Guidelines for Water Quality Monitoring

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Foreword

For drawing up and implementing any water quality management plan, water quality monitoring is essential in identification of water bodies or their part(s) in need of restoration and also nature and magnitude of pollution control required. It also helps in prioritization of pollution control efforts and evaluating trends and effectiveness of such efforts.

Since there are a number of agencies involved in water quality monitoring, in order to optimize and rationalize the monitoring programme, it is important that all these agencies follow the same monitoring protocol. Water Quality Assessment Authority (WQAA) created under Environment (Protection) Act, 1986 has notified a "Protocol for Water Quality Monitoring". In order to effectively implement this Protocol, water quality monitoring Guidelines are necessary. The present Document is an attempt to fulfill this need. The Document brings out major considerations to design water quality monitoring network, procedures for sampling, laboratory analysis, data storage, data analysis, presentation, interpretation, reporting and quality assurance. I hope this Document will be useful to all involved in water quality monitoring.

(J.M. Mauskar)

Contents

1.   **Introduction**

Water is one of the most important and basic natural resources. Water is not only one of the most essential commodities of our day-to-day life, but the development of this natural resource also plays a crucial role in economic and social development processes. While the total amount of water available in the world is constant and is generally said to be adequate to meet all the demands of mankind, its quality and distribution over different regions of the world is uneven and causes problems of scarcity and suitability. It is therefore imperative that man develops, uses and manages this scarce commodity as rationally and efficiently as possible. In order to execute this task, accurate and adequate information must be available about the quality of the this natural resource under constantly changing human pressures and natural forces.

Water quality management is for a great deal controlled by authorization of discharges of dangerous substances for which monitoring of discharges, effluents and influenced surface water is essential. On national and state levels, we have several policies and regulation like Water (Prevention and Control of Pollution) Act, 1974 to regulate pollution discharges and restore water quality of our aquatic resources including the prescription of monitoring activities (Box-1,2 and 3). Under Water Act, 1974, pollution control boards were created, who are responsible for implementation of its provisions. One of the important provision of the Water Act, 1974 is to maintain and restore the 'wholesomeness' of our aquatic resources. To define the level of 'wholesomeness to be maintained or restored a system of water use classification was developed. Under this system water uses are classified in 5 classes (Box-4). If a water body or its part is used for multipurpose, then the use which demands highest quality of water is designated as 'designated best use' and accordingly water body or its part is designated. Now through regular water quality monitoring existing water quality is assessed and compared with the desired quality as identified under designated best use class and gaps are identified. Based on the identified gaps the water body or its part is identified as polluted.

Box 1: 'Protection of Environment' Provisions in India's Constitution

The Forty Second Amendment to the Constitution in 1976 underscored the importance of 'green thinking'. Article 48A enjoins the state to protect and improve the environment and safeguard the forests and wildlife in the country. Further, Article 51A(g) states that the "fundamental duty of every citizen is to protect and improve the natural environment including forests, lakes, rivers and wildlife and to have compassion for living creatures".

Box 2: Policy Documents on Natural Resource Conservation

Policy Statement for Abatement of Pollution **(1992)** has suggested developing relevant legislation and regulation, fiscal incentives, voluntary agreements and educational programs and information campaigns. It emphasizes the need for integration by incorporating environmental considerations into decision making at all levels by adopting frameworks namely, pollution prevention at source, application of best practicable solution, ensure polluter pays for control of pollution, focus on heavily polluted areas and river stretches and involve public in decision-making.

The National Conservation Strategy and Policy Statement on Environment and Development, 1992 aimed at "integrating environmental concerns with developmental imperatives…. [to] meet the challenges….by redirecting the thrust of our developmental process so that the basic needs of our people could be fulfilled by making judicious and sustainable use of natural resources." The priorities mentioned in this policy document include the sustainable use of land and water resources, prevention and control of pollution and preservation of biodiversity.

The National Water Policy, 2002 contains provisions for developing, conserving, sustainable utilizing and managing this important water resources and need to be governed by national perspectives. Concern due to water logging, ingress of soil salinity and over–exploitation of groundwater will be addressed on the basis of common policies and strategies. The policy includes improvements in existing strategies, innovation of new techniques to eliminate the pollution of surface and groundwater resources to improve water quality. It has emphasized on water resource planning, development of institutional mechanism, water allocation, groundwater development and participatory approach to water resource management. Regular

water quality monitoring programme for both surface and groundwater will be undertaken with particular emphasis on pollution control at source.

Box 3: Indian Laws and Regulation on Water Quality Management
The conservation of water resources expressed in the Constitution is embodied in the following regulations:

The Water (Prevention & Control of Pollution) Act, 1974 as amended deals comprehensively with water issues. It empowers the Government to constitute Pollution Control Boards to maintain the wholesomeness of national water bodies. It enables Central and State Pollution Control Boards to prescribe standards and has provisions for monitoring & compliance and penal provisions against the violators of the Act. It provides the permit system i.e. **"Consent"** procedure to prevent and control of water pollution. The Act empowers State Boards to issue directions to the defaulters.

Water Cess Act, 1977 was adopted to strengthen the Pollution control Boards financially, to promote water conservation. This Act empowers the Central Government to impose a **Cess** on water abstracted from natural resources by industries and local authorities.

Environment (Protection) Act, 1986 has a broad coverage in which 'Environment' includes **water**, air and land and there exists an interrelationship among water, air, land, human beings and other creatures. It empowers to take measures in protecting and improving the quality of the environment through preventing, controlling and abating environmental pollution. The Government is authorized to set national standards for ambient environmental quality and controlling discharges to regulate industrial locations, to prescribe procedure for hazardous substance management and to collect and disseminate information regarding environmental pollution. The Act provides for severe penalties for those who fail to comply with or contravenes any provision of the Act.

The Manufacture, Storage, Import of Hazardous Chemicals Rules, 1989 and its amendments under EPA, 1986 has identified the responsibilities of various stakeholders for management of chemicals and containment of spillage.
The Hazardous Wastes (Management and Handling) Rules, 1989 and its subsequent Amendment 2000 were created to provide 'cradle-to grave' or comprehensive guidance to the generators, transporters and operators of disposal facilities among others, and monitoring norms for State governments.
The Municipal Wastes (Management & Handling) Rules,1999 fix responsibilities to every municipalities responsible for the collection ,segregation, storage, transportation and disposal of municipal wastes.
The Bio-medical waste (Management & Handling) Rules, 1998 are likewise directed at institutions that generate and bio-medical wastes in any form.

Designated Best Use Classification of Surface water

Designated best use	Quality Class	Primary Water Quality Criteria
Drinking water source without conventional treatment but with chlorination	A	Total coliform organisms (MPN*/100 ml) shall be 50 or less pH between 6.5 and 8.5 Dissolved Oxygen 6 mg/l or more, and Biochemical Oxygen Demand 2 mg/l or less
Outdoor bathing (organized)	B	Total coliform organisms(MPN/100 ml) shall be 500 or less pH between 6.5 and 8.5 Dissolved Oxygen 5 mg/l or more, and Biochemical Oxygen Demand 3 mg/l or less
Drinking water source with conventional treatment	C	Total coliform organisms(MPN/100 ml) shall be 5000 or less pH between 6 and 9 Dissolved Oxygen 4 mg/l or more, and Biochemical Oxygen Demand 3 mg/l or less
Propagation of wildlife and fisheries	D	pH between 6.5 and 8.5 Dissolved Oxygen 4 mg/l or more, and Free ammonia (as N) 1.2 mg/l or less
Irrigation, industrial cooling, and controlled disposal	E	pH between 6.0 and 8.5 Electrical conductivity less than 2250 micro mhos/cm, Sodium Aborption Ratio less than 26, and Boron less than 2 mg/l.

* MPN: Most Probable Number
(Source: CPCB, 1978)

Water quality monitoring is one of the first steps required in the rational development and management of water resources. In the field of water quality management, there has been a steady evolution in procedures for designing system to obtain information on the

changes of water quality. The 'monitoring' comprise all activities to obtain 'information' with respect to the water system.

Water quality monitoring is a complex subject, and the scope of it is both deep and wide. Water quality monitoring has a direct relation with chemistry, biology, statistics and also economics. Its scope is also related to the types of water uses and functions which are manifold and the nature of the sources of water such as surface water (rivers and lakes), sea water groundwater.

The Central Pollution Control Board (CPCB) is an apex body in the field of water quality management in India. For rational planning of any water quality management programme, CPCB needs to know the nature and extent of water quality degradation. Therefore, a sound scientific water quality monitoring programme is prerequisite. Realising this fact, water quality monitoring was started in 1976 by CPCB with 18 stations on the Yamuna river. The programme was gradually extended. Today, there are 1032 monitoring stations in the country spread over all important water bodies.

2.   Water Quality

Water quality is a complex subject, which involves physical, chemical, hydrological and biological characteristics of water and their complex and delicate relations. From the user's point of view, the term "water quality" is defined as "those physical, chemical or biological characteristics of water by which the user evaluates the acceptability of water". For example for drinking water should be pure, wholesome, and potable. Similarly, for irrigation dissolved solids and toxicants are important, for outdoor bathing pathogens are important and water quality is controlled accordingly. Textiles, paper, brewing, and dozens of other industries using water, have their specific water quality needs.

3.   What is monitoring ?

Webster's dictionary defines monitoring as **(1)** to check and sometimes to adjust for quality or fidelity, **(2)** to watch, observe or check, especially for a special purpose, **(3)** to keep track of, regulate or control (as a process for the operation of a machine). Note that both (1) and (3) involve adjustment, regulation, or control, which fit well with the various types of monitoring information. A distiction can be made between different monitoring activities:

Survey: short term observation(s) on water quality (in present context) to fulfil definite objective(s);

Surveillance: a continued programme of surveys systematically undertaken to provide a series of observations in definite time period;

Monitoring: continuous surveillance undertaken to fulfil set of objectives.
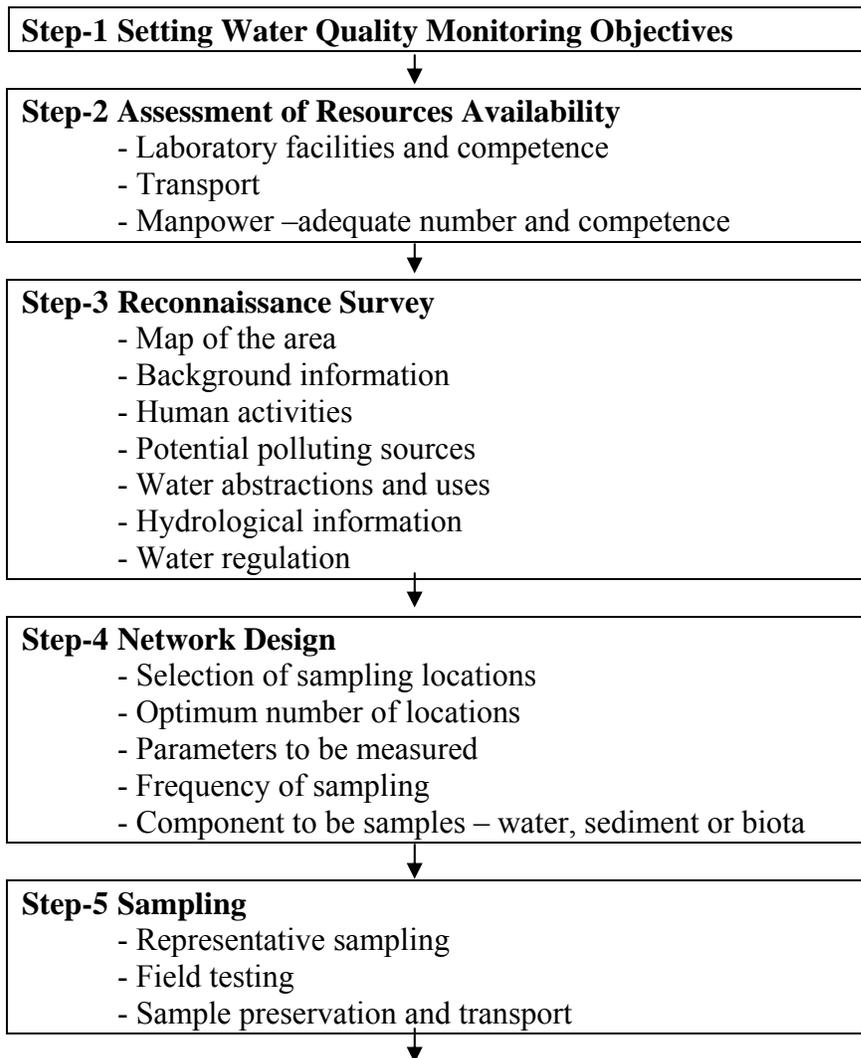
4.   Monitoring Strategy

Due to economic and practical considerations, monitoring network design, sampling frequencies, choice of variables and frequency of laboratory analysis should be determined on the basis of the information requirements, the hydraulic and hydrologic constraints, variability in water body characteristics, the end-use of water that drains to and from the

water body, the overall objectives of the monitoring programme, and finally of course on costs involved and budgets allocated to the programme. It is also important to optimise the amount of efforts required and information generated and its importance to fulfil the set objectives.

The scoping and designing step is the foundation of the entire water quality monitoring programme. The main objective of the design should be to minimise the cost of monitoring without sacrificing the desired information to the level of precision. Scoping and designing of water quality monitoring programme is based on clear scientific understanding of:

1. issues;
2. relevant background information;
3. monitoring objectives;
4. desired outcomes;
5. appropriate methods;
6. the dynamics and characteristics of water systems

Water quality monitoring involves 8 steps as explained below:

Step-1 Setting Water Quality Monitoring Objectives

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Step-2 Assessment of Resources Availability
- Laboratory facilities and competence
- Transport
- Manpower –adequate number and competence

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Step-3 Reconnaissance Survey
- Map of the area
- Background information
- Human activities
- Potential polluting sources
- Water abstractions and uses
- Hydrological information
- Water regulation

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Step-4 Network Design
- Selection of sampling locations
- Optimum number of locations
- Parameters to be measured
- Frequency of sampling
- Component to be samples – water, sediment or biota

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Step-5 Sampling
- Representative sampling
- Field testing
- Sample preservation and transport

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Step-6 Laboratory Work
        - Laboratory procedures
        - Physical, chemical analysis
        - Microbiological and biological analysis
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Step-7 Data Management
        - Storage
        - Statistical analysis
        - Presentation
        - Interpretation
        - Reporting
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Step-8 Quality Assurance
        - Production of reliable data
        - Quality control
        - Internal AQC
        - External AQC
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For each of the above steps following guidelines are provided:

5.   Step-1 Setting Water Quality Monitoring objectives

Before formulation of any water quality monitoring programme it is very important to have clear understanding on the monitoring objectives. Everybody of the programme team should be fully aware of the objectives, methodology, quality assurance, data validation and other aspects. Clearly environmental monitoring must have a purpose and a function in the process of risk assessment and pollution control. In risk management, monitoring is essential in the stage of problem recognition (indication of water quality deviations), the stage of analysis (with respect to the expected changes) and the stage of management (verification or control of strategy results).

A number of purposes for monitoring can be discerned:

-       The **signal or alarm function** for the detection of suddenly occurring (adverse) changes in the environment. Preferably the monitoring system should be designed to immediately enable the tracing of causes;

-       The **control function** to assess the general quality of water in relation to adopted water quality requirements or objectives, and for verification on the effectivity of pollution control strategies as well as a check on permitted effluent quality compliance;

-       The **trend (recognition) function** based on time series analysis to enable the prediction of future developments;

-       The **instrument function** to help in the recognition and clarification of underlying processes.

Water quality monitoring is carried out for various reasons and the objectives of a particular monitoring programme have a direct bearing on the costs of carrying out the programme.

The most important objectives of water and effluent quality monitoring programmes kept in mind by CPCB/SPCBs/PCCs include:

- rational planning of pollution control strategies;
- to identify nature and magnitude of pollution control required;
- to evaluate effectiveness of pollution control efforts already in existence;
- identification of state and trends in water quality, both in terms of concentrations and effects;
- identification of the mass flow of contaminants in surface water and effluents;
- formulation of standards and permit requirements;
- testing of compliance with standards and classifications for waters and effluents;
- early warning and detection of pollution.

In practise, data from routine monitoring programmes are generally used for a variety of purposes in addition to those for which the programmes were designed. Identification of the state and trends in water quality is mainly important for policy and management, while the identification of the mass flow in rivers and waste water discharges is of particular importance at the boundaries between states countries, districts or water systems. Mass flows are subject of international, national or state disputes, negotiations are an input for mass balances for specific substances. Testing of compliance with standards (control) is related to the water quality objectives for surface water as prescribed in both national and international standards. The early warning monitoring programme to signal pollution due to (accidental) spills by industry and ships is especially important if surface water of that particular river or water system is used for public water supply. Finally, data will be used for various projects including research.

Water quality monitoring is an important aspect of overall water quality management and water resources development. A well planned and well managed water quality monitoring system is required to **signal**, **control** or **predict** changes or trends of changes in the quality of a particular water body, so that curative or preventive measures can be taken to restore and maintain ecological balance in the water body. Monitoring is essential for the successful implementation of environmental legislation: to ensure that standards and criteria set by CPCB/SPCBs/PCCs are maintained on a continuing basis.

6. Step-2 Assessment Resources Availability

Once the monitoring objectives are known, it is important to look into the availability of resources for monitoring. Generally a compromise is made between quality and quantity of data required to fulfil certain objective(s) and resources available. Before planning water quality monitoring programme it is important to ensure that following resources are available:

a. Sampling equipment (as per checklist)
b. Transport for sampling
c. Laboratory facilities
d. Trained Manpower adequate number and competence
e. Equipment/instruments for desired parameters analysis
f. Chemicals/glasswares and other gadgets for analysis of desired parameters

g.   Funds for operation and maintenance of laboratory

7.   Step-3: Reconnaissance Survey

Most water quality monitoring programs have the objective of defining pollution, and relating it to its sources. After this the reductions in discharges, which are necessary to remedy the problem, can be determined. A few days spent reviewing all available reports and records concerning the water quality of all waste discharges and of the receiving water body may save several days of field work and may prevent the collection of useless data. It is important to make a reconnaissance survey of the river during the planning stage, noting all sources of wastes, all entering tributaries that might contribute a potential pollutant, and all uses and abstractions of the water. This action will also include a survey of background information such as geography, topography, climate and weather, hydrology, hydrogeology, land use, urbanization, industrialization and agriculture, including farming in the riverbed. This information will help in an appropriate siting of sampling locations.

For groundwater quality monitoring network, it is important to conduct survey to identify potential sources of pollution. For groundwater pollution monitoring generally existing structures in the potentially polluted sites are selected. Since variation in groundwater quality is very high and unpredictable, it is practically not possible to cover assessment of groundwater quality of a particular area fully. It is also not practicable to create so many groundwater structures for sampling. Thus, a compromise has to be made between resources available and criticality of information required. It commonly agreed that groundwater quality is generally degraded in the urban, industrial, solid wastes (both municipal and hazardous from industries) dumpsites and agricultural areas. In such areas a reasonable network is adopted for groundwater quality monitoring depending on resources available. Sometimes groundwater structures need to be created in view of the criticality of the information needed for a particular area. Because of the heavy cost involved in sampling and analysis, it is well worth devoting time and effort to careful planning of a monitoring system.

This survey will give an overview of the geographical location of the water body to be monitored, its accessibility all kind of human influences to decide appropriate sampling location and also appropriate number of sampling locations. The survey may include acquisition of following information:
a.   Location map
b.   Background information on water body
c.   Human activities around the water body like mass bathing, melon farming, cattle wading etc
d.   Identification of potential polluting sources
e.   Water abstraction – quantity and uses
f.   Water flow regulation - schedule, quantity etc

The above information will help in proper designing the network and also planning the schedule for sampling.

8.   Step-4: Network Design
In designing the sampling network, it is important to consider optimum number of sampling location, sampling frequency and parameters required to fulfil the desired objectives. Under NWMP, CPCB has set certain important criteria for selection of sampling location.

Criteria for Site Selection
The sampling site selection is generally linked with water quality monitoring objectives. For example if the monitoring is carried out for judging suitability of water for drinking water source then the monitoring site should be closer to the intake point whereas for outdoor bathing it should be near bathing ghats.

After understanding the factors affecting water quality thoroughly, it is necessary to select specific reaches or areas of the stream or river to sample. There is no set number of sampling stations that will be sufficient to monitor all the possible types of waste discharges. There is no routine methodology for site selection on a cook book basis. However, there are some basic rules. If these rules are carefully followed, a basically sound sampling design will be the result.

Some general criteria for selecting appropriate sampling sites will be summarized under the following points:

1) Always have a reference station up-stream of all possible discharge points. The usual purpose of a monitoring exercise is to determine the degree of man induced pollution, and the damage that is caused to aquatic life. The reference station serves to assess the situation with respect to background water quality and biological aspects, which may vary locally and regionally.
2) Drinking water intake points, bathing ghats, irrigation canal off-take points should be considered for monitoring.
3) Sampling stations should be located upstream and downstream of significant pollution outfalls like city sewage drains and industrial effluent outfalls.
4) All samples must be representative, which means that the determinants in the sample must have the same value as the water body at the place and time of sampling. In order to achieve this it is important that the sample is collected from well-mixed zone. A homogeneity test must be performed to identify the well-mixed zone.
5) Additional downstream stations are necessary to assess the extent of the influence of an outfall, and locate the point of recovery.
6) In large rivers like Ganga, Yamuna, Narmada, Krishna and Godavari, where mixing is poor and incomplete, the effluent may tend to follow one bank. Stations on both sides downstream are useful to make an estimate of the extent of the mixing zone.
7) In large rivers a balance has to be found between the selection of a few stations giving poor coverage, and the selection of more stations having different substrates and dissimilar fauna, which can not be compared spatially.

8) In order to enable comparisons among sampling stations, it is essential that all stations be sampled approximately at the same time. Not more than two weeks should elapse between the sampling of the first and last station in a river.

9) Sites for biological sampling should match with sites for chemical sampling.

10) Biological sampling stations need to be selected with proper attention to representative habitats (kind of substrate, depth and flow). All sampling stations in a certain river should preferably be ecologically similar. To increase biological and chemical comparability, they should have similar substrate (sand, gravel, rock, or mud), depth, presence of rifles and pools, stream width, flow velocity, bank cover, human disturbances, etc.

11) The conventional location of macro-invertebrate sampling stations in rivers arises not only from an assumed uniformity of substrate and fauna, but also from the ease with which it may be sampled by means of handnets and stone-lifting or kicking, and from the ease of access.

12) For the estimation of the oxygen exchange rate of the river, a measurement of cross section is required. Any station should be typical with respect to the cross section of the river.

13) The sampling team normally has to carry an appreciable burden of sampling gear and water samples, and the distance they can walk is limited. Easily accessible sites should be selected. The site should also be accessible under all conditions of weather and riverflow. Accessibility is therefore an important consideration.

14) With respect to preservation, samples are taken to perform analysis on three types of parameters: for some parameters, such as heavy metals, the samples need not be preserved. For other parameters, samples can be preserved by cold storage or by the addition of certain preservatives. However, the samples for analysis of parameters like BOD and bacterial counts cannot be preserved and need to reach the laboratory shortly after taking the sample. The need to transport the samples to the laboratory will govern the range of determinations which can be carried out for a particular sampling site. Travel time greater than 24 hours between the site and laboratory is not recommended.

15) The collection of samples can be hazardous at some locations in bad weather (such as high flow). Such sampling sites can better be avoided.

16) There are many disturbing influences in the rivers, especially cattle wading, melon farming, fishing, sand recovery, etc.. These disturbances can drastically influence chemical processes and the nature of the biological community. Dams and barrages provide a different kind of habitat. Such sampling sites should be avoided.

17) Availability of sampling facilities such as bridges, boats, and possibilities for wading are important criteria in the selection of sampling sites.

18) In case of ghroundwater sampling select only wells (tubewell, dug-well, handpump), which are in use.

19) For groundwater pollution monitoring generally existing structures in the potentially polluted sites is selected.

20) Since variation in groundwater quality is very high and unpredictable, it is practically not possible to cover assessment of groundwater quality of a particular area fully.

21) It is also not practicable to create so many groundwater structures for sampling. Thus, a compromise has to be made between resources available and criticality of information required. It commonly agreed that groundwater quality is generally degraded in the urban, industrial, solid wastes (both municipal and hazardous from industries) dumpsites and agricultural areas. In such areas a reasonable network is adopted for groundwater quality monitoring depending on resources available. Sometimes groundwater structures need to be created in view of the criticality of the information needed for a particular area.

Zonation

The occurrence of two general types of zonation in water bodies should be mentioned here because of their significance for the planning and execution of large scale sampling programs.

Cross-sectional zonation. A cross-section of the river and lakes will usually reveal gradients in depth, current velocities and sediment and water characteristics.

Longitudinal zonation. On a large geographical scale rivers may be classified in a number of zones: highland brooks and lowland courses both subdivided in upper and lower reaches.

Sampling frequency

The sampling frequency is governed by the level of variation in water quality of a water body. If variations are large in a short duration of time, a larger frequency is required to cover such variations. On the other hand, if there is no significant variation in water quality, frequent collection of sample is not required. The water quality variations could be of two types i.e. random and cyclic or seasonal. In case of random variations e.g. due to sudden rainfall in the catchment or sudden release of water from the dam etc., increased frequency may not help much as such variations are highly unpredictable. Thus, within the available resources it is not cost effective to cover such variations. In case of the water bodies having cyclic variations more frequently, sampling on monthly basis is justified. But for all those water bodies having stable water quality round the year, monthly sampling is not justified.

Frequency and Parameters

- On routine basis, a combination of general parameters, nutrients, oxygen consuming substances and major ions should be analyzed at all stations. Depending upon the industrial activities and anticipated at the upstream of the sampling station other parameters like micro-pollutants, pesticides or other site specific variables may be included at lower frequency. Such stations need to be identified.

- A list of parameters to be considered for analysis and frequency of sampling is provided in the "Protocol for Water Quality Monitoring" notified by Govt of India. These are provided in Table 1 and 2.
- It was also emphasized that biological monitoring should form an important part of our water quality monitoring programme due to its inherent advantages. The SPCBs/PCCs agreed to initiate such exercise initially at limited stations.
- Sediment needs to be analyzed for micro pollutant in some stretches as most of micro pollutants are associated with sediment. This should form part of monitoring programme.

Table 1:   Parameters and frequency of monitoring in surface waters

Type of Station	Frequency	Parameter
Baseline:	**Perennial rivers and Lakes :** Four times a year **Seasonal rivers** : 3-4 times (at equal spacing) during flow period. **Lake**: 4 times a year	**(A) Pre-monsoon**: Once a year Analyse 25 parameters as listed below : 　**(a)General** : Colour, odour, temp, pH, EC, DO, turbidity, TDS 　**(b) Nutrients** : NH_3-N, $NO_2 + NO_3$, Total P 　**(c)Organic Matter** : BOD, COD 　**(d)Major ions** : K, Na, Ca, Mg, CO_3, HCO_3,　　Cl, SO_4, 　**(e)Other inorganics** : F, B and other location-specific parameter, if any 　**(f)Microbiological** : Total and Faecal Coliforms **(B)Rest of the year** (after the pre-monsoon sampling) at every three months' interval: Analyse 10 parameters: Colour, Odour, Temp., pH, EC, DO, $NO_2 + NO_3$, BOD, Total and Faecal Coliforms.
Trend:	Once every month starting April-May (pre-monsoon), i.e. 12 times a year	**(A)Pre-monsoon**: Analyse 25 parameters as listed for baseline monitoring **(B)Other months** : Analyse 15 parameters as listed below 　**(a)General** : Colour, Odour, Temp, pH, EC, DO and Turbidity 　**(b)Nutrients** : NH_3-N, $NO_2 + NO_3$, Total P 　**(c)Organic Matter** : BOD, COD 　**(d)Major ions** : Cl 　**(e)Microbiological** : Total and Faecal coliforms **(C)Micropollutant** :Once in a year in monsoon season 　**(i)Pesticides**-Alpha BHC, Beta BHC, Gama BHC (Lindane), OP-DDT, PP-DDT, Alpha Endosulphan, Beta Endosulphan, Aldrin, Dieldrin, 2,4-D, Carboryl (Carbamate), Malathian, Methyl Parathian, Anilophos, Chloropyriphos

		(ii)Toxic Metals-As,Cd,Hg,Zn,Cr,Pb,Ni,Fe (Pesticides & Toxic metals may be analysed once a year)

➢ This does not, however, restrict analysis of more parameters depending upon specific requirements of the analysing agency and its manpower availability.
➢ For lakes/reservoirs, monitoring of additional parameters, like Total Kjeldhal Nitrogen, Chlorophyll, total plankton count and productivity, are to be included in the list of parameters.
➢ If bio-monitoring is done in rivers/lakes/reservoirs, additional parameters, like Photosynthesis-Respiration (P/R) ratio, saprobity index and diversity index are to be included.
➢ The list of pesticides & toxic metals is flexible and should be decided on need basis.

Table 2: Parameters and frequency of monitoring in Groundwaters

Type of Station	Frequency	Parameters
Baseline	Twice a year in Pre & Post monsoon season. The frequency may be reviewed after 3 years of monitoring	**(A)Pre & Post Monsoon season**: Analyse 20 parameters as listed below : **(a)General** : Colour, odour, temp, pH, EC, TDS **(b)Nutrients** : $NO_2 + NO_3$, ortho-phosphate **(c) Organic Matter** : COD **(d)Major ions** : K^+, Na^+, Ca^{++}, Mg^{++}, CO_3, HCO_3, Cl, SO_4, **(e)Other inorganics** : F, B and other location-specific parameter, if any
Trend	Four times every year (once in pre-monsoon, April-May, and thereafter at intervals of 3 months)	**(A)April-May** : Analyse 20 parameters as listed for Baseline monitoring. **(B)Other times**: Analyse 14 parameters as listed below **(a)General** : Colour, odour, temp, EC, pH, TDS **(b)Nutrients** : $NO_2 + NO_3$, ortho-phosphate **(c)Organic Matter** : COD **(d)Major ions** : Cl **(e)Other organics** : F, B **(f)Microbiological** : Total and faecal coliforms **(C) Micropollutant** : **(i)Pesticides**- Alpha BHC, Beta BHC, Gama BHC (Lindane), OP-DDT, PP-DDT, Alpha Endosulphan, Beta Endosulphan, Aldrin, Dieldrin, 2,4-D, Carboryl (Carbamate), Malathian, Methyl Parathian, Anilophos, Chloropyriphos **(ii) Toxic metals-** Fe, Cu, Cr, Ni, Pb, Cd, Zn, Hg, As

➢ The parameters to be analysed as mentioned above are the minimal requirement. This does not, however, restrict analysis of more parameters depending upon specific requirements of the analysing agency and its man power availability.

➢ If COD value exceeds 20 mg/l , the sample is to be analysed for BOD also. The list of pesticides & toxic metals is flexible & should be decided on need basis

9. Step-5: Sampling

Planning for Sampling

When planning a sampling programme the number of sampling stations or wells that can be sampled in one day is required. For this is necessary to know the required time needed for sampling, and other actions required, at the site. Since purging is a time consuming activity an estimate of the required purging time is a must to arrive at a fair estimate of the sampling time.

Check list for the field visit

Table 3 contains a list of items which should be checked before starting on a sampling mission. At least one day before sampling, make sure that all the arrangements are made as per the check list. Make sure that you know how to reach sampling site(s). Take help of location map for each site which shows the sample collection point with respect to prominent landmarks in the area. In case there is any deviation in the collection point, record it on the sample identification form giving reason. Note that depending on the local conditions, type of water body, analysis requirements, etc., not all items on the check list may be necessary. Other items, not listed, may sometimes be required. The field operator may make his or her own personal checklist based on Table 3. Decide on the number of each item that would be required depending on the number of samples to be collected. It is always safer to carry a few numbers in excess. If for any reason the laboratory conducting analyses is different from the laboratory preparing sample bottles, ensure that the concerned laboratory is informed of the programme and ready to receive samples, particularly those which would need immediate attention.

Table 3:   Checklist for Field Visit

• Itinerary for the trip (route, stations to be covered, start and return time)	• Personnel and sample transport arrangement
• Area map	• Sampling site location map
• Icebox filled with ice or icepacks or ice	• Weighted bottle sampler
• BOD bottles	• Rope
• Special sample containers: bacteriological, heavy metals, etc.	• Sample containers
• Sample preservatives (e.g. acid solutions)	• Thermometer
• Tissue paper	• Other field measurement kit, as required

• Sample identification forms	• Labels for sample containers
• Field notebook	• Pen / pencil / marker
• Soap and towel	• Match box
• Spirit lamp	• Torch
• Drinking water	• Knife
• First-aid box	• Gloves and eye protection
• Dump sampler to check well conditions	• Submersible pump and accessories

General Guidelines for Sampling
- Rinse the sample container three times with the sample before it is filled.
- Leave a small air space in the bottle to allow mixing of sample at the time of analysis.
- Label the sample container properly, preferably by attaching an appropriately inscribed tag or label. The sample code and the sampling date should be clearly marked on the sample container or the tag.
- Complete the sample identification form for each sample.
- The sample identification form should be filled for each sampling occasion at a monitoring station. Note that if more than one bottle is filled at a site, this is to be registered on the same form.
- Sample identification forms should all be kept in a master file at the laboratory where the sample is analysed.

Surface water Sampling
- Samples will be collected from well-mixed section of the river (main stream) 30 cm below the water surface using a weighted bottle or DO sampler.
- Samples from reservoir sites will be collected from the outgoing canal, power channel or water intake structure, in case water is pumped. When there is no discharge in the canal, sample will be collected from the upstream side of the regulator structure, directly from the reservoir.
- DO is determined in a sample collected in a DO bottle using a DO sampler. The DO in the sample must be fixed immediately after collection, using chemical reagents. DO concentration can then be determined either in the field or later, in a level I or level II laboratory.

Groundwater Sampling
- Samples for groundwater quality monitoring would be collected from one of the following three types of wells:
- *Open dug wells* in use for domestic or irrigation water supply,
- *Tube wells* fitted with a hand pump or a power-driven pump for domestic water supply or irrigation
- *Piezometers*, purpose-built for recording of water level and water quality monitoring.

- Open dug wells, which are not in use or have been abandoned, will not be considered as water quality monitoring station. However, such wells could be considered for water level monitoring.
- Use a weighted sample bottle to collect sample from an open well about 30 cm below the surface of the water. Do not use a plastic bucket, which is likely to skim the surface layer only.
- Samples from the production tube wells will be collected after running the well for about 5 minutes.
- Non-production piezometers should be purged using a submersible pump. The purged water volume should equal 4 to 5 times the standing water volume, before sample is collected.
- For bacteriological samples, when collected from tubewells/hand pump, the spout/outlet of the pump should be sterilised under flame by spirit lamp before collection of sample in container.

Sample Labeling

Label the sample container properly, preferably by attaching an appropriately inscribed tag or label. Alternatively, the bottle can be labelled directly with a water-proof marker. Information on the sample container or the tag should include:

- sample code number (identifying location)
- date and time of sampling
- source and type of sample
- pre-treatment or preservation carried out on the sample
- any special notes for the analyst
- sampler's name

Sample Preservation and Transport

Preserve the collected samples as specified in Tables 1. Samples for BOD and bacteriological analyses should be stored at a temperature below $4^{o}C$ and in the dark as soon as possible after sampling. In the field this usually means placing them in an insulated cool box together with ice or cold packs. Once in the laboratory, samples should be transferred as soon as possible to a refrigerator. If samples collected for chemical oxygen demand (COD) analysis cannot be analysed on the day of collection they should be preserved below pH 2 by addition of concentrated sulphuric acid. This procedure should also be followed for samples for ammoniacal nitrogen, total oxidised nitrogen and phenol analysis. Samples which are to be analysed for the presence of metals, should be acidified to below pH 2 with concentrated nitric acid. Such samples can then be kept up to six months before they need to be analysed; mercury determinations should be carried out within five weeks, however. After labeling and preservation, the samples should be placed in an insulated ice box for transportation. Samples should be transported to concerned laboratory as soon as possible, preferably within 48 hours. Analysis of bacteriological samples should be started and analysed within 24 hours of collection. If samples are being brought to the laboratory they should be transported in less than 24 hours.

The result of any test on the quality of the environment is no better than the result of all efforts that lead to this final result: collection of the samples, the handling and chemical treatment, the method of storage, the chemical analysis, the calculation and interpretation of the data. If any of these steps are carried out with insufficient care, the final result (e.g. the concentration of a given compound) will be no more than a figure without relation to the actual situation in the environment, and therefore be useless: the entire operation has been a waste of energy, time and money.

In a situation where the tasks of sampling (and preservation) and chemical analysis belong to different specialized groups, lack of communication may easily lead to erroneous results. The optimum situation is there, where the entire procedure, from sampling to final analysis, is within the hands of one group of experts. However, this is due to managerial aspects not always possible. Therefore, instead of blaming each other for evident errors in analysis (often without proof), it is essential that both sampling team and chemical analysts work together to optimize the integrated task: the analysis. Both groups are specialized: the sampling party has the knowledge of the actual situation in the field, with the consequential restrictions and possibilities in terms of e.g. logistics (transport, accessability, local condition) and should already in the planning phase be consulted, the analytical party (chemical or biological) is specialized in aspects related to contamination control, sample- and sampling-bottle selection, cleaning and preservation methods etc. The necessity for close cooperation is evident and serves the ultimate goal: reliable analysis that reflect the actual situation in the environment.

Importance of the sampling procedures
It will be obvious that the result of any chemical or biological analysis can be no better than the sample that is offered to the analytical laboratory. Often the quality control aspects are only related to the analytical part, whereas the control procedures for the sampling are neglected. There appears to be a need for a detailed description of the sampling and preservation procedures. It is not possible, however, to specify one detailed description, valid for all parameters of interest, because of varied purposes and specific needs required in the analytical process. Therefore in this report a detailed description is offered per parameter (or set of parameters) in the following sections. The present section deals with general considerations.

The objective of sampling is to collect a portion of material from an environmental compartment (either water, sediment or biota) small enough in volume to be conveniently transported and handled in the laboratory, while still accurately retaining is representativity. This implies that the relative proportions or concentrations of the components of interest should be the same in the samples when they are being analysed , as they were originally in the environment. This requires that the sample will be handled and, if necessary, treated in such a way that no significant changes in composition occur that may hamper proper analysis. In other words, no addition (e.g. contamination), loss (e.g. adsorption to the wall of the sample bottle) or deterioration (e.g. physico-chemical or biological degradation or transformation) can be allowed.

Sampling devices

Many sampling devices have been developed during the last century. Not only became the design more reliable, also new materials were introduced. It goes too far, to give a complete list of the different sampling gear available and their (im)possibilities (Hellawell, 1986; Kramer, 1988; Holme & McIntyre, 1984; Sournia, 1978). The most important sampling devices are the following:

Water
For the compartment water several type of sampling devices are available:

a - Bottle. The same bottle used for storage is used for collection. Only (sub)surface samples can be collected.

b - Sampler. Operated on a line or wire for deep water sampling. Several samplers can be mounted together on one wire. They are closed by messenger (metal weight gliding along the wire) or by electronic means. In this paper the Van Dorn type is mentioned (see the following figure), but also Niskin-, NIO-, Nansen- samplers (and others) are available, and can often be used. A large variation in sizes is available. Specific purposes (sampling for bacteria (thus sterile), trace metals (metal free), pesticides (no plastics)) require specially designed samplers.

c - Pumping. Automatic sampling devices, using pumping systems are available. They usually can be preset to desired volume and/or time of sampling; depending on the collection bottles installed, either a series of spot samples or one composite sample may be collected.

Sediment For sediment sampling one may use one of the following techniques:

d - Coring. A PVC or perspex tube (ca. 1 m x 8 cm φ) is used to extract relatively undisturbed sediment.

e - Grabbing. A larger volume of sediment, disturbed, however, can be collected. Useful also for the collection of organisms.
f - Others. Special types of sediment samplers have been developed, e.g. for use in the deep sea (piston corers), for use in sandy sediments (vibro-corers), for large sections of the sediment (box-corers). They are beyond the scope of this report, however.

Biota Sampling methods for biota may be roughly divided into active and passive methods. Among the passive methods belong:
- methods that extract and separate the organisms from their habitat (which at the same time will be disturbed);
- methods that remove an undisturbed part of the habitat from which the organisms are then extracted.

- Among the active methods belong various artificial experimental designs like:

- colonization substrates from which the biota are collected;

- exposure techniques with different species by which some environmental problems can be studied under conditions that are under control.

Apart from the organisms that are collected in the above mentioned compartments, such as phytoplankton and bacteria in water samples, meiofauna in sediments, a multitude of special sampling gear has been developed for the collection of organisms.
We can summarize to the following types, without even trying to be complete: local conditions and habits often necessitate own adaptations or modifications of existing designs.

g - <u>Nets</u>. Hand nets for macro-invertebrates, plankton nets with various mesh sizes for phyto- and zoo-plankton, fish nets of various designs like fykes, seines or (beam) trawls;

h - <u>Dredges</u>. like naturalists' dredge, rock dredges, anchor dredge

i - <u>Suction samplers</u>

j - <u>Colonization samplers</u> like baskets filled with various substrates (e.g. bricks) or microscope glass slide holders;

k - <u>Exposure cages</u> of various design for different organisms as molluscs, crustaceans or fish;

l - <u>Collection by hand</u> is an easy and valuable technique, especially for sessile organisms (molluscs, water plants) or floating species (e.g. water hyacinth). For deeper water the use of divers should be considered. An advantage of manual picking is that already during sampling one may select special organisms (e.g. in size/age) and one is more able to prevent damage to the organisms than when using a mechanical device.

A variety of sampling equipement is depicted on the following pages. In some cases the method of applying the instruments is also graphically demonstrated.

Types of Samples
Apart from a separation into compartments (water, sediment and biota) different types of samples can be collected:

1) <u>Grab sample</u> (also called spot - or catch samples)
One sample is taken at a given location and time. In case of a flowing river, they are usually taken from the middle of the flowing water (main) stream and in the middle of the water column. When a source is known to vary with time, spot samples collected at suitable time intervals and analyzed separately, can document the extent, frequency and duration of these variations. Sampling intervals are to be chosen on the basis of the expected frequency with which changes occur. This may vary from continuous recording, or sampling every 5 minutes, to several hours or more.

2)   composite samples
In most cases, these samples refer to a mixture of spot samples collected at the same sampling site at different times. This method of collection reduces the analytical effort, because variations are middled out in one analysis. It is a useful technique when daily variations occur and seasonal variations are the objective of the programme. If, however, the series of spot samples are not mixed but analyzed individually, also information on the daily variability can be obtained, and afterwards the average can be computed.

Sometimes the indication 'time-composite' is used to distinguish from 'location-composite' sampling. Time-composite sampling representing a 24-hour period is often used. For many determinations, the time interval between sampling events being 1-3 hours. To evaluate the nature of special discharges (e.g. variable in volume or irregular in time), samples should be collected at time intervals representing the period during which such discharges occur. Especially in effluents, one may sample a volume that is propor-tional to the discharge (flow based composite). This type of sampling is also required to measure the flux of pollution load discharged through a point source.

Biota that is only active during certain periods of the day (e.g. activity during the night) can only be sampled accordingly.

For parameters that will change after collection, and that can not be preserved, in-situ determinations should be applied if possible. If preservatives are to be added, add them to each sample and not in the end to the composite sample.

3)   Integrated samples
Sometimes samples are collected at the same location but, due to horizontal or vertical variation in the composition of the river (or in water flow) or lake, they come from different points in the cross-section that are regarded with a different relative importance. To evaluate the average composition, total load or mass balance, integrated samples are collected, often in proportion to the river flow of the areas of sample collection.

4)   In-situ measurements
Some determinations are more likely to be affected by sampling and sample storage than others. In several cases the expected changes are so large, that it is impossible to store the sampled material for a correct analysis at a later moment. If possible, these parameters should be analyzed on the sampling site or, even better, in-situ. Most important parameters that should (and can) be analyzed in situ are the pH, dissolved oxygen, temperature, conductivity and sometimes turbidity. For several measurements special portable measuring devices are available.

The estimation on numbers and diversity of organisms is also to be considered as in situ analysis.

 Contamination control
Special attention should be given to the minimization of contamination. As said earlier, unintentional additions to the sample of the compound under consideration, will increase the concentration (contamination) and make further analysis quite useless. The levels of

many constituents, especially of pollutants in the water are, although they may be elevated, still very low (μg/l levels are common for dissolved trace metals, while ng/l levels occur in case of organic micropollutants). Therefore, contamination will easily occur: from the sampling equipment, from the sample bottle, from preservatives, from the ambient atmosphere, from the personnel taking the sample etc. Utmost care should therefore be maintained, - and the mind should always be focused on this topic during sampling - in order to prevent contamination.

Often sampling bottles need to be cleaned in a special way, depending on the parameter. To avoid cross-contamination, the same bottles should be used only for identical selected parameters, even when they are cleaned in between. Separate sets of bottles should be used for (low concentration) natural waters and for (high concentration) effluents. To prevent contamination by the hands, plastic (PE) gloves are needed. Atmospheric dust and (exhaust) fumes are readily available to contaminate the sample: minimum contact of the sample with the atmosphere is essential, here. A (portable) laminar flow "clean bench" is of great use for adding preservatives and for filtration under controlled conditions. The person taking a sample (and the analyst) should take care not to touch the inside of bottle and cap. The sampling bottles should be kept clean from dust and dirt. In between cap and bottle dust can accumulate that is not easily washed away. The (cleaned) bottles should therefore leave the analytical laboratory protected by a polythene plastic bag; only on the sampling site this bag should temporarily be removed to allow sampling. Then, after addition of preservative(s) if necessary, the bottles should be stored in the plastic bag again. Pipettes or pipette tips should (in the field and in the laboratory) only be used once. Biota, especially those that are collected for chemical analysis of the concentration of pollutants, require special attention with regard to contamination control. Be aware of the intention of the programme (and the compounds to be analyzed) and take appropriate measures. Prevent the use of metal equipment for the collection or storage of organisms in case of trace metal analyses (no zinc plated steel buckets or storage boxes, no copper mesh sieves). For trace organic analysis, try to stick to glass and stainless steel equipment. Handle the organisms with care, remove excessive sediment or algae, and collect them in clean (plastic or glass) wide mouth bottles. Prevent contact of the collected organisms with the (shore) sediment, effluent water, deck of the ship etc.

Cleaning procedures
The cleaning of samplers, sampling bottles and other labware, that comes into contact with the sample, is essentially a task for the analytical chemical laboratory, not for the sampling team. Depending on the parameter, different cleaning procedures can be applied.
For heavy metals rinsing with:

-       1:1 diluted Nitric acid (supra pure quality) for 1 week is needed, followed by:

-       three times washing with double distilled water.

Bottles for trace organic (chlorinated) compounds, like pesticides, should be cleaned with the solvent used for extraction (also of high purity quality).

Samples for the general physical-chemical characterization allow less vigorous methods. Thorough cleaning with water to remove particulates and two times rinsing with distilled water will usually be sufficient.

Organisms that are to be preserved (alcohol, formalin) should be stored in glass bottles. The samples for chemical analysis follow the selection and cleaning procedures for the water and sediment compartments (wide mouth bottles facilitate the entry of the organisms.

All bottles should arrive at the sampling site in a fully cleaned state, protected from accidental contamination.

The last cleaning step is in most cases (NOT all: not for the trace organics, in case a solvent is already present in the bottle, and not for microbiological samples) rinsing 2-3 times with the water to be sampled. This cleaning should be done, one bottle at the time, at the sampling point and both bottle and cap should be cleaned: fill the bottle (1/3), put on the cap, shake and empty. Repeat this procedure 2 times.

Sample Containers

The sample containers needed for a sampling campaign are prepared by the laboratory and given to the person collecting samples. An overview of the types of containers and preservation is given in Table 4. More detailed information on the specific containers needed for each parameter is given in Table 1.

Table 4:   Container Types and Volumes Needed for Sampling

	Analysis	Container		Volume	Preservatio
0	On-site analysis	PE bowl	or	±200	-
1	General (SS, TDS, major, ions	Glass, PE		1000	-
2	COD, NH3, NO2-+NO3-	Glass, PE		500	H_2SO_4, pH
3	o-PO4	Glass		100	-
4	BOD	Glass, PE		1000	$4^{o}C$, Dark
5	Coliforms	Glass,	PE,	300	$4^{o}C$, Dark
6	Heavy metals (Cd, Zn)	Glass, PE		500	HNO_3, pH
7	Mercury	Glass		1000	HNO_3, pH
8	Pesticides	Glass, Teflon		1000	$4^{o}C$, Dark

Reagent Solutions

For some of the field analyses, reagent solutions are necessary for the analysis. All necessary reagent solutions should be prepared in the laboratory and brought to the field by the sample collector.In all cases, sample preservatives and DO fixing solutions, if applicable, *must* be brought to the field and added to the samples immediately after collection.

For analysis of pH, buffer solutions are necessary to standardise the pH meter: Buffer solutions should be prepared in the laboratory, or purchased, for pH = 4, 7, and 9.

For analysis of Electrical Conductivity, standard potassium chloride solution, KCl (0.01*M*) is needed to standardise the conductivity meter.

For preservation of certain samples, concentrated nitric acid, concentrated sulfuric acid, ZoBell's solution, etc., are needed.

A supply of distilled water is needed for rinsing equipment.

Instruments

Some instruments and equipment are necessary to make the field analyses. Instruments and equipment must be brought to the field. *Temperature should always be measured in the field*:

- For measurement of Temperature, a (mercury) thermometer or thermistor is needed.
- For analysis of Electrical Conductivity, a conductivity meter is needed.
- For analysis of pH, a pH meter is needed.
- For analysis of Redox Potential, a pH meter (mV scale), reference electrode and oxidation-reduction indicator electrode are needed.

Note: It is possible that instead of separate meters for temperature, pH and conductivity, there is a single instrument with different probes which will measure all three parameters. These are called field monitoring kits.

A supply of batteries and standard spare parts should also be carried along with the field instruments.

Field Analysis

Measurements of colour, odour, temperature, electrical conductivity, pH and dissolved oxygen are considered to be 'Field Determinations' and should be made as soon as possible after collecting a sample.

Measurement of these parameters can be made in the field if field meters are available. This is the best option, as the analyses will be made immediately. If samples are brought to the level II/II$^+$ laboratory, the travel time should be *very* short, so that parameter values do not change between the time the sample is collected at the time of analysis.

Colour

Determining the colour in the field is relatively easy. Pour an aliquot of approximately 10mL of sample into a glass test tube and judge the colour observed. Consider one of the following options:

(1) Light brown
(2) Brown
(3) Dark brown
(4) Light green
(5) Green
(6) Dark green
(7) Clear
(8) Other specify

Odour

Determining the odour should always be done in the field, as soon as possible after collecting a sample. After collection, fill a cleaned odourless bottle half-full of sample, insert stopper, shake vigorously for 2-3 seconds and then quickly smell the odour. Alternatively, pour an aliquot of approximately 5mL of sample into a glass test tube and judge the odour. Consider one of the following options:

(1) Odour free
(2) Rotten eggs
(3) Burnt sugar
(4) Soapy
(5) Fishy
(6) Septic
(7) Aromatic
(8) Chlorinous
(9) Alcoholic
(10)   Unpleasant

Temperature

Water temperature should be measured in degrees Celsius, using a mercury thermometer or a thermistor. Normally, if temperature is measured electronically using a thermistor this device is built into an instrument which is capable of making other water quality measurements (e.g., pH and EC). Whenever possible, the temperature should be measured by directly dipping the thermometer in the natural body of water being studied. In case it is not possible, collect about 500 mL sample in a plastic or glass container and measure temperature by immersing the thermometer in the sample. Read the temperature after equilibration (no more change in the temperature reading). Report the Temperature on the sample identification form in degrees Celsius with 1 digit after the decimal point e.g. $13.2\,^{o}C$.

pH

The most accurate method of measuring water pH in the field is by means of a portable purpose designed meter. Such meters are normally capable of measuring pH to the nearest 0.05 of a pH unit by using a 'glass' and a 'reference' electrode (although these are often combined in a single probe). Before measuring pH, it is necessary to calibrate the meter. This should be done at least once per day, before the first pH measurement is attempted. The procedure of this is as follows:

➢ After removing their protective caps, the electrodes are rinsed in distilled water and carefully blotted dry with soft absorbent paper. *NOTE: Care needs to be exercised here as the electrodes are very fragile.*
➢ The electrodes are then placed in a fresh buffer solution and after following time for meter stabilisation, the pH reading of the meter is adjusted to the pH the buffer solution (normally pH = 7).
➢ The electrodes are then rinsed again with distilled water and blotted dry.
➢ If a pH measurement is not to be taken immediately, the electrodes should be replaced in their protective caps. Normally, the glass electrode cap is filled with distilled water before replacement to prevent the electrode drying out.

➢ Report the pH on the sample identification form in pH units showing one digit after the decimal point, e.g. 7.6.

Once calibrated, the pH meter can be used to measure the pH directly by placing the electrodes in water sample immediately after it is obtained. Care should be taken to ensure that the electrodes are rinsed with distilled water before and after each determination and that distilled water is placed in to the glass electrode cap for transportation.

Electrical Conductivity (EC)
EC can be measured in the field with a purpose-designed meter, see section 2.3. Before measuring conductivity it is necessary to calibrate the meter. This should be carried out at least once per day, before the first measurement is taken. Calibration is achieved by determining the conductivity of a known, fresh solution of potassium chloride and adjusting the meter accordingly. In order to ensure the conductivity reading is accurate, it is necessary to adjust the conductivity reading to compensate for temperature changes. In most modern meter this is done automatically. Once calibrated, the conductivity of the water can be measured by immersing electrode in a sample of water as soon as it is taken. It is important to remember that conductivity meters often take some minutes to stabilise. The reading must, therefore be taken after this stabilisation has occurred. Report the EC at 25° C preferably in μmhos/cm with no figure after the decimal point, e.g. 1135 μmhos/cm.

Documentation of sampling and analysis
A special form has to be prepared where the details of the sampling event and the in-situ/on site analysis can be filled in. The form ("field data protocol") should at least contain room for the following items:

Field Data protocol

  a. Sampling team members
  b. Date and time (24 hr method) of collection (time span in case of composite - sampling)
  c. Nature of the sample: spot/composite/integrated
  d. Results of performed in-situ/on site analyses (water/air temperature, dissolved oxygen, pH (field or lab), conductivity (field or lab), turbidity, macrofauna composition (BMWP score), macrofauna diversity (SCI), and 24 hr oxygen production / respiration ratio)
  e. Exact sampling location (location along the river, distance from shore) and depth of collection
  f. Definition of sampling intervals and volumes in case of composite sampling
  g. Maximum depth of the river, lake and current velocity in case of river (only if actually measured with a current meter)
  h. Weather conditions with respect to clouds, precipitation, wind (direction and force)
  i. Consistency of sediment (sandy, silty etc.)

j. Comments on smell, colour, discharges etc.
k. Parameter(s) that will be analyzed
l. Sample bottle (number, type, material, volume, and an indication if a preservative is already present)
m. The method of preservation/storage

Especially if a large number of different sample bottles have to be filled for various observations, it is convenient to have a space on the form to tick-off when the sample has been collected. At the end of the sampling event it is then easy to check, if all samples have been collected in the correct number.

Analytical result sheets
When offering the samples to the analytical laboratory, each and every series of replicate sample containers has to be accompanied by a prefilled "result sheet". This sheet is marked with sample specifications identical to the specs marked on the bottle. The individual parameters to be measured in the sample are tabulated, together with the units they should be reported in. The sheet leaves space for the analytical lab to fill in the results of replicate analysis.

10. Step 6: Laboratory Work

Work Assignment and Personnel Register
- The laboratory incharge should maintain a bound register for assignment of work. This register would link the lab. sample number to the analyst who makes specific analyses, such as pH, EC, BOD, etc.
- An estimate of time needed for performing the analyses may also be entered in the register.
- Each laboratory analyst should have his/her own bound register, where all laboratory readings and calculations are to be entered.
- When analysis and calculations are completed, the results must be recorded in a register containing data record sheets described in the next section.

Laboratory Analysis
The laboratory analysis is to be performed by the laboratory staff within stipulated time and precision. It is observed that many laboratories have their own procedures traditionally being followed. Not only that they also use different units to present the results and sometimes many digits after decimal. This create un-necessary problem in integrating the results. In order to make the procedures uniform and also presentation methods uniform a guideline is prepared. The analytical methods are prescribed for each parameter along with measurement unit and significant figure in the following table 5. It is important that all the agencies monitoring water quality and putting the data on website through EDB use the table 5 strictly.
Table 5:
Measurement methods, units and significant figures for different paprametrs used in water quality monitoring

Parameters	Unit	Measurement Methods	Significant figures after Decimal

Colour	-	Visual method	
Odour	-	Manual	
Temperature	°C	Thermameter	1
pH	-	pH meter	1
Electrical Conductivity	µS/cm	Conductivity meter	0
Dissolved Oxygen	mg/L	DO Meter or Winkler modified method	1
Turbidity	NTU	Nephelometer	1
Total Dissolved Solids	mg/L	Gravimetry	0
Ammonical Nitrogen (NH_4-N)	mgN/L	Colorimetry	1
Nitrite + Nitrate-N	mgN/L	Colorimetry	1
Total Phosphate	mg/L	Colorimery	4
Orthophosphate	mg/L	Colorimetry	4
Biochemical Oxygen Demand (BOD)	mg/L	DO consumption in 3 days at 27 °C	1
Chemical Oxygen Demand (COD)	mg/L	Potassium dichromate method	1
Sodium	mg/L	Flame photometry	1
Potassium	Mg/L	Flame photometry	1
Calcium	$mgCaCO_3$/L	EDTA Titrimetric	1
Magnesium	mg $CaCO_3$/L	EDTA Titrimetric	1
Carbonate as CaCo3	mg $CaCO_3$/L	Titrimetric	1
Bicarbonate, as CaCo3	mg $CaCO_3$/L	Titrimetric	1
Chloride	mg/L	Argentometric titration	1
Sulphate	mg/L	Turbidimetry	1
Fluoride	mg/L	Ion meter, Colorimetry	2
Boron	mg/L	Ion meter, curcumin method	2
Total Coliform	No./100mL	MPN or MF method	0
Fecal Coliform	No/100mL	MPN or MF method	0
% Sodium	-	Calculation	2
SAR	-	Calculation	2
1 Specific Parameters			
Arsenic	µg/L	Cold vapour AAS	1
Mercury	µg/L	Cold Vapour AAS	1
All other heavy metals	µg/L	AAS	1

Pesticides and other organics	µg/L	GC, GCMS	1

11.   Step 7: Data Management

Data Storage and Validation
- A recommended format for recording data is given in EDB. It includes all parameters, except heavy metals and trace organics that may be analysed in the water quality monitoring programme currently envisaged. Note that ordinarily a sample would NOT be analysed for all the listed parameters in EDB.
- Record of analyses for heavy metals and trace organics, which would be performed on a limited   number of samples, would be kept separately in a similar format.

Data Validation
- Absolute checking/Data entry
- Checking if data is within the detection limits of a particular method
- Checking if the data is within the expected ranges for a parameter
- Checking if there are too many (or too few) significant digits reported
- Checking if data are physically or scientifically possible (general checks)
- Checking correlation of parameters (Some conditional checks like BOD/COD relation, TC/FC relation)
- Checking the correlation between EC and TDS
- Checking cation/anion balance
- Total coliforms must be greater than faecal coliforms
- Total iron must be greater than dissolved iron
- Total phosphorus must be greater than dissolved (ortho-)phosphorus
- Total iron must be greater than dissolved iron

General checks:

Total solids	$\geq$ Total dissolved solids
Total solids	$\geq$ Total settleable solids
COD	> BOD
Total Coli	$\geq$ Faecal Coli
Total Iron	$\geq Fe^{+2}, Fe^{+3}$
Total P	$\geq PO4^{-3}$
EC (µS/cm)	$\geq$ TDS (mg/l)
Total oxidized nitrogen	$\geq$ Nitrate, nitrite
Total oxidized nitrogen	= Nitrate + nitrite
Total hardness	= Ca hardness + Mg hardness

Conditional Checks
When there are known correlations between one or more water quality parameters these can be used to
Some of the more well known correlations between parameters are:
- Total dissolved solids specific conductance

- pH and carbonate species
- pH and free metal concentrations
- Dissolved oxygen and nitrate
- If pH <8.3 then Carbonate = 0
- If DO = 0, then nitrate = 0
- If DO >0, then nitrate >0
- If DO > 7m, then ferrous ions = 0
- If nitrite >0, then ferrous ions = 0
- If ferrous ions >0, then nitrite = 0

Data Analysis and Presentation

It is often useful to subject data to some simple statistical analysis. It may be, for example, that such an analysis could be used to summarise the data; to transform them to aid understanding or to compare them with a water quality standard that is couched in statistical terms (annual mean, standard deviation, trend, seasonal changes or a percentile for certain parameters). The data can also be summarized in form of index. Statistical analysis like parametric correlation, seasonal fluctuations, seasonal trends over a period of time are also common. The data after analysis can be presented in different format. For a river usually river profiles are commonly presented. For groundwater contours are plotted over a geographical area.

Graphical Presentation

1. Time Series Graphs
2. Histograms
3. Pie Charts
4. Profile Plots (river profiles)
5. Geographical Plots (contours)

Data Interpretation

The data interpretation involves understanding on the water chemistry, biology and hydrology. Normally data analysed and interpreted in terms of chemical quality, quality fluctuations, and their possible effect on different uses and ecosystem. A comparison is made with predefined criteria or standards set for protection of different uses. The quality fluctuation are explained in view of possible sources of pollution and their fates in aquatic environment and their effects.

12.   Step 8: Quality Assurance

The QA programme for a laboratory or a group of laboratories should contain a set of operating principles, written down and agreed upon by the organisation, delineating specific functions and responsibilities of each person involved and the chain of command. The following sections describe various aspects of the programmes

Sample control and documentation: Procedures regarding sample collection, labelling, preservation, transport, preparation of its derivatives, where required, and the chain-of-custody.

Standard analytical procedures: Procedures giving detailed analytical method for the analysis of each parameter giving results of acceptable accuracy.

Analyst qualifications: Qualifications and training requirements of the analysts must be specified. The number of repetitive analyses required to obtain result of acceptable accuracy also depends on the experience of the analyst.

Equipment maintenance: For each instrument, a strict preventive maintenance programme should be followed. It will reduce instrument malfunctions, maintain calibration and reduce downtime. Corrective actions to be taken in case of malfunctions should be specified.

Calibration procedures: In analyses where an instrument has to be calibrated, the procedure for preparing a standard curve must be specified, e.g., the minimum number of different dilutions of a standard to be used, method detection limit (MDL), range of calibration, verification of the standard curve during routine analyses, etc.

Data reduction, validation and reporting: Data obtained from analytical procedures, where required, must be corrected for sample size, extraction efficiency, instrument efficiency, and background value. The correction factors as well as validation procedures should be specified. Results should be reported in standard units. A prescribed method should be used for reporting results below MDL.

An important aspect of reporting the results is use of correct number of significant figures. In order to decide the number of significant digits the uncertainty associated with the reading(s) in the procedure should be known. Knowledge of standard deviation will help in rounding off the figures that are not significant. Procedures regarding rounding off must be followed.

Analytical quality control: This includes both *within-laboratory* AQC and *inter-laboratory AQC.*

Under the within-laboratory programme studies may include: recovery of known additions to evaluate matrix effect and suitability of analytical method; analysis of reagent blanks to monitor purity of chemicals and reagent water; analysis of sample blanks to evaluate sample preservation, storage and transportation; analysis of duplicates to asses method precision; and analysis of individual samples or sets of samples (to obtain mean values) from same control standard to check random error. Inter-laboratory programmes are designed to evaluate laboratory bias. It may be added that for various determinands all of the AQC actions listed may not be necessary. Further, these are not one time exercises but rather internal mechanisms for checking performance and protecting laboratory work from errors that may creep in. Laboratories who accept these control checks will find that it results in only about 5 percent extra work.

Within Laboratory Exercise
Shewhart Control Chart
If a set of analytical results is obtained for a control sample under conditions of routine analysis, some variation of the observed values will be evident. The information is said to be statistically uniform and the analytical procedure is said to be under statistical control if this variation arises solely from random variability. The function of a control chart is to identify any deviation from the state of statistical control.

Shewhart control chart is most widely used form of control charts. In its simplest form, results of individual measurements made on a control sample are plotted on a chart in a

time series. The control sample is analyzed in the same way as the routine samples at fixed time intervals, once or twice every week, or after 20 to 50 routine samples.

Assuming the results for the control sample follow the Normal frequency distribution, it would be expected that only 0.3% of results would fall outside lines drawn at 3 standard deviations above and below the mean value called upper and lower control limits, UCL and LCL, respectively. Individual results would be expected to fall outside these limit so seldom (3 out of 1000 results), that such an event would justify the assumption that the analytical procedure was no longer in statistical control, i.e., a real change in accuracy has occurred.

The chart is constructed from 20 or more replicate analysis results of a control or standard samples. Two lines are inserted on the chart at 2 standard deviations above and below the mean value called upper and lower warning limits, UWL and LWL, respectively. If the method is under control, approximately 4.5% of results may be expected to fall outside these lines.

This type of chart provides a check on both random and systematic error gauged from the spread of results and their displacement, respectively. Standard Methods lists the following actions that may be taken based on analysis results in comparison to the standard deviation.

Control limit: If one measurement exceeds the limits, repeat the analysis immediately. If the repeated analysis result is within the UCL and LCL, continue analyses; if it exceeds the action limits again, discontinue analyses and correct the problem.

Warning limit: If two out of three successive points exceeds the limits, analyse another sample. If the next point is within the UWL and LWL, continue analyses; if the next point exceeds the warning limits, discontinue analyses and correct the problem.

Standard deviation: If four out of five successive points exceed one standard deviation, or are in increasing or decreasing order, analyse another sample. If the next point is less than one standard deviation away from the mean, or changes the order, continue analyses; otherwise discontinue analyses and correct the problem.

Central line: If six successive points are on one side of the mean line, analyse another sample. If the next point changes the side continue the analyses; otherwise discontinue analyses and correct the problem.

Figure 8.5 to Figure 8.6 illustrate the cases of loss of statistical control for analysis of individual samples based on the above criteria.

Precision: The most important parameter to evaluate in the results is the precision. The statistical term to evaluate precision is standard deviation. The numerical value of the standard deviation depends on the average concentration (standard deviation also has the unit of concentration). Numerical values of standard deviations of low concentration solutions are usually smaller than those of solutions with higher concentrations. Therefore the coefficient of variation, defined earlier, should be used to evaluate precision. This is particularly useful when comparing results of analysis for samples having different concentrations. Before evaluating the results one should answer the question 'what is the desired precision for an analyses?'. In fact this question should be answered by the so called 'data users'. The use of the data determines the required precision, e.g. detection of trends may require more precise results (in order to actually detect small changes with time) than checking water for use, say for irrigation.

Laboratory staff should always ask for the purpose for which they are performing the requested test.

As a minimum goal for precision, however, the precision that can be obtained by correctly and adequately following the method prescribed by the APHA Standard Methods for the examination of water and wastewater may be adopted

Calculating revised limits when continuing the exercise: Warning and control limits should be recalculated periodically. Especially when new techniques are introduced, the precision improves when experience is gained with the technique. A good time for recalculating the control and warning limits is at the time when the control chart is full and a new graph has to be created anyway. At this point, use the 20 most recent data on the old chart for construction of LCL, LWL, average, UWL and UCL.

Errors that cannot be detected by within-laborartory AQC: The within-laboratory AQC exercise focusses mainly on precision. A laboratory on its own cannot detect many sources of bias. A good example to illustrate this is the total hardness method. If the analytical balance in a lab always reads 10% too much all solution prepared will have a 10% higher concentration: the Standard $CaCO_3$ solution, the EDTA titrant and also the control sample containing $CaCO_3$. This error can only be detected by analysing a sample prepared by a laboratory with a correctly functioning balance. The current laboratory will underestimate the concentration of such a inter-laboratory sample by 10% because their EDTA titrant is '10% too strong'. In some cases freshly introduced bias may be detected. For example, if the measurements consistently fall on one side of the previously calculated mean, it indicates a freshly introduced bias.

Inter-Laboratory AQC

CPCB regularly carry out Inter-laboratory AQC involving about 140 laboratories in the country.

The objectives of an *inter*-laboratory AQC programme are:

1 To test for possible bias in measurements in a laboratory.
2 To provide direct evidence of comparability of results among laboratories in a common water quality monitoring programme. Some related objectives and benefits are listed below:

- to assess the status of analytical facilities and capabilities of participating laboratories.

- to identify the serious constraints (random & systematic) in the working environment of laboratories.

- to provide necessary assistance to the concerned laboratories to overcome the short comings in the analytical capabilities.

- to promote the scientific and analytical competence of the concerned laboratories to the level of excellence for better output.

- to enhance the internal and external quality control of the concerned laboratories

Inter-laboratory AQC should form the routine part of monitoring programme. Such exercises will give more confidence on results.

13. Guidelines on Management Aspects

Following important aspects are included:

a. Before planning for any water quality monitoring programme ensure that adequate resources are available as prescribed.

b. Ensure that every body who is involved in monitoring is fully aware of the objectives, procedures, time schedule, quality assurance and importance of this programme.

c. Ensure that people are motivated and working with full interest.

d. Ensure that accountability of every body is fixed.

e. Ensure that there is enough communication among all the groups involved in monitoring.

f. All the field data collected should be properly transferred to the laboratory people.

g. Data should be transferred as soon as acquired through electronic mean (EDB).

h. Adequate funds are available with the field staff and laboratory people to take care of emergency measures.

i. Private transport facility should be available to the sampling team.

j. There should be annual maintenance contract (AMC) for the repair and maintenance of laboratory equipment/instruments.

k. There should be regular AQC exercises both internal and external and the results of these exercises are available to any body.