories for specified analyses is well known and is being performed by national institutes, like NAMAS (UK), and STERLAB (The Netherlands), based on European standards produced by the CEN (European Committee for Standardization).

More specific elements of quality management, relating to specific tasks performed within a monitoring programme, are addressed in the subsequent chapters, combined with a discussion of other aspects of these specific tasks.

3. Assessment of water quality; the meaning of criteria and objectives

The process of assessing water quality is generally seen as an evaluation of the physico-chemical and biological status of waters in relation to [Enderlein, 1994a]:

(a) the natural hydrological regime, the morphological character and background concentration levels;
(b) the anthropogenic impact;
(c) the requirements for intended uses, such as drinking-water, industry and agriculture, fisheries and recreation, as well as the functioning of aquatic ecosystems, and
(d) the effectiveness of pollution reduction measures.

The definition of water quality as the physical, chemical and biological characteristics of water necessary to sustain desired water uses, can never result in a universally applicable set of numbers for assessment, because measurements that need to be made to assess the suitability of water for one use are not the same as those required for another use, and not all potential uses can be foreseen [McBride, 1986].

The Helsinki Convention provides for the definition of water quality criteria and objectives, amongst others accounting for the individual use categories [UN/ECE, 1992, Article 3 paragraph 3] (see also article 9 paragraph 2(e)):

3. In addition, each party shall define, where appropriate, water quality objectives and adopt water quality criteria for preventing, controlling and reducing transboundary impact. General guidance for developing such objectives and criteria is given in annex III to this Convention (given below). When necessary, the parties shall endeavour to update this annex.

Annex III (Guidelines for developing water quality objectives and criteria)

Water quality objectives and criteria shall:

(a) Take into account the aim of maintaining and, where necessary, improving the existing water quality;
(b) Aim at the reduction of average pollution loads (in particular hazardous substances) to a certain degree within a certain period of time;
(c) Take into account specific water quality requirements (raw water for drinking-water purposes, irrigation, etc.)
(d) Take into account specific requirements regarding sensitive and specially protected waters and their environment, e.g. lakes and groundwater resources;
(e) Be based on the application of ecological classification methods and chemical indices for the medium- and long-term review of water quality maintenance and improvement;
(f) Take into account the degree to which objectives are reached and the additional protective measures, based on emission limits, which may be required in individual cases.

A recent UN/ECE study on 'Water quality Criteria and Objectives', including policy recommendations to ECE Governments, may assist UN/ECE countries in jointly defining water quality criteria and objectives for maintaining and, where necessary, improving water quality in transboundary waters [UN/ECE, 1993]. In addition, it may help countries to define levels of significant transboundary pollution, resolve problems related to responsibility and liability or transboundary water pollution, and select technology for wastewater treatment.

An review of existing methods in member countries for assessing the status of surface waters and for defining water quality criteria and objectives is provided. These methods have the aim of maintaining and, where necessary, improving the existing water quality, in particular of transboundary waters. Existing cooperative arrangements on this subject made by riparian countries in the UN/ECE region are also presented [UN/ECE, 1993].

Water quality assessment and classification

Water quality assessment and classification is generally based on a reference system against which the current water quality is compared. The purpose of a reference system is to describe, as far as possible, the natural conditions of a water body or to describe basic requirements posed on water quality for different uses. The system of EC-Council directives [EC, 1975] [EC, 1975a] [EC, 1978] [EC, 1979] [EC, 1980] relates to the latter. There are numerous difficulties in setting up such a reference system, in particular relating to catchment areas that have been subject to anthropogenic stress over decades, and to the use category 'aquatic life' (ecosystem functioning). For this purpose, many UN/ECE countries now use a system of water quality criteria, expressed as maximum levels for the concentration of a substance in water (ambient water quality standards), sediment and/or biota, respectively. Other countries carry out specific hydrochemical investigations of the catchment area concerned in order to establish an appropriate reference system [UN/ECE, 1993].

It is impossible to establish a reference system for all water quality variables. Assessments of water quality and subsequent classification have therefore often been confined to a study of a selected number of criteria considering, in particular the most important water pollution problems in a country. Expert judgement is often used to ascertain appropriate water quality variables relevant to specific water quality problems, resulting e.g. in the so-called 'black and grey lists' [EC, 1976].

Water quality objectives

Water quality objectives aim at compliance with specified levels of variables to define water quality within a certain period or at the reduction of average pollution loads (in particular hazardous substances) to a certain degree within a certain period [IRC, 1987] [NAP, 1988]. It is generally recognized that in order to meet water quality objectives, the combined use of emission limits (based on best available technology) or point source pollution control, and best environmental practice for non-point source pollution control is necessary. These are integral procedures for prevention, control and reduction of pollution in inland surface waters [UN/ECE, 1993]. Water quality objectives may be used as an instrument to evaluate whether additional efforts are needed in water pollution control.

3.1 Physico-chemical assessment

Water quality criteria for physico-chemical assessment define threshold values for physical and chemical variables in water, sediment and/or biota. These variables may include temperature, pH, oxygen regime, chlorophyll concentration, suspended solids, turbidity, minimum flow, nutrients, chloride and other natural variables. These can be maximum or minimum values depending on the type of variable considered. Maximum/minimum acceptable values are set to prevent harmful impact to specific water uses.

In setting water quality criteria, particular attention should be paid to substances that may cause acute and chronic toxic effects at low concentrations, as well as to substances that cause (or are suspected of causing) carcinogenic, mutagenic and teratogenic effects [Van Leeuwen, 1994]. However, it remains ambiguous which characteristics should constitute the minimum necessary to describe a hazard, i.e. whether a substance should be classified as hazardous because of its toxicity[1] only, because of its toxicity combined with either persistence[2] or bio-accumulation[3], or because it possesses all three characteristics [UN/ECE, 1993]. Furthermore, it remains ambiguous which fraction of a hazardous substance should be taken for developing water quality criteria (the total recoverable and/or the dissolved form of a substance). Criteria for these fractions may be quite different (see also paragraph 4.1.2(D)).

Recommendations for assessing the toxic effects of chemicals adsorbed on suspended particulate matter and sediments have been proposed by the OECD [OECD, 1992]. The use of equilibrium partitioning coefficients for individual chemicals, or doseresponse data for individual chemicals and chemical mixtures (spiked sediment toxicity) can predict aquatic concentrations under field conditions. More thorough methodologies, however, might prove to be more amenable. Ideally, regulatory decisions should be based upon sediment assessments such as the sediment quality triad where all the following data would be available: benthic community structure, toxicity test results and chemical analyses, the so-called TRIAD-approach [Van de Guchte, 1992]. With respect to sediment toxicity, toxicity identification evaluation (TIE) procedures that utilise toxicity-based fraction approaches are the only methods currently available to link toxicity to specific contaminants in a causal manner for field-collected sediments [Hill *et al,* 1993].

Some general considerations with respect to the development of water quality criteria for individual use categories are summarised below [UN/ECE, 1993]:

Note

1) Among toxicity parameters used in assessment schemes, acute aquatic toxicity (the concentration of a substance at which 50 per cent of test organisms die within 96 hours, or the concentration thas causes immobilization of 50 per cent of test organisms within 48 hours) and chronic aquatic toxicity (the concentration level which produces 'no-adverse effects' on the test organisms on lifetime exposure) are widespread.

2) The persistence (usually based on the aquatic half-life of a substance) is generally influenced by a range of physical, chemical and biological processes.

3) Bioaccumulation describes effects of uptake of a substance from the environment upon a target organism. As with persistence, bioaccumulation may constitute a risk only in combination with effects parameters such as toxicity.

Considerations with respect to the development of water quality criteria for individual use categories:

(1) Criteria for raw water used for drinking water supply:
- Criteria are generally based on toxicological data.
- Extrapolation of toxicological data from animals to man is often a problem.
- The potential of additive, synergistic and antagonistic effects should be considered.
- Increasing knowledge on organic pollutants, hazardous in water at low concentrations, has led some countries to narrow the gap between drinking water criteria and raw-water criteria.

(2) Criteria for irrigation:
- Criteria are generally based on characteristics such as crop tolerance to salinity, sodium concentration and phytotoxic trace elements.
- Criteria may differ considerably from one country to another, due to different annual application rates of irrigation water.

(3) Criteria for livestock watering:
- The purpose of quality criteria for water used for livestock watering is to protect both the livestock and the consumer.

(4) Criteria for recreation and amenities:
- Criteria are often set for indicators of faecal pollution, such as faecal coliforms and pathogens.
- Usually recreational water quality criteria do not take into account hazardous substances such as heavy metals and organic micro pollutants. Due to the short exposure of swimmers, recreational water quality criteria for these substances would be less stringent than similar criteria established for other water uses.
- Some criteria have been established in UN/ECE countries aimed at the protection of the aesthetic properties of water.

(5) Criteria for commercial and sports fishing:
- Criteria for commercial and sports fishing take into account, in particular, the bio-accumulation of contaminants through successive levels of the food web, which can make fish unsuitable for human consumption.

(6) Criteria for the protection of aquatic life:
- Water quality criteria for the protection of aquatic life may consider only physico-chemical variables that tend to define a water quality that protects and maintains aquatic life, ideally in all its forms and life stages, or they may consider the whole aquatic ecosystem (see section 3.2).

A particular problem is the estimation of criteria for the use category 'aquatic life'. Classification criteria for a number of polluting substances that are a risk to aquatic life have been proposed by UN/ECE, primarily based on ecotoxicological considerations [UN/ECE, 1993b]. Ambient water quality standards for ecosystem functioning are often formulated for ecotoxicological 'no-effect' levels (NOEC values) [Van Straalen *et al.*, 1994]. However, this type of standards is not fully developed yet, as ecotoxicological risk assessment is complicated due to some uncertainties (e.g. lack of data, variability between species and also between tests with a single species, laboratory-field extrapolation). The pressure to prioritise large lists of industrial chemicals for further attention has led to QSAR techniques being used where no test data are available; most frequently based on molecular weight and octanol-water partition coefficients (log P or log K_{ow}) [OECD, 1992a].

Compensation factors are usually applied to extrapolate laboratory test data to the actual situation of the water body and to compensate for any missing data (Note: compensation factors are also applied to set criteria for other use categories such as human consumption). The lower the level of knowledge of the harmful effects, particularly with respect to the long-term effects of low concentrations, the wider the safety margin to be established between the effects data and the quality criteria based on this must be. Most UN/ECE countries use a safety factor of 10 with data on chronic toxicity for sensitive aquatic species [UN/ECE, 1993]. If only data on acute toxicity are available, a larger factor, most commonly 100 or 1000, is used unless information on the ratio between acute/chronic toxicity is available. A recommendation, relating the assessment factor to the amount of data available, was formulated at an OECD workshop on extrapolation of laboratory aquatic toxicity data [OECD, 1992a]. Three distinct situations were recognized

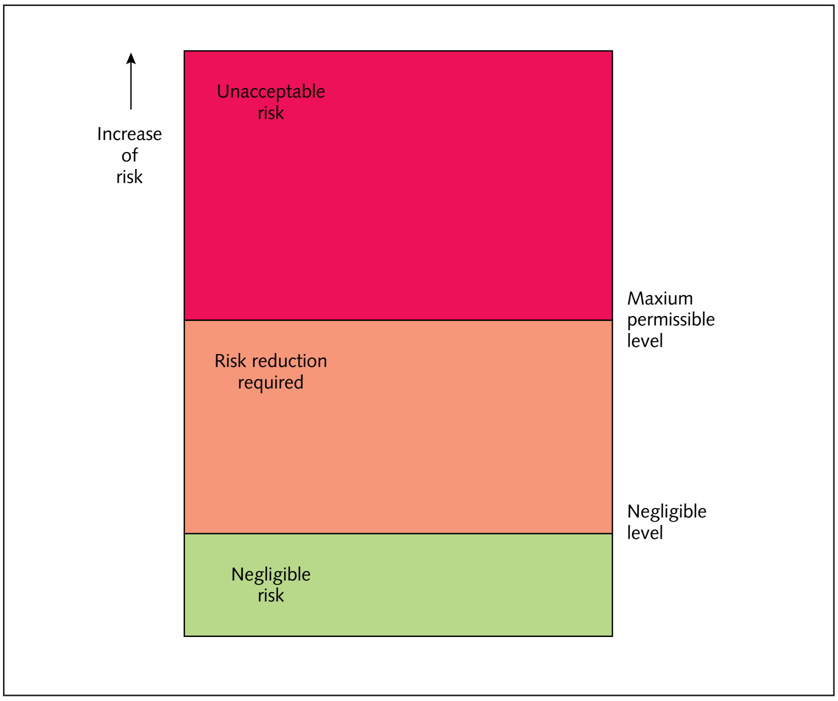
Available information	**Assessment factor or extrapolation factor**[1]
Lowest acute LC_{50}, EC_{50} or QSAR estimate within a data set on one or two aquatic species	1000
Lowest acute LC_{50}, EC_{50} or QSAR estimate in a set comprising at a minimum algae, crustaceans and fish	100
Lowest NOEC value or QSAR estimate in a set comprising at a minimum algae, crustaceans and fish	10

[1] An assessment factor is the number used to adjust the effects concentration (laboratory $L(E)C_{50}$, NOEC, etc.) to estimate an environmental concern level, i.e. that concentration of a chemical at and above which ecosystems could be adversely affected.

In the past decade there has been growing support for defining two risk levels [Van Leeuwen, 1994]. One level represents the ultimate goal at which no adverse effects on the considered human water uses would occur and functions of the aquatic ecosystems would be maintained and/or protected. This level, the 'negligible level' (NL), corresponds in most countries with the most stringent water quality criterion among all of the considered water uses, with some modifications to account for specific site conditions. A second level is also being defined that should be reached within a fixed period of time. This level, the maximum permissible level (MPL), is generally the result of a balance between what is desirable from an environmental point of view and what is feasible from an economic and technical point of view. These two risk limits create three zones (figure 3.1) a black (high-risk) zone, a grey (medium-risk) zone and a white (low-risk) zone.

Water quality management goals typically aim at fitting the maximum permissible risk level, in a step-by-step approach, which finally leads to the negligible level. Additionally, some countries recommend a phased approach, which starts with rivers and catchments of sensitive waters and is progressively extended to other water bodies in a second phase [UN/ECE, 1993]. Though current approaches to the elaboration and setting of water quality objectives differ between (UN/ECE) countries and within various international conventions, many of them bear some characteristics of the above general strategy [IRC, 1987] [IKSR, 1991]. They may or may not be based on water quality classification schemes [NRA, 1994].

Figure 3.1:
Risk limits and risk reduction requirements [Van Leeuwen, 1994]



Concern for extrapolation of data from standard laboratory species to complex aquatic ecosystems has led to multiple species testing and more recently, the attempts to develop integrated field, laboratory and mesocosm approaches. Current methods for toxicity testing may also fail to deal with ecosystem complexity resulting from multiple causality and synergy of multiple stresses acting simultaneously within the ecosystem.

With respect to synergy, establishing quality criteria for mixtures, based on the hypothesis of simple addition effects for molecules with similar modes of action, may well provide good results [Calamari and Vighi, 1991]. Advances in defining the effects of mixtures of chemicals seem to demonstrate that, in mixtures of organic toxicants with the same modes of action, even very low portions of the individual NOEC values can additively contribute to the final effect on aquatic organisms. A single criterium for several organic substances in combination, if they have been demonstrated to have a common mode of action, may prove to be adequate [Van Loon and Hermens, 1995].

It is unclear whether an approach based on scarce toxicological data should be pursued until realistic criteria for all single substances have been set, which surely will never be the case. The precautionary approach is adopted in most international conventions [Dogterom and Buijs, 1995].

As a final remark, it should be noted that toxicity, being a measurable variable itself, can be prone to setting of criteria as well. Some countries (e.g. France, Germany, Ireland, Norway, Sweden, Canada, USA) already apply toxicity criteria (on a case by case basis) for the assessment of effluent quality [De Zwart, 1995]

3.2 Biological assessment

Biological assessments are particularly useful in the context of ecosystem functioning. The selection of the reference base for the use category 'aquatic life' is a particular problem. Efforts have been made to develop and apply requirements that relate directly to the nature and composition of biological communities themselves rather than to surrogate or indirect chemical criteria.

In some UN/ECE countries, research is underway on the development of biocriteria that quantitatively express water quality criteria in terms of the resident aquatic community's structure and function. Biocriteria are understood as measures of 'biological integrity' that can be used to assess cumulative ecological impact from multiple sources and stress agents. Considerable efforts have been made to identify key species that may serve as useful integrative indicators of the functional integrity of aquatic ecosystems (see Guidelines on the Ecosystem approach on water management [UN/ECE, 1993a]).

Biocriteria are an integral part of biological assessment methods. The species (or families) included in these biological assessment methods, the weight assigned to individual species (or families) and consideration of species abundance depends completely on the biological assessment methods under concern. In turn, the biocriteria (the 'assessment endpoint') depend on these methodology characteristics. These characteristics are briefly outlined below for the three major classes of biological assessment methods that can be recognized (i.e. Diversity and comparative indices, Saprobic systems and Biotic indices and scores) [Knoben *et al.,* 1995].

Diversity indices and comparative indices provide an appraisal of aquatic community structure based on the number of observed species (richness) in relation to the number of individuals (abundance), either or not in comparison with a 'genuine' reference community. Sometimes the uniformity of the distribution (evenness) is included in the assessment method as well. There is no weight attached to the individual species, nor are any specific predetermined implications attached to the diversity assessed (there is no clear 'assessment endpoint'). These biological assessment methods merely embark on diversity as a basic feature of the structure of a community or ecosystem [Odum, 1971]. However, it should be noted that, if the assessment includes appraisal against the diversity of a reference community, this can be regarded as applying a relative (not predetermined) criterion.

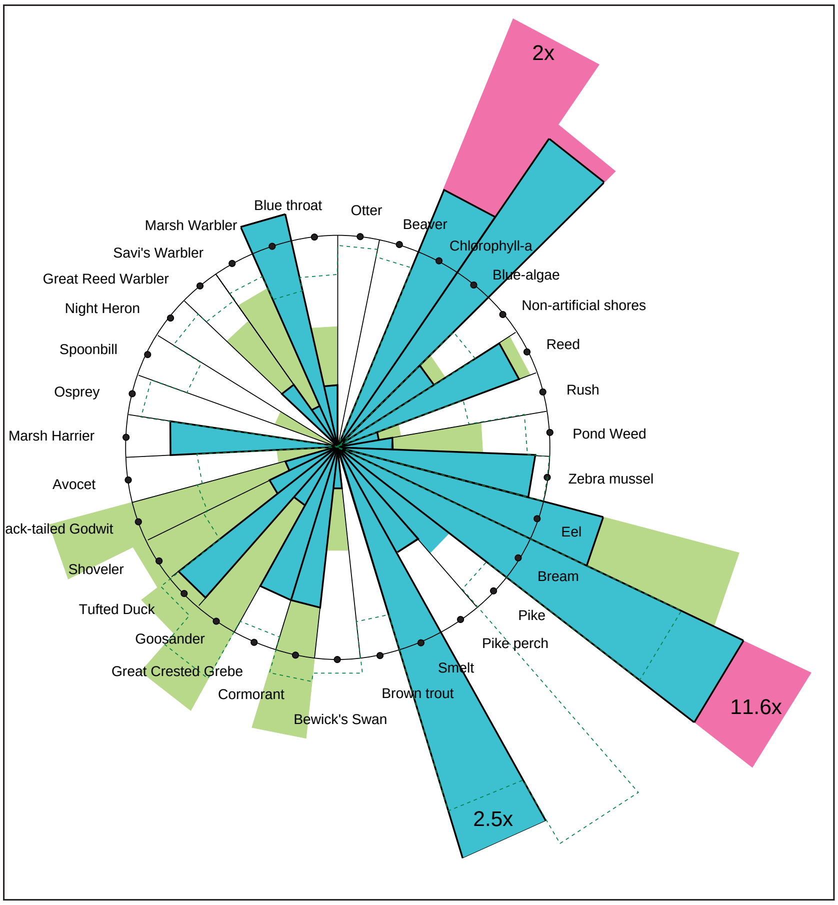
Saprobic systems provide a water quality classification ranging from pure to polluted by means of a system of aquatic organisms, which indicate by their presence and vital activity the different levels of water quality [Sládecek, 1973]. The (known) tolerance of the various species included against (organic) pollution is expressed in a saprobic indicator value. Apart from the presence of the various species included, their (relative) abundance is taken into account. Furthermore, some saprobic systems assign a weight to the various species included [Zelinka and Marvan, 1961]. From these data, the saprobic index or saprobity level, which can only have a limited number of values, is calculated and assessed against a predetermined assessment endpoint (set of biocriteria). The result is a classification system with a distinct number of classes (typically 5 -7), ranging from pure to polluted.

Biotic indices and biotic scores are based on the indicative presence of a selected number of benthic macro-invertebrate (families). The various taxa included are assigned a weight factor that may even be negative in some systems. Species abundance is only included in biotic score systems. Calculation of biotic indices and biotic scores results in a number on a certain scale (i.e. 1 – 10). The value of the index can be used to classify the aquatic systems sampled against predetermined biocriteria, into a distinct number of water quality classes.

The application of the ecosystem approach in water management has led to the development of objectives for safeguarding the functional integrity of aquatic ecosystems. Ecosystem objectives may specify the level or condition of certain biological properties that could serve as indicator of the overall condition or 'health' of the aquatic ecosystem. Ecosystem objectives are used in combination with water quality objectives, and objectives relating to hydrological conditions [UN/ECE, 1993]. Ecosystem objectives are expressed by a set of (mostly biological) variables, called the target variables. The target variables as a whole are usually a cross section of the aquatic ecosystem, providing a fairly representative picture of ecosystem conditions.

An interesting example of the use of biological indices and scores is provided by the Netherlands approach [Klapwijk *et al.,* 1994]. The third National Policy document on Water Management for the Netherlands includes objectives for specific target organisms. These target organisms are selected not only as being characteristic of the water system concerned, but also as having a clear relationship with steerable (water manageable) factors such as pollution, navigation and flooding regime. A related method, using the so called 'Amoeba' (A general Method Of Ecological and Biological Assessment) provides a transparent method of visualizing the difference between the desired abundance of the selected species and the actual situation [Laane and Peters, 1993] [Ten Brink *et al.*, 1991] [Cappon, 1991] [RIZA, 1993]. An example of the Amoeba is presented in figure 3.2.

Figure 3.2:
The Amoeba for Lake Ketelmeer and Lake Zwartemeer [Laane and Peters, 1993]



3.3 Hydrological assessment

There is a close relationship between the quality of a water body and quantitative characteristics. Assessment of changes in water quality are not possible without understanding quality-quantity relationships.
A significant proportion of the variations of water quality can be related to variations in river flow. An increase of river flow usually leads to [WMO, 1994]:

- the dilution of pollutants entering with waste water;
- the increase in suspended solids from surface runoff and from disturbance of bottom sediments;
- the release of materials absorbed by or precipitated in the sediments (e.g. phosphates, heavy metals);
- the increase in biochemical oxygen demand caused by stirring up reducing substances from the river bed;
- the decrease in the ratio of groundwater to surface runoff in the river flow, usually leading to a lower pH;
- the washing out of benthic micro-organisms, reduced concentration of aquatic micro-organisms and reduced residence time;
- the attenuation of effects of sudden inputs of pollutants;
- the reduced absorption of solar radiation and related decline in photosynthetic activity;
- higher turbulence and better aeration.

Low flow periods usually lead to effects that are opposite to those caused by flow increases. In addition to natural variations in river flow and levels, man made hydrological projects like dams, weirs and river training works also affect water quality. By raising upstream water levels, a dam and, to lesser extent a weir, usually causes the following effects on water quality in the upstream reach of the river:

a. intensification of self-purification processes and more deposition of suspended solids due to increased residence time in the reach, resulting in increased solar-radiation absorption and in changes in the sediment characteristics of the river bed;
b. a rise in phytoplankton production, increased day-night fluctuations in oxygen, pH and carbon dioxide, and potential oxygen depletion if eutrophication conditions exist.

Fish migration may be disturbed by the physical barrier and by changes in water quality. Changes in bank vegetation, which is governed by local topography, climate and water-level variation, may also affect water quality.

The impact of a dam or weir on water quality in the downstream reach depends on the upstream storage volume, dam design and operation and other factors. The most important effects are the following:

- reductions in suspended solid load, pollution load and turbidity;
- changes in the chemical characteristics of the water (often a lower concentration of dissolved oxygen and nitrates and increases in phosphate, carbon dioxide and hydrogen sulphide, the latter particularly when anaerobic conditions prevail upstream);
- decreases in the summer water temperature and increase in the winter temperature;
- reductions of the day-night temperature fluctuation to which the river flora and fauna are adapted.

River-training works lead to reduced self-purification processes because the straightening of the banks eliminates stagnant water zones both as areas of self-purification and as a favourable environment for animal and plant life development. The reduced surface-to-volume ratio leads to a reduction in the solar-radiation absorption and re-aeration. The re-aeration reduction may be partly compensated for if river training leads to higher water velocities.

In order to assess natural and man made effects, extensive networks and frequent measurements for the collection of hydrological data are necessary. The most important variables for quality assessment are water levels, velocity, discharge and sediment transport. Many direct and indirect methods exist to measure level, velocity (m/sec), discharges (m3/sec) and sediment transport in rivers, and at weirs and dams [WMO, 1980] [WMO, 1989] [ICWS, 1989] [ISO, 1993a] [ISO, 1977] [ISO, 1986].

3.4 Effluent assessment and early warning

Assessment methods for effluents of industrial and municipal waste water treatment plants are used to evaluate for environmental risks and compliance with permits, independently of surface water quality assessment. In early warning, risk assessment is used to determine the precautionary measures in case of accidental pollution or alarm phases in case of calamities. These issues will be dealt with in chapters 5 and 6.

4. Surface water quality monitoring

4.1 Introduction

In the previous chapters it was outlined that policy objectives and management strategies define the information needs, which should be met by monitoring programmes. It was emphasised that the overall systems view of monitoring requires that network design be derived from information objectives and that it directly support data analysis, reporting and ultimately information utilization [Ward *et al.,* 1990]. It was emphasized as well that the design process should start with an in-depth investigation of all factors and activities that influence, directly or indirectly, water quality. Inventories of the geographical features in the area, water uses, habitats of special interests and pollution sources (present and expected) have to be prepared. It cannot be overemphasised that the benefits of an optimal monitoring operation drawn from careful preliminary planning and investigation by far outweigh the efforts spent during the initial phase. Mistakes and oversights during this part of the programme may lead to costly deficiencies, or overspending, during many years of routine monitoring [Meybeck *et al.,* 1992].

This chapter provides information on 'State of the Art' practices of how to structure surface water quality monitoring programmes, based on the principles mentioned. It is to be expected that international Treaties and Conventions will deal with transnational obligations with respect to the structure of transnational monitoring programmes [see also: Danube, 1994 and EC, 1977a], a process to which many countries have already committed themselves based on the **Helsinki Convention,** that states (Article 4 and Article 11):

Article 4 (Monitoring):
The parties shall establish programmes for monitoring the conditions of transboundary waters.

Article 11 (Joint monitoring and assessment):
1. In the framework of general cooperation mentioned in article 9 of this Convention, or specific arrangements, the Riparian Parties shall establish and implement joint programmes for monitoring the conditions of transboundary waters, including floods and ice drifts, as well as transboundary impact.

2. The Riparian Parties shall agree upon pollution variables and pollutants whose discharges and concentration in transboundary waters shall be regularly monitored.

3. The Riparian Parties shall, at regular intervals, carry out joint or coordinated assessments of the conditions of transboundary waters and the effectiveness of measures taken for the prevention, control and reduction of transboundary impact. The results of these assessments shall be made available to the public in accordance with the provisions set out in article 16 of this Convention.

4. For these purposes, the riparian Parties shall harmonize rules for the setting up and operation of monitoring programmes, measurement systems, devices, analytical techniques, data processing and evaluation procedures, and methods for the registration of pollutants discharged.

To realize these obligations, knowledge of the type of monitoring programme needed (i.e. what should be measured, where and when) is required. More specifically, the following issues must be decided:
- how to select pollution 'variables'[1] and pollutants that require regular monitoring;
- how to determine whether sampling locations can be considered representative;
- how to determine sampling frequencies, so that information requirements can be met with satisfactory significance;
- which aspects must be considered when selecting sampling techniques and when taking samples;
- which aspects must be considered when selecting analytical techniques and performing analyses;
- what kind of data interpretation and presentation methods are most powerful in assessing the conditions of (transboundary) waters and changes in these conditions.

The following sections will deal with these aspects.

4.2 Various types of water quality monitoring

Various types of water quality monitoring can be distinguished, including:

Note
1) In this report the term variables is used instead of parameters (see section 4.1.2.).

ground water monitoring, (wet) deposition monitoring, effluent monitoring, early warning monitoring and surface water monitoring (including river basin, lake, estuary, and marine monitoring). This chapter deals with surface water monitoring of running waters only.

If the nature of the monitoring programme is considered, a distinction can be made between monitoring, survey and surveillance as different types of monitoring activities:

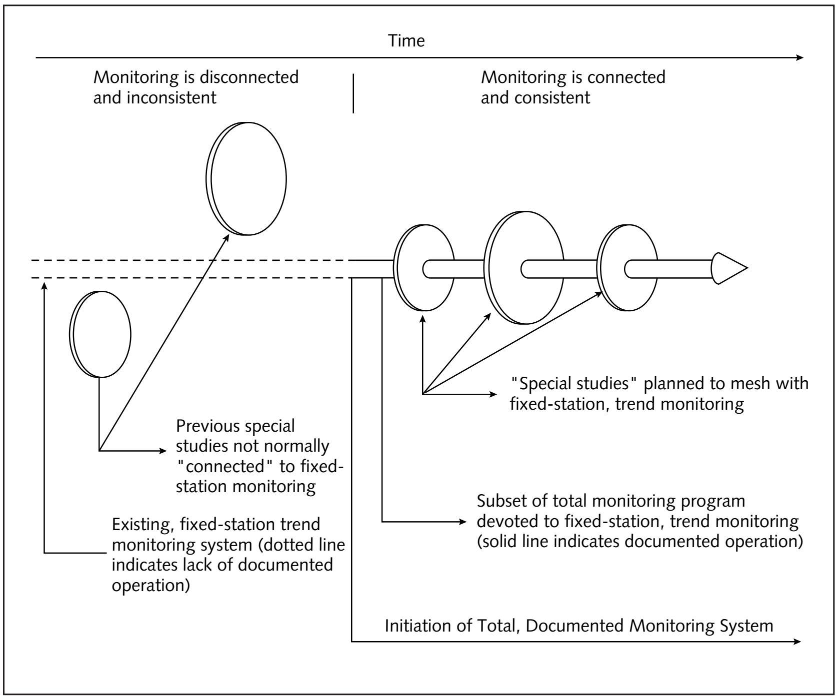
Monitoring is defined as a long term standardized measurement, observation, evaluation and reporting of the environment in order to define status and trends [Meybeck *et al.,* 1992]. Monitoring in this definition is organized on a routine base with a well defined set of variables and standardized methods. Stations, sampling frequencies and sampling intervals are fixed. Evaluation is standardized and reporting is according to an agreed format. Transnational monitoring networks should comply with these conditions. Monitoring of surface water according to these principles can also be referred to as *ambient water quality monitoring* [Ward *et al.,* 1990].

Survey is defined as a finite duration, intensive programme to measure, evaluate and report the quality of the environment for a specific purpose [Meybeck *et al.,* 1992]. Surveys usually aim at providing information required for designing, redesigning, or 'optimizing' of an ambient monitoring programme, but they may serve a purpose of their own as well. Some examples of surveys performed to assist in the setting up of an ambient monitoring network are [Adriaanse *et al.,* 1995]:

- Surveys into the actual occurrence or nonoccurrence of substances that are considered to be possible problem substances (in water, sediments and/or biota).
- Surveys into the occurrence of substances (in water, sediments and/or biota) that may not have been contemplated previously, searching based on specific analytical characteristics rather than based on known substances (generally called screening).
- Surveys into the potential toxicity of water or sediments.
- Surveys into the distribution of aquatic species or communities within (a part of) a river basin [Friedrich *et al.,* 1992].
- Surveys into the homogeneity of water quality over a river cross section.
- Surveys into the variability of water quality in time and space, aiming at determining representative sampling sites and frequencies.

The close connection that exists between surveys and ambient monitoring is nicely indicated in the wheel-and axle model, as described by [Payne and Ford, 1988] [Pollack and Ford, 1989].

Figure 4.1:
The generalized 'wheel and axle' framework for the complete integration of special surveys with ambient water quality monitoring [Ward *et al.,* 1990]



The wheels represent special surveys or intensified sampling efforts, whereas the axle represents ambient monitoring.

The exact distinction between surveys and ambient monitoring has become vague with recent proposals to study watershed units with intensive monitoring efforts for a 2 to 5 year period, followed by periods when monitoring will be less intense [Wiederholm *et al.,* 1992].

Surveillance is defined as continuous, specific measurement, observation and reporting for the purpose of environmental quality management and operational activities [Meybeck *et al.,* 1992]. Surface water monitoring efforts for early warning purposes can be considered surveillance, as well as industrial monitoring for process control of, for instance, a reactor or a wastewater treatment plant (see chapters 5 and 6).

In the present report, the term monitoring is used in a more general way to encompass all three types of monitoring activities. The next sections (4.3 to 4.5) deal with the design of ambient water quality monitoring programmes.

4.3 Indicators, variables and media

The choice of variables for a specific monitoring programme, ideally, would be related to policy and management objectives. If desired uses of water resources in a river basin have to be promoted and protected, the quality of water resources needs to be assessed in terms of the desired use. This is what actually happened in the EU in the seventies, when use related directives were established. For strictly economic uses (cooling water, irrigation), fewer variables need to be monitored then for more critical uses (the production of drinking water, see section 2.1). The choice of variables and the media to monitor are thus directly linked to the desired uses and – eventually – their prioritization.

Since monitoring authorities are confronted with ever increasing numbers of potentially harmful compounds in surface water (see section 2.3.2), logistic and financial constraints push for a more limited choice of individual compounds to monitor or for variables that allow for an integrated assessment. Historically, monitoring programmes started with physical and chemical variables, and now include aggregate variables and biological variables. Statistical techniques allow the number of variables to be limited by using surrogate variables [Sanders and Loftis, 1994]. The choice of media to monitor is governed by compound specific chemical characteristics, like absorption.

An additional future development could be the establishment or use of function specific indicators, which are relevant to activities or events occurring in the watershed.
A 'core-set' of indicator variables would enable early assessment of use-related surface water quality. Early assessment, based on indicators that assess pressures on the water system rather than damage, would limit the number of variables to be monitored considerably. Such indicators could be the use of fertilizer and pesticides, the extent of erosion or the industrial production [Dogterom and Buijs, 1995].

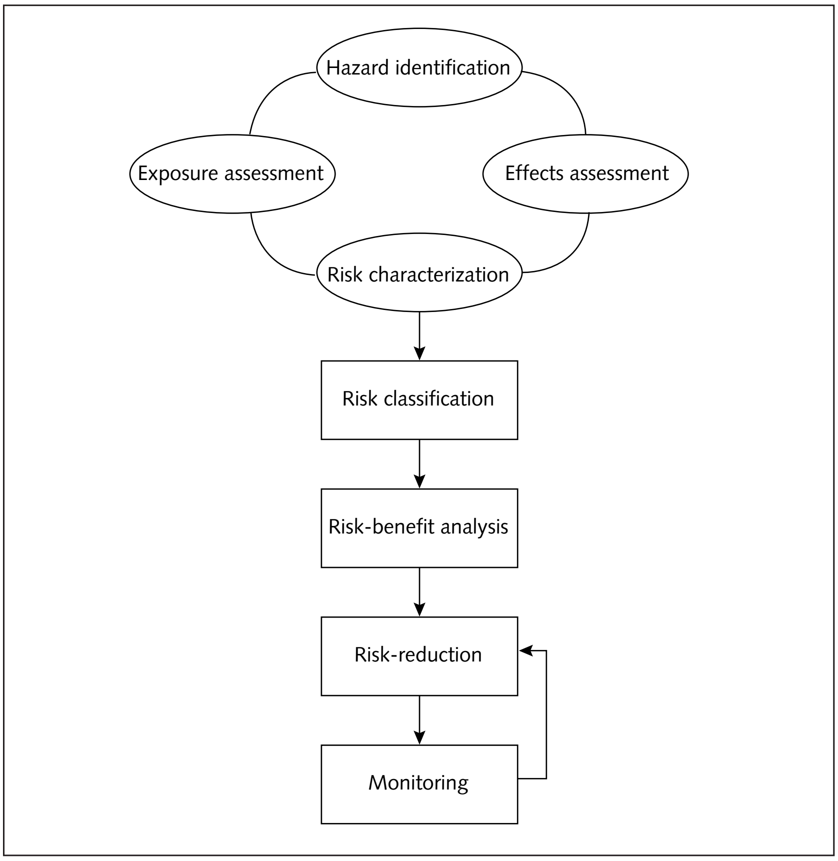
Considerations with respect to the selection of physico-chemical, surrogate and aggregate variables and biological variables are presented in the following sections.

4.3.1 Physico-chemical variables

Assessment programmes define the set of physico-chemical variables to be included in monitoring programmes. This can be at the international, e.g. in EC-directives and in Conventions, or at national level, e.g. in national water resources management programmes.

The European Community Council directive 75/464/EEC of 4 May 1976 'On pollution caused by certain dangerous substances discharged into the aquatic environment of the Community (amended in 1990)' [EC, 1976], provides a list of 132 compounds, selected on the basis of their toxicity, persistence and bioaccumulation (the 'black list'). Other EC directives are focused on variables related to specific water uses [EC, 1975), 1975a , 1978 , 1979].

Figure 4.2:
Steps in the risk management process [Van Leeuwen, 1994]



Experience gained in some transboundary waters, such as the Elbe, Oder, Rhine, Moselle and Saar Rivers, suggests that additional catchment area specific variables for a monitoring programme should be chosen. The water uses in the catchment area, the hazardous substances which are handled in the area, and the risk involved should be the major criteria in this respect [Enderlein, 1994a]. To this end, catchment specific inventories and priority lists of hazardous substances (toxic, carcinogenic, mutagenic, teratogenic) have to be drawn up. Some other properties of these substances, such as the potential for bio-accumulation and persistence should be considered as well. Risk assessment is of major importance in such an approach [Van Leeuwen, 1994]. Such assessments tie the hazardous characteristics of substances to the possibility of exposure to such substances. Embedded in a risk management procedure (figure 4.2 and table 4.1), such considerations may lead to inclusion of specific substances in monitoring programmes.

Table 4.1:
Meaning of the terms commonly used in the field of risk assessment and variable selection [Van Leeuwen, 1994]

Hazard identification (step 1).
Identification of the adverse effects that a substance has an inherent capacity to cause. It involves gathering and evaluating data on the types of health injury or disease that may be caused by a chemical and on the condition of exposure under which environmental damage, injury or disease occurs.

Effects assessment (step 2).
Identification and quantification of the potential adverse effects of chemicals on individuals, populations or ecosystems by means of laboratory testing or field observations (examples of endpoints: dose causing death, reproductive failure or reduction of species diversity).

Exposure assessment (step 3).
Determination of the emissions, pathways and rates of movement of a substance and its transformation or degradation, to estimate the concentrations/doses to which human populations or environmental compartments are or may be exposed.

Risk characterization (step 4).
Estimation of the incidence and severity of the adverse effects likely to occur in a human population or environmental compartment due to actual or predicted exposure to a substance, potentially including 'risk estimation', i.e. the quantification of that likelihood. This generally involves the integration of the previous three steps.

Risk classification (step 5).
Valuation of risks in order to decide if risk reduction is required.

Risk-benefit analysis (step 6).
Drawing up of a balance sheet of the respective risks and benefits of a proposed risk-reducing action.

Risk reduction (step 7).
Taking measures for the protection of man and/or the environment from the risks identified.

Monitoring (step 8).
Surveillance undertaken to ensure that previously formulated

In summary, the following criteria are of importance for the selection of variables to monitor [Adriaanse *et al.,* 1995]:

1. The **properties** and **occurrence** (extent of the emissions and present concentrations) of chemical substances, encompassing such aspects as:
   – adverse effects on biodiversity of natural compounds in high concentrations (nutrients causing eutrophication, oxygen depleting substances);
   – the known (or suspected) toxic nature of pollutants for the ecosystem and other water uses (NOEC, LC50, carcinogenicity, mutagenicity);
   – the properties of chemicals in the water environment (bio-accumulation, persistence, half-life time, toxic properties);
   – the extent of production, emission and use of pollutants in the area concerned;
   – the occurrence of pollutants in high concentrations in surface water.

2. The availability of **reliable** and **affordable** analytical methods for determination of chemical substances, encompassing such aspects as:
   – can the substance be measured with sufficient reliability

(quantifiable) in the selected medium (water, suspended matter, sediment, organisms)?
- are analytical methods operational (at a reasonable distance from the place where the sample is taken)?
- are the costs of monitoring a specific pollutant reasonable in relation to the available monitoring budget?

3. **Demonstrable efficiency** of substance control by water policy and water management, as related to quantified objectives (e.g. required percentages for the reduction of emissions, standards to be aimed at, reductions in transnational loads). Factors that may play a role include:
   - the indicative value of a variable for the state and the use of water (nutrients, oxygen balance (O2, COD and BOD) and additional indicators or aggregate variables like Adsorbable Organic Halogen (AOX), Dissolved Organic Carbon (DOC), Total Organic Carbon (TOC) and Choline esterase inhibition);
   - the sensitivity and controllability of a variable to water management measures (measurability of effects: selected individual variables like metals and pesticides, aggregate variables like oil index, phenolic index, Polycyclic Aromatic Hydrocarbons (PAH, 6 of Borneff) and Poly Chlorinated Biphenyls (PCB, indicator congeners), but also for instance AOX);
   - the requirements formulated concerning the specific functions that are served by the management of water (water for swimming, drinking water preparation, etc.; e.g. most of the above mentioned variables).

A brief overview, emphasising the significance of some generally recommended variables and groups of variables, differentiated by the environmental problems they relate to, is presented below [Chapman and Kimstach, 1992]. Firstly, some essential hydrological and general variables are considered.

A *Quantitative and other hydrological variables*
River flow measurements are essential if mass flow or mass balance calculations have to be performed. The characteristics and the amount of *suspended matter and sediments* are essential variables for the purpose of scaling the concentration of compounds adsorbed on suspended matter and therefore accumulated in sedimentation areas.

B *General variables*
Temperature is an important general variable as it affects some physical, chemical and biological processes in water bodies and, thereby the concentration of many other variables.
Humic and fulvic acids, due to their chelating capacity, are indicative in relation to toxic pollution with heavy metals. For specific water uses, some major ions (e.g. chloride for agriculture) may be relevant variables as well.

C *Trophic status variables*
The chemical side of characterizing trophic status involves such variables as inorganic and organic *nitrogen* (i.e. total nitrogen, nitrate (NO_3-), nitrite (NO_2-), ammonium[1] (NH_4+), molecular nitrogen (N2) and organic nitrogen), *phosphorous* (i.e. total phosphorous and ortho-phosphate) and *chlorophyll* (indicative of algal biomass).

Note
[1)] Ammonium is also a useful indicator of organic pollution.

D Acidification variables
For the assessment of acidification pH is the most important variable. Additionally, *acidity* and *alkalinity* (base- and acid-neutralising capacities of water) must also be considered.

E Organic matter pollution variables
Chemical assessment of organic matter pollution is based on variables such as *Organic Carbon* (Total (TOC), Dissolved (DOC) and Purgeable (POC)), *Chemical Oxygen Demand (COD), Biochemical Oxygen Demand (BOD)* and Dissolved Oxygen. It should be noted that apart from organic matter pollution, dissolved oxygen is influenced by characteristics such as temperature and salinity.

F Toxic pollution variables
Two major classes of potentially toxic pollutants can be recognized: *trace metals* (e.g. Cd, Cu, Cr, Pb, Hg, Ni, and Zn, and less well-known metals like Be, Tl, V, Sb, Mo) and *organic micro-pollutants* (e.g. pesticides , PolyChlorinated Biphenyls (PCB), Polycyclic Aromatic Hydrocarbons (PAH), phenols, and their metabolites). Trace metals and organic micro-pollutants in natural waters can exist in truly dissolved, colloidal or suspended forms, depending on the compound under concern and some general water characteristics.

G Microbiological pollution variables
Microbiological pollution variables are often included in physico-chemical monitoring programmes. The most common water-borne *bacterial pathogens* are Salmonella, Shigella, Escherichia coli, Campylobacter, Vibrio and Yerisinia [Friedrich *et al.,* 1992]. Other pathogens occasionally found include Myobacterium, Pasteurella, Leptospira and Legionella and the enteroviruses (poliovirus, echo virus and Coxsackie virus). Either the pathogen itself or an indicator (e.g. coliform bacteria, faecal streptococci, or Clostridia perfringens) can be monitored. Furthermore, viruses like adenoviruses, reoviruses, rotaviruses and the hepatitis virus may be important monitoring variables.

4.3.2 From variables to surrogate variables and aggregate variables

The number of chemicals which might affect the water quality is uncountable (see also section 2.2.2, page 9). An inventory of harmful compounds that are discharged in a river basin will generally reveal numerous compounds and it will virtually be impossible to monitor each compound individually (even if analytical methods for each of them existed).
Fortunately, it is generally not necessary to measure each compound individually. There is often considerable information from certain water quality variables called *surrogates,* that can be correlated to other variables [Ward *et al.,* 1990]. Surrogate variables include [Sanders and Loftis, 1994]: e.g. Faecal Coliform/Faecal Streptococcus, specific conductance, dissolved oxygen, pH. Furthermore, PCB and PAH are generally assessed based on the measurement of a few indicator PCB and PAH (i.e. the seven ‘indicator PCBs’ and the six PAHs of Borneff).

Aggregate variables provide the possibility to ‘quantify’ a group of related compounds based on a similar characteristic. Such characteristics are generally related to the analytical method applied (e.g. as in Adsorbable Organic Halogen (AOX); the halogenated organic compounds that can be adsorbed on active carbon) and are more thoroughly discussed in section 4.8. Progress is being made in developing new aggregate variables based on chemical methodologies [Van Loon and Hermens, 1995, 1994] as well as the mode of toxic action of aquatic pollutants [Verhaar *et al.,* 1994]. Some examples of aggregate variables are [Sanders and Loftis, 1994]: Nutrients, organic carbon (TOC, DOC, POC), BOD, COD, and various forms of Organic Halogen (e.g. AOX, EOX, VOX).

Biological variables have aggregate variable characteristics. The functioning or structure of communities is indicative of ecosystem health and thereby of possible[1] chemical anthropogenic impact (see [Cairns, 1989]). Toxicity tests, apart from providing information about the variable 'toxicity', are also indicative of presence of harmful substances.

4.3.3 Biological variables

With respect to variables for biological monitoring, the following differentiation can be made:
1. *Biological methods* (Analysis of biological communities of the water body);
2. *Physiological and biochemical methods* (e.g. oxygen production and consumption, respiration, growth, etc. of organisms suspended in the water;
3. *Monitoring of the eco-toxicological effects* (behavioral, lethal, or sub-lethal) of samples on organisms under defined laboratory conditions (toxicity tests and bioassays), or in-situ / on-site (continuous field or 'dynamic' tests);
4. *Observation of histological and morphological changes, embryological development or early life stage tests.*

1. Biological methods
The presence or absence of certain species, or the total species number and abundance, can be utilized as a means of measuring environmental degradation. As such, the actual variables in biological monitoring are aquatic vegetation, phyto- and zooplankton, macroinvertebrates, fish, or even water birds or mammals. The (family of) species (variables) chosen depends completely on the assessment methodologies (the biological index) that will be applied.

Biological indices are usually specific for certain types of pollution, since they are based on the presence or absence of indicator organisms (bioindicators), which are unlikely to be equally sensitive to all types of pollution. Some biological monitoring methods use families of organisms (taxonomically less complex) instead of species. However, the ecological requirements of families of organisms are so broad that the family level is satisfactory for use in biological indices in only a few cases .

In many cases, the biological indices (those based on selected species) only work well for the water bodies in the regions in which they were developed and may give anomalous results in other types of water bodies. This is largely due to natural variations in species distributions [Woodiwiss, 1980a,b][Ghetti and Bonazzi, 1980]. A brief overview of species selection

Note
[1] Caution should be taken as for example natural causes and/or habitat changes may also affect community structure.

within the three major classes of biological methods is presented below [Friedrich *et al.,* 1992].

It is important to realize that the flora and fauna present in an aquatic system are a function of and respond to the combined effects of various hydrological, physical and chemical factors [Friedrich *et al.,* 1992]. Apart from pollution of anthropogenic origin, important factors include: (alterations in) hydrological and physical characteristics, natural changes in nutrient and dissolved oxygen concentration, and (alterations in) habitat. Therefore, it is important that biological methods are not used in isolation, but together with all other data available to ensure correct interpretation of the results. Furthermore, the duration of exposure and the bio-availability of a substance may affect the response [Friedrich *et al.,* 1992]. Many aquatic organisms react very rapidly against toxic substances, but for instance the effect of nutrient enrichment (eutrophication) in a water body is a long-term effect.

Community structure indices (Abundance and diversity indices and similarity indices) are used to assess situations with organic, toxic or physical pollution which impose general stress [Hawkes, 1977].

Indices based on selected species (saprobic indices and biotic indices) may not work well in rivers which have toxic pollution or which have been canalised, since most indices were designed specifically for use in upland rivers or for use with organic matter pollution causing oxygen depletion [Woodiwiss, 1980a,b] [Ghetti and Bonazzi, 1980].

Macro- and microphytes and phytoplankton as indicators of water quality. Algal species may be used to assess acidification of surface waters [Battarbee and Charles, 1986] [NRC, 1986] [Smol *et al.,* 1986] or trophic status, but difficulties still remain.
In order to develop systems based on macrophytes, a thorough understanding of the local species and their preferred aquatic environments, including physical, chemical and hydrological features, is necessary.

2. Physiological and biochemical methods
The physiological response of an organism to changes in its environment can also be a variable in the biological assessment of water quality [De Zwart, 1995]. Many of the methods that have been developed are most suitable for occasional assessments or basic surveys. Few methods are suitable for routine monitoring and assessment because they are often developed in relation to specific water bodies and because they are highly qualitative or rather complex and expensive to perform. Some examples of physiological responses that can be measured include: growth rate of algae and bacteria, phytoplankton oxygen production potential, bacterial additional consumption, and chlorophyll fluorescence.

3. Monitoring of eco-toxicological effects (toxicity tests and bioassays)
The testing of samples and compounds for toxicity under controlled laboratory conditions is widely used for pollution monitoring and control. The actual variable in these tests is ‘toxicity’ (an observable effect inflicted on the test organisms). A distinction is made between acute or chronic toxicity and lethal and sub-lethal effects. Toxicity testing can be applied independently, with the important advantage that unknown toxicants can be addressed, or it can be applied as a first and relatively cheap step in a tiered system of water quality assessment [Van Leeuwen, 1994]. It should be noted, that species differ in their sensitivity towards various toxic compounds. This should be considered when selecting a species for

toxicity testing. Using more than one type of toxicity test may be advantageous [Beim, 1986].

4. Histological and morphological methods
The presence of pollutants may lead to chronic and/or sub-lethal effects in the 'health' of an organism which may be manifested as morphological or histological changes [Friedrich *et al.,* 1992]. The actual variables observed with these methods are again the biological responses (e.g. body tumours, damage or inflammation on fish gills).

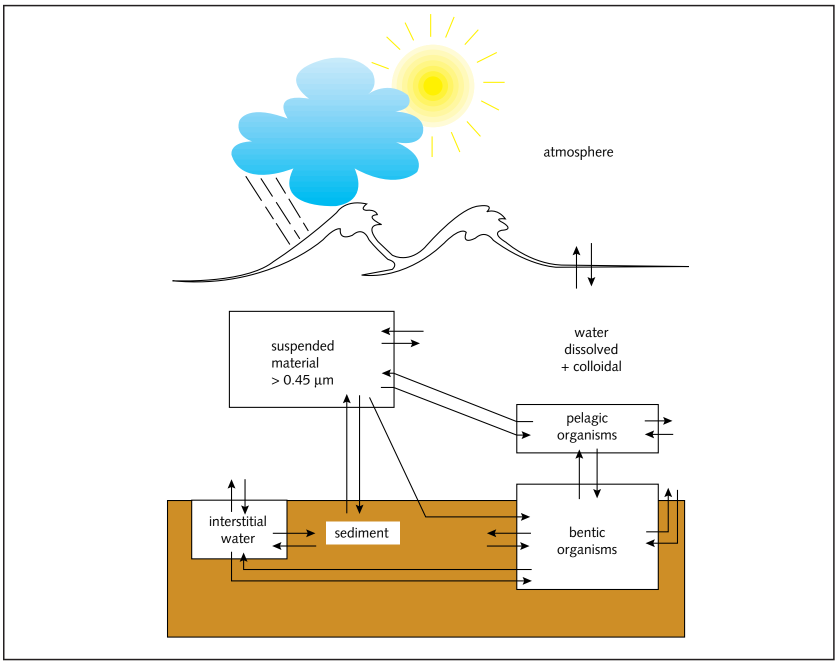
4.3.4 Selection of the media

Three principal media can be used for aquatic monitoring: water, particulate matter (suspended matter and sediments), and living organisms [Meybeck *et al.,* 1992]. Figure 4.3 shows the patterns of exchange of pollutants between these most important media.

The distribution of the various micro-pollutants between the different media will be determined by transport of water and particulate matter, by chemical and biological transformation processes and by distribution processes, such as absorption and desorption on sediment and suspended material, evaporation from the water phase and bioaccumulation in organisms.

Although the dissolved forms of pollutants in the water are directly involved in biological processes (bioavailable forms) and directly affect most of the water uses, many toxic pollutants (e.g. heavy metals, hydrophobic organic micropollutants) are associated with particulate matter [Litherathy, 1994]. As a result of biological and chemical influences or transformations, these toxic substances can be mobilized to affect water uses. In the Elbe, Rhine, Moselle and Saar Rivers, measuring programmes are increasingly focusing on the medium in which the most efficient measurement can be made, i.e. water for substances which mainly occur in solution, and suspended matter or bottom sediments for highly adsorbable substances [Enderlein, 1994a]. More measurements to detect possible contaminations of flora and fauna are also envisaged.

Figure 4.3:
Transport processes of micro pollutants (exchange between media) [Adriaanse *et al.,* 1995]



A beneficial tool in the selection of the preferred medium for the determination of a specific variable is the equilibrium partitioning coefficient (either empirically or semi-empirically determined). The equilibrium partition coefficient (K_p) is a measure for the distribution of a substance between water and particulate material. The coefficient K_p is defined as:

$$K_p = \frac{\text{concentration in suspended material}}{\text{dissolved concentration in water}} = \frac{C_s}{C_w} \text{ [l/g]}$$

K_p can be calculated by measuring the concentration in particulate matter and the dissolved concentration in water. However, for a number of organic micro-pollutants, the dissolved concentration cannot be measured, because the concentration levels are below the detection limits. Assuming equilibrium partitioning, an estimate of the partition coefficient can be obtained with the help of an empirically-determined octanol-water partition coefficient K_{ow} and the organic carbon fraction f_{oc} [CUWVO, 1990].

$$K_p = \frac{K_{ow} * 10^{-0.21} * f_{ox}}{1000}$$

The derived partition coefficient provides an indication of the preferable medium for a compound to be measured in. In general the following rule of thumb may be used:

– partition coefficient > 330 l/g or log K_{ow} > 7	Sampling of suspended material or sediments
– 3 l/g < partition coefficient < 330 l/g or 5 < log K_{ow} < 7 material and/or sediments	Sampling of surface water and/or suspended
– partition coefficient < 3 l/g or log K_{ow} < 5	Sampling of surface water

It should be noted that deciding which medium to sample, based only on a theoretical partitioning coefficient or a log Kow and the rule of thumb, should be done with great care, as many (sometimes unknown) factors can influence the actual value of the partition coefficient in a real environmental system. For instance, calculation of the partition coefficient for chromium, from actual data for the dissolved and suspended solid adsorbed fractions in various surface water systems, provided values ranging from 126 to 786 l/g [Stortelder *et al.,* 1989]. This range shows significant uncertainty as to whether there is any justification for measuring chromium in the water compartment.

Many lipophilic compounds and heavy metals possess the potential to *accumulate in organisms,* either through direct intake, or through food chain transfer [Friedrich *et al.,* 1992]. Measuring some chemical variables in organisms, or organs from these[1], can prove to be advantageous in two respects: (1) bioaccumulated pollutants may be easily detectable and (2) information about bioavailability is obtained.

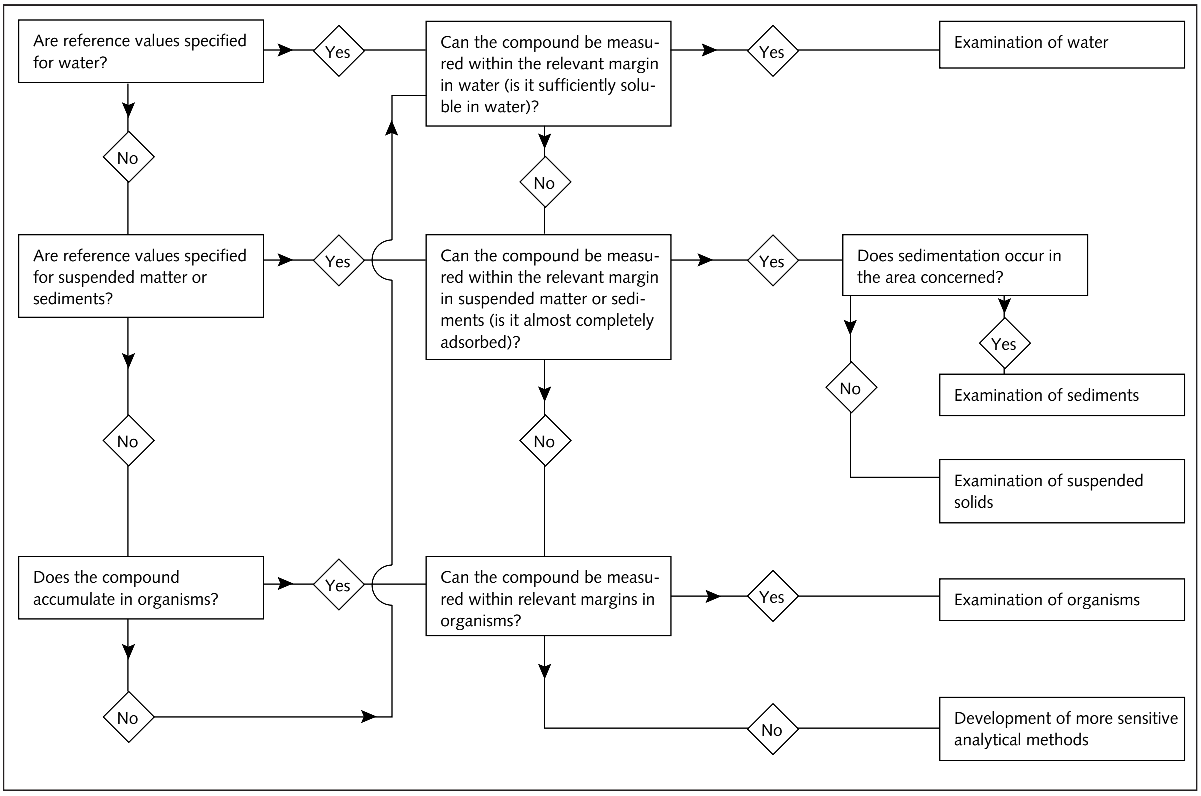
Note

1) Persistent organic chemicals are frequently associated with tissues with a high lipid content. Therefore, it may be more economical, and effective, to collect and analyze only certain tissues {Friedrich *et. al.* (1992)}.

Collecting the organisms from the environment for chemical analysis is known as ‘passive biomonitoring’. However, deliberate exposure of organisms (’active biomonitoring’) to chemicals or possibly polluted environments can also provide useful information, particularly when chemical analysis of water samples is difficult due to extremely low concentrations.

Some general criteria for organism suitability for bioaccumulation monitoring are: accumulation without toxic effect, correlation with water concentration, accumulation to a sufficiently high level, typically immobile or unlikely to travel far. Both plants and animals have been found suitable in many bioaccumulation studies [Philips, 1980] [Burton, 1986] [Whitton, 1988] [Samiullah, 1990]. Fish are widely used, as they are high in the food chain. Substrate bound organisms have the advantage that they are entirely immobile and easy to sample, especially if artificial substrates are used [Sládeckova, 1962] [Friedrich, 1973]. Some aquatic plants, particularly mosses, have also been shown to have a good correlation between tissue concentrations of some metals and the concentrations occurring in the surrounding water.

Figure 4.4:
A decision-tree for selection of the appropriate medium for monitoring [Adriaanse *et al.,* 1995]



4.4 Variability in water quality and relevant margins

Temporal and spatial variability in water quality is caused by natural processes and human activities. Hydrological and meteorological factors (e.g. storms, rainfall, river flow), as well as the physical, biological and chemical factors (e.g. flow-dependency of suspended material and many other variables, seasonal growth and decay of vegetation, temperature dependency of purification and nutrition) cause natural variations. These variations have to be documented with the other analytical data and have to be taken into account when interpreting monitoring data. Information on the importance of such phenomena have to be given to the users of the information to avoid mistakes in the evaluation and interpretation. Man-made changes in variables will be caused by pollution run-off, leaching, operation of sewer overflows, accidental spills and leakages.

Different time scales can be distinguished in the variability of surface water. Meybeck [Meybeck *et al.,* 1992] named five major types of variability:

a. Minute-to-minute to day-to-day variability resulting from water mixing, fluctuations in inputs etc., mostly linked to meteorological conditions and water body size (e.g. variations during river floods).
b. Diurnal variability (24-hour variations) linked to biological and light/dark cycles etc. (e.g. O_2, nutrients, pH), and to cycles in pollution inputs (e.g. domestic wastes).
c. Days to months variability, mostly in connection with climatic factors (river regime, lake overturn etc.) and pollution sources (e.g. industrial waste waters, run-off from agricultural land).
d. The seasonal hydrological and biological cycles (mostly in connection with climatic factors).
e. Year-to-year trends, due mostly to human influences.

To this inherent variability is the variability resulting from coincidental errors introduced during the various activities contained in monitoring and the variability of the analytical measurements. Variability is reflected in the precision of the data that are obtained and leads to an uncertainty interval around the numerical information that is generated on interpretation of the data (i.e. depending on the natural and experimental variability and the amount of data used in the interpretation phase). This uncertainty interval should preferably be less than the relevant margin.

The *relevant margin* is a measure that can be best characterised as the margin in the information that is still relevant for the policy and management of surface water [Adriaanse, 1994] [Adriaanse, 1993], or stated more directly: the margin in the information which the user of the information is bothering about. The relevant margin will be determined by the aim and use of the information (water quality policy and management) and is thus independent of measurement accuracy or limits of detection. The relevant margin is determined not only by the toxicological properties, but also by the extent to which the current concentrations in surface water are different from the standards and the future developments expected (production and use of chemicals). A relevant margin has therefore an interpretative character and is dated. Furthermore, relevant margins depend on the variable and the monitoring objective considered (trend assessment, load assessment, assessment of compliance with standards) [Adriaanse *et al.,* 1995].

The relevant margin is essential basic information when performing an examination of water quality. Usually the user of information can give a reasonable indication of the order of magnitude of the relevant margin that will, as such, be usable for network design. The desirable level of accuracy made explicit in this way will determine the lay-out of the measurement network. The density of points and the frequency of measurements will, at least, have to be sufficiently high to assure a precision that matches the relevant margin. Furthermore, the relevant margin will determine the suitability of analytical methods; limits of detection must allow for detection of concentrations preferably below the relevant margin. Even the final decision whether or not to measure quality variables is determined by the relevant margin, depending on actual occurrence at concentrations above or below the relevant margin.

4.5 Site selection

Identifying sampling sites requires several levels of specification. First, the macro level defines the river reach to be sampled. These macro level locations are generally a function of the information objectives. Selection of sampling locations at the macro level should take the water uses in the river basin into consideration. The micro level defines the place within the river reach to obtain a representative sample within the macro location. At the micro level, selection of sampling locations, horizontally and vertically, has to account for inhomogeneity of the cross-section caused by the incomplete mixing of waste discharges and tributaries [Litherathy, 1994].

For ambient monitoring, a sampling location will preferably be selected where full mixing of inflows has taken place. In some cases, because of the proximity of inflows, such a spot may not exist and multiple samples in the cross-section may be needed. These can then be combined to obtain a composite sample or alternatively, each sample can be analyzed separately and the results combined [Ward *et al.,* 1990] [Ward, 1986]. Representativeness at the micro level is of greater importance for the objectives of load estimation and testing for compliance with standards, then it is for trend detection. Logically this is only true in cases of known and invariable inhomogeneity.

In general, the same principles for site selection (but also sampling frequency and number of samples collected) for monitoring of water or sediment apply to biological assessments [Friedrich *et al.,* 1992]. It is important to understand the distribution of the species or communities to be sampled so that methods for sample collection and data analysis can be properly selected. For biological monitoring, sampling at different sites within a specific micro-habitat is necessary to avoid unrepresentative sampling. Preliminary surveys may be essential to indicate the number of samples required (for a given method) for a particular aquatic habitat, to achieve a certain degree of precision and confidence. Statistical methods relating to the sampling of benthic invertebrate communities are described by Elliott [Elliott, 1977] and general information on environmental sampling and analysis is given in Gilbert [Gilbert, 1987].

Samples of biota required for methods based on biotic indices, community analysis or species counts must often be taken from sites with specific hydrological features or substrate type. General guidelines for sampling biota are given by the International Standards Organization (ISO) in ISO Standard 7828 [ISO, 1985] and 9391 [ISO, 1991] and in the German Standard DIN 38410 T.1 [DIN, 1987].

For purposes of integration, abiotic and biotic data should be collected as much as possible at the same sites and at the same time. This is required to ensure that the interrelationships within ecosystems can be fully analyzed. With this information, conceptual and even dynamic models can be synthesized for ongoing guidance of water managers [UN/ECE, 1993a]. Long term monitoring programmes of this multi-media, multidisciplinary nature are important for the ecosystem approach, as they often provide the key to understanding cycles which may follow patterns of several years duration.

Data for ecosystems-based water management should be taken or developed from existing observation networks and supplemented, where necessary, by integrated monitoring programmes to provide for comprehensive assessments of ecosystems conditions, including interlinkages between abiotic and biotic factors operating within the same catchment area. Chemical variables and the movement of elements into and out of the catchment area, should be studied. Furthermore, encroachments and changes in human activities and the corresponding habitat changes along water bodies, that may affect the aquatic ecosystem, should be monitored.

4.6 Sampling frequency

It should be realized that in practice, sampling is never random; there is always some systematic component [Ward *et al.*, 1990]. This is the inevitable consequence of the practical realities of running a sampling programme. Specifying the frequency for sampling within a water quality monitoring system requires integrating a number of factors [Ward *et al.*, 1990]. These include:

1. Information sought (such as magnitude of trend to be detected or degree of standard compliance, including the agreed error risks).
2. Statistical methods employed to obtain the information.
3. Statistical characteristics of the water quality ‘population’ being sampled.
4. Budget available to support travel to sampling sites.
5. Distance of sampling sites from the laboratory.
6. Number of sampling sites within the network.
7. Ability of laboratory to process samples.

The first three considerations relate to actual design criteria based on information goals, whereas the latter four involve operational and financial constraints on the monitoring system that do not relate to the information goals.

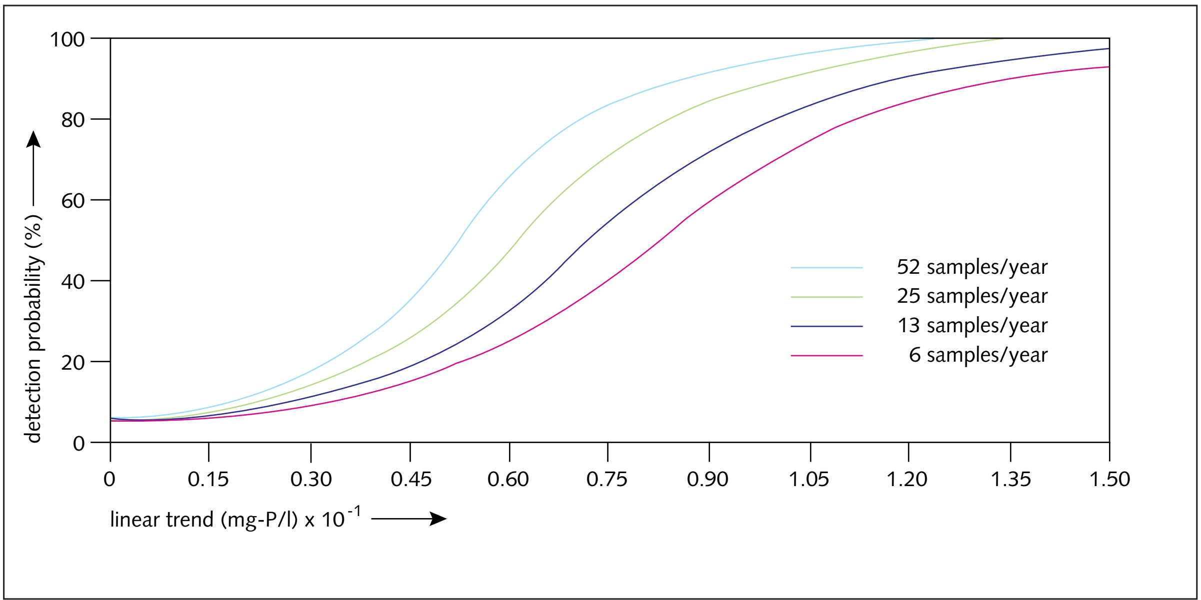
Information needs that focus upon critical hydrological events occurring frequently at certain times of the year can be identified [Hines *et al.*, 1975]. Examples include concerns about the assimilative capacity of streams for oxygen demanding waste-water effluents during low streamflows in late summer (high temperatures) or winter periods (low temperatures) or with controls of suspended sediment loads associated with high streamflows [Steele, 1986]. Sampling strategies could focus on such events.

Based on such considerations, operational surveillance should focus on the worst possible conditions such as summer dry periods and on extreme values of concentration. Impact surveys which must also determine pollutant fluxes should, in case of rivers, include surveys during high flow periods [Meybeck *et al.*, 1992]. The same is true for trend monitoring. Comparing different methods for estimating annual loads for the Rhine and Meuse Rivers, it was concluded that the reliability of estimates was mainly determined by the monitoring strategy (sampling frequency) [De Vries and Klavers, 1994].

In many monitoring programmes, it may be best to evaluate logical alternative sampling frequencies in terms of their ability to satisfy multiple objectives. This may be better than to optimizing the sampling frequency for one specific objective [Ward *et al.*, 1990]. For example, it may be logical to sample at such a spacing in time that the samples can be assumed to be independent.

Sampling frequencies that satisfy multiple objectives may still differ for individual variables. Each variable has, in principle, its own variability, its own relevant margin and optimal sampling frequency. However, it is usually sufficient to perform frequency studies for a limited number of variables that are representative of groups of variables with similar behaviour. For this purpose, time-series analysis can provide relevant information [Mueller, 1989]. Such analysis requires that e.g. dependencies on river flow, suspended matter content and seasonal variability is eliminated from the measurement series [Hirsch R.M., 1988] [Hirsch *et al.*, 1991]. The gains to be made by increasing the frequency are often limited, however. In some cases, the demonstration of trends, of the order of the relevant margin, is only feasible after an extravagantly large increase in the measurement effort. This is illustrated in figure 4.5 for the P content (relevant margin 0.01 μg/l) in the lower part of the Rhine [Adriaanse, 1993].

Figure 4.5:
Trend detection probability as a function of the actual linear trend in mg-P/l for four distinct sampling frequencies [Adriaanse, 1993]



Naturally, as data are collected, sampling programs can be refined and improved [Ward *et al.,* 1990]. However, there are advantages to maintaining sampling frequencies over the long term for at least some locations. Furthermore, attention can be focused on:

- the possibility of mixing and storing composite samples of particulate matter which then enables the analysis of only one sample per year;
- determining biotic indices during the low water stage when quality is usually at its worst; or
- taking composite water samples through automatic samplers.

In transboundary surface waters, samples for the analysis of chemical and some biological variables are usually taken 12 or 13 times a year [Enderlein, 1994a]. Attempts have recently been made to adjust sampling frequencies to the variability of the physico-chemical and biological regimes along the transboundary watercourse. This sometimes requires an increase in sampling frequency or the composite sampling of water over a period of 7 or 14 days. Experience in transboundary waters is scarce, however.

Specific considerations for sampling frequency related to biomonitoring:
For toxicity testing and other bioassay techniques, no additional remarks are needed. However, with respect to the biological monitoring and monitoring of physiological or biochemical characteristics, the life cycle of the species that have to be sampled, or on which the measurement is based, has to be considered in setting sampling schemes. Sampling could be done such that the same part of the life-cycle is sampled each year. The representativeness of the environmental conditions of such a sample depends on the species sampled. Micro-organisms such as ciliated protozoa, periphytic algae or bacteria reflect the water quality of only one or two weeks prior to their sampling and analysis, whereas insect larvae, worms, snails, and other macroinvertebrate organisms reflect more than a month, and possibly several years [Friedrich *et al.,* 1992].

4.7 Field work

4.7.1 Sampling methods

To achieve the purpose of sampling, i.e. to take a sample that is representative of the system sampled for the variable to be determined, three major aspects of sampling have to be considered.
A type of sampling
B insuring sample authenticity
C general sampling procedures

A Type of sampling
In addition to the selection of sampling site and frequency (see section 4.1.4 and 4.1.5), the possibility to choose from a number of types of sampling provides a further possibility to guarantee near field and temporal representativeness. Inhomogeneity of the medium to be sampled (e.g. water, sediment or biota), either in time or in space, can usually be accounted for by the type of sampling applied.

The major types of samples that can be distinguished are summarized below [Adriaanse *et al.,* 1995]:

- grab sample: a container of water (or sediment), taken at a selected place, depth and time;
- depth-integrated grab sample: the sample is collected over a predetermined part of the entire depth of the water column at a selected location and time;
- time proportional composite sample: the sample is composed of a mixture of equal volumes of water collected at regular time intervals;
- flow-proportional composite sample: the sample is composed of a mixture of equal volumes of water collected at time intervals that are inversely proportional to the flow;
- space composite sample: the sample is composed of a mixture of equal volumes of water (or sediment, biota) collected at selected space intervals.

The extension of the technical possibilities for water sampling in recent times as a result of automation, has made, in principle, any type of proportional sampling possible [Smith, 1990]. Practicable solutions only depend on the availability of a specific sensor (time, flow, conductivity, etc.) to be applied in combination with an automatic sampler.

B Ensuring sample authenticity
Sample authenticity can be disturbed by contamination with any possible impurity that might interfere with the analysis that will be performed on the sample, occurring at some stage during sampling, preservation or transportation. Great care must be taken in the selection of materials (e.g. samplers, containers, filters, filter apparatus, preservatives), the cleaning of equipment and in the checking for purity of chemicals (preservatives, reagents) used. Samples for the determination of different variables call for different sampling, preservation and storage methods [Chapman and Kimstach, 1992].

- Samples collected for the determination of heavy metals require plastic (polyethylene) bottles, whereas samples for the determination of organic micro-pollutants should be in glass or stainless steel.
- Samples for bacteriological analysis must be taken in sterile glass or non-toxic plastic bottles and all subsequent handling of the samples must be done under sterile conditions.

As the risk of contamination cannot be completely eliminated, provisions to trace the possible occurrences of contamination are important. Contamination is best identified through use of a formal program of blanks. A field blanks program must be maintained on a regular basis, with contingency provisions for a major effort to resolve any contamination problem once identified [Clark and Whitfield, 1993]. Arrangements to prevent and identify possible contamination make up an integrated part of sampling procedure protocols as discussed below.

For biological monitoring sample authenticity is to be checked as well; after periods of flooding organisms might have drifted from upstream to lower stream stretches.

C Sampling procedures
When sampling, it is always necessary to follow recommended procedures to avoid collection of unrepresentative samples [Meybeck *et al.,* 1992]. In order to assure sample representativeness, it is of major importance to incorporate such produces in sampling protocols [Ward, 1994] [Clark and Whitfield, 1993].

Within recommended procedures, considerations such as the materials and equipment to be used, the way a sample should be collected (generally associated) and how the sample should be pretreated, preserved and stored, may differ depending on the variable to be determined and the medium sampled. Detailed descriptions of these sampling and pretreatment methods for both physico-chemical and biological variables, including sampling of (substrate bound) organisms and hanging out 'cultivated' organisms, are available in a number of standard reference guides published by various international organisations and programmes, or national agencies [Semenov, 1977] [CMEA, 1987] [WHO, 1987] [NIH, 1987-88] [APHA, 1989] [Edmondson and Winberg, 1971] [Vollenweider, 1974] [Eliott and Tullett, 1978]. Moreover, the International Standards Organization (ISO), publishes approved 'International Standards' concerning sampling and sample pretreatment, including general guidelines for sampling biota (e.g. ISO Standard 7828 [ISO, 1985] and 9391 [ISO, 1991] and [ISO, 1990]).

In addition to sampling procedures, protocols should provide guidance on topics such as [Clark and Whitfield, 1993]:
- documentation of field operations and observations and sample characteristics,

- unique identification of samples,
- a field blanks program,
- communicating of missing samples.

Documentation of field operations and observations and sample characteristics (e.g. location, date, time, collector, collection equipment, site conditions, sample details, unusual features or events) is of major importance for quality control, especially if the operator might deviate from predetermined procedures.

Ensuring that all protocols, including those related to the QA/QC part of the plan, are executed in a proper way requires that the personnel in charge of sample collection, field handling and field measurements be specially trained for their tasks [Meybeck *et al.,* 1992]. This is of special importance in ecosystem monitoring, where field workers should be properly trained to collect all the environmental information needed to aid interpretation of the biological data [Friedrich *et al.,* 1992]. In addition, it is desirable that the field vehicle can also be used as a mobile 'laboratory' for filtration, field measurements, preservation and sample storage [Chapman and Kimstach, 1992]. A lack of proper facilities will increase the risk of deviations from the protocol(s) as well as the risk of contamination.

4.7.2 In situ measurements

Some variables, typically some general characteristics of the system to be sampled, have to be determined in the field. These include variables such as temperature, pH, Dissolved Oxygen (DO), conductivity, turbidity, colour and transparency [WMO, 1988]. It should be noted that such field measurements should never be performed inside the sample bottles; no foreign objects whatsoever must be placed into any sample bottle [Clark and Whitfield, 1993]. Ideally, individual aliquots, which cannot be used for further analytical work, should be used or in situ measurements should be performed [Meybeck *et al.,* 1992] [Clark and Whitfield, 1993].

Apart from field measurements to determine general characteristics, rinsing, selection and counting of organisms for ecosystem monitoring can be performed in the field. However, these activities are preferably done in a laboratory, and are therefore discussed elsewhere.

As with the field work discussed previously, detailed protocols are required for all the operations that have to be performed in the context of doing field measurements (including calibration of the measurement equipment).

4.8 Analytical work

4.8.1 Chemical analyses in water

The analytical techniques applied for freshwater monitoring primarily depend on the variables that have to be measured. However, the cost effectiveness in relation to the level of precision required by the objectives of the programme is of importance as well [Chapman and Kimstach, 1992].

Detailed descriptions of analytical methods, including 'classical' methods are available in a number of standard reference guides published by various international organisations and programmes, or national agencies

[Semenov, 1977) [CMEA, 1987] [WHO, 1987] [NIH, 1987-88] [APHA, 1989]. Furthermore, a large series of 'International Standards' for chemical analysis in water have been published by the International Standards Organization (ISO) [ISO, 1993]. A division of analytical techniques into some general categories provides a basic view of the main analytical disciplines that can be recognized and the variables covered by these methodologies [Adriaanse *et al.,* 1995] [Chapman and Kimstach, 1992]. A number of advanced techniques are listed.

Atomic spectroscopic methods include Atomic Absorption Spectroscopy (AAS) with electrothermal (graphite furnace) or flame atomization and Atomic Emission Spectroscopy (AES) with Inductively Coupled Plasma (ICP) atomization and excitation. AAS is conventionally used for the analysis of trace metals, but AES has recently gained a lot of attention due to its broad applicability for elemental analysis. ICP with mass spectrometric (ICP-MS) detection has also gained considerable interest for trace element analysis.

Gas Chromatographic (GC) separation methods can be coupled with various detection methodologies, including Flame Ionisation Detection (FID), Electron Capture Detection (ECD), Nitrogen Phosphorous Detection (NPD) and Mass Spectrometric Detection (MS). Both the chromatographic conditions and the detection method applied depend on the variables that have to be determined. Gas Chromatography is used for the analysis and identification of individual organic compounds[1], with a very high resolution (separation power). The compounds to be analyzed have to be sufficiently volatile and thermally stable.

(High Performance) Liquid Chromatographic ((HP)LC) separation methods can be coupled with various detection methodologies, including single wavelength Ultra Violet absorption detection (UV), Diode Array Detection (DAD), Fluorescence Detection (FD). Furthermore, MS detection in combination with HPLC has recently gained a lot of interest. Both the Chromatographic conditions and the detection method applied depend on the variables that have to be determined. HPLC is used for the analysis and identification of individual organic compounds[2], with a resolving power that is less than that of GC analysis. The methodology is most suitable for the analysis of polar or thermolabile compounds that cannot be analyzed with GC analysis.

Both GC and HPLC are now often used in combination with (on-line) provisions for effective pre-concentration, or liquid – or solid phase extraction [Van Loon and Hermens, 1995]. This provides the advantage of concentrating the compounds present in the sample, which makes them more easily detectable. Moreover, this allows for a specific chemically defined fraction of the sample to be isolated before chromatographic separation and detection, thereby increasing the selectivity and diminishing matrix disturbances. The isolated fraction depends on the materials used for pre-concentration/extraction [Van Loon and Hermens, 1995].

Note

1) e.g. Organo Chloro Pesticides (OCP), Organo Phosphorous Pesticides (OPP), Triazines, 'derivatized' chlorophenoxycarboxylic acids, volatile Polycyclic Aromatic Hydrocarbons (PAH), Poly Chloro Biphenyls (PCB), other halogenated organic compounds, etc.

2) Organo Chloro Pesticides (OCP), Organo Phosphorous Pesticides (OPP), Triazines, Phenylureaherbicides, Carbamates, Chlorophenoxycarboxylic acids, Polycyclic Aromatic Hydrocarbons (PAH), etc.

Spectroscopic methods cover a broad area of methodologies for the detection and identification of a wide range of compounds, based on some spectral feature of the compound or derivative. This group of analytical methods includes e.g. AAS, AES, MS, UV, DAD and FD as discussed above. Furthermore, some very specific analytical methods are included in this category, such as the determination of phosphate / ortho-phosphate (colorimetrically), Nitrate and nitrite (colorimetrically) and oil (UV, or infra red spectroscopy (IR)).

Variable specific methods provide a result that relates to a broad characteristic of the sample, rather than to a narrowly specified set of compounds present. Furthermore, the result depends on the analytical method applied, which is generally specifically developed for the determination of that single variable. As a result, it is extremely important that the same method is followed each time, so that the results are comparable. The variables determined by such analytical methods are termed **aggregate variables,** and they are generally referred to by the name of the analytical method. Examples of such aggregate variables are:

- Organic Carbon: Total (TOC), Dissolved (DOC), Purgeable (POC): Determined as CO2 after complete oxidation.
- Organic Halogen: Adsorbable (AOX), Extractable (EOX), Volatile (VOX): Determined as the hydrogen halogenide after complete destruction.
- Kjeldahl Nitrogen (organic-N and ammonia): Determined as ammonia after reduction of all reducible nitrogen.
- Chemical Oxygen Demand (COD): Determined as loss of a chemical oxidant after chemical oxidation.
- Biological Oxygen Demand ('usually five days'; BOD5): Determined as loss of oxygen due to biological activity.

Many more aggregate variables have been, and are being developed, since they provide an interesting indication of a specific aspect of general water quality [Van Loon and Hermens, 1995].

4.8.2 Chemical analyses in suspended solids and sediments

For a number of variables the appropriate media for analysis are suspended solids or sediments rather than the water phase (see section 4.3). For most variables, the analytical principles applied in that case are basically the same as presented above for their analysis in water. However, isolation of the compounds to be determined often requires some additional effort. Digestion or destruction of the particulate material or extraction of the compounds of interest from the particulate matter is generally required [Adriaanse *et al.,* 1995] [Thomas and Meybeck, 1992].

There is a general relationship between the concentration of pollutants adsorbed on particulate matter and the 'grain size distribution' of the particulate matter. This is directly associated with the much higher specific surface area of the small particles (silt (2 – 63 μm) and clay (< 2 μm) fraction) as compared to the larger particles (sand fraction (> 63 μm)), ranging from 10 to 0.01 $m^2 g^{-1}$ [Thomas and Meybeck, 1992]. As a result, characterization of the grain size of the particulate matter for scaling purposes is of major importance. Basically two different methods, gravidimetric and laser spectroscopy, are available for this purpose [Adriaanse *et al.,* 1995]. The gravidimetric method is well standardized, but needs large amounts of the particulate matter, which is a problem when suspended matter is considered. The laser methods requires only small amounts of particulate matter (mg's). However, although a good intra-laboratory reproducibility is possible with the laser method, there is a large variability between different laboratories.

Normalization procedures can be applied, taking into consideration the ratio of the concentration of the variable of interest to some other sediment element or component that quantifies the geochemically active and/or geochemically inactive fraction. Such ratios can be undertaken using e.g. organic matter, aluminum, or sand (quartz). As organic compounds are mainly bonded to the organic matter of the particulate matter, this variable is of great importance for assessment of the bioavailability of organic micropollutants in water systems with transport of particulate matter. The organic matter is most often measured as TOC.

4.8.3 Microbiological analyses and analysis of biodiversity

A Microbiological methods

Microbiological analysis involves the enumeration of the virulent organisms and identification of special organisms indicative of hygienically suspect contamination or even pathogens themselves [Knoben *et al.*, 1995].

Assessing pathogenic and facultative pathogenic bacterial organisms (e.g. coliform bacteria, Salmonella, Shigella, Escherichia (E.coli) and Erminia) involves measuring turbidity, the growth of colonies, or the evolution of gas after incubation of a sample on a suitable (solidified or liquid) medium [Friedrich *et al.*, 1992]. Selection of incubation medium and temperature depends on the species or species group that has to be identified. Approved 'International Standards' concerning the analysis of bacteria have been produced by the ISO (ISO 9308-1 (E.coli) [ISO, 1990]).

Identification of viruses involves immunological methodologies. Although this methodology for identification of viruses is constantly being improved and simplified, many tests still require advanced and expensive laboratory facilities [Friedrich *et al.*, 1992].

B Biological methods

The analytical work associated with biological assessment methods constitutes of cataloguing of the species sampled and, if assessment requires, counting the number of individuals for each of these species [Knoben *et al.*, 1995]. The species included depend on the type of assessment that will be performed with the data [Knoben *et al.*, 1995]:

- Diversity and comparative indices: mostly macro-invertebrates and algae
- Saprobic systems: bacteria, phytoplankton, zooplankton and/or macro-invertebrates
- Biotic indices and biotic scores: benthic macro-invertebrates

As the identification of species requires a considerable knowledge of taxonomy, this is generally the work of taxonomical experts. As taxonomy is not always far enough advanced and can be quite controversial, this may prove to be a complex task, especially if assessment requires identification of micro-organisms (e.g. bacteria, phytoplankton, zooplankton). At present, only a few specialists may be able to adequately identify the algae present [Friedrich *et al.*, 1992]. It should be noted, however, that the recent development of Optical Plankton Analysers (OPA's) provides interesting possibilities for the automated characterization and counting of algal species [Dubbelaar *et al.*, 1990]. These OPA's are based on the light scattering and fluorescence characteristics of algal species (flow cytometry) and the pattern recognition capabilities of artificial neural networks.

4.8.4 Toxicity testing and other physiological biochemical and morphological methods

A Methods for assessing toxic pollution in controlled environments
A large number of different tests exist for the evaluation of the distinctive adverse effects that can be inflicted on various species [OECD, 1984]:

- Acute toxicity (severe effects (often death) inflicted on e.g. Fish, Invertebrates, Bacteria, Algae, Protozoa).
- Sub-lethal toxicity (behavioral or functional effects inflicted on e.g. bivalve molluscs (shell movement), fish (swimming behaviour), phytoplankton species (chlorophyll fluorescence)).
- Mutagenity (e.g. 'AMES' test [Ames *et al.*, 1975] [Maron and Ames, 1983] [Levi *et al.*, 1989]).
- Carcinogenity, teratogenity (specific morphological effects inflicted on species or their offspring)

Many tests for acute toxicity have been standardised by national and international water organisations and are described in detail in national water quality assessment guidebooks (e.g. [Nat. Comm. USSR, 1987] [Nat. Comm. USSR, 1989] [APHA, 1989]). However, only few tests for sub-lethal toxicity, carcinogenity, teratogenity and mutagenity ('AMES' test, [OECD, 1983]) have been standardised. Further information on the variety of tests available is provided in various reports and articles [EIFAC, 1975] [US EPA, 1985a] [Beim, 1986] [Lillelund *et al.*, 1987] [OECD, 1987] [De Kruijf *et al.*, 1988] [Abel, 1989].

Toxicity tests reduce the necessity for highly sophisticated instruments and trained staff that are otherwise needed for effective chemical monitoring. Moreover, they provide an interesting possibility to assess the overall environmental risk associated with complex mixtures (typically effluent discharges). It is very difficult, if possible, to reconstitute from compound-specific chemical data alone [Van Loon and Hermens, 1995]. At present toxicity tests are principally used in the assessment of effluent discharges. Natural water samples often have to be concentrated many times to get a measurable effect making the results difficult to relate to the natural environment [Friedrich *et al.*, 1992]. Toxicity testing, following concentration, does not differ substantially from the methodologies applied for effluent toxicity testing. A more detailed discussion of toxicity testing is therefore postponed until chapter 5 (Effluent Monitoring).

If a specific or selective (solid or liquid phase) extraction procedure is applied for sample concentration, a type of chemically defined group variable is obtained. Such group variables can provide interesting information, complementary to whole sample toxicity testing, since the toxicant fractions are much more defined [Van Loon and Hermens, 1995]. This type of toxicity testing is, therefore, a suitable primary testing method in a tiered approach. Examples of tiered testing systems are provided by the EPA [US EPA, 1991] the OECD [OECD, 1987] and Pedersen et al. [Pedersen *et al.*, 1994].

B Physiological and biochemical methods
Complementary to toxicity testing under controlled conditions in the laboratory, the functional, biochemical or morphological effects of toxic pollution inflicted on organisms in their natural environment can be assessed. Observables examined in this category of biomonitoring techniques include [Friedrich *et al.,* 1992]:

- Oxygen production potential of the native plankton in water samples under light and dark conditions;
- Bacterial respiration (increased oxygen consumption) associated with the reduction of substrate (i.e. peptone or glucose) added to the sample (Zusätzliche Zehrung (ZZ), or additional consumption method [Knöpp, 1986]);
- Alteration, or inhibition of algal chlorophyll fluorescence, generally correlated to e.g. cell number or extracted chlorophyll;
- Morphological deformities or distortions (e.g. tumours, inflammation, and other deformities) in sampled organisms (e.g. fish, macro-invertebrates).

4.8.5 Chemical analysis in organisms

As was already presented in section 4.3.3, some variables are better determined in organisms, or organs taken from these organisms, than in the water phase. Freshwater mussels for instance can be very effective biomonitors [Herve, 1991]. The analysis of chlorinated organic compounds in the soft tissues of freshwater mussels (Anodontia piscinalis), set out in surface waters in Finland, showed high concentrations of chlorophenols near pulp bleach mills with no biological treatment facilities. Considerable amounts of polychlorinated biphenyls were also detected in some receiving waters.

For most variables, the analytical principles applied for chemical analysis in organisms are basically the same as presented above for chemical analysis in water. However, isolation of the compounds to be determined often requires some additional effort. Grinding of the organisms or organs, subsequent extraction, saponification, or digestion by concentrated acid and specific cleanup procedures are generally required [Barceló, 1993].

When measuring whole body contaminant levels, physiological condition/fitness, sex and reproductive cycles of an organism must be taken into account. The amount of, for instance, fat tissue relative to total body weight and thus bioaccumulation may be affected by such characteristics [Friedrich *et al.,* 1992].

4.8.6 Analytical quality assurance

Experts agree that 10 to 20 percent of resources for analytical work, including manpower, should be directed towards insuring the quality of analytical determinations for common water quality variables (WHO, 1987 in Meybeck *et al.,* 1992)). When trace pollutants (e.g. pesticides and trace elements) are measured, the resources required for quality control may even reach 50 percent. Insuring the quality of analytical work requires a number of prerequisite to be fulfilled, including validation, provision of SOP's, overall QA/QC programmes, inter laboratory testing, etc. These prerequisites are specified in some more detail below [Clark and Whitfield, 1993] [Adriaanse *et al.,* 1995].

Validation of the analytical methods applied is of primary importance. The performance characteristics of the analysis should be adequate with respect to accuracy, precision, linearity (range), sensitivity and selectivity. Sensitivity and precision have to be in accordance with the relevant margin of the variable concerned. Furthermore, the analysis has to be robust in regard of critical factors of the sample and the analytical circumstances. Validated analytical methods have to be documented in *Standard Operating Procedures (SOP's, Protocols).*

SOP's for analytical methods are part of a much more comprehensive *in-house programme for systematic quality assurance and quality control* (QA/QC). Such a programme includes standard procedures for documentation of results, instrument condition, maintenance activities, method changes, etc. Furthermore, SOP's for calibration and a programme of reference samples, blanks, and spiked samples is part of the overall QA/QC Programme. Finally, a final check of the results, by a competent person, before they leave the laboratory is mandatory.

Application of reference samples assures the traceability of results. However, due to the lack of certified reference material and the importance of comparability of analytical results, *inter-laboratory tests (Round Robin testing)* are indispensable. Within this context, it should primarily be noted that the comparability of water quality data from different laboratories can only be ensured if identical or, at least, similar methods are used. The application of 'internationally standardized' methods as referred to in the previous paragraphs is therefore of major importance in this respect.

Furthermore, data comparability problems may result from replacement of existing methods with newer, more elaborate and more efficient, ones. This can cause problems in the statistical analysis of data time series. Therefore, studies of the comparability of new with old analytical methods must be undertaken. If a new method is accepted into a monitoring programme an overlap period is required where samples are analyzed by both the new and the old methods. In addition, method changes have to be documented and archived. For (inter)national standardization of new methods, validation is performed by large method-evaluating inter-laboratory tests.

4.9 Data validation and storage

4.9.1 Validation

Data validation is an important element in the quality management of monitoring programmes. It assures that inaccuracies in the data are traced on a timely basis, before they are included in a database or reports or lead to misinterpretations when performing data analysis. Data validation checks typically include statistical analysis of replicate and spiked sample data, of blanks and of standard reference materials data, and also of the historical data records [Clark and Whitfield, 1993]. Protocols for data validation must include details as to what methods and checks are to be utilized to ensure the data on record are valid. As revision of taxonomic nomenclature occurs quite frequently, it must be checked whether the most recent nomenclature is used.

When data are found to be questionable, they should preferably be flagged or moved to a secondary file rather than being destroyed. The detection of abnormal values should lead to re-checks of the analysis, related computations and data transcriptions. Documentation of irregularities or deviations from protocols during e.g. sampling, preservation, or analysis can provide helpful information in these cases. Such information may provide an explanation as to the cause of aberrations in the data.

Checking of data for 'outliers' may also be part of data validation (alternatively it is part of data interpretation). An outlier is a value that does not conform to the general pattern of a data set [Demayo, 1992]. However, data that appear as outliers may also be occasional, but appropriate members of a measurement series. If such data are improperly excluded, then the true range may be seriously underestimated. Inclusion of erroneous data, however, may lead to a much more pessimistic evaluation than warranted. It is important not to exclude data solely on the basis of some statistical test. An expert should also review the data and make the final decision.

Subsequent data approval is a formal process where the reviewers formally, through signature, take responsibility for the data being of scientific level quality. If different levels of data validation have been used through a study (see PTI Environmental Services [PTI, 1991]), then the quality management protocols must ensure that there is no ambiguity as to the level of validation applied to each specific subset of data. Data released for publication, without having gone through the entire data validation and data approval process, must be clearly identified as 'Preliminary' or 'Not Validated'.

4.9.2 Data storage

Most risk of errors during data storage is associated with human error during written transcription or during 'keying-in' via a computer keyboard [Meybeck *et al.,* 1992]. Therefore, it is important to have databases checked periodically by an expert who is capable of spotting obvious errors. Another common problem is loss of data due to accidental erasure of computer files. In order to prevent this, there should always be at least a second, and possibly even a third, copy of the master file (e.g. on diskette) in a location away from the computer, where it is safe from fire, theft etc. The back-up file needs to be updated frequently to minimize loss if the main file is erased.

When entering data into a database, some secondary data must also be stored for the unambiguous identification of the measurement data to allow further processing, interpretation and presentation at a later date. Secondary information is generally stored in coded form.
A comprehensive check list of the secondary data that has to be considered for inclusion in the database files has been published by Chapman [Demayo, 1992]. Depending upon local conditions and the use of the database, additional secondary data, not included in the check list, can be meaningful as well [GEMS, 1992]:

1. Sampling location or station inventory
- geographical coordinates
- name of the body of water
- basin and sub-basin
- state, province, municipality, etc.
- type of water, e.g. river, lake, reservoir, effluent, rain, etc.

2. Sample information

- sampling location
- date and time of sampling
- medium sampled, e.g. water, suspended solids, sediments, biota
- sample matrix, e.g. grab, depth integrated, composite, replicate (e.g. duplicate or triplicate), split, spiked or blank
- sampling method and/or sampling apparatus
- depth of sampling
- preservation method, if any
- any other field pre-treatment, e.g. filtration, centrifuging, solvent or resin extraction
- name of collector
- identification of project

3. Measurement results

- variable measured
- location where the measurement was made, e.g. in situ, field, field laboratory or regular laboratory
- analytical method used, including the instrument used to make the measurement
- actual result of the measurement, including the units

A additional subject that requires attention is censoring of data. The lack of measurement precision encountered near the limit of detection is generally resolved by censoring of the data [Porter, 1986]. However, censoring removes information that may be useful for statistical data analysis and often creates the false impression that results near but above the LOD are sufficiently precise. Such results are usually reported as e.g. ‘not-detected’ (ND), less-then values (< or LT), half limit-of-detection (0.5 LOD), or zeros [Demayo, 1992]. Further complications when censoring data may occur if the detection limit has changed over the period of record. Multiple censoring levels generally occur when different analytical techniques have been employed over the period of record [Steele, 1986]. As a result, censored data should always be recognizable as such and information should be included on the type of censoring that has been used.

4.10 Data interpretation

Data interpretation includes performing descriptive statistics, calculation of trends and loads and testing for compliance with standards. The first step in data interpretation should be to view the data (i.e. in a graphical format). Viewing the data helps to gain an understanding of water quality behaviour which can be used in interpreting statistical results. That is, use Exploratory Data Analysis (EDA), provided by modern statistical packages [Ward *et al.,* 1990].

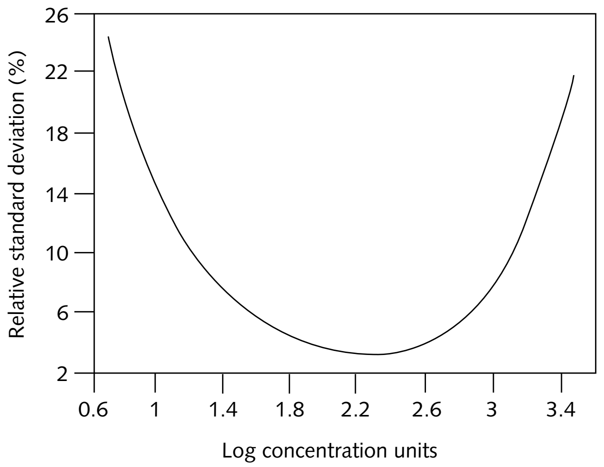
In further (statistical) data interpretation the role of a data analysis protocol (DAP) is crucial. A DAP connects raw data directly to the information goals for which the data are collected in the first place. A data analysis protocol must, at a minimum, contain five components:

1. a statement of the exact information to be produced;
2. procedures to be used to prepare a raw data record for graphical and statistical analysis;
3. means to visually summarize the behaviours of the water quality variables;
4. recommended statistical methods which yield the desired information;
5. reporting formats for the resulting information.

Another main component of a DAP is specifying exactly how to address some common data limitations that may complicate the analysis of data series, before data analysis proceeds. These limitations include [Ward *et al.*, 1990]:

1. missing values;
2. sampling frequencies that change over the period of record;
3. multiple observations within one sampling period;
4. uncertainty in the measurement procedures;
5. censoring the measurement signals;
6. small sample size (insufficient for proper analysis);
7. outliers.

Figure 4.6:
Relative standard deviation of an analytical signal as a function of concentration [Porter, 1986]



Random analytical error associated with water quality measurements should be considered when performing statistical data interpretations [Porter, 1986]. Such analytical error is generally correlated with the analytical signal obtained. The relative standard deviation is high for measurements close to the limit of detection, decreases at higher analytical signals and increases again for signals at the upper end of the analytical reach. A typical example of relative standard deviation as a function of analytical signal is presented in figure 4.6.

Moreover, analytical error may not be constant even despite a rigorous quality assurance programme. Especially for extreme data (at the lower and upper end of the analytical range) it is of major importance to account for random analytical error.

Finally, as an important part of most data interpretation techniques is hypothesis testing, some general aspects related to error probabilities in hypothesis testing have to be regarded. An overview of the error probability terminology that is associated with hypothesis testing is presented in table 4.2.

Table 4.2:
Four possible outcomes of hypothesis testing and their probabilities

	'TRUTH'	
TEST RESULT	**H_0 TRUE**	**H_A TRUE**
H_0true	1 – α (Confidence level)	β (Type II error risk)
H_A true	α (Significance level) (Type I error risk)	1 – β (Power)

Much attention is generally given to the probability of making a Type I error, i.e rejecting the null hypothesis[1] when it is actually true (the significance level). In contrast, only little attention is generally given to the probability of making a Type II error, i.e accepting the null hypothesis when it is actually false. The power of hypothesis testing, being directly related to the probability of making a Type II error (see table 4.2), is therefore hardly ever taken into account [McBride and Loftis, 1994]. As the power is strongly related to the sampling frequency (number of data used), it is recommended that attention should also be given to the probability of making a Type II error when performing (and reporting the results of) hypothesis testing.

Some more specific aspects of data interpretation related to specific data interpretation methods are presented below.

4.10.1 Descriptive statistics

Performing descriptive statistics is of major importance for characterization of the data. Many statistical data interpretation methods, e.g for the detection of trends or testing of compliance with standards, require that the data are normally distributed and free of serial correlation (e.g. autocorrelation and seasonal variation) [Ward *et al.,* 1990]. Such data characteristics can be evaluated with descriptive statistics. If deviations from required characteristics are observed, these can generally be adjusted by applying data transformations.

Other aspects of statistical data characterization are central tendency (e.g. mean, median) and spread (standard deviation, range/maximum-minimum). The median is generally recommended in water quality data analysis instead of the geometric mean, to avoid the problems with using data transformations [Ward *et al.,* 1990]. Methodologies for performing descriptive statistics are generally included in most statistical text books, modern statistical software packages and specific analytical textbooks [Kateman and Buydens, 1993] [Demayo, 1992].

4.10.2 Trend detection

The detection and quantification of trends is an objective of major importance in water quality examination. Identification of trends offers a possibility of timely detection of deteriorations, or improvements, in water

Note
1) In water quality testing the null hypothesis is usualy one of no change or no difference (e.g. no difference in the mean value of a water quality variable at two locations, or no trend in water quality present.

quality. As such, trend detection is indispensable for the evaluation and preparation of policy or management in water quality control. Both trends in concentration (more precisely the absolute value of a variable) and trends in load can be considered.

A trend in the measurement information occurs when a systematic, statistically significant change takes place during a certain period of time that cannot be explained by known hydrological or meteorological factors, such as high or low flow, suspended matter content, etc. A trend can be caused, for example, by a reduction in emissions. In most cases trends are modelled by some step function (representing an abrupt water quality change) or a linear function (representing a gradual change of water quality). Both parametric and nonparametric statistical methods can be used for their detection [Hirsch *et al.,* 1991]. Well known theoretical tools for the detection of trends include Student's t-statistic, Mann-Whitney's and Spearman's tests [Somlyody *et al.,* 1986].

It is worth while to emphasize that the above mentioned classical tests are directly applicable only for analyzing independent time series data. Therefore suitable extensions are necessary for handling the dependent observations which occur in practice [Bayley and Hammersley, 1946] [Lettenmaier, 1976]. Serial correlation, like seasonality, violates the assumption of independence inherent in many statistical tests [McBride and Loftis, 1994]. Before performing trend detection calculations, the raw data should be adjusted for flow dependency, suspended material content dependency, seasonal variability and other variabilities that might blur recognition of the actual trend.

Special care should be taken when analyzing data series that 'contain' missing values, values below the detection limit, or otherwise censored data. Software specifically developed for the analysis of water quality data (e.g. WQSTAT) generally include such statistical methodologies and methods for handling data limitations [Aaldrink, 1992]. Special software programmes exist to check for trends and correlations between biotic and abiotic variables (TWINSPAN, DECORANA, CANOCO) [Jongman *et al.,* 1987].

Finally, it should be noted that the highest discrimination for trends is possible with calculations made with individual measurement data, not with aggregated data such as annual means. This applies both to quality data and to loads. When using the original measurement data, the relative error is by far the smallest.

4.10.3 Estimation of loads

Load estimations are of major importance for the evaluation and preparation of policy and management for water quality control, especially in cases where transboundary impact of pollution is considered, or where effects on pollutant 'sinks', like e.g. sedimentation areas, lakes, reservoirs and seas, are considered. Various models and equations for the estimation of loads are available, ranging from very simple to highly advanced interpolation and correlation techniques [De Vries and Klavers, 1994]. In selecting an equation or model, insight into the characteristics of the variable for which the load has to be calculated, is required; e.g. is a compound strongly adsorbed on suspended matter, is the load subject to fluctuations in suspended matter, or does variability relate to the anthropogenic or natural source(s) of the variable? Characteristics may be different for individual variables and within different river basins.

It is concluded that the reliability of load estimates is mainly determined by the sampling frequency. The load estimation model that is applied is generally of secondary importance [De Vries and Klavers, 1994].

4.10.4 Testing for compliance with standards

Testing of compliance with standards involves the comparison of measurement data with criteria and objectives, as discussed in chapter 3, or possibly with other standards formulated for specific purposes. The results of physical/chemical monitoring and toxicity testing are generally tested for the individual variables determined [Stortelder *et al.,* 1989]. Occasionally, the sum of a number of compounds or an ‘index’, based on a larger number of substances or groups of substances, is tested against the standards. In ecological assessments the indexes, being an integral part of the assessment methodology, are tested as an integrated part of the assessment strategy [see chapter 3].

Both selection of a technique for testing compliance with standards and the implications of the results depend, to a major extend, on how compliance with a standard has been formulated and whether or not specific testing requirements are prescribed. Standards may be formulated as hard criteria or as an indicative value, and either as a single value or as a ‘range’ that allows for various compliance rankings [IKSR, 1993].

Testing procedures for compliance testing are based on comparing a specific result of descriptive statistical data analysis (e.g. 90th percentile, or the median, (or the 10th percentile for e.g. dissolved oxygen)) with the standard [NRA, 1994] [IKSR, 1993a] [Ellis and Newman, 1993]. The 90th percentile value instead of the maximum absolute value and the median instead of the mean is generally used, to avoid the possible influence of extreme peaks [Stortelder *et al.,* 1989] [IKSR, 1993]. For toxic substances, the upper limit from the series is often used, because short term exceeding of standards may have a deleterious influence on the water system. In order to calculate percentile or median values with sufficient accuracy, specific measurement frequencies are required [IKSR, 1993a]. A thorough analysis of the accuracy of statistical interpreted data as a function of sampling frequency has been reported by Valiela and Whitfield [Valiela and Whitfield, 1989].

For surface water and suspended matter, a series of measurements (generally a fixed number per year) are usually tested against the standard. For assessment of the quality of sediments, individual samples or composite samples may be used from the area concerned. Furthermore, when testing the quality of suspended matter and sediments the DAP should specify directions for including the characteristics of the suspended material in the testing procedure. Both ‘grain size distribution’ and organic matter content may have a marked influence on the concentration of adsorbed pollutants [Van der Kooij *et al.,* 1990].

4.11 Presenting and reporting the results of quality assessment

Interpreting data and assessing water quality as discussed in section 4.10, is only a first step in conveying actual information to the target audience for whom the information is meant. Preparation of reports and dissemination of information is another significant part of an information system. To inform decision makers, concise presentation is conditio-

sine-qua-non. To achieve this, State of the Environment Reports (SOE) and Environmental Indicator Reports have been introduced by several countries and international organizations [OECD, 1995] [Adriaanse, 1993a]. SOE reports normally include [Adriaanse and Lindgaard, 1995]:
– the state of the environment;
– changes and trends in the state of the environment;
– links between human and environmental health and human activities including the economy;
– the actions taken by the society to protect and restore the environment.

Environmental Indicator Reports are presentations of selected indicators to evaluate their development in time. They include development in environmental quality, economy, demography, investment, industrial production, traffic and others. For surface water quality, useful indicators are dissolved oxygen, BOD, nitrate extent of waste water treatment, use of fertilizers and pesticides and others.

For the production of reports on surface water quality the following issues have to be considered [Villars and Groot, 1995]:

A audience definition
Several audience categories can be identified (i.e. interested public/ concerned citizens, media/general public, policy makers, resource managers, scientists). Reporting should be tailored to meet the information needs of the expected reader audience.

B monitoring objective definition
If a monitoring programme is well designed, monitoring objectives have been defined before the actual monitoring programme started [see section 2.4]. These monitoring objectives have to be considered again when reporting the results. Too often, report information is presented in a self standing manner, and the connection with the original objectives is not given.

C format definition
Formatting decisions should be based on the type of audience the document is trying to reach, and should make the information comprehensible to them. Items that should be considered within this context are presentation method (tables, graphs and charts, maps, or possibly even electronic presentation), level of detail and lay-out.

Below, some important aspects of various types of presentation methods are discussed. Consideration is given to the type of information that can be displayed and level of detail that can be obtained.

For the rapid interpretation of the frequently large amounts of water quality data that monitoring networks produce, it can be useful to aggregate the data to a higher and more understandable level. Bulky reports containing large amounts of raw data will not normally lead to a good understanding of the information that is enclosed. Moreover, it will generally agitate the audience that is addressed [Hofstra, 1994].

A very high level of aggregation can sometimes be obtained. The British NRA, for example, has proposed that the results of biological grading[1] can be used to add a higher degree of confidence to the Chemical grading

Note
1) These are based on the ‘Biological Monitoring Working Party’ (BMWP) scores in combination with the ‘River Invertebrate Prediction and Classification System’ (RIVPAC).

system (the new General Quality Assessment (GQA) system) [NRA, 1994]. A fundamental level of correlation between the two grading systems has been established.

Data aggregation is already inherent to some assessment methods (e.g. ecological indices). By using indexes the results for several variables can be converted to one quality evaluation which creates a rapid manner in which to express the complex concept of ‘water quality’ as a single evaluation figure. The concept of indices remains promising for conveying the results of routine water monitoring to non-technical users and to the public (For four examples see Smith, 1989) ref. in Ward *et al.,* 1990)). However, for many assessment methods (e.g. physico-chemical assessment) such a high inherent level of aggregation is not easily obtained. Only a few indices have been developed for data included in such types of monitoring.

An example of such a water quality index is the IMP index. First developed for the purposes of the Netherlands water quality policy, this index has been used later in other European countries [Chambolle, 1993] [V&W, 1975]. The index is based on the variables oxygen, BOD and NH4, and for this reason is particularly suited for the evaluation of the organic load.

If aggregation by means of indexing is not practical, proper graphical presentation is ever so important. Nevertheless, calculated ‘indices’ are often presented graphically as well, providing a better view and allowing any trends to be recognised at a glance.

Further general aspects of data presentation consider standardization and public access to information. A questionnaire given to representatives of all EC member states revealed that there is a general desire for further standardization in the area of reporting [Villars and Groot, 1995]. A procedural framework, as with data analysis, was recommended. Reporting protocols could be defined by each monitoring organization and could thus be flexible to meet the goals of individual monitoring programmes.

As stated in section 2.3, consumer's support and general public awareness is necessary for successful implementation of any water quality management strategy. Therefore, at the European level, agreements as to the public availability to information should be made. If information can become more freely available, the distribution of reports can be more easily organized. Implementation of EU directive 90/313/EEC, 1990) on free access to environmental information is to be stimulated.

4.11.1 Data tables

As was already recognized above, using tables with measurement data will not normally shed any light on the overall results of monitoring. If, however, it is absolutely necessary to use extensive data tables, they should preferably be added to a report as appendices. A better insight is obtained if, instead of the individual results, the results of data interpretation (e.g. central tendencies and standard deviation, the numerical value of a detected trend, yearly loads) are presented tablewise. Depending on the audience, such aggregated numerical data presentations may even be required. However, if such a presentation leads to large tables these are also better added to a report as appendices.

A further important aspect of presenting aggregated numerical data involves adding information concerning the methodologies that have been used to analyze the data. A sufficient amount of appropriate supplementary information should be included to provide a clear understanding of the significance of the results.

Finally, decisions as to the detail in the data (i.e. significant figures) that should be presented. Relevant margins, as defined in section 4.4, provide a suitable measure with respect to the amount of detail that is still relevant to the target audience.

4.11.2 Graphs and charts

Graphical displays are probably the most useful approach for conveying information to a wide variety of both technical and non-technical audiences [Ward *et al.,* 1990]. Various standard types of graphical presentation methods are available. Each type of graphical presentation method is inherently best suited to display a specific type of information [Demayo and Whitlow, 1993].

Box-and-whisker plots are especially powerful at providing a visual indication of data distributions (central tendency and spread) and indicate how distributions change over time of between locations. Line graphs, often in combination with a scatter plot can provide a good view of tendencies, like e.g. seasonal variations, and trends in time series. If data are plotted against data for another variable such graphs can nicely display correlations with this other variable, like e.g. flow, or suspended matter content. Bar charts, pie charts and histograms are good presentation methods to display loads and/or relative contributions to loads. However, they are suited for many other uses as well. If, for example, frequency counts are displayed they can provide a lucid indication of the normality of a distribution.

The information can further be put into perspective by showing standards or other references in the graph [Adriaanse *et al.,* 1995]. For example adding a line, displaying the criteria against which is tested, provides an good way of presenting the results of compliance testing, especially if testing involves comparing a percentile or a mean value to be compared with the criteria. The same is true for comparing loads with a load criterium or objective in a bar chart.

Graphical methods are also very useful as a check on statistical methods. For example one should not generally believe that a time trend in water quality is 'significant' if it is not apparent from a time series plot or an annual box-and-whiskers plot of the data, unless, perhaps, the data record is extremely long [Ward *et al.,* 1990].

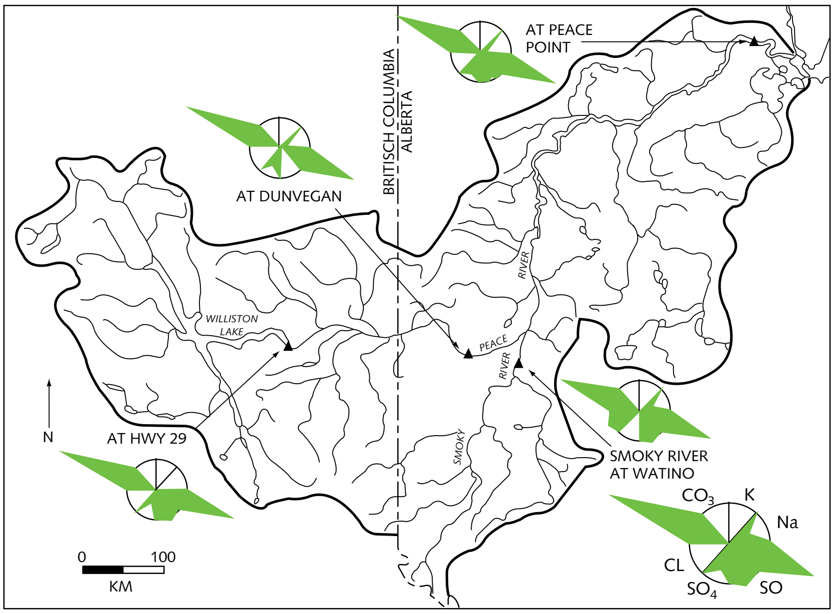
In addition, some graphical presentation methods have been specifically developed to display a specific type of information. An example of such a presentation method is the so-called 'AMOEBA' and acronym for 'A general Method Of Ecological and Biological Assessment' [Laane and Peters, 1993] [Ten Brink et al. 1991]. This method has been developed to present the results of ecological monitoring for specific target organisms (figure 3.2 in section 3.2). Both reference and present values are visualized. The reference values form a circle around the centre of this diagram. The present values are represented as percentage of the reference values and are connected to form an amoeba-like shape. A third set of values, representing a ‘target situation’ in between the present and the reference situation, may also be presented in the AMOEBA [Noordhuis *et al.*, 1994].

As with displaying information in tables, a sufficient amount of appropriate supplementary information should be included to provide a clear understanding of the significance of the results.

4.11.3 Maps

Maps are a powerful tool for presenting aggregated information [Demayo and Whitlow, 1993]. Using colour coding can give a direct impression of the distribution of a specific variable in space, or of areas of a distinct water quality class. Many countries apply such presentation methods to display the annual results of water quality classification [NRA, 1994]. Simple black and white patterns or isopleths may often be valuable as well. Pie carts, bar charts, ‘amoebae type’ charts (figure 4.7) or other graphs or plots can be added to a map, connected to a specific location with, for example, an arrow.

Figure 4.7:
Example of a map, expressing medians for selected ions at selected sites, as related to reference values in an ‘amoebae type’ presentation [Demayo and Whitlow, 1986]



By means of geographic information systems (GIS), quality data from a diversity of sources (monitoring programme, satellite observations etc.) can be inter-related by means of multiple layers of geographically-referenced information. The use of multiple map layers, that can be presented superimposed on each other according to requirements, is a useful means of interpreting the data. For presentation purposes GIS systems can be used to insert the desired presentation for locations or areas (water system) onto a national map.

5. Effluent monitoring

The US EPA defines effluent as ‘Waste water (either treated or untreated) that flows out of a treatment plant, sewer or industrial outfall. This generally refers to wastes discharged into surface waters’ [US EPA, 1989]. Effluent is most commonly related to point sources, but also can apply to non-point (diffuse) sources. According to Behrendt (quoting Novotny and Chesters, 1981; Novotny, 1988) sources of pollution to surface waters can be differentiated as follows:

- *Point sources* are fairly steady in flow and quality, and variability ranges are less than one order of magnitude. The magnitude of pollution is less than or not related to the magnitude of meteorological factors. Sources are identifiable points.
- *Diffuse sources* are mostly highly dynamic but occur at random, intermittent intervals. The variability ranges are often more than several orders of magnitude. The amount of pollution is closely related to meteorological variables such as precipitation. Often sources cannot be identified or defined [Behrendt, 1993]. Meybeck [Meybeck and Helmer, 1992] further subdivides non-point sources into:
  - atmospheric diffuse sources:
    - combustion of fossil fuels for energy generation,
    - combustion of fossil fuels for cars/transport, or heating in cold climates,
    - industrial needs (e.g. steel making),
    - ore smelting (mainly sulphides),
    - wind blown soils from arid and agricultural regions, and
    - volatilisation from agriculture, waste disposal and previously polluted regions); and
  - non-atmospheric diffuse sources:
    - agricultural run-off,
    - urban run-off,
    - waste disposal sites,
    - and miscellaneous sources.

Examples of point sources are direct discharges of industrial and municipal waste waters. However, from the viewpoint of the final waste water treatment plant, industrial waste waters discharged in a mixed sewer system are often considered as non-point sources. Stormwater overflows of sewer systems are also often regarded as non-point sources. Runoff of nutrients from agricultural lands is a good example of a diffuse source.

The distinction between point and non-point sources is relevant in the framework of monitoring and assessment. Because loads from non-point sources occur at irregular intervals, their origin cannot be traced down to few, discrete locations. Thus, monitoring of non-point sources is complicated or virtually impossible. Although monitoring of non-point sources will be addressed in section 5.1.5, the contents of this chapter mainly will deal with effluent monitoring of point-sources (industrial and municipal waste waters).

Some characteristic differences between effluent monitoring and surface water monitoring can be indicated. Surface water acts as a collector, in which many separate discharges are integrated and concentrations are decreased after dilution and dispersion. In contrast, with effluent monitoring:

- the number of substances that occur can be limited (e.g. depending on the type of industry);
- the concentrations are relatively high;
- the sampling location is fixed;
- the variability of the discharge with time may be very high (e.g. by discontinuities in operational processes and internal management of effluent flows by industries).

5.1 Monitoring strategy

General monitoring objectives which apply to effluent monitoring include:

- testing of compliance with standards (enforcement and control);
- estimation of mass flows;
- trend developments;
- early warning (chapter 6);
- screening.

Additional objectives, which are more specific for effluent monitoring, can be added:

- control of operational processes;
- prediction of effects occurring in receiving water bodies.

5.1.1 Legal and organizational aspects

Testing of compliance with standards, in the framework of enforcement and control, can be considered as the main objective for effluent monitoring. Various internationally applicable statements and agreements show the rationale of this objective, which can be summarized as: water policy and water management directed toward reducing and bringing surface water pollution under control. As an example, the text box below contains an excerpt of the Helsinki convention [UN/ECE, 1992, Article 3 paragraph 2], additional to paragraph 1/b to d presented in section 2.2.

> 2. …each party shall set emission limits for discharges from point sources into surface waters based on the best available technology, which are specifically applicable to individual industrial sectors or industries from which hazardous substances derive.
>   The appropriate measures mentioned in paragraph 1 of this article to prevent, control and reduce the input of hazardous substances from point and diffuse sources into waters, may, inter alia, include total or partial prohibition of the production or use of such substances. Existing lists of such industrial sectors or industries and of such hazardous substances in international conventions or regulations, which are applicable in the area covered by this Convention, shall be taken into account.

Another example is shown in following text box, being part the 'Recommendations to ECE governments on economic instruments for rational utilization of water resources' [UN/ECE, 1980, Article 5 and Article 11].

5. The concept of effluent charges and of fines and sanctions for violation of pollution abatement regulations should be oriented towards, and consistent with, prevailing policy principles, such as 'the polluter pays', compensation for damage, and equivalent conditions for economic development. Serious consideration should be given to charges, fines and sanctions which have an economic influence on mitigating and counteracting damage caused by pollution. Charges should be based on the amount discharged and on the pollution load. Fines and sanctions would intervene and should be increased if established limits, standards or norms are exceeded.

11. Efforts should also be made to establish or improve methods of statistical data collection and analysis. This should be done for evaluating the effects of economic incentives in water management on the development of rational utilization and conservation of water resources in all sectors of the national economy.

Previous examples illustrate the various characteristics which in general apply to waste water discharges, namely their embedment in legal and political frameworks and the use of discharge permits. In various European countries, the instruments of emission policy are contained in Water Acts, which control water pollution and permit the establishment of pollution charging schemes [Cartwright, 1990] [Zabel, 1993]. Generally, in these acts it is regulated that:

- an effluent discharge license in which the conditions of discharge are specified in detail, is needed for discharges into surface water;
- a discharge is subjected to an effluent charge, by which the discharger is levied in proportion to the quantity of waste water discharged or the number of pollution equivalents discharged.

As an essential part of the discharge license, clearly specified measurement obligations are specified for the discharger (self-monitoring). Enforcement and control as well as setting of the actual effluent charges is generally based on control measurements performed by the authorities. An overall view of the discharges into surface water, obtained through effluent monitoring, can be utilized for environmental management and policy making. Thus, with effluent monitoring, two actors can be discriminated: the discharger and the competent authority. A summary of various types of effluent monitoring laid down upon the discharger, or performed by the authorities and the purpose that the resulting data is generally used for (objectives), is presented in the function matrices below [Adriaanse *et al.*, 1995] (for types of sampling, see section 5.2.2).

Table 5.1:
Various types of effluent monitoring

self-monitoring by the discharger based on:	company policy and management	self enforcement, setting of effluent limits	early warning purposes	screening for the occurrence of pollutants	calculation of loads[2]	steering the treatment process
	utilization of the result					
grab samples	x	x[1]		x[3]		x
composite samples	x	x		x	x	
continuous monitor	x		x			x

monitoring by the competent authorities based on:	government policy and management	enforcement and setting of effluent charges	early warning purposes	screening for the occurrence of pollutants	calculation of loads[2]
	utilization of the results				
grab samples	x	x		x[3]	
composite samples	x	x		x	x
continuous monitor	x				

1: Not in relation to effluent charging, which is based on monitoring by the competent authorities.
2: Actual calculation is generally based on the data gathered by the discharger (higher frequency), whereas the data gathered by the competent authorities are used for validation purposes.
3: Especially for detection of volatile compounds

5.1.2 Industrial effluents

The monitoring strategy for industrial effluents is largely dictated by the discharge permit. Self-monitoring though can be of the discharger's own interest. As Smith puts it 'Companies are also becoming aware that sampling their waste water can provide valuable information about production efficiency, often providing an indication of where savings can be made' [Smith, 1990]. In addition, effluent monitoring can indicate malfunctioning, calamities or accidental spills somewhere in the production process, thus to a certain extent provides an 'early warning function'.

5.1.3 Municipal effluents

Similar objectives as mentioned for industrial effluents also apply to municipal effluents, if being treated in a waste water treatment plant. Control of operational processes focuses on the performance of the waste water treatment plant. Examples of systematic monitoring of municipal waste waters which are discharged without treatment are not known. Dedicated sampling might occur if for instance an outbreak of diseases, related to usage of the receiving surface waters, is observed.

5.1.4 Stormwater overflows

Stormwater overflows generally are not subjected to systematic monitoring. Their irregular and often 'peak-wise' occurrence, depending on precipitation and melting of snow and ice, hamper this. If they exist at all, standards for stormwater overflows are expressed as a maximum frequency of their occurrence in a certain period. The latter is often already included in the design of the sewer network. Data on the amount of pollutants being 'discharged' with stormwater overflows often consist of studies in limited areas for limited periods. Because of various area specific characteristics, the extrapolation of such data to a basin- or nationwide scale is questionable.

5.1.5 Non-point sources

As mentioned in the introduction of this chapter, non-point sources in fact consist of a heterogeneous group of pollution sources. Monitoring of non-point sources, for purposes of estimating pollutant loads from these sources to surface waters in terms of 'water quality sampling and flow measurements', is hardly feasible. In practice, loads from non-point sources can be estimated by calculating the loads from point sources and loads from natural background and subtracting this from the total river load. A general development in relation to non-point sources is the use of (computer) models to estimate loads. Many applications have been developed in many countries. The tendency up to now seems to be that each country or even each organization prefers their own applications; internationally no specific programme seems to prevail. General restriction of most models is calibration: testing the validity of the calculate results with field measurements. An in depth discussion on the various approaches, methods, models etcetera for non-point sources is out of the scope of present report.

5.2 In situ measurements

Ideally, a discharge permit includes prescribed measuring frequencies, sampling procedures, methods of analysis to be applied, test criteria, reporting formats and frequencies, etc. Most discharge permits are 'custom-made', i.e. fitted to the characteristics of for instance the specific branch of industry. Especially for industrial effluents, a great variety of permits exists. Despite of all variations, some generally applicable principles can be mentioned.

It should be mentioned in advance that various aspects of monitoring are mutually dependant. Hartmann (1989) for instance illustrates how sampling strategy (either grab or composite samples), methods of analysis (including inter laboratorial variations) and assessment method (testing the average of 5 samples, or testing '4 out of 5 samples') can effect the final outcome, regardless of whether or not the effluent complies with the standards.

5.2.1 Selection of sampling points

A distinction can be made between an emission-based and the water quality based approach. The selection of approach is either a decision made by the competent authorities or it is already national policy (see section 2.2.3). The emission-based approach requires that discharges into a body of water must be treated at the very least to certain defined limiting values. The water quality-based approach starts out from the actual or desirable state of the receiving water body. In the emission-based approach, monitoring will take place in the effluent (e.g. end-of-pipe). In the water quality-based approach, monitoring will be carried out in the receiving water, at a certain distance from the outlet [Tonkes et al, 1995].

Effluent monitoring does not necessarily imply a sampling position just before the discharging point. It is important though that the location be chosen such that changes in effluent composition will not occur, and representative flow measurements and sampling can be carried out. Depending on the characteristics of the discharge, positions of flow measurement and sampling can differ.

5.2.2 Sampling and flow measurement methods

Three types of sampling can be discriminated:

- grab samples;
- composite samples;
- continuous sampling.

The type of sampling conducted depends on several factors. Combinations of methods are also possible.

Grab samples are most easily collected, but in principle require a discharge of fairly constant quality. Grab samples also preferable for substances which need quick analysis before degradation, volatilization or other processes occur. With effluents, the composition can vary over time, thus grab samples might give either overestimates or underestimates of the average concentration. This can be compensated for by collected more, though this might conflict with the need to be cost-efficient. Grab sampling in principle does not support early warning purposes.

Composite samples (time or flow proportional) are often used because of the significance of discharged loads in the context of effluent monitoring (levies based on discharged volumes/masses). With composite sampling, short-term variations in the composition of the effluent are integrated. The optimum interval for composite sampling is site-specific.

Continuous sampling actually is on-line monitoring of the waste waters. This occurs in effluent as well as in influent. Analysis of influent is a tool to prevent malfunctioning of the treatment plant. Continuous monitoring is most suitable for early warning and alarm purposes. The usual variables for continuous monitoring are COD (and other oxygen balance associated variables), TOC, oil, suspended solids and general variables (temperature, pH). In recent years, there has been a rapid increase in the developments of on-line monitoring for compounds such as heavy metals, and organic micropollutants as well as toxicity. Requirements of sufficient sensitivity, discrimination in compounds and response time (relevant for toxicity testing) are important points of consideration.

Various ISO standards have been developed for measuring waste water flows. Numerous types of equipment exists for this purpose.

5.2.3 Selection of variables

Traditionally, effluent concentrations of suspended solids and BOD5 are used as general treatment plant performance indicators. Selection of variables to be monitored will be mainly dictated by the discharge permit. Different types of variables can identified:

- *General variables,* such as temperature, pH, suspended solids etc.
- *Specific variables* (including bacteria), specific for the type of waste water discharged (certain industrial branch, municipal waste water), compounds from black and/or grey lists.
- *Aggregate variables,* which might prevail because analytical efforts could be significantly reduced. German initiatives for instance, aim at setting an emission standard for AOX in stead of for individual halogenated organic compounds. Wunderlich reported that AOX completely covered the four single substances regulated in the EC Directive 90/415 [Wunderlich, 1994]. General discussions on using aggregate variables, instead of individual compounds, boil down to the representativeness of the aggregate variable for specific individual compounds of interest in a certain group.
- *Toxicity tests.* Quoting Van der Gaag, 1991 '…A full scale identification of all substances in a waste water is impossible. Depending on the type of pollutants present, only a minor fraction can be analyzed. If the compounds are identified, further assessment of the impact of the waste water discharge is hampered by the lack of toxicity data. Discharge allowances will therefore be based on the knowledge concerning only a minor part of the effluent, without any indication about the potential harmful impact of the unknown fraction. In this situation, simple toxicity assays are a welcome supplement during the initial assessment of possible negative effects of the unknown fraction.' Thus, instead of focusing on specific compounds, the potential (biological) impact of the entire effluent is assessed [US EPA, 1991]. Effluent toxicity monitoring supports the following basic objectives for monitoring [De Zwart, 1995]:
  - Testing and steering the progress of technology based remediation of effluent quality, and finally deriving permit criteria for ecotoxicity.
  - Permit compliance monitoring, provided that toxicological criteria are part of the permit formulation. An example is fish toxicity, which expressed as Gf-values can be part of discharge permits in Germany.
  - early warning of calamities and accidental spills, provided that measures can be taken to contain the released toxicity.

For additional remarks on variables for effluent toxicity monitoring, see also section 5.3.2.

5.2.4 Sampling frequencies

The sampling frequency, both for self-monitoring as well as for monitoring by the competent authorities, can be part of the discharge permit. Alternatively, it can be placed under the discharger's responsibilities to provide an accurate discharge estimate (with penalties and an increase in charges when checks by the State prove that there has been an underestimation). A sampling frequency is relevant for both grab and composite samples. The exact number of samples to be collected depends on several aspects. There can be an enormous variability in the waste water flow, both in the quantities discharged and in the concentrations in the effluent, depending on the process operations. The sampling method and measuring frequency should be adapted to these variations.

Various examples indicate that the larger the ratio of effluent volume/discharged load, the higher the sampling frequency. For example, in the EC Directive 91/271/EEC concerning Urban Waste Water Treatment, a minimum sampling frequency for compliance testing by the competent authorities or appropriate bodies, is related to the size of the waste water treatment plant (size in Population Equivalent: PE):

Table 5.2:
Minimum sampling frequency according to EC Directive 91/271/EEC

Size of WWTP	No. of samples per year
2000- 9999 PE	4 (if proper operation is proved)
10000-49999 PE	12
50000 PE	24

WWTP: waste water treatment plant
PE : population equivalent

In principle, statistical inaccuracies associated with (compliance) testing have to be considered and may be relevant in setting the sampling frequency. The EC Directive 91/271/EEC includes a maximum allowed number of samples not complying with the standards, ranging from 1 when 4-7 samples are taken yearly, to 25 for an annual sampling frequency of 351-365. Another example of using a relation between size of the discharge and sampling frequency is the practice in the International Rhine Committee [IKSR, 1992].

The sampling frequency for self-monitoring usually ranges from daily to once per two months. Up to a maximum of 12 samples a year are collected from the larger sewage treatment plants for compliance purposes. This is equivalent to approximately 10% of the samples taken for self-monitoring. Similar considerations apply to compliance testing at industrial discharges.

If trend detection is part of the effluent monitoring strategy, measuring frequencies should be sufficient to support the statistical requirements. The statistical principles do not basically differ from those for surface water monitoring.

5.3 Analytical work

5.3.1 Analyses on individual substances and aggregate variables

Basically the analytical methods for the monitoring of discharges of waste water are the same as those for ambient monitoring (chapter 4). Generally, compared to surface water, the concentration levels in effluent are higher. As a result, less sensitive methods are often sufficient for monitoring of discharges. In most cases, for example, flame-AAS or ICP analytical methods will be adequate for the monitoring of heavy metals in waste water. However, due to a higher complexity of the sample matrix, a much higher selectivity is often required. For instance, the analysis of organic micropollutants in municipal waste waters is often hindered by matrix complexity. Furthermore, sensitive methods (GC-MS, HPLC) may still be required for the analysis of trace compounds (e.g. dioxins), especially when the waste water flow is relatively high. In several countries, such as Germany, the Netherlands and France, specific methods for waste water have been developed.

5.3.2 Analyses of toxicity

Analyses of toxicity first of all need a clear definition of which effluent properties are to be addressed. Different types of toxicity are identified ([De Zwart, 1995]):

- **Acute toxicity** is indicative for acute effects (e.g. fish kills) possibly in the immediate vicinity of the discharge.
- **Chronic toxicity** is reflecting the extent of possible sublethal ecological effects occurring in a larger proportion of the receiving water.
- **Genotoxicity** reveals the risks for interference with the ecological gene pool and the occurrence of deceases in biota and man. Unlike the normal toxicity, the incidence of genotoxic effects is thought to be only partially related to concentration (one hit model).
- **Bioaccumulation and biomagnification capacity** is proportional to the risk of delayed effects and food chain intoxication.

The following modifying aspects must also be considered:

- **Persistence and degradation of toxicity** determines the exposure duration and the affected area in the receiving water body.
- **Bioavailability** strongly influences the expression of toxicity, and may be changing during transport.
- **Reactivity and combination toxicity** may positively or negatively alter the biological responses to the effluent.
- **Dilution (effluent load per unit time vs retention time and flow in the receiving water)** strongly influences the expression of toxicity in the receiving water.

The complexity of toxicity testing has already been illustrated in previous descriptions. A positive result when testing acute toxicity does not indicate or predict potential negative impacts on a longer term e.g. genotoxic effect. Testing on genotoxicity though does not support monitoring for early warning and alarm purposes. Toxic impacts can result when directly testing the effluent, which might not appear when testing after dilution of the effluent. The issue gets even more complicated when it comes to selecting the specific organism for which toxicity is to be analyzed: bacteria, algae, water fleas, fish, seals or humans.

Various surveys show that numerous toxicity tests exist all over the world [De Zwart, 1995] [Tonkes and Botterweg, 1994]. The most common approach is to investigate short-term effects, such as death in short-term tests at four trophic levels, which are fish, water fleas (Daphnia Magna), bacteria and algae [Van der Gaag, 1991]. At the moment, only the acute ecotoxicity tests on Daphnia, fish and luminescent bacteria are (in the process of being) internationally standardized; for more chronic exposure, international standardization relates to fish, algae and Daphnia only [De Zwart, 1995]. Examples for two countries, showing strategies to tackle some of the complications are elaborated below. These examples contain elements which also are applied to varying degrees for effluent toxicity monitoring in other countries all over the world.

In Canada, the so called Potential Ecotoxic Effects Probe (PEEP) index has been developed [De Zwart, 1995]. The PEEP-index is used as an evaluation system, based on effluent toxicity testing, capable of ranking the environmental hazards of industrial effluents. In the index, no allowance has been made for in-stream dilution, therefore the actual risk for environmental effects is NOT modelled. On each effluent, defined tests are performed using the following organisms:

- bacterial assay *(Photobacterium phosphoreum,* Microtox);
- microalgal assay *(Selenastrum capricornutum);*
- crustacean assay *(Ceriodaphnia dubia);*
- bacteriological genotoxicity test *(E.coli).*

All test results are finally transformed to represent toxic units (TU) and are processed in the numerical formula:

$$\mathrm{PEEP} = \log_{10}\left[1 + n\left(\frac{\sum_{i=1}^{n} TU_i}{N}\right) Q\right]$$

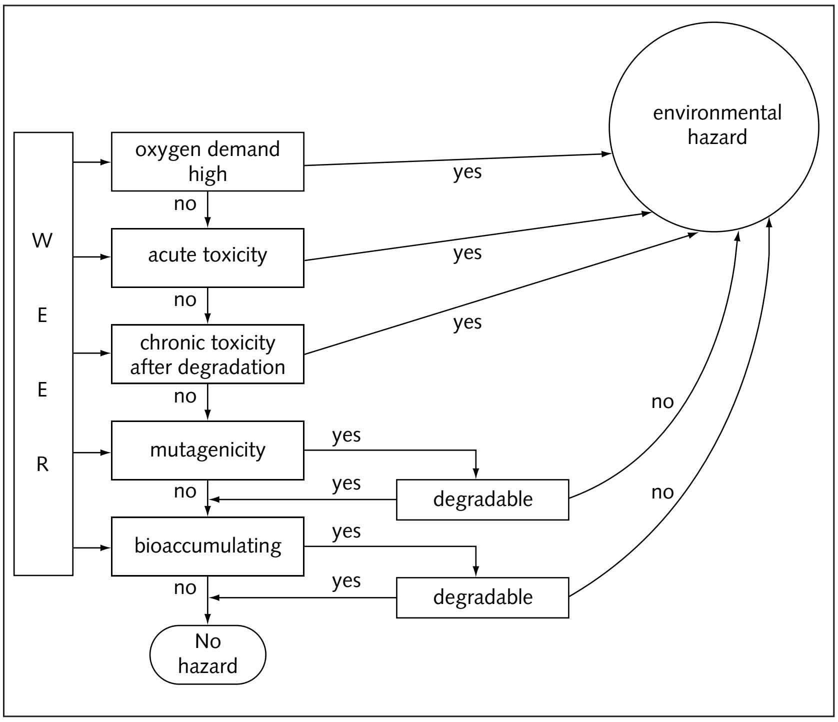
In the Netherlands the process of developing a methodology is referred to as Whole Effluent Environmental Risk (WEER) [Tonkes and Botterweg, 1994]. The WEER method first of all is meant for complex mixtures to complete the assessment of unknown components in the chemical approach. The concept underlying the WEER method is shown in figure 5.1.

For testing methods and criteria, one organism per trophic level (maximum of 4 trophic levels) is proposed in WEER, namely:

- Oxygen demand: BOD, COD
- Acute toxicity
- * algae: green algae
  * bacteria: *Photobacterium phosphoreum* (like Microtox or Lumistox)
  * crustacea: *Daphnia magna* (freshwater); *Acartia tonsa* (marine water)
  * fish: *Poecilia reticulata* (temporary; maybe to replaced by *Brachydanio rerio or Salmon* spec.)
- Chronic toxicity
- * crustacea: *Daphnia magna* (maybe in future: *Ceriodaphnia)*
- * fish: *Brachydanio rerio* (fresh); *Cyprinodon variegatus* (marine)
- Mutagenicity
  Notobranchius; Ames test
- Bioaccumulation
  (standardized method to be expected)
- Persistence (degradation)
  (no standardized method identified yet)

Regarding the tests, reference is made to various standardized methods (OECD, NEN, ISO, EPA, PARCOM).

Figure 5.1
Whole Effluent Environmental Risk (proposed WEER methodology) [Tonkes and Botterweg, 1994]



5.3.3 Analytical quality assurance

General guidelines for analytical quality assurance as presented in chapter 4 also apply to effluent monitoring and assessment. Specific to effluent monitoring is that in principle, separate bodies independently collect data on effluent discharges:

- the discharger;
- the supervising governmental authority; depending on the country's organization, various supervising authorities can be involved.

Considering aspects such as testing for compliance with standards and raising of levies/penalties, the basic data from the two parties (concentrations and flows) should be mutually comparable. Options to achieve such are:

- to strive at a precise and uniform standardization for methods to be used by both parties;
- to exchange duplicate samples on a regular basis, to be analyzed by the laboratory used by the other party (like round-robin tests);
- to agree upon application of methods of analysis, whose performance characteristics (sensitivity, interlaboratory reproducibility, selectivity, etc.) are known and well documented.

The tendency seems to be for an introduction of this last option last (application of agreed methods with known performance). This is motivated amongst other factors by financial and logistical restraints (laboratory capacity).

5.4 Data validation and storage

Compared to data validation and storage for ambient water quality

monitoring and assessment, the following factors are more specifically relevant for effluent monitoring:
because (at least) two actors are involved, more emphasis has to be put on the comparability and exchangeability of data, as well as on their interpretation (assessment);
the relevance of latter aspects are even more significant, because charges and penalties can be imposed (arbitrage).

The handling of data gathered in the context of effluent monitoring varies greatly over the world. Instead of attempting to describe various systems, general points of consideration are listed below.

5.4.1 Validation

Because sampling frequencies of competent authorities are usually lower, the data gathered by the discharger provide the most information on discharge effluent. For comparing both data sets, general guidelines should exist, such as:

- the criterium used to flag deviations (e.g. 10% of value observed by one of both parties);
- the additional information to be used for interpretation of the deviation data (analytical errors, logbooks, calamity reports, etcetera); and
- the procedure to be followed to gain consensus for deviating data.

5.4.2 Data storage

In principle, two different media exist for data storage:

- paper;
- digitized computer formats.

For reporting effluent monitoring data on paper, formats and contents are usually described in the discharge permit. For primary data exchange, mainly written reports are used. For compiling e.g. country or basin wide overviews, support of computerized systems is generally unavoidable for data management. Considerations and criteria for creating databases for effluent data do not deviate from those used for storage of data gathered in the framework of ambient water quality monitoring. For effluent data, the following options can be added:

- Inclusion of all raw data or agreed upon values (the practise in the Netherlands is that data are discussed by discharger and authority before they are made available to other parties)
- Inclusion of supporting information for proper evaluation of data included, for instance:
  - method of sampling/ sampling frequency;
  - analytical method applied (AAS, ICP, GC/MS, etc.);
  - overview of flows (yearly, monthly, daily);
  - description of method used for load calculation.
- Inclusion of not only the monitoring data, but also those elements of the discharge permit describing the effluent boundary conditions. These latter allow the possibility to evaluate whether general policy pollution abatement objectives (like 50% emission reduction from point sources in 10 years) are feasible, considering the amount of pollutants that theoretically can be discharged as formally agreed upon in the discharge permit.

5.5 Data interpretation and presentation

Effluent assessment classically is based on the prescriptions, incorporated in discharge permits. These include usually general variables: flow, maximum temperature, a range for pH, total suspended solids, electrical conductivity and others. Chemical variables and aggregate variables include maximum levels for: BOD, COD, individual chemical compounds (hazardous and nonhazardous), AOX and others. Requirements for self-monitoring by the discharger are usually part of the permit. Water authorities usually have the right for independent and unannounced control. More recent permits also set maxima for loads of individual compounds as a total per day or per month or as a maximum of discharged compounds related to the level of production. Phased introduction of best available technology in industry can be an intrinsic part of a permit.

Introduction of whole environmental effluent risk provides a base for toxicological assessment of effluents. For an inventory on specific toxicity tests, the reader is referred to section 5.3. Some countries have introduced such systems (USA, Canada, Sweden), others are on the verge of introducing such a system (Denmark, UK).

5.6 License control and charging

Normally, the discharge permit describes the conditions to which the effluent has to comply with, including the criteria to assess whether the effluent discharge met the standards set. For charging two possibilities are to be discriminated.

Levies are raised for the regular discharge. In principle, pollution units are combined with a certain amount of money, e.g. per ton pollutant discharged over a year. The system of levies can vary from relatively simple systems using few pollutants like BOD, to complex systems in which the total levy is calculated by weighing the relative share of specific pollutants (e.g. the costs for discharging a pollution unit mercury are significant higher compared to a pollution unit BOD). Flexible systems, setting various prices for various compounds can be one of the governmental instruments for abatement of specific pollutants. Some countries have introduced levies bases on effluent toxicity (France, Canada, Brazil and others).

Penalties can be raised when the effluent discharge does not comply with the standards, as set in the discharge permit. The amount to be paid as a penalty will of course depend on the exceeding (duration, volume, specific substances). Finally settling the penalty to be paid might even be decided by a court of law.

Estimation of loads
The method to be used for calculating/estimating discharged loads partially will depend on the sampling scheme (sampling frequency; grab or composite samples). As for the calculation of (yearly) river loads, various methods could be applied:

- Calculation of the annual average of daily loads (based upon daily measurements), eventually followed by extrapolation.
- The (annual) average concentration of the composite samples, multiplied by the mean daily flow times the number of days of discharging.

- The (annual) average concentration of the grab samples, multiplied by the mean daily flow times the number of days of discharging.
- Mean momentary load (derived from grab samples and flow during sampling) multiplied by the number of days of discharging.

The number of days of discharge can arbitrarily be set, using general information about the specific discharge. For instance, for large industries working all around the year and for municipal waste water treatment plants, 365 days of discharge per year can be assumed. For medium- and smaller sized industries, 250 days can be assumed. Because the number of samples gathered by the discharger is usually higher (sections 5.1.1 and 5.2.4), statistically more reliable loads can be obtained by using the data collected by the discharger.

If compounds are discharged with batches or if the production processes change over the year, additional information is needed to derive annual loads. The latter requires more detailed knowledge about the specific industry, its production processes, the duration of the specific discharge, etc.

5.7 Presentation

Accessibility to data gathered for effluent monitoring will partly depend on the legislative and organizational framework. This especially applies to public access of data gathered with effluent monitoring by the specific discharger. Usually, public access to such data is arranged by (national) laws. The EU guideline 90/313/EEC concerning free access to environmental information, provides the Member States with a general framework for arranging this in their national policy. Protection of commercial interests could be a reason for limited or no public access.

Guidelines for presentation of data collected with effluent monitoring partially will be dictated by who will use the data for which purpose. It is often difficult to generate simple overviews from detailed data tables. Bar, pie or other types of graphical overviews might lack sufficient level of detail. Levels of aggregation for potential target groups are for instance (per compound/group of compounds):

- total loads discharged by point sources;
- total load discharged by (direct) industrial point sources and total load discharged with municipal waste waters;
- loads discharged per industrial sector (mining, chemistry, food processing, etc.).

Aggregation levels for geographical scopes are for instance: per country, per river basin, per country/per basin, per sub-basin/watershed etc. Examples of the usage of a combination of various options are the emission inventories for the Rhine basin published by the International Rhine Committee [IKSR, 1994], and of the National Rivers Authorities (England/Wales) which e.g. summarize data for pollution input per region into the North Sea [NRA, 1992].

6. Early warning

6.1 Introduction

Early warning is important in cases of accidental pollution of surface water (surface water early warning) and in cases of direct danger for accidental pollution of surface water by effluent. Early warning has as objectives to provide an alarm (protection) as well as to trace dischargers or process operation failures (detection).

Timely alarm for sudden pollution is important for water users. These are mainly drinking water companies treating surface water for potable water production, but also, to a lesser extent, all other direct users of river water for animal husbandry, arable farming, industry, etc. where water quality is of importance.

Early warning can lead to the suspending of intake and use of water, and to measures to limit the spread of the pollutant to certain less vulnerable areas by water management measures (control of locks/weirs, water distribution, etc.). Specifically for effluent early warning, continued calamitous discharge can be prevented [Adriaanse *et al.,* 1995].

The Helsinki Convention states [UN/ECE, 1992), Article 14]:

> Article 14 (Warning and alarm systems):
>
> The Riparian Parties shall without delay inform each other about any critical situation that may have transboundary impact. The Riparian Parties shall set up, where appropriate, and operate coordinated or joint communication, warning and alarm systems with the aim of obtaining and transmitting information. These systems shall operate on the basis of compatible data transmission and treatment procedures and facilities to be agreed upon by the Riparian Parties. The Riparian Parties shall inform each other about competent authorities or points of contact designated for this purpose.

6.2 The concept of early warning

As accidents cannot be entirely precluded, a system for early warning to be used in cases of accidental water pollution should be developed. This would constitute an information and early warning system for the responsible authorities in the riparian states. The necessary information is obtained from monitoring locations that (continuously) investigate the water quality in the form of chemical analyses and biomonitoring. But also information from the polluting agency, shipping, concerned citizens and river police may play an important role in early warning.

The objectives of an early warning system can be summarized as follows [Spreafico, 1994]:

- information and warning of the responsible authorities of the riparian states after an accidental spill;
- initiation of prevention and control measures;
- definition of the causes;
- detection of the source of pollutants;
- determination of measures for the reparation of the damages and avoidance of secondary damages.

Early warning systems can be both substance and effect-oriented. Chemical screening methods can detect substance-specific increases in concentration levels. Only a few of the many substances that occur can actually be measured on-line. Biological early warning systems (fish, water fleas, algae, bacteria) can detect a decrease in water quality, without specifically indicating which pollutants are involved.

An important part of early warning can be provided by early warning provisions established by dischargers (see also chapter 5). In addition to prevention of (continued) calamitous discharge effluent, early warning systems can be of major importance in timely warning of the water users. Within the context of the working group on 'accidental discharges' (Störfallvorsorge 'S') of the International Rhine Commission (Internationale Kommission zum Schutze des Rheins gegen Verunreinigung, IKSR) agreements have been made for the announcement of all relevant accidental discharges [IKSR, 1991a]. These agreements provide for effluent monitoring for early warning purposes in all Rhine basin countries. Measurement responsibilities are shared by the dischargers and the proper authorities, based on national agreements [Adriaanse *et al.,* 1995].

The following design criteria can be derived from the early warning objectives (alarm and detection) [Adriaanse *et al.,* 1995]:

- significant disastrous pollution occurring shall be reliably detected and recognised;
- measurement information, on which the warning is based, shall be available at a given time (for example, several hours) before the pollutant reaches the water-use site, so that timely action will be possible (e.g. closing water-intake, modified control of locks, weirs etc., warning the inhabitants);
- measurement information from effluent early warning systems shall be available on a timely basis for prevention of (continued) calamitous discharge.

6.3 Early warning monitoring

The need for early warning depends on the water uses downstream and the risk for accidents upstream. Accordingly, the location of the monitoring, the type of monitoring, the monitoring variables and the monitoring frequency depend on the uses of the surface water downstream and the risk for accidents upstream (industries, agriculture, shipping).

Location

The position of the sampling site will be set by the early warning response time. The response time is defined as the total time required for sampling and analysis, interpretation and raising the alarm. The response time, together with the time required for action, must be less than the transit time for the water pollutant from the sampling site to the interest under threat (e.g. water supply intake). This principle can be expressed in the formula [Adriaanse *et al.*, 1995]:

$$t_w > t_{an} + t_{al} + t_{ak}$$

where: t_w = transit time in water
t_{an} = sampling and analysis time
t_{al} = interpretation and alarm time
t_{ak} = time for action

The response time is dependent on the analytical systems available, the sampling times selected, and the personnel available (for validation, interpretation, and issuing an alarm). The response times with the present on-line measurement systems are of the order of magnitude of several hours. Using an advanced system of collection and analysis, composite samples are collected over periods of the order of a half-day, for the analysis of organic micro-pollutants. In this case, the response time is three hours longer than the sampling time.

There is certainly a direct relationship between the transit time and the distance from the sampling site and the water users concerned. Since the transit time is inversely proportional to the river flow, high river flow conditions are the most critical. The transit time can be expressed in terms of the river velocity, as:

$$t_W = \frac{L}{V_{cr}}$$

where: L = distance sampling site – water user
V_{cr} = velocity with which the water pollution is transferred along the river at critical river flow

This imposes a requirement for the distance form the sampling site to the water user:

$$L > V_{cr} (t_{an} + t_{al} + t_{ak})$$

Before an early warning sampling site is chosen, there should first be a study of the extent to which sampling sites are representative, looking for any horizontal or vertical concentration gradients at the monitoring site under consideration.

Sampling sites should be so allocated that no pollutants will be missed; if sampling from the banks is the only possibility, then water intake points should be on both banks or, in any case, at least on the bank where most of the pollutants flow in (tributaries, discharges).

The above presented calculation for sampling site selection is very straightforward, providing a safe estimate of sampling site distance from the water user. Models applied to calculate substance propagation in case of actual detection of an accidental spill should take many other hydrological and substance specific aspects into account. A comprehensive review of these aspects has been produced by the World Meteorological Organization (WMO) [WMO, 1992].

Frequency

The sampling frequency for early warning is, as it is for ambient monitoring and effluent monitoring, dependent upon the information objective. It is essential that the frequency is sufficiently high that a wave of pollution not be ‘missed’, that a timely alarm can be given to relevant water users, and that timely measures can be undertaken to prevent (continued) calamitous discharge [Adriaanse *et al.,* 1995].

Whenever a pollutant gets into the water, it will spread itself downstream as an increasingly longer wave of pollution. Depending upon the flow in the river and the distance between the point of discharge and the monitoring station, it can be hours or even days before the pollutant has reached and passed the monitoring station.

As an illustration, the measurement frequencies needed for the monitoring stations on the Netherlands Meuse and Rhine Rivers were determined in 1991. It was then determined that for the monitoring station at Lobith on the German-Netherlands frontier, a measurement frequency of twice a day under critical river flow conditions would suffice to catch a wave of pollutant and give a timely warning to the water supply company. Lobith is at a distance of about 80 km from an important water supply intake point (and about 60 – 100 km downstream of the most important sources of pollution).

In contrast, for the monitoring station near Eysden on the Belgian/Netherlands frontier, a sampling frequency of once every two hours is needed, due to the short transit time between the potential source (industry in Liege) and the monitoring station. It then takes days for a wave of pollution to reach the water intake points in the lower reaches of the Meuse in The Netherlands [Adriaanse *et al.,* 1995].

Similar considerations apply for the alarm stations in the Ile de France region. Each of the eight automatic analysis stations requires high sampling frequencies due to their proximity to the three drinking water production plants in the region [Mousty *et al.,* 1990].

Variables

It is necessary to have criteria for deciding which variables to chose for early warning monitoring. These criteria are basically the same as the criteria used in the selection of variables in routine monitoring (chapter 4). However, the criteria for selection of variables in early warning monitoring can be more specific because the objectives of early warning monitoring are more specific than in routine monitoring.

The function of the downstream area to be protected by early warning is an important factor to be considered in selecting monitoring variables. Different variables in different concentration levels are hazardous for drinking water production, irrigation or recreation. On the other hand, the use of the river upstream (type of industries, shipping, agriculture) determines the expected accidental pollution.

A number of the frequently occurring local risk substances will then preferably be monitored as target compounds, and alarm levels will be determined for these substances. A risk analysis for the discharge situation in the upstream area can make clear what the potential problem substances or groups of substances (e.g. metals, Cl, CN) are. In the Daugava River in Latvia, for example, a sample is taken twice a day for analysis of cyanide only, for the protection of the drinking water supply. In the Tagus River in Portugal, early warning is specifically focused on radionuclides [Hupkes, 1995].

For effluent discharges, it is generally known which substances might be expected during a calamitous discharge, based on their application and creation in production processes and their presence in raw materials. It can therefore be anticipated that analysis of indicator or signal variables in combination with knowledge of process circumstances may often be sufficient to trace the cause of a calamitous discharge and thus the substance(s) discharged.

Results of the on-line analyses at the early warning stations have to be produced quickly. The information needed immediately does not have to be exact concerning substances and amounts spilled, but it should give an indication of whether water quality has deteriorated to the point where water quality standards are exceeded. Additional analyses should be performed only in accidental pollution situations where standards are exceeded, in order to investigate the compound causing the alarm and its precise concentration [Adriaanse *et al.,* 1995].

6.4 From monitoring to alarm

Changes in the water quality as they are registered by the early warning monitoring may or may not lead to an alarm. In addition to the measurements themselves an important role in early warning systems is played by the following components:

- a list of warning and alarm values;
- a substances file (database) is needed to estimate the deleterious properties of substances;
- a model for the calculation of the transit time of a confirmed accidental pollution from a warning centre or a monitoring station to the place where water is used;
- a communication system, in which warning procedures are defined and through which all those involved in the river basin can be informed quickly.

These components have to be integrated in an adequate early warning system. There have been major developments in early warning systems in the last 20 years. Integrated early warning systems have been developed for e.g. the river basins of the Rhine [Spreafico, 1994], the Ile de France region [Mousty *et al.,* 1990], and the Elbe [IKSE, 1992] [De Vries, 1993]. An integrated system is now under development for the Danube river basin [Task Force for the Environmental Programme for the Danube River Basin, 1994].

Warning and alarm values

For assessment in early warning, a preset list of warning and alarm values for different types of variables, both substance and effect oriented, is an indispensable tool. Types of variables used in early warning will be discussed in section 6.4. Pre-set warning and alarm values will be defined on the basis of the type of variable, the sensitivity of the monitoring system and ambient water quality standards, as prescribed in international or national directives. Exceedence of warning or alarm values will trigger warning procedures.

Database

Databases are used to retrieve information about the toxicity and the chemical/physical properties of pollutants. This data is necessary to evaluate the behaviour of the pollutant in water. Different processes in water are for instance evaporation, degradation and adsorption to suspended solid. These processes have different implications for the pollution in the water and can greatly influence its impacts. Some processes enhance pollutant effects, while some diminish them. The handling of the pollution, for instance by the fire brigade (when removing the pollution from the water), requires data on pollutant properties.

The information in databases should consist of basic characteristics of substances, such as identification (CAS, ADR, or UN numbers, etc.), description (formula, brandnames, colour, smell), danger classification, behaviour (evaporation, reactions), as well as recommended health protection and fire fighting measures. Specific characteristics, such as ecotoxicological values and specific behaviour should also be available. With this information, it is possible to predict the impact of the pollution on the different users of the surface water [Mulder, 1994].

In the Netherlands a computerized decision support system for calamity handling called AQUABEL is being built. The system consists of a reporting module, a database for toxic compounds, predictive models, and information about local authorities (responsibilities and locations of cleaning equipment). The reporting module and the database are now completed and these are now implemented by different users in the Netherlands. The other modules will be developed in a later stage. In the reporting module, all necessary information is gathered in a structured form. This is essential because different sorts of pollutants require different information or different handling. For some pollutants, the water temperature is needed because of evaporation of the pollutant. For oil, it is essential to get information about where equipment to remove the oil from the water is located. The database is used in cooperation with German industry and government. Parts of this system will be integrated in the ENVIRONET-project for data communication along the Rhine River [Mulder, 1994].

Models

After an accidental discharge, the pollutant is mixed in the river water. As a result of mixing and inflow from tributaries, the concentration of the pollutant decreases to the point where no impact can be seen for users of the surface water or for the environment. A model can be used to predict the concentration of the pollution at critical points in the river as well as the time of arrival of the polluted water to a specific point. The estimated time of arrival allows water companies or other water users to stop their water intake at the proper time when the intake situation is critical.

The predictions can be made most easily with the aid of computer models, which are simple and easy to use. For the Rhine River for instance the development of a Rhine Alarm Model was started after the Sandoz accident in 1986. The first version was finished in 1988, but was uncalibrated. Later versions had better descriptions of actual situations and were calibrated with tracer experiments. The input of this model is hydrological information (water levels and weir programmes) and pollutant information (point of discharge, amount, time of discharge). The output is the concentration and arrival time of the pollutant at a desired point along the river [Mulder, 1994]. Figure 6.1 shows an example of the output of the alarm model [Spreafico, 1994].

An alarm model for predicting substance propagation has to fulfil the following prerequisites [Spreafico, 1994]:

- The model should be ready for operational use in cases of accidental pollution, i.e. the results must be available promptly;
- The model must be based on input data that can be provided real time. These data are information concerning the accident (i.e. substance, volume spilled and time and location of accident) and hydrologic data (i.e. flows and water levels), which the warning centres can obtain from the measurement stations by telemetering transmissions.
- The model design should be as simple as possible and it should be suitable to be implemented on PC's, so that it can be used without difficulty by the alarm centres.

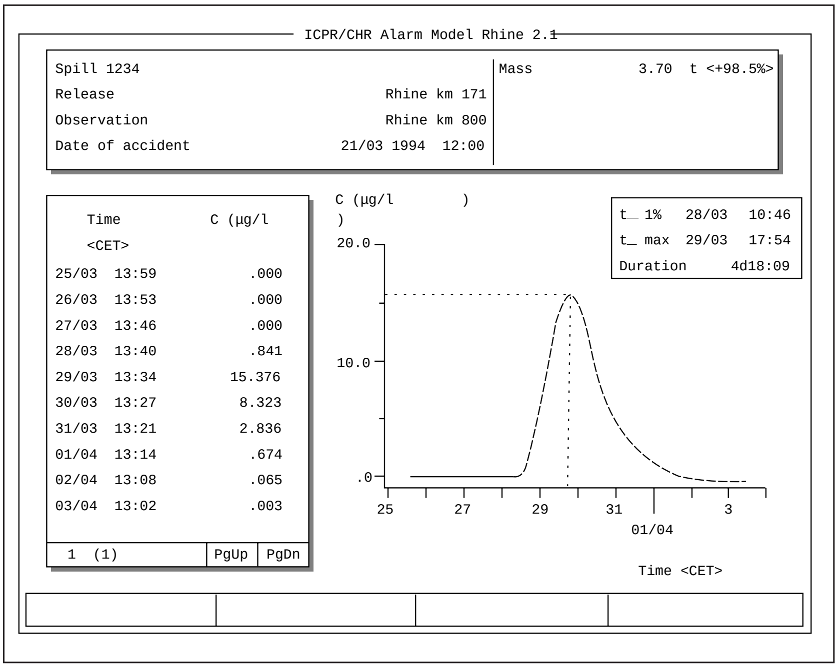


Figure 6.1
An example of the output of the Rhine Alarm Model [Spreafico, 1994]

Communication

The establishment of joint communication in warning and alarm systems is another important element of cooperation on transboundary waters. The international warning and alarm system for the Rhine River developed under the auspices of the Rhine Commission, ensures the exchange of information among eight international warning centres in emergency situations. The Elbe Commission is installing and testing a joint warning and alarm system for the Elbe River consisting of in total 18 monitoring stations. Joint or coordinated warning services have been also set up for some other transboundary rivers [De Vries, 1993].

6.5 Analytical-chemical and biological techniques

Early warning monitoring is aimed at a rapid detection of sudden changes in the water quality. When such a change in the water quality occurs, water samples should be analyzed to establish the nature of the pollutant and the concentration in the river water. As argued in chapter 6.3 the frequency of monitoring depends much on the location of the monitoring station, regarding both the distance to the source of pollution and the distance to the area(s) of concern.

To establish reliably that there is a cause for alarm, two steps can be distinguished [Mulder, 1994]:

- (semi) continuous monitoring at the measurement station (by measurement of indicator variables, biological effects, analytical windows and alarm levels) to determine if there is something wrong ;
- automatic sampling and advanced analysis to precisely identify the pollutant using advanced equipment in a supporting laboratory).

Biological early warning systems (using fish, water fleas, algae, bacteria) are effect-oriented and detect a deterioration in water quality, without indicating which pollutants are involved. Chemical analysis screening methods are substance-oriented and detect specific changes in concentration levels. These concentration levels are often relative and rather indicate a change in the concentration than an actual concentration.

The importance of on line measurement of the classic variables (e.g. pH, ammonia, dissolved O2), for which sensors are available, is usually in itself limited. These basic variables can fulfil a useful function as indicators or signals of more serious pollution if the concentration variations resulting from pollution are sufficiently significant and discriminatory when compared with natural variations. When these requirements are met, even a simple temperature or pH monitor can sometimes be valuable for tracing irregularities in the waste water flow [Mulder, 1994].

Early warning in the Thames Region in the UK is based on the principle of monitoring of a few macro-chemical variables, accompanied by automatic sampling. Samples are analyzed when the on-line information gives reason. This system (ARQM) gathers information either every hour (fresh water) or every 15 minutes (tidal zone). During a pollution incident, more frequent intervals can be manually initiated from the central control room. Similar systems operate in other regions in the UK [Griffiths and Reeder, 1992].

In the early seventies a start was made with the measurements of simple classic variables, like pH and dissolved oxygen. At the beginning of the eighties, an accidental spill of an organic micro-pollutant (chlornitrobenzene) in the Rhine River initiated the extension of the measured variables. Starting from 1978 (Ile de France) [Philipot *et al.*, 1989] and 1984 (Rhine and Meuse) instrumentation has been installed that enabled heavy metals to be measured on an on-line base and organic micro-pollutants to be measured daily. The range of compounds measured has, since then, been extended continuously. Some specific attention will be given to the sensor systems. Analytical methods used after the detection of a change in the water are dealt with in chapter 4.

As far as effluent monitoring is concerned, most industrial processes provide possibilities for the detection of calamitous contamination of the waste water at stages prior to their occurrence in the effluent discharge. In cases where there is an effluent treatment plant, observation of the process operation of the plant should provide for timely detection of failures and would thus serve early warning purposes. Furthermore, a single effluent discharge is often fed by various principal waste water flows (water used for cooling and water used in various process operations). Monitoring of these primary flows will provide a far more timely detection of disturbances than end-of-pipe monitoring of the actual discharge into surface water. Last but not least, process control observation can provide valuable information. Often the temperature, pH, pressure, or other variables of process operations are being monitored for process steering purposes. Irregularities in these variables provide the earliest possible opportunity for detection of malfunctions. If not already practised for process control, establishing such early monitoring possibilities especially for early warning purposes can be indispensable. The need for such early warning possibilities has been explicitly included in the agreements made within the context of the IKSR working group on ‘Disturbance precaution’ [IKSR, 1991a].

Sensor systems used in early warning

Sensor systems can provide information on a short term. This information is not necessarily exact, as far as substances and amounts are concerned, but it should give an indication of whether water quality has deteriorated to the point where water quality standards are exceeded. Additional analyses should be performed only in accidental pollution situations where standards are exceeded for the purpose of investigating the compound causing the alarm and its precise concentration.

The viability of any continuous monitoring system depends primarily on the ready commercial availability of a sufficiently wide range of reliable sensors [Lynggaard-Jensen, 1994].

Sensors can be divided into three groups according to the type of variables they measure. These groups are:

- Physical measurements
- Chemical measurements
- Biological measurements

Most available sensors are placed in group 1, some in group 2 and a few in group 3. When measuring biological waste water treatment processes and biological systems in receiving waters, this distribution of available sensors is clearly unfavourable, because the best information would be obtained by group 3 sensors. However, one of the most important measurements – the flow measurement – is placed in group 1, and many different technologies are available to this [Lynggaard-Jensen, 1994].

Application of on-line instrumentation is at present limited. On-line measurement of the classic variables (including salts and nutrients) is common practice (e.g. for the Rhine and Elbe Rivers, and in France and the UK). Metals are measured only in the Rhine, the Dutch part of the Meuse and in the Ile the France region. This also applies to the on-line measurement of organic micro-pollutants.

A review of analytical methods for early warning monitoring of effluent discharges [Tebodin, 1988] showed that most methods presented for surface waters can also be applied to effluent discharges. In addition some alternative methods were presented. However, many of those methods still require some application research.

A system for the detection of organic micro-pollutants is operational in Netherlands monitoring stations on the Rhine and Meuse. The system for the detection of increased concentrations of non-polar to moderately polar organic compounds (SIVEGOM) was introduced in 1984. The system is based on the concentration of pollutants on a resin (XAD-4, a copolymer of styrene and divinylbenzene) and analysis by gas chromatography (GC-FID). The system is still, at present, partly manual (drying, elution and analysis), but will be automated within 2 years. If the pre-set alarm values are exceeded, a sample will be taken immediately to the central laboratory for identification and quantification of the pollutant by GC-MS. A system for the detection of volatile organic micro-pollutants (SIVEVOC) was introduced in 1990. A special sampling device had been developed and, together with a purge and trap GC analysis, a fully-automated system was completed [Mulder, 1994].

Neither of the above-mentioned systems cover polar chemicals which are very important in the water phase. Many pesticides and herbicides belong to this group. The European Community standards for these chemicals are very stringent (0.1 µg/l for individual chemicals). Early warning of these polar chemicals is very relevant because many of them are difficult to remove during the production of drinking water. An automated screening system (SAMOS) for polar organic micro-pollutants, based on High Performance Liquid Chromatography (HPLC), has been developed and was installed for the Rhine and Meuse Rivers in 1993. During the system test-phase, a considerable increase in the concentration of Diuron in the Meuse was detected. Based on this measurement, the intake of river water for the production of drinking water was suspended for one week. The detection limits for the organic systems range between 0.1 and 1.0 µg/l, depending on the specific compound [Mulder, 1994].

With the three 'analytical windows' shown, for non-polar, volatile and polar organic micro-pollutants, a broad range of organic substances is covered. They provide powerful tools for early warning.

Bio-sensors are sometimes used in continuous monitoring, such as on-line tests of acute toxicity using fish, daphnia and bacteria. 'Dynamic' toxicity tests are useful as early warning mechanisms for drinking water supplies, or as a general safeguard for the ecosystem. A continuous flow of water from the water body is routed through a specially constructed apparatus containing the test organisms. Many years of experience with a dynamic test have been obtained on the Rhine River with a fish test and more recently with a Daphnia (crustacean) test [Kramer and Botterweg, 1991] [Friedrich *et al.,* 1992]).

A bio-fluorometer uses the changes of fluorescence properties of standard solutions, e.g. algae, while algae are exposed to the water to be investigated. Dangerous substances, e.g. pesticides, can influence the photosynthesis of living algae causing an inhibition of fluorescence, changes in induction curves (kautsky-effect) or delayed fluorescence [Noack, 1989] [Gerhardt and Putzger, 1993]. Another type of biosensor is based on (own) luminescence of bacteria, which generate an enhanced luminescence signal when exposed to toxic substances [Mittenzwey, 1994].

Recent developments in sensor technology:

The developments of low cost multiple sensor arrays based on semiconductor technology and based on immobilization of reagents on optical fibres are of distinct relevance. One of the most attractive possibilities for measuring such variables as heavy metal ions and trace organics is the deposition of appropriate sensitive materials on the gates of an array of metal oxidized effect transistors (MOSFETS) which are integrated with a microprocessor onto a single chip. Clear advantages are low cost if the market allows volume production, miniaturisation, the ability to utilise a good deal of redundancy and thus better reliability, and the ability to deploy in-situ cleaning and calibration. Additionally, if ratio measurements are satisfactory, then these technologies are particularly useful.

The use of electro-optics and optical fibres coupled with microprocessors offers an attractive solution to many water industry problems, particularly those associated with measurement in or communication from hazardous areas where intrinsic safety considerations are paramount. Additionally the use of fibre optics and multiple light sensor arrays coupled with pattern recognition techniques can be particularly useful as a means of monitoring plant and equipment status. These technologies have been described in greater detail elsewhere [Briggs, 1994] [Briggs and Grattan, 1990].

Ahmad [Ahmad, 1991] has summarized the possibility of developing remote sensing techniques for the detection and possible quantification of a wide range of molecular species. Methods are typically base on Raman Scattering, or optical fluorescence. Recent research has demonstrated the possibility of determining residual chlorine concentrations (as ClO-) in the range 100 ppb to 10 ppm by direct absorption of light at 290 nm (in the ultra-violet), based on measurements before and after destruction of the ClO- ion. Work is currently under way leading to the development of a multivariable, optically-based monitor, initially aimed at intake protection. The basis of the proposed instrument is a solid state (no moving parts) diode array detector based spectrophotometer, which can be fibre optically coupled to a number of sampling points. Scans will be carried out throughout by U.V., visible and infra red spectrum and advanced signal processing techniques utilised, not only to obtain bulk measurements of organic matter and suspended matter but also to quantify specific organic contaminants.

Interesting possibilities for the development of small volume, point source, low cost fibre optic sensors are for example the use of Bragg gratings in fibres and interferometric chemical sensors. The potential of this approach to the sensing of chemical species, as well as physical variables such as temperature, pressure, vibration and flow must be considerable. Additionally the use of chemically sensitive materials or gels that change their refractive index or length (volume) when a particular chemical is absorbed may well form the basis of alternative sensors [Badini *et al.*, 1989] as it is refractive index or length that is changed, this can be detected with high sensitivity by incorporating the material into an interferometric arrangement.

7. Conclusions and recommendations

This chapter provides a summary of conclusions and recommendations on topics of special interest and state of the art approaches and techniques.

A: Water resource management; the need for information

1. The **goal of water resource management** can be summarised as promoting and protecting desirable water uses, including ecosystem functioning. In such a multifunctional approach, environmental issues and competing interests of water uses are managed in a balanced way.
2. Promoting sustainability of all water uses requires an **integrated approach** (addressing all uses), which combines:
   - River basin approach (recognising that use conflicts are confined to hydrological – rather than to administrative borders);
   - Ecosystem approach (which is more capable of determining cause-effect relations);
   - A shared emission based / water quality based approach (accounting for both economic viability of the dischargers and protection of other water uses).
3. The **process of monitoring and assessment** should principally be seen as a sequence of related activities that starts with defining the need for information and ends up in utilisation of the information product. Each component in this sequence imposes conditions on the type and quality of information flowing in from the previous component.
4. Explicit definition of the **information needs** of water resource management (based on policy and legal documents and by the staff charged with implementation) and the monitoring strategy (monitoring objectives) are of primary importance to the success of any water quality assessment system design.

B: Assessment criteria and objectives

5. Water quality **criteria** (quality standards) and **objectives** provide a reference system for water quality assessment, classification and evaluation of management efforts, respectively. In setting criteria and objectives, serious attention should be given to: defining risk levels (for various use categories), uncertainties in (QSAR estimates of) No Observable Effect Levels (NOEC), ecosystem complexity, bio-availability, synergy and variable characteristics (e.g. solubility). Furthermore, the potential of setting standards for aggregate variables, indicators, environmental effects (e.g. toxicity), and/or integrity of biological communities should be considered.

C: Ambient Water Quality Monitoring.

6. The **variables** included in a monitoring programme are the features for which assessment is performed. As such, selection of variables and setting of criteria and objectives is closely associated. Selection of the variables should account for:
   - production, emission, use, and actual occurrence of pollutants;
   - hazardous characteristics, bio-accumulation, and persistence of pollutants;
   - reliable and affordable analytical determination;
   - efficiency of pollutant source management.

   The potential of including aggregate variables, indicators, environmental effect variables (e.g. toxicity), and/or integrity of biological communities should be considered too.

7. The preferred sampling **media** (water, particulate matter, or organisms) may differ for each variable. Selection of the media should account for distribution of pollutants over the possible sampling media, bio-availability, bio-accumulation and ease of analytical determination.
8. **Variability** in water quality leads to uncertainty intervals in the data and information produced. These uncertainty intervals should, however, be less than the **relevant margin,** i.e. the margin in the information that is still relevant to the intended user of the information. The consequences of this requirement have to be reflected in the selection of sampling sites and frequencies and may differ, together with variability and relevant margins themselves, from variable to variable and for each monitoring objective.
9. The selection of **sampling sites** should account for the location (distribution) of water users (including biological communities) in a river basin and the associated risk of conflicts (macro level), as well as the inhomogeneity of the sampling media and variability in space (micro level).
10. Selection of **sampling frequency** should account for variability in time, and must take into consideration the intended procedures for statistical data analysis. Operational and financial constraints (e.g. budget, number of sites) should be considered as well.
11. **Sample collection and laboratory analysis** are the critical operational activities of monitoring and assessment systems. Special attention should therefore be given to avoiding additional uncertainties (such as caused by possible contamination at any stage during sampling, field measurements, conservation, storage and transport). On the other hand, depending on the type of sampling performed (e.g. depth integrated composite, or flow proportional versus simple grab sampling), sampling procedures may also reduce variability in time and/or space.
12. With respect the choice of **analytical methods,** attention should be given to the required precision and general performance characteristics of the analytical method, as well as on cost effectiveness. Furthermore, it should be noted that, with aggregate variables, toxicity testing and biological indices, the analytical method is more or less fixed by the variable description.
13. **Data validation and storage** are concurrent activities. They provide a last possibility to check data and to add annotations. In this process, questionable data should be flagged rather than thrown away. Furthermore, all valuable secondary information (meta information) should be stored with the data.
14. **Data interpretation** is the step where data are converted to information. Exploratory data analysis (viewing the data) and careful selection of statistical methods (accounting for variable characteristics such as normality, random analytical error, serial correlation, correlation with other variables, etc.) are invaluable for data interpretation. Furthermore, individual, rather than aggregated-data should be used for interpretation and all error probabilities in hypothesis testing should be considered.
15. Finally, the type of **presentation** (tables, graphs, maps), as well as the amount of detail (versus aggregation) and visualisation provided, should match the requirements of the (intended) audience. A proper definition of the intended audience and its specific information needs is therefore required.

D: Additional remarks with respect to effluent monitoring

16. As a direct consequence of the legal and political framework in which effluent monitoring is embedded, relatively much emphasis is put on the **monitoring objective** of testing of compliance with quality standards. Additional objectives of effluent monitoring can be the control of operational processes and the prediction of environmental impact in the receiving water body. Most additional considerations and recommendations for effluent monitoring, however, stem from the objective of testing of compliance with standards, which are generally made explicit by means of discharge permitting.
17. A **discharge permit** will usually contain an obligation for (self) monitoring by the discharger, including obligatory variables, frequencies, compliance criteria, and data validation, storage, interpretation and presentation procedures.
18. The selection of **variables, sampling frequencies and analytical methods** should depend on information with respect to the discharged pollutants and their interrelations, their concentration levels and their variability.
19. In effluent monitoring, **toxicity testing** can be of special significance as a means of assessing possible negative environmental effects of the unknown fraction (the pollutants not covered by application of other analytical methods).

E: Additional remarks with respect to early warning monitoring

20. Early warning systems for surface water and effluent discharges fulfil a very important need in the protection of downstream water uses. The **information need** and therewith the **monitoring objectives,** to provide an alarm, and to trace the cause (discharger or process operation failure) in case of the accidental pollution, differ considerably from those of ambient water quality monitoring. Additional considerations and recommendations for early warning monitoring stem from these monitoring objectives.
21. The need for reliable and timely early warning will put special emphasis on the selection of **sampling sites, sampling frequencies, variables and analytical methods.** Within this context, the potential of including dynamic toxicity testing and observation of process operations should be considered.
22. An **early warning system** should, apart from a monitoring system, intrinsically include: clearly defined warning and alarm values, a decision support system for calamity handling (including database files with substance information, reporting formats and information about local authorities), computer models for calculation of transit times (simple, ready to be used operationally and based on real time input data), and communication systems.

F: Quality management

23. Assuring the reliability and interchangeability of produced information calls for a well designed and operated **quality management** programme. Such a programme should:
    - include protocols (standard operating procedures) for a/o sampling and field measurement procedures, analytical work and data analysis;
    - provide for documentation of actual operations performed (primarily for sampling and analytical work);
    - contain a well designed programme for validation and inter laboratory testing, possibly leading to standardisation and/or accreditation (such procedures, now mainly in use for analytical work, may extend to other monitoring and assessment activities).

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