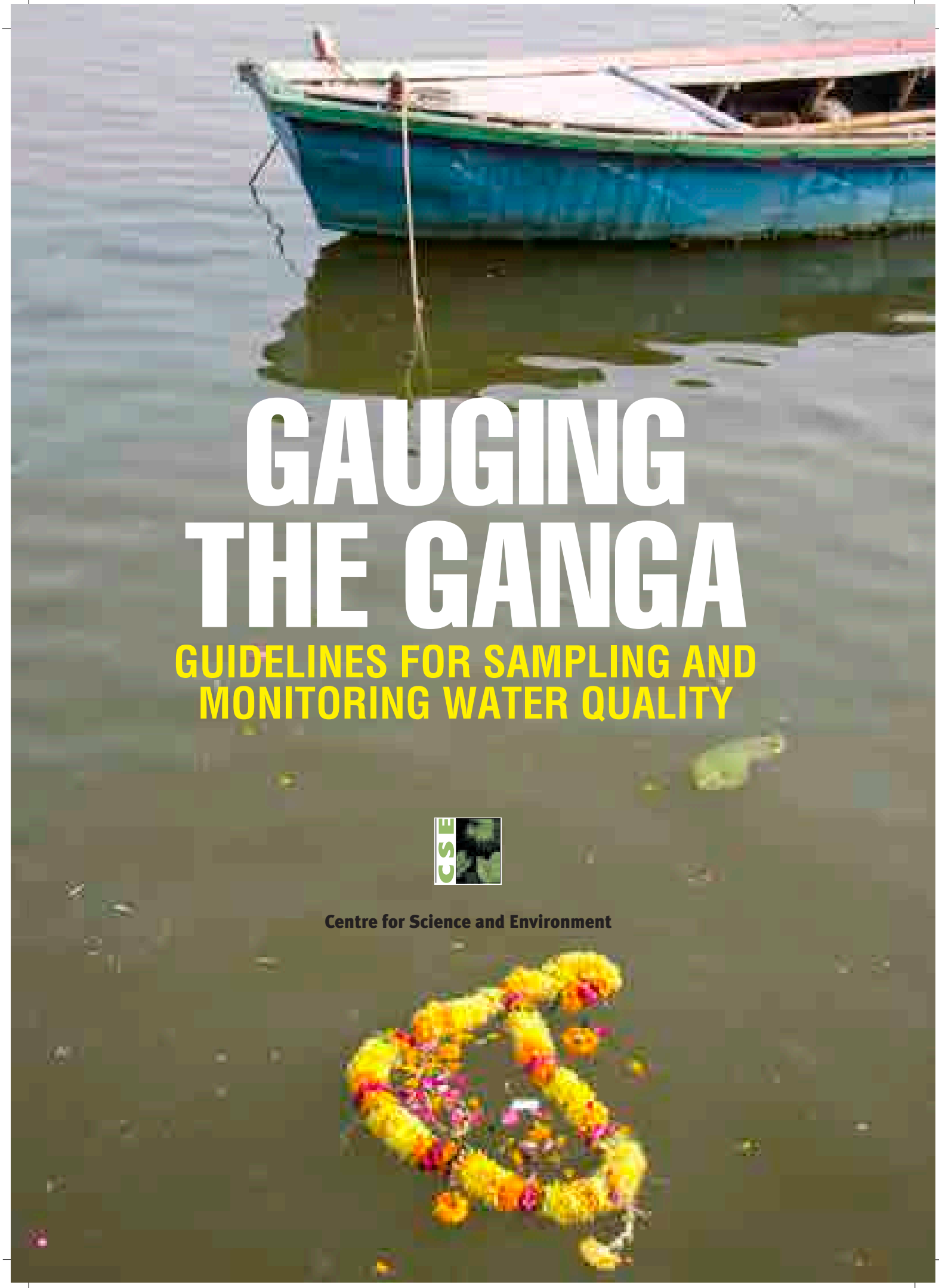

GAUGING THE GANGA

GUIDELINES FOR SAMPLING AND MONITORING WATER QUALITY

Centre for Science and Environment

Research direction: Chandra Bhushan

Writer: Dr DD Basu

Research support: Nivit Kumar Yadav and Rahul Singh

Editor: Arif Ayaz Parrey

Design and cover: Ajit Bajaj

Layout: Kirpal Singh

Production: Rakesh Shrivastava, Gundhar Das

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Phone: 91-11-40616000
Fax: 91-11-29955879
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GAUGING THE GANGA

GUIDELINES FOR SAMPLING AND MONITORING WATER QUALITY

Centre for Science and Environment

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Introduction

The objective of water quality management, as stated in the preamble of the Water (Prevention and Control of Pollution) Act, 1974, is to provide for the prevention and control of water pollution and the maintaining or restoring of wholesomeness of water.

Section 2 of the Act defines pollution as 'such contamination of water or such alteration of the physical, chemical or biological properties of water or such discharge of any sewage or trade effluent or any other liquid, gaseous or solid substance into water (whether directly or indirectly) as may or is likely to create a nuisance or render such water harmful or injurious to public health or safety, or to domestic, commercial, industrial, agricultural or other legitimate uses, or to the life and health of animals or plant or aquatic organisms.' Wholesomeness of water refers to the physicochemical characteristics that harbour aquatic flora, fauna and ensure various uses for human beings in aquatic ecosystems that act as a dynamic biological machine.

Logically, therefore, water quality management not only restores or maintains aquatic ecosystems but also ensures legitimate use of rivers. This requires proper monitoring to ensure balance between use and quality control.

Water quality is a complex subject. It requires monitoring and management of a wide range of parameters. In case of monitoring of a riverine system, a number of monitoring stations are needed along the length of the system, to measure the ever-changing hydrological and anthropogenic activities. The spatial and technical range of monitoring needs to be housed within a uniform protocol so that the generation of data is comprehensive and synergized.

Though some guidelines exist for water quality monitoring in the country and abroad, specific protocols for particular riverine systems streamlines the processes to a large extent. Centre for Science and Environment (CSE) is developing a water quality monitoring programme for River Ganga.

In this document, CSE suggests a standard protocol for Ganga monitoring. The document is divided into two parts. The first part presents an outline of water quality monitoring protocol, by borrowing judiciously from the experiences of guidelines developed by several agencies, both international and national. The second part presents CSE's proposal for the water quality monitoring programme.

PART 1

OUTLINE FOR THE WATER QUALITY MONITORING PROGRAMME (RIVERINE)

1. Monitoring

The International Organization for Standardization (ISO) defines water quality monitoring as the programmed process of sampling, measurement and subsequent recording or signaling or both, of various water characteristics, often with the aim of assessing conformity to specific objectives. This general definition can be differentiated into three types of monitoring activities that distinguish between continuous short-term and long-term monitoring programmes as follows:

- Surveillance is continuous, specific measurement and observation for the purpose of water quality management and operational activities.
- Surveys are finite duration, intensive programmes to measure and observe the quality of the aquatic environment for a specific purpose.
- Monitoring is the long-term, standardized measurement and observation of the aquatic environment in order to define status and trends.

1.1 MONITORING PROGRAMME

Monitoring is systematic observation in order to draw inferences (prediction) about an experiment or phenomena for which it is designed. Systematic observation refers to periodic observation with regular intervals. It consists of three important sub-components:

- When (how often) to observe→ Frequency of observation in science refers to measurement
- What to measure→ Parameters to be defined
- Where to sample→ Location of sampling point

1.2 MONITORING STRATEGY

The main strategy of designing a water quality monitoring programme is minimizing the cost of monitoring without sacrificing the quality and detail of the information sought by the process. Information refers to the variability in spatial and temporal trends. Spatial variability is generally governed by factors like water withdrawn and wastewater discharged, whereas temporal variability is caused by seasonal and yearly variations. In general, hydraulic and hydrological factors are responsible for all variations, and thus it is necessary to have background information of the river basin.

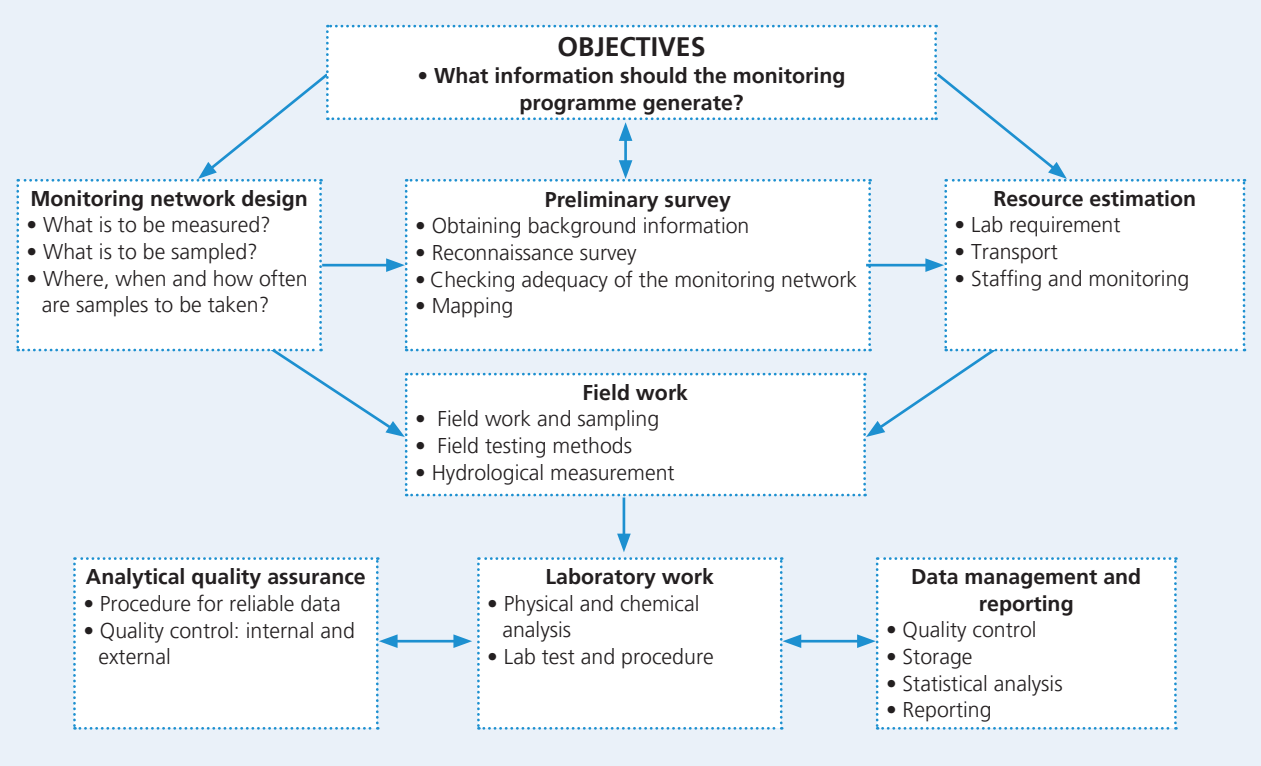
In a long river, the number of sampling points will be high, increasing the cost of analysis. Measuring more parameters—and doing it frequently—will keep adding to the overall cost.

It is, therefore, necessary to assess the resources for monitoring. Scoping and designing of water quality monitoring programme must be based on a clear understanding of:

- Relevant background information of the riverine system
- Monitoring objective(s)
- Desired outcomes
- Appropriate methods
- The dynamics and characteristics of the water system

Within this background the strategy to monitor water quality is summarized in *Figure 1: Strategy to monitor water quality.*

Figure 1: Strategy to monitor water quality



Source: *Water quality monitoring—a practical guide to the design and implementation of fresh water quality studies and monitoring programme*, UNEP/WHO

2. Eight steps towards a water quality monitoring programme

Water quality monitoring programme involves eight steps as illustrated in *Figure 2: Steps to monitor water quality*.

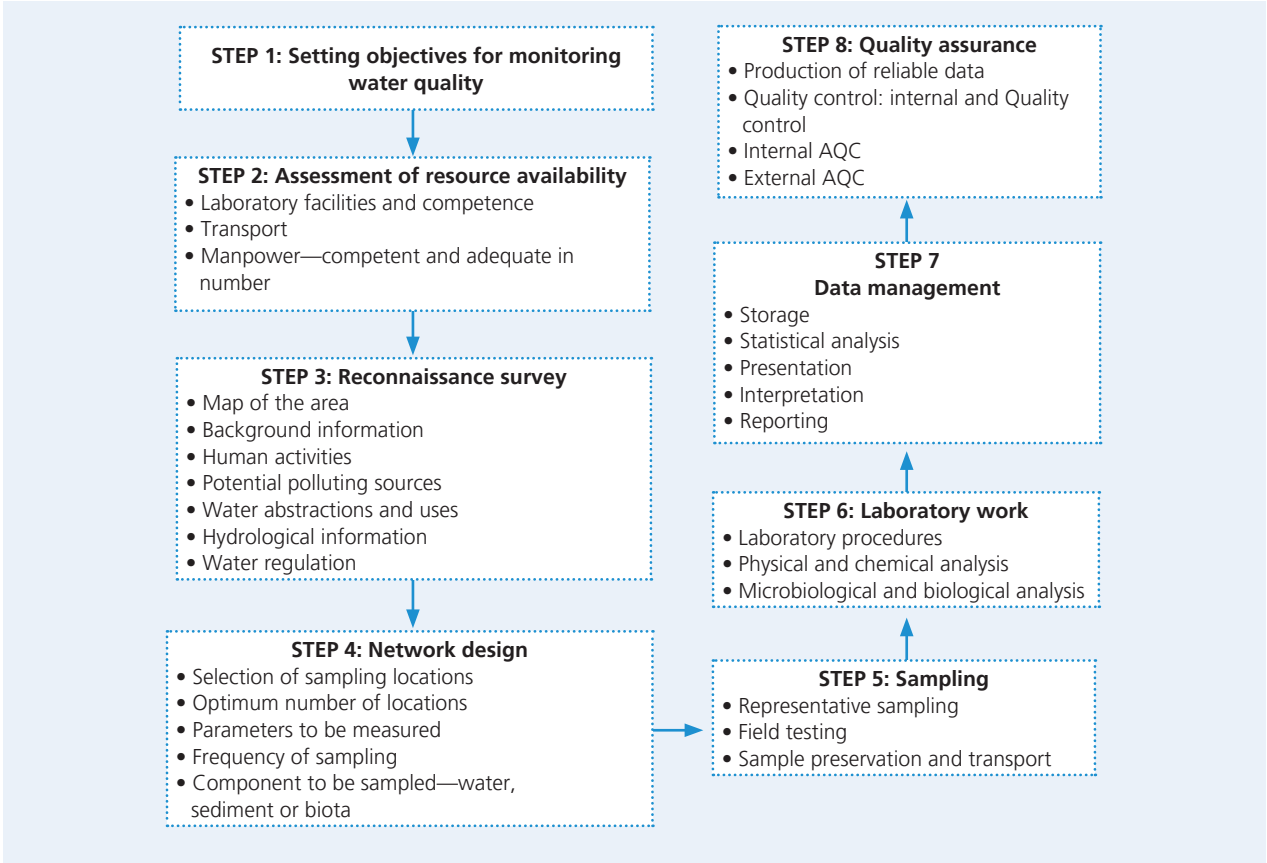
Guidelines to accomplish these eight steps are provided as follows.

2.1 SETTING WATER QUALITY OBJECTIVES

Before formulating any water quality monitoring programme, it is very important to have a clear understanding on the objectives of the monitoring. Water quality monitoring has various purposes, which are summarized as follows:

- Signal or alarm functions for detecting sudden adverse changes in the environment. The monitoring systems should preferably be able to track the causes of the changes immediately.
- Control functions to assess the general quality of the water in relation to adopted water quality requirements or objectives, checking permitted effluent quality compliance, and for verification of the effect of pollution control strategies.
- Trend (recognition) functions to enable the prediction of future developments.

Figure 2: Steps to monitor water quality



Source: *Guidelines for water quality monitoring*, CPCB (MINARS/27/2007–08

Keeping these purposes in mind, the objectives of water quality monitoring may be stated as follows:

- Rational planning of pollution control strategies.
- Identification of the nature and magnitude of the pollution control required.
- Evaluation of the effectiveness of pollution control of effluent discharge.
- Identification of the status and trends in water quality, both in terms of concentrations and effects.
- Identification of the mass flow of contaminants in surface waters and effluents.

Monitoring of water quality is essential to take preventive or curative measures to maintain the ecological balance of riverine systems. Continuous monitoring is also essential for the successful implementation of environmental legislations.

2.2 ASSESSMENT OF RESOURCES

Once the objectives of monitoring are known, it is important to consider the availability of resources for monitoring. Generally, a compromise is made between the quality and quantity of the data required to fulfil the objectives, and resource availability. Before planning a programme to monitor water quality, it is important to ensure that the following resources are available:

2.2.1 Sampling equipment

A basic list of requirements essential to carry out the survey smoothly are summarized in *Table 1: Checklist for field visits*.

2.2.2 Transport for sampling

Any vehicle hired or purchased to transport personnel for water quality sampling must be able to accommodate at least three people besides the driver, and should have enough space to spare for the sampling kit described in Section 2.2.1.

A sampling van can designed according to the following parameters:

- Seating for six passengers
- Length—6.065 m
- Width—1.975 m
- Height—2.550 m
- Fully air conditioned with portable generators
- Deep freeze facility available onboard
- Space for sampling kits, one folding table, and two folding chairs
- Multi-parameters box that can measure pH, dissolved oxygen (DO),

Table 1: Checklist for field visits

• Itinerary for the trip (route, stations to be covered, start and return time)	• Personnel and sample transport arrangements
• Area map	• Sampling site location map
• Icebox filled with ice or icepacks	• Weighed 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 kits, as required
• Sample identification form	• Labels for sample containers
• Field notebook	• Pens, pencils and markers
• Soap and towel	• Matchbox
• Spirit lamp	• Torch
• Drinking water	• Knife
• First-aid box	• Gloves and eye protection
• Dump sampler to check well conditions	• Submersible pump and accessories

Source: *Guidelines for water quality monitoring*, CPCB (MINARS/27/2007–08

Table 2: Three-tier laboratory manpower

S. no.	Job description	Qualification
1	Supervisor	M.Sc. in chemistry, life or environmental sciences with at least five years' experience
2	Analysis and sampling	M.Sc. in chemistry, life or environmental science with at least three years' experience, or B.Sc. with eight years' experience
3	Lab/field attendant	Higher secondary with science

Source: Dr DD Basu/CSE

conductivity (can be placed in table drawer with provision of keeping it in a fixed position
- One rack to hold the sample and reagent bottles

2.2.3 Laboratory facilities

A water laboratory with a floor area of at least 100 sq m is a must. It should have dedicated areas as follows:

- Analytical lab
- Balance room
- Instrument room
- Microbiology lab
- Space for sample receipt and storage room
- Staff room with computer facilities

There should also be dedicated spaces for distillation assembly, sample digestion, and the hood system. The laboratory should have a dedicated power supply and a DG set as a backup arrangement. Continuous water supply is also important.

2.2.4 Trained manpower

One of the most important factors for producing reliable analytical results in a laboratory is skilled and educated analysts in adequate numbers. Three-tier manpower is necessary, as stated in *Table 2: Three-tier laboratory manpower*.

2.2.5 Chemicals and glassware

Selection of laboratory chemicals of an appropriate quality is an important factor for achieving results with desired accuracy. The quality of chemicals or solvents used in the analytical laboratory may vary from laboratory grade to analytical or guaranteed grade (analar or AR or GR).

2.2.6 Funds for operation and maintenance of the laboratory and sampling programme

Generally, funds are needed for two purposes in the context of the laboratory:

- Infrastructure, including purchasing of equipment, instruments, laboratory furniture, and civil works.
- Operation and maintenance cost for day-to-day activities, including salary of manpower, cost for sampling, glassware and chemicals. Maintenance of instruments and equipment is included in the operation and maintenance cost.

3. Identification of monitoring stations

One of the most important aspects of water quality monitoring is the identification of location of sampling (monitoring station). Monitoring stations can be of many types, as described in the next section.

3.1 TYPES OF MONITORING STATIONS

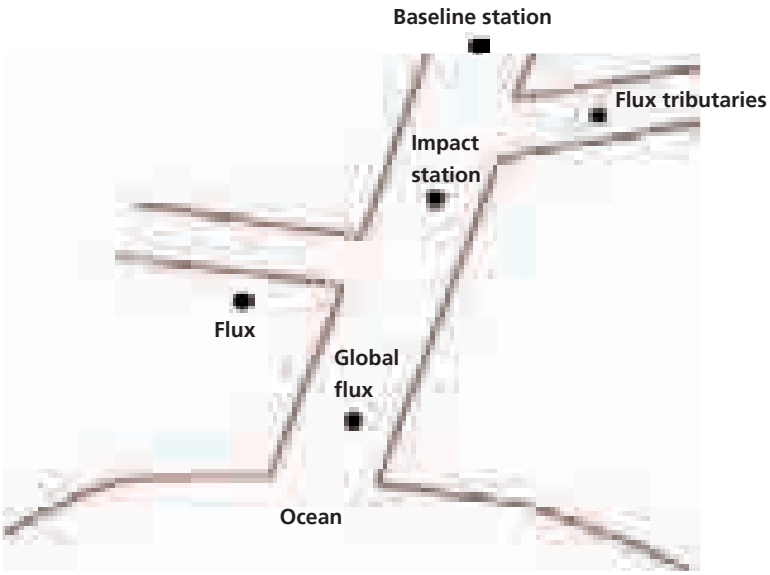
- **Baseline station** refers to a monitoring location where no human activities affect water quality.
- **Flux station** refers to a monitoring location where the pollution load is discharged by tributaries, irrigation or storm-water drains etc. into the mainstream.
- **Trend station** refers to a monitoring location designed to show how the parameters at a specific point on a water course vary over time due to the influence of human activities.
- **Impact station** refers to a station where a pollutant is mixed with water of the mainstream (see *Figure 3: Types of monitoring stations*).

3.2 GENERAL CRITERIA FOR SELECTING SITES

The following is the general criteria for selecting appropriate sampling sites:

1) Always have a reference station upstream from all possible discharge points. The usual purpose of a monitoring exercise is to determine the degree of man-induced pollution and damage caused to aquatic life. The reference station provides data on the original quality of the water and its biological aspects, which may vary locally and regionally.
2) Intake points of drinking water, bathing *ghats*, and irrigation canal take-off points should be considered for monitoring.
3) Sampling stations should be located upstream and downstream of significant pollution outfalls, such as city sewage

Figure 3: Types of monitoring stations



Source: Dr DD Basu/CSE

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 a well-mixed zone. A homogeneity test must be performed to identify the 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 such as Ganga, Yamuna, Narmada, Krishna and Godavari, where mixing is poor and incomplete, the effluent may tend to follow one bank. Stations on both sides are useful to make an estimate of the extent of the mixing.
7) In large rivers, a balance has to be found between the selection of a few stations giving poor coverage, and selection of more stations with different substrates and dissimilar fauna that cannot be compared spatially.
8) To enable comparisons among sampling stations, it is essential that all stations be sampled around the same time. Not more than two weeks should elapse between sampling of the first and last stations in a river.
9) Sites for biological sampling stations should match sites for chemical sampling.
10) To estimate the oxygen exchange rate of a river, a measurement of the cross-section is required. Typically, every station should be aligned with the cross-section of the river.
11) Since the sampling team has to carry an appreciable burden of sampling gear and water samples in most cases, the distance they are able to walk is limited. Therefore, easily accessible sites should be selected. Sites should also be accessible under all weather conditions and river flows.
12) With respect to preservation, samples are taken to perform analysis on three types of parameter. For some parameters, such as heavy metals, the samples need not be preserved. For other parameters, samples can be reserved by cold storage or by addition of certain preventatives. 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.
13) Collection of samples should be avoided at locations where there is high turbulence or flow.
14) There are many disrupting influences in rivers, especially cattle wading, melon farming, fishing, sand recovery, etc. These 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.
15) Availability of sampling facilities, such as bridges and boats, and possibilities for wading, is important in the selection of sampling sites.

3.3 APPROACH TO SELECT A MONITORING STATION

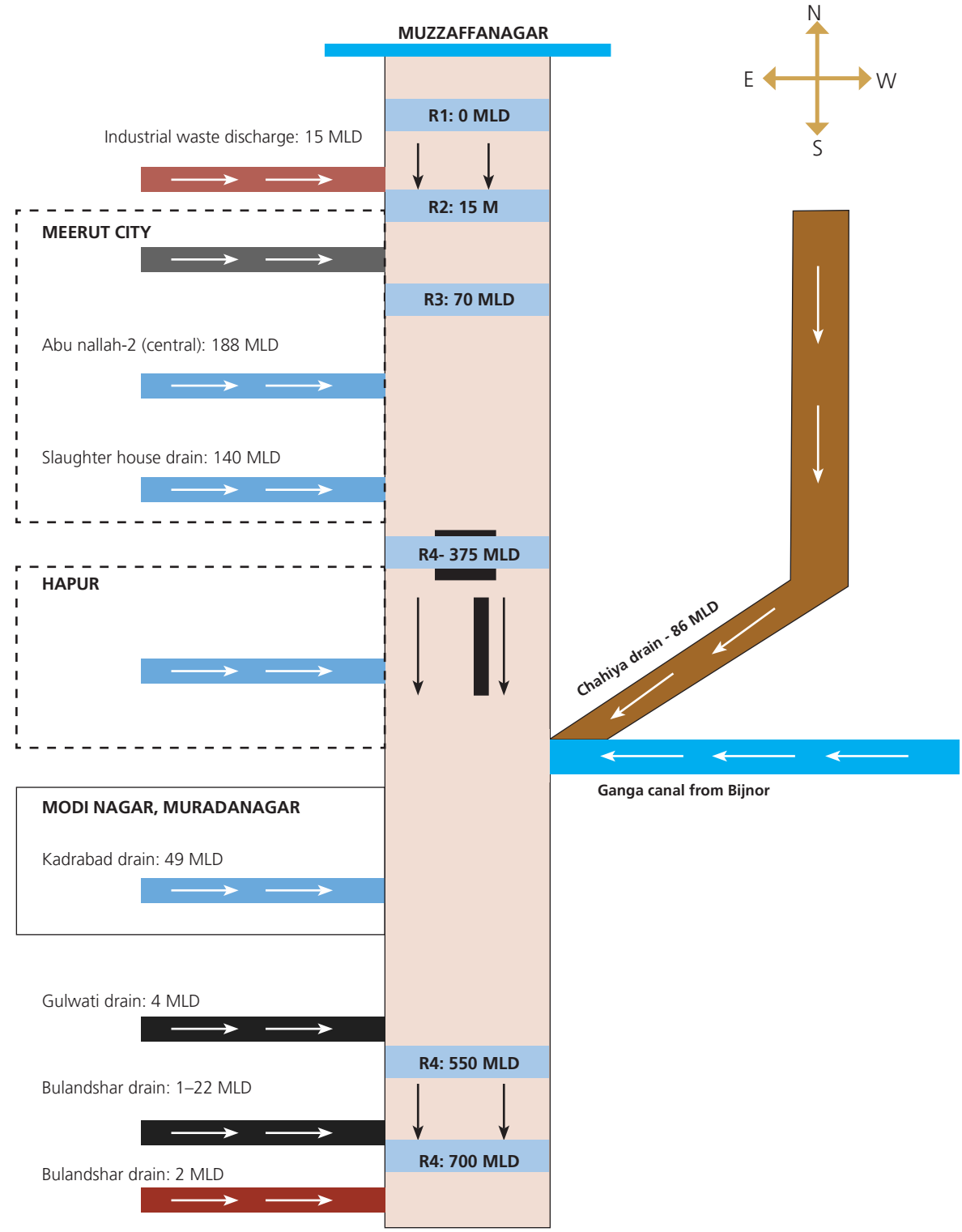
Four steps are involved in selecting a monitoring station, as follows:

- Reconnaissance survey
- Mixing zone
- Depth
- Minimum distance

3.3.1 Reconnaissance survey

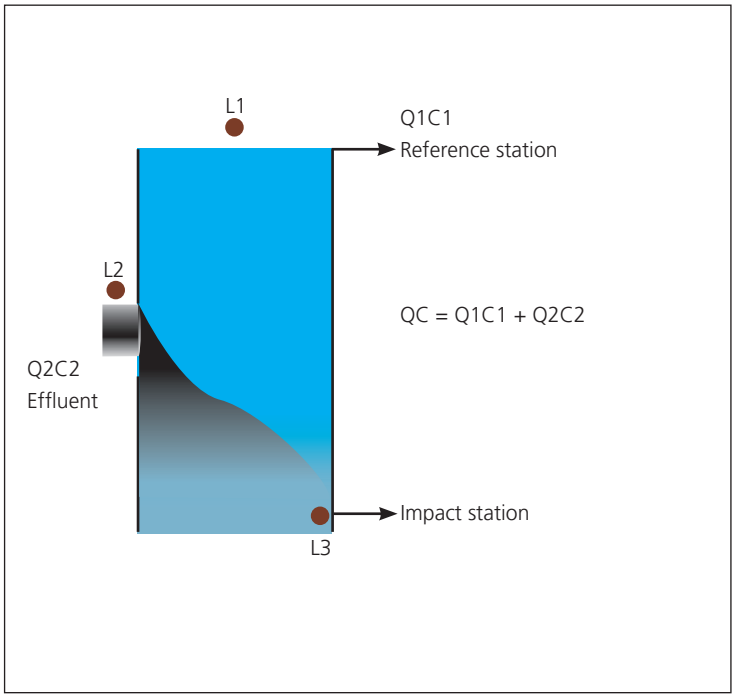
This survey will give an overview of the geographical location of the water body to be monitored, and its susceptibility to human influences to help decide appropriate sampling locations and the appropriate number of sampling locations.

Figure 4: Reconnaissance survey of pollution load of the river Kali and identification of monitoring stations



Source: CPCB

Figure 5: Mixing zone



Source: Dr DD Basu/CSE

Table 3: Mixing zone and depth

Average width (m)	Mean depth (m)	Estimated distance for complete mixing (km)
5	1	0.08–0.7
	2	0.05–0.3
	3	0.03–0.2
10	1	0.3–2.7
	2	0.2–1.4
	3	0.1–0.9
	4	0.08–0.7
	5	0.07–0.5
20	1	1.3–11
	3	0.4–4
	5	0.3–2
	7	0.2–1.5
50	1	8–70
	3	3–20
	5	2–14
	10	0.8–7
	20	0.4–3

Source: *Water quality monitoring—a practical guide to the design and implementation of fresh water quality studies and monitoring programme*, UNEP/WHO

The survey can include acquisition of the following information:

- Location map
- Background information of the water body
- Human activities around the water body, such as mass bathing, melon farming, cattle wading etc.
- Identification of potential polluting sources
- Water abstraction—quality and uses
- Water flow regulation—schedule, quality etc.
- Usage pattern

This information will help in proper designing of the network and planning the schedule for sampling. For example, *Figure 4: Reconnaissance survey of pollution load of the river Kali and identification of monitoring stations*, shows that all wastewater drains have been identified and the impact stations spotted on the river. There is one point where freshwater intake into the river is also identified, besides an impact station at the beginning of the baseline station.

3.3.2 Mixing zone or depth

This is one of the most important parameters for selecting the right point of sampling in a riverine system. After various point sources, such as tributaries, drainage from agriculture and urban systems and wastewater discharges from industries to the main stream of the water body are identified, water needs to be mixed well for sampling. Sampling, by definition, involves selection of elements from a collection in such a way that every element of the collection has the same chance of being selected. Thus, a sample with a specified number of items (objects or bits of information) is drawn from a population. Population is defined as a larger body of collection of items or objects.

Table 4: Minimum stations

Average discharge (cubic metre per second)	Type of stream or river	Number of sampling points	Number of sampling depths
< 5	Small stream	2	1
5–140	Stream	4	2
150–1,000	River	6	3
≥ 1,000	Large river	≥ 6	4

Source: *Water quality monitoring—A practical guide to the design and implementation of fresh water quality studies and monitoring programme*, UNEP/WHO

Representative samples are drawn after the water bodies merge so that representatives of all the merging water bodies are evenly collected. Otherwise, there is a greater chance of taking a sample of the domain of one water body over the other.

Experiments must be carried out to find the exact mixing zone of two water bodies. One such experiment with a sample of the cross-section of the main stream of the water body is shown in *Figure 5: Mixing zone*. The relation between the width and depth of the river, and the distance of mixing from the point source has been summarized in *Table 3: Mixing zone and depth*.

In India, programmes to oversee water quality monitoring programmes generally consider a depth of 1 meter and 1 km downstream from a point source as the depth and mixing zone respectively. The minimum number of stations on a river is generally decided on the basis of water discharge. UNEP and WHO guidelines suggest the number of stations with respect to discharge (see *Table 4: Minimum stations*).

It has also been observed that large rivers such as Ganga, Brahmaputra and Kaveri need one station every 10 km. Ganga, which has a length of 2,525 km, needs around 250 stations, but has only about 60 monitoring stations, i.e. one station per 40 km—baseline stations interspersed with impact line stations.

4. Water quality parameters and sampling frequency

4.1 PARAMETERS OF WATER QUALITY

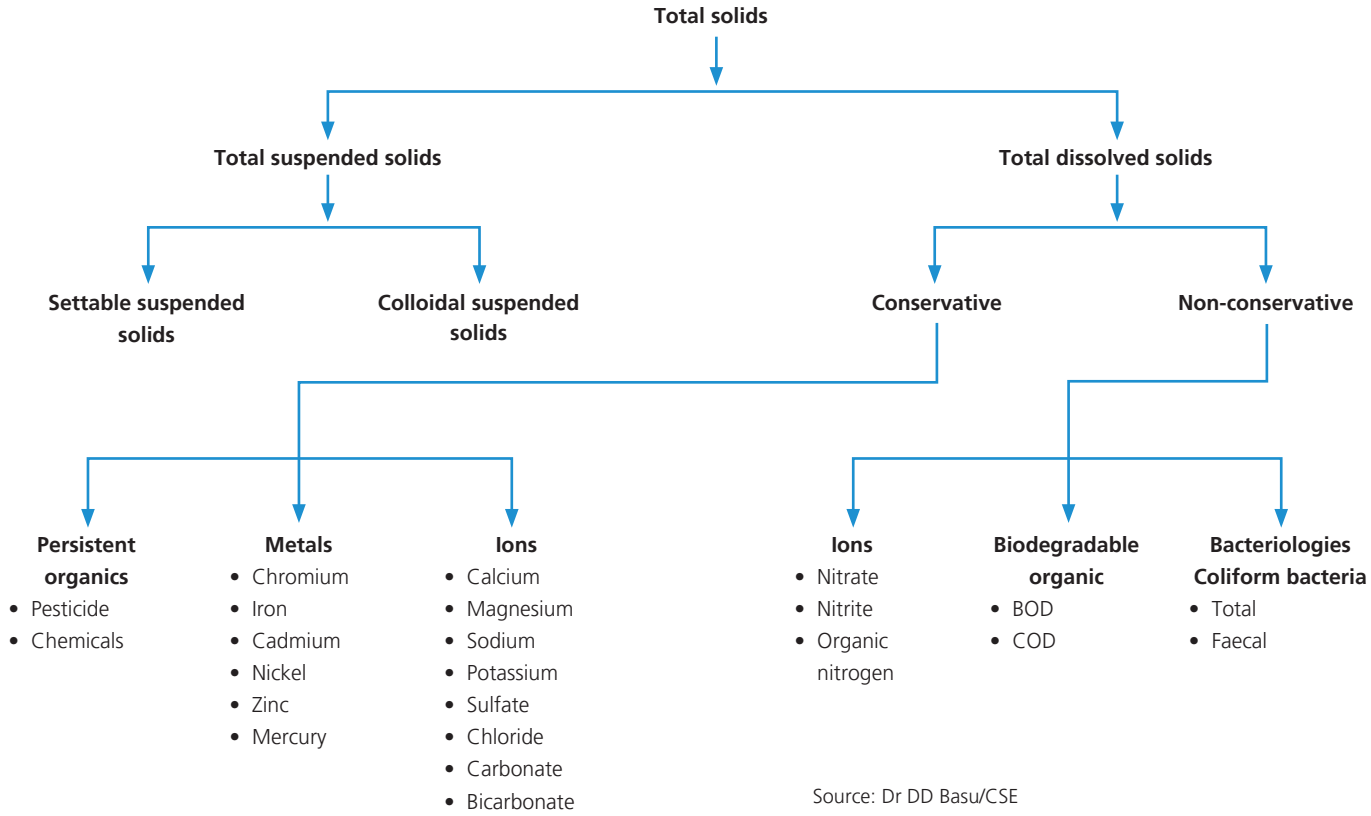
Water quality is a complex subject as water itself is a unique solvent. It dissolves a range of chemicals, including trace metals and organics, besides common ions and biodegradable organics, and a variety of microorganisms and planktons (see *Figure 6: Solids forming water quality*).

Common ions, biodegradable organics and Coliform bacteria are the dominating parameters of water quality, and they vary seasonally. The Central Pollution Control Board (CPCB), therefore, enlists them as core or general parameters in its monitoring programmes, including the national water quality monitoring programme (see *Table 5: List of parameters monitored under the national programme for monitoring water quality*).

4.2 SAMPLING FREQUENCY

Sampling frequency is governed by the level of variations in the quality of water. If large variations occur in a short duration of time, sampling needs to be done frequently. Variations in water quality could be of two types: random, and cyclic or seasonal. Variations are not predictable in the case of random variations, e.g., variations due to sudden rainfall in the catchment or unscheduled release of water from a dam. In such cases, increasing the frequency would not help much as it would not be possible to be cost effective in measuring such random

Figure 6: Solids forming water quality



Source: Dr DD Basu/CSE

Table 5: List of parameters monitored under the national programme for monitoring water quality

Observation	Core parameters (9)	General parameters (19)	Bio-monitoring (3)	Trace metals (µg/ml) (9)	Pesticides (30)
Weather	pH	Turbidity	Diversity index	Arsenic (µg/l)	Alpha BHC (µg/l)
Depth of main stream/depth of water table	Temperature	Phenolphthalein alkalinity, as ($CaCO_3$)	Saprobity index	Cadmium (µg/l)	Beta BHC (µg/l)
Colour and intensity	Conductivity (µmhos/cm)	Total alkalinity, as ($CaCO_3$)	P/R ratio	Copper (µg/l)	Gamma BHC (lindane) (µg/l)
Odour	Dissolved Oxygen (mg/l)	Chlorides (mg/l)		Lead (µg/l)	OP DDT (µg/l)
Visible effluent discharge	BOD (mg/l)	COD (mg/l)		Chromium (Total) (µg/l))	PP DDT (µg/l)
Station detail	Nitrate-N (mg/l)	Total Kjeldahl-N (Nmg/l)		Nickel (µg/l)	Alpha Endosulphan (µg/l)
Human activities	Nitrite-N (mg/l)	Ammonia-N (Nmg/l)		Zinc (µg/l)	Beta Endosulphan (µg/l)
	Faecal Coliform MPN/100 ml)	Hardness, as ($CaCO_3$)		Mercury (µg/l)	Aldrin (µg/l)
	Total Coliform (MPN/100 ml)	Calcium, as ($CaCO_3$)		Iron (total) (µg/l)	Dieldrin (µg/l)
		Sulphate (mg/l)			Carboryl (Carbamate) (µg/l)
		Sodium (mg/l)			2,4 D (µg/l)
		Total dissolved solids (mg/l)			Malathian (µg/l)
		Total fixed dissolved solids (mg/l)			Methyl Parathian (µg/l)
		Total suspended solid (mg/l)			Anilophos (µg/l)
		Phosphate (mg/l)			Chloropyriphos (µg/l)
		Boron (mg/l)			Corbamat (µg/l)
		Magnesium ($CaCO_3$)			Methyl Parathion (µg/l)
		Potassium (mg/l))			HCH Alpha Beta Delta (µg/l)
		Flouride (mg/l)			Isoprofuron (µg/l)
					Alachlor (µg/l)
					Atrazine (µg/l)
					Monochorotophos (µg/l)
					Ethion (µg/l)
					Phorate (µg/l)
					Butachlor (µg/l)
					Chlorandane (µg/l)
					Heptachlor (µg/l)
					Hexachlorobenzene (µg/l)
					Phosphamidon (µg/l)
					Diomethoate Diazinon (µg/l)

Source: CPCB

variations. For water bodies that have frequent cyclic variations, sampling on a monthly basis is justified.

4.3 FREQUENCY OF REPORTING PARAMETERS

A combination of general parameters, nutrients, oxygen-consuming substances and major ions should be analyzed at all stations on a routine basis. Depending on the industrial activities and other anticipated activities upstream from the sampling station, more parameters such as micro-pollutants, pesticides and other site-specific variables may be investigated less frequently.

A list of parameters to be considered for analysis and frequency of sampling is provided in the *Protocol for Water Quality Monitoring* notified by the government of India (see *Table 6: Parameters for and frequency of monitoring surface water*). But the following must be kept in consideration in this regard:

- The list does not restrict analysis of more parameters depending upon specific requirements of the analyzing agency and its available manpower.
- For lakes and reservoirs, monitoring of additional parameters, such as total Kjeldhal nitrogen, chlorophyll, total plankton count and productivity are to be included.
- The list of pesticides and toxic metals is flexible and should be decided case-by-case.

Table 6: Parameters for and frequency of monitoring surface water

1	2	3
Type of station	**Frequency**	**Parameters**
Baseline	Perennial rivers and lakes: Four times a year (seasonal) Seasonal rivers: Three to four times (at equal spacing) during the flow period Lakes: Four times a year (seasonal)	(A) Pre-monsoon: Once a year analyze 25 parameters as listed below: a) General: Colour, odour, temperature, pH, electrical conductivity (EC), dissolved oxygen (DO), turbidity, total dissolved solids (TDS) b) Nutrients: Ammoniacal nitrogen (NH_4 -N), nitrite and nitrate nitrogen (NO_2 + NO_3) total phosphate (Total P) c) Demand parameters: Biological oxygen demand (BOD), Chemical oxygen demand (COD) d) Major ions: Sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), carbonate (CO_3) bicarbonate (HCO_3), chloride (Cl), sulfate (SO_4) e) Other inorganic: Fluoride (F), boron (B), and any other location specific parameter. f) Microbiological: Total Coliform and faecal Coliform (B) Rest of the year (after the pre-monsoon sampling) at three months intervals: Analyze 10 parameters: Colour, odour, temperature, pH, EC, DO, NO_2 + NO_3 , BOD, total Coliform and faecal Coliform
Trend or flux or impact	Once every month starting April–May (pre-monsoon), i.e. 12 times a year	(A) Pre-monsoon: Analyze 25 parameters as listed for baseline monitoring (B) Other months: Analyze 15 parameters as listed below : a) General: Colour, odour, temperature, 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) Micro pollutant: Once a year/pre-monsoon a) Pesticides—Alpha benzenehexachloride (BHC), beta BHC, gama BHC (Lindane), OP-Dichlorodiphenyltrichloroethane (OP-DDT), PP-DDT, alpha endosulphan, beta endosulphan, aldrin, dieldrin, carbaryl (carbamate), malathion, methyl parathion, anilophos, chloropyriphos b) Toxic metals: Arsenic (As), cadmium (Cd), mercury (Hg), zinc (Zn), chromium (Cr), lead (Pb), nickel (Ni), iron (Fe) (The parameters may be selected based on the basis of local need)

Source: *Guidelines for water quality monitoring*, CPCB (MINARS/27/2007–08

5. Sampling programme and field activities

5.1 PLANNING FOR SAMPLING

When planning a sampling programme, an estimate of the number of sampling stations or wells that can be sampled in a day is required. For this, it is necessary to know the time required at each site.

5.2 CHECKLIST FOR FIELD VISIT

At least one day before sampling, it should be ensured that all arrangements are made as per *Table 1: Checklist for field visit*. Location maps should be kept handy, to flag the prominent landmarks in the vicinity of the sampling site(s). If there are any deviations from the fixed collection point, they must be recorded and reasons must be cited. If the laboratory conducting analysis is different from the one preparing the sample bottles, it must be ensured that the former should be informed about the programme and should be ready to receive the samples, particularly those which need immediate attention.

5.3 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 analyzed.

5.3.1 Surface-water sampling

- Samples should be collected with a weighed bottle or DO sampler from a well-mixed section of the river 30 cm below the water surface.
- Samples from reservoir sites should be collected from the outgoing canal, power channel or water intake structure. When there is no discharge into the canal, samples should be collected at the exit point of the reservoir itself.
- DO is determined in a sample collected in a bottle specialized for this purpose using a DO sampler. The DO in the sample must be fixed immediately after collection, using chemical reagents. DO concentration can be determined either in the field, or later, in a laboratory.

5.4 SAMPLE LABELLING

Sample containers should be labelled properly, preferably by attaching an appropriately inscribed tag or label. Alternatively, the bottle can be labeled directly with a waterproof 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

Table 7: Container types and preservatives needed for sampling

1	2	3
Analysis	**Container**	**Preservation**
General	Glass, PE	4°C, dark
BOD	Glass, PE	4°C, dark
COD, NH_3, NH_2, NO_3	Glass, PE	H_2SO_4, pH < 2
Coli form	Glass, PE, sterilized	4°C, dark
DO	BOD bottle	DO fixing chemicals
Fluoride	PE	None
P	Glass	None
Pesticides	Glass, Teflon	4°C, dark
Toxic metals	Glass, PE	HNO_3, pH < 2

Source: *Guidelines for water quality monitoring*, CPCB (MINARS/27/2007–08

5.5 SAMPLE CONTAINER, PRESERVATION AND TRANSPORTATION

1. The type of containers and sample preservation to be adopted shall be as mentioned in *Table 7: Container type and preservatives needed for sampling*.
2. Samples shall be transported to the concerned laboratory as soon as possible, preferably within 48 hours of collection.
3. Analysis for Coliforms shall be started within 24 hours of collection of sample. If the time is exceeded, it should be recorded with the result.
4. Samples containing μg/l level metal concentration should be stored at 4°C and analyzed as soon as possible. If the concentration is of mg/l level, it can be stored for up to six months, except mercury, for which the limit is five weeks.
5. Sample identification of the analysis for surface-water extracts shall be as mentioned in *Form I: Sample identification for surface-water analysis and record*.

FORM I: Sample identification for surface-water analysis and record

Sample code											
Observer			Agency			Project					
Date:			Station code								
Time:											
Parameter code	Container				Preservation				Treatment		
	Glass	PVC	PE	Teflon	None	Cool	Acid	Other	None	Decant	Filter
(1) General											
(2) Bacteriology											
(3) BOD											
(4) COD, NH_3, NO_3											
(5) Toxic Metals											
(6) Trace Organics											

Source of sample				
Water	Point	Approach	Medium	Matrix
o River o Drain o Canal o Reservoir (lake / tank / pond)	o Main current o Right bank o Left bank	o Bridge o Boat o Wading	o Water o Suspended matter o Biota o Sediment	o Fresh o Brackish o Salt o Effluent
Sample type	o Grab o Time component o Flow component o Depth-integral o Width-integral			
Sample device	o Weighted bottle o Pump o Depth sampler			

Field determination			
Temperature °C	pH	EC µMho/cm	DO mg/l

Odour code	(1) Odour-free (6) Septic (2) Rotten eggs (7) Aromatic (3) Burnt sugar (8) Chlorinous (4) Soapy (9) Alcoholic (5) Fishy (10) Unpleasant	Colour code	(1) Light brown (6) Dark green (2) Brown (7) Clear (3) Dark brown (8) Other(specify) (4) Light green (5) Green

Remarks	
Weather	o Sunny o Cloudy o Rainy o Windy
Water velocity (m/sec)	o High (> 0.5) o Medium (0.1–0.5) o Low (< 0.1) o Standing
Water use	o None o Cultivation o Bathing and washing o Cattle washing o Melon or vegetable farming in river bed o Organized water supply

Source: Dr DD Basu/CSE

5.6 TYPES OF SAMPLES

5.6.1 Grab sample (also called spot or catch sample)

One sample is taken at a given location and time. In the case of a flowing river, it is usually taken from the middle of the flowing water 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 of the changes and may vary from continuous recording or sampling every five minutes, to several hours or more.

5.6.2 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 averaged out in 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, information on the daily variability can also be obtained, and the averages computed later.

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 should be one–three 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 proportional 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.

5.6.3 Integrated samples

Sometimes, samples are collected at the same location but, because of horizontal or vertical variations in the composition of the river (or in the water flow) or lake, they come from different points in the cross-section and are accorded 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.

5.7 IN SITU MEASUREMENTS

Some determinants 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 later. If possible, these parameters should be analyzed on the sampling site or, even better, in situ. Most important parameters that should be analyzed in situ are pH, DO, 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.

5.7.1 Colour

Determining the colour in the field is relatively easy. Pour an aliquot of approximately 10 ml of sample into a glass test-tube and judge the colour observed. Options can be listed as:

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

5.7.2 Odour

Odour should always be determined in the field, as soon as possible after collecting a sample. After collection, fill a clean and odourless bottle half with the sample, cover with a stopper, shake vigorously for two–three seconds, open the stopper and quickly smell. Alternatively, pour an aliquot of approximately 5 ml of sample into a glass

test tube and judge the odour. Consider one of the following options:

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

5.7.3 Temperature

Water temperature should be measured in °C, using a mercury thermometer or a thermistor. Most electronic thermistors are built into larger devices which can also measure pH and electrical conductivity (EC) of the sample. Whenever possible, the temperature should be measured by directly dipping the thermometer in the natural body of water being studied. In case that 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 calibration (no more change in the temperature reading). Report the temperature on the sample identification form in °C with one digit after the decimal point (e.g. 13.2°C).

5.7.4 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 using a 'glass' and a 'reference' electrode (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 for this is as follows:

- After removing their protective caps, the electrodes are rinsed in distilled water and carefully dried 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 suitable time for meter stabilization has passed, the pH reading of the meter is adjusted to the pH of the buffer solution (normally seven).
- The electrodes are then rinsed again with distilled water and dried.
- If the 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 electrodes from drying out.
- The pH should be reported 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 a 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 a glass electrode cap for transportation.

5.7.5 EC

EC can be measured in the field with a purpose-designed meter. Before measuring conductivity, it is necessary to calibrate the meter. This should be done at least once every 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 that the reading is accurate, it is necessary to adjust the conductivity reading to compensate for temperature changes. In most modern meters, this is done automatically. Once calibrated, the conductivity of the water can be measured by immersing the 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 stabilize. The reading must, therefore, be taken after this stabilization has occurred. Report the EC at 25°C, preferably in µMho/cm with no figure after decimal point (e.g. 1,135 µMho/cm).

Table 8: Container types and volumes needed for sampling

1	2	3	4
Analysis	Container	Volume	Preservation
On-site analysis	PE bowl	±200	-
General (SS, TDS, major ions)	Glass, PE	1000	-
COD, NH_3,NH_2,NO_3	Glass, PE	500	H_2SO_4, PH < 2
o-PO_4	Glass	100	-
BOD	Glass, PE	1000	4°C, Dark
Coliform	Glass, PE, sterilized	300	4°C, Dark
Heavy metals (Cd, Zn)	Glass, PE	500	HNO_3, pH < 2
Mercury	Glass	1000	HNO_3, pH < 2
Pesticides	Glass, Teflon	1000	4°C, Dark

Source: *Guidelines for water quality monitoring*, CPCB (MINARS/27/2007–08

5.7.6 Instruments for field measurement

There is a basic list of instruments and equipment which must be brought to the sampling sites. For example, 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.

5.7.7 Sample containers

Sample containers needed for the campaign are prepared by the laboratory and given to the person collecting samples (see *Table 8: Container types and volumes needed for sampling*).

5.7.8 Reagent solutions

In some field analysis, reagent solutions are necessary. They must be prepared in the laboratory and brought to the field by a responsible sample collector. In all cases, sample preservatives and DO-fixing solutions, as applicable, must be brought to the field and added to the samples immediately after collection.

For analysis of pH, buffer solutions, for pH – 4, 7 and 9, are necessary to standardize the pH meter. For analysis of EC, standard potassium chloride solution, KCl (0.01 M) is needed to standardize the conductivity meter. For preservation of certain samples, concentrated sulphuric acid, ZoBell's solution etc. are needed. A supply of distilled water is needed for rinsing equipment.

5.7.9 Field data protocol

a) Sampling team members
b) Date and time (24-hour method) of collection (timespan; in case of composite sampling)
c) Nature of the sample: Spot or composite or integrated
d) Results of in situ or on-site analysis performed (water or air, temperature, DO, pH (field or laboratory), EC (field or laboratory), turbidity, macro-fauna composition (bio-monitoring working party score), macro-fauna diversity (strategic bio-monitoring initiatives) and 24-hour oxygen production/ respiration ratio)
e) Exact sampling location (location along the river and 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 or lake, and current velocity in case of composite sampling
h) Weather conditions with respect to clouds, precipitation and wind (direction and force)
i) Consistency of sediment (sandy, silty etc.)
j) Comments on smell, colour, discharge 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 or storage

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. It makes it easy at the end of the sampling event to check if all samples have been collected in the correct number.

5.7.10 Analytical result sheets

When offering the samples to the analytical laboratory, every series of replicate sample containers has to be accompanied by a prefilled 'result sheet'. This sheet is marked with sample specifications identical to those 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.

6. Laboratory work and analysis

6.1 WORK ASSIGNMENT AND PERSONNEL REGISTER

- The laboratory in-charge should maintain a bound register for assignment of work.
- This register would link the laboratory and sample numbers 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 into the register.
- Each laboratory analyst should have a bound register where all laboratory readings and calculations are to be entered.
- When analyses and calculation are completed, the results must be recorded in a register or computer containing data records sheets described in the next section.

6.2 LABORATORY ANALYSIS

It has been observed that many laboratories have developed their own procedures. They also use different units to present results and, sometimes, place several digits after the decimal. This creates problems in integrating results. To make the procedure and presentation methods uniform, a guideline has been prepared (see *Table 9: Measurement methods, units and significant figures for different parameters used in monitoring water quality*). It is important that all agencies monitoring water quality and entering date into websites must follow this procedure to achieve unity.

6.3. OUTLINE ON QUALITY ASSURANCE AND CONTROL

6.3.1. Quality assurance

Quality assurance programme for a laboratory or group of laboratories should contain a set of operating principles, written down and agreed upon by the organization, delineating specific functions and responsibilities for each person involved, and the chain of command. Following points describe various aspects of the programmes:

- **Sample control and documentation**
  Procedures regarding sample collection, labelling, preservation, transportation, preparation of derivatives, where required, and the chain of custody.
- **Standard analytical procedures**
  Procedures detailing methods for the analysis of each parameter giving results of acceptable accuracy.
- **Analytical qualification**
  Qualifications and the training requirements of the analysts must be specified. The number of repetitive analyses required to obtain results of acceptable accuracy also depends on the experience of the analyst.
- **Equipment maintenance**
  For each instrument, a strict preventive maintenance programme should be followed. This reduces instrument malfunctions, maintains calibration and reduces downtime. Corrective actions to be taken in case of malfunction 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 numbers of different dilutions of a standard to be used, method detection limit (MDL), range of calibration and verification of the standard curve during routine analyses.
- **Data reduction, validation and reporting**
  Data obtained from analytical procedures must be corrected, where required, for sample size, extraction

Table 9: Measurement methods, units and significant figures for different parameters used in monitoring water quality

Parameters	Unit	Measurement methods	Significant figures after decimal
Colour	-	Visual method	
Odour	-	Manual	
Temperature	℃	Thermometer	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	Colorimetry	4
Orthophosphate	mg/L	Colorimetry	4
BOD	mg/L	DO consumption in 3 days at 27 °C	1
COD	mg/L	Potassium dichromate method	1
Sodium	mg/L	Flame photometry	1
Potassium	Mg/L	Flame photometry	1
Calcium	mg$CaCO_3$/L	EDTA Titrimetric	1
Magnesium	mg $CaCO_3$/L	EDTA Titrimetric	1
Carbonate as $CaCO_3$	mg $CaCO_3$/L	Titrimetric	1
Bicarbonate, as $CaCO_3$	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
Faecal Coliform	No/100mL	MPN or MF method	0
Per cent sodium	-	Calculation	2
SAR	-	Calculation	2
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

Source: *Guidelines for recognition of environmental laboratories under the EPA, 1986* (LATS/9/2008–9).

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 results is the use of the correct number of significant figures. To decide on 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 figures that are not significant. Procedures regarding rounding off must be followed.

6.3.2. Analytical quality control (AQC)
This includes both within-laboratory and inter-laboratory AQC.

In the within-laboratory programme, studies may include recovery of known additions to evaluate the matrix effect and suitability of analytical method, and analysis of reagent blanks, to monitor purity of chemicals and reagent water; sample blanks, to evaluate sample preservation, storage and transportation; duplicates, to asses method precision; individual samples or sets of samples, to obtain mean values from the same control standard to check for random errors.

Inter-laboratory programmes are designed to evaluate laboratory bias. All the listed AQC actions may not be necessary for various determinants. Further, these are not one-time exercises but internal mechanisms for checking performance and protecting laboratory work from errors. These checks do not add to the workload of laboratories significantly.

6.3.3 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 statistically controlled 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.

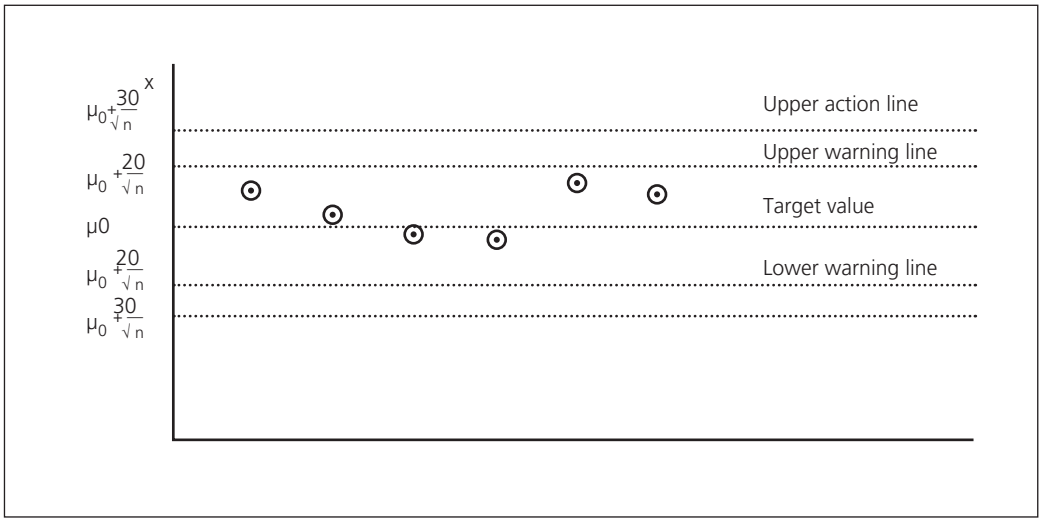
Shewhart Control Charts are the most widely used form of control charts. In its simplest form, results of individual measurements made on a control sample are plotted on a chart in a time series. The control sample is analyzed in the same way as routine samples at fixed intervals, once or twice every week, after 20–50 routine samples.

Assuming the results for the control sample follow the normal frequency distribution, it would be expected that only 0.3 per cent of results would fall outside lines drawn at three 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 limits so seldom (three out of 1,000 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 sample. Two lines are inserted on the chart at two 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 per cent of results may be expected to fall outside these lines.

A Shewhart Control Chart provides a check on both random and systematic errors gauged from the spread of results and their displacement respectively. The standard methods list the following actions that may be taken based on analysis results in comparison to the standard deviation.

Figure 7: A typical Shewhart Control Chart



Source: *Statistics for Analytical Chemistry*, J. C. Miller

- **Control limit:** If one measurement exceeds the limits, repeat the analysis immediately. If the repeated analysis results are within the UCL and LCL, continue the analysis; if they exceed the action limits again, discontinue analysis and correct the problem.

- **Warning limit:** If two out of three successive points exceed the limits, analyze another sample. If the next point is within the UWL and LWL, continue analysis; if the next point exceeds the warning limits, discontinue analysis and correct the problem (see *Figure 7: A typical Shewhart Control Chart*).

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

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

- **Precision:** The most important parameter to evaluate in the results is 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), the ratio of variation of standard deviation, and mean is the coefficient of variation and cancels the unit to become a dimensionless number. 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 analyses for samples with different concentrations. Before evaluating the results one should answer the question, 'What is the desired precision for analysis?' In fact, this question should be answered by the designated 'data users'. The use of 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 in, say, irrigation. Laboratory staff should always ask for the purpose for which they are performing the requested test. As a minimum goal, however, the precision that can be obtained by correctly and adequately following the method prescribed by the APHA (American Public Health Association) 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. Precision improves, especially when new techniques are introduced, when experience is gained with the technique. A good time for recalculating the control and warning limits is when the control chart is full and a new graph has to be created anyway. At this point, use the 20 most recent data points on the old chart for construction of LCL, LWL, average, UWL and UCL.

- **Errors that cannot be detected by within-laboratory AQC:** The within-laboratory AQC exercise focuses mainly on precision. A laboratory cannot detect many sources of its own bias. A good example to illustrate this is the total-hardness method. If the analytical balance in a laboratory always reads 10 per cent too much, all solutions prepared will have a 10 per cent higher concentration of the standard $CaCO_3$. This error can only be detected by analyzing a sample prepared by the laboratory with a correctly functioning balance. A laboratory without such bias will underestimate the concentration of such an inter-laboratory sample by 10 per cent. In some cases, a 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.

6.3.4. Inter-laboratory AQC

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 programme to monitor water quality

Some related objectives and benefits are listed as follows:

- To assess the status of analytical facilities and capabilities of participating laboratories
- To identify the serious constraints (random and systematic) in the working environment of laboratories
- To provide necessary assistance to the concerned laboratories to overcome the shortcomings in the analytical capabilities
- To promote 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 a routine part of the monitoring programme. Such exercises will engender more confidence in results.

7. Data management

Data management has the following steps (also *see Figure 8: Data management flowchart*):

- Data storage
- Data validation
- Statistical analysis
- Data interpretation

7.1 DATA STORAGE

- A recommended format for recording data is given in pre-set formats in several softwares. It includes all parameters, except heavy metals and trace organics, which may be analyzed in the water-quality monitoring programme currently envisaged. Note that, ordinarily, a sample would not be analyzed 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.

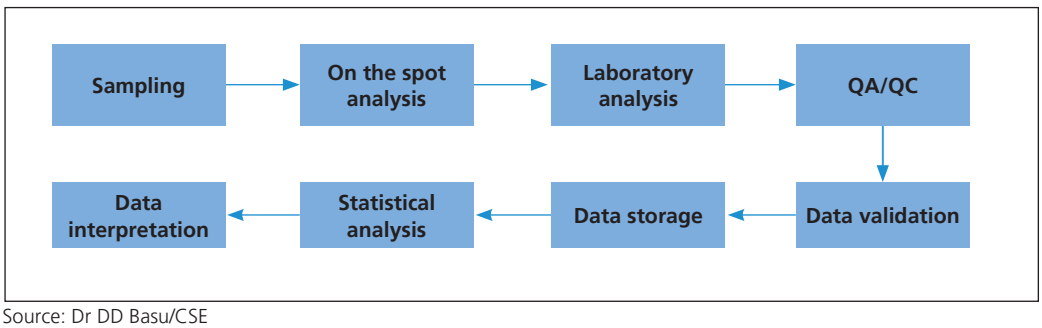
7.2 DATA VALIDATION

- Absolute checking and 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 is physically or scientifically possible (general checks)
- Checking correlation of parameters (some conditional checks like BOD–COD relation, total Coliform–faecal Coliform 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

7.3 DATA ANALYSIS AND PRESENTATION

It is often useful to subject data to simple statistical analysis. Analysis could, for example, be used to summarize the data, to transform it to aid understanding or compare it 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 the

Figure 8: Data management flowchart



Source: Dr DD Basu/CSE

form of an index. Statistical analyses such as parametric correlation, seasonal fluctuations and seasonal trends over a period of time are also common. After analysis, the data can be presented in different formats, for example, in a river, river profiles are commonly presented.

Graphical representation

1. Time-series graphs
2. Histograms
3. Pie charts
4. Profile plots (river profiles)
5. Geographical plots (contours)

7.4 DATA INTERPRETATION

Data interpretation involves understanding the water chemistry, biology and hydrology. Normally, data is analyzed and interpreted in terms of chemical quality, and quantity 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 (like drinking, bathing and washing). Quality fluctuations are explained in view of possible sources of pollution, their fates in aquatic environment and their effects.

PART 2

GUIDELINES FOR WATER QUALITY MONITORING PROGRAMME

PROPOSED BY

CENTRE FOR SCIENCE AND ENVIRONMENT

8. Proposed programme to monitor water quality in Ganga

8.1 INTRODUCTION

The water quality programme in Ganga is led by the CPCB, in association with the state pollution control boards (SPCBs) of the states located on the mainstream of the river. The states include Uttarakhand (UK), Uttar Pradesh (UP), Bihar and Jharkhand (JK).

This is in accordance with statutory obligation of the CBCB and SBCBs under the Water (Prevention and Control of pollution) Act, 1974.

While developing the Ganga Action Plan (GAP), it was felt that there is a need for third party involvement to assess the water quality of the river. In the first phase of GAP, institutions other than regulatory bodies were involved in monitoring the water quality of Ganga.

The idea of involving a non-governmental organization for monitoring Ganga, however, has been considered for the first time. The Centre for Science and Environment (CSE), a premiere non-government institution, has been selected to coordinate the programme with the help of local academic institutions and organizations to accomplish the said task.

8.2 OBJECTIVES

CSE has set down the following objectives for the programme:

I. Delineating the water quality of Ganga
II. Identifying spatial and temporal trends of the water quality
III. Identifying polluted stretches and comparing them with the findings of the pollution control boards
IV. Spreading awareness about the use of water in specific stretches of the river, and the criteria, status and involvement of people to clean it up

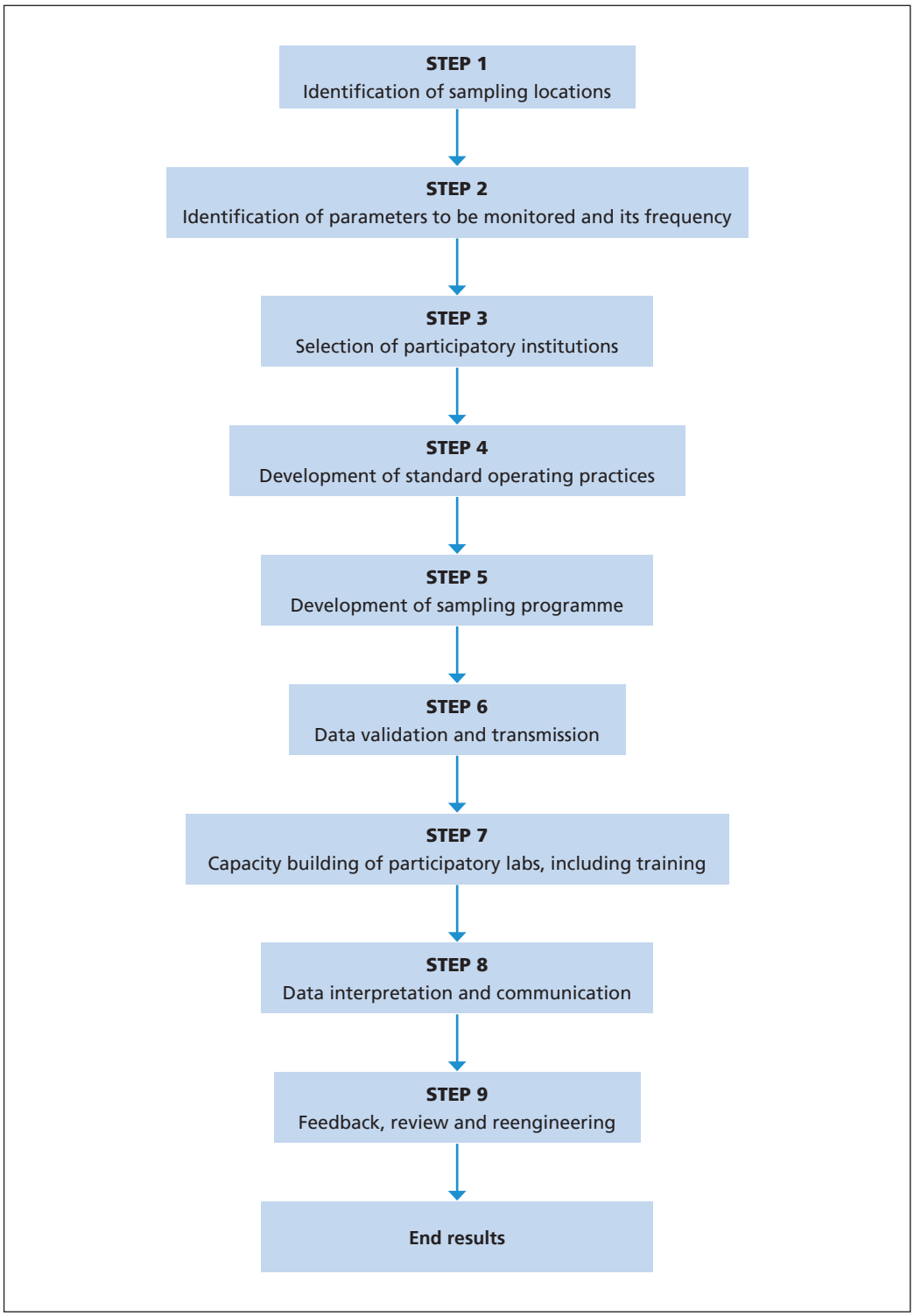
8.3 PROPOSED NETWORK DESIGNING

As stated earlier (*Chapter 1: Monitoring*), water quality programmes have to take into account three factors:

- Location and number of monitoring stations
- Water quality parameters to be monitored
- Frequency

In this backdrop, CSE shall work according to the following steps given in *Figure 9: Steps of the proposed water quality monitoring programme*. These steps are described in detail in the next chapter.

Figure 9: Steps of the proposed water quality monitoring programme



Source: Dr DD Basu/CSE

9. Number and location of monitoring stations

The main stream of Ganga is 2,525 km long. Such a long stretch cannot be monitored without an extensive network of stations. The ideal is to have a monitoring station every 10 km which, however, is a costly proposition in terms of logistics, infrastructure and manpower.

It was, therefore, decided that the proposed monitoring programme would make use of the existing network of pollution control boards. A list of monitoring stations of CPCB and SPCBs is provided in *Annexure I*. A list of the monitoring stations proposed by CSE is provided in *Annexure II*. State-wise distribution of existing CPCB-SPCB network and the proposed CSE programme is provided in *Table 10: Water quality monitoring stations in different states*.

Table 10: Water quality monitoring stations in different states

State	Number of locations	
	CPCB-SPCB network	CSE's proposed network
Uttarakhand	11	3
Uttar Pradesh	20	12
Bihar	15	11
Jharkhand	1	-
West Bengal	10	7*
Total	57	33

*Two stations out of seven shall be of groundwater near the bank of Ganga
Source: Dr DD Basu/CSE

Two of the stations will exclusively focus on monitoring groundwater. The exact location of these stations will be finalized in consultation with the Groundwater Board. The number of monitoring stations proposed by CSE is only a fraction of the total number in the CPCB-SPCB network. The stations in the CSE network are located to assess the impact of wastewater discharge from major urban agglomerations, with a few additional baseline stations for each state. Location of stations are depicted in *Maps 1* to *5*.

9.1 WATER QUALITY PARAMETERS

The existing monitoring network of CPCB has identified nine core parameters and 19 general parameters. Besides these, they have also identified trace metals and pesticides as parameters in their network. The parameters are described as follows:

- Physical: pH, temperature, turbidity, and conductivity
- To assess the organics: BOD and COD
- Related to eutrophication: nitrates, nitrites and total phosphorous
- Common ions: K^+, Na^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}, and TDS
- Pathogens: Total and faecal Coliform

CSE proposes that core parameters be analyzed monthly and general parameters quarterly. These parameters should be analyzed by identified laboratories. Trace metals and pesticides can be analyzed twice a year by CSE itself. In this case, samples shall be collected by identified laboratories and sent to CSE for the analysis.

9.2 SELECTION OF PARTICIPATORY LABORATORIES

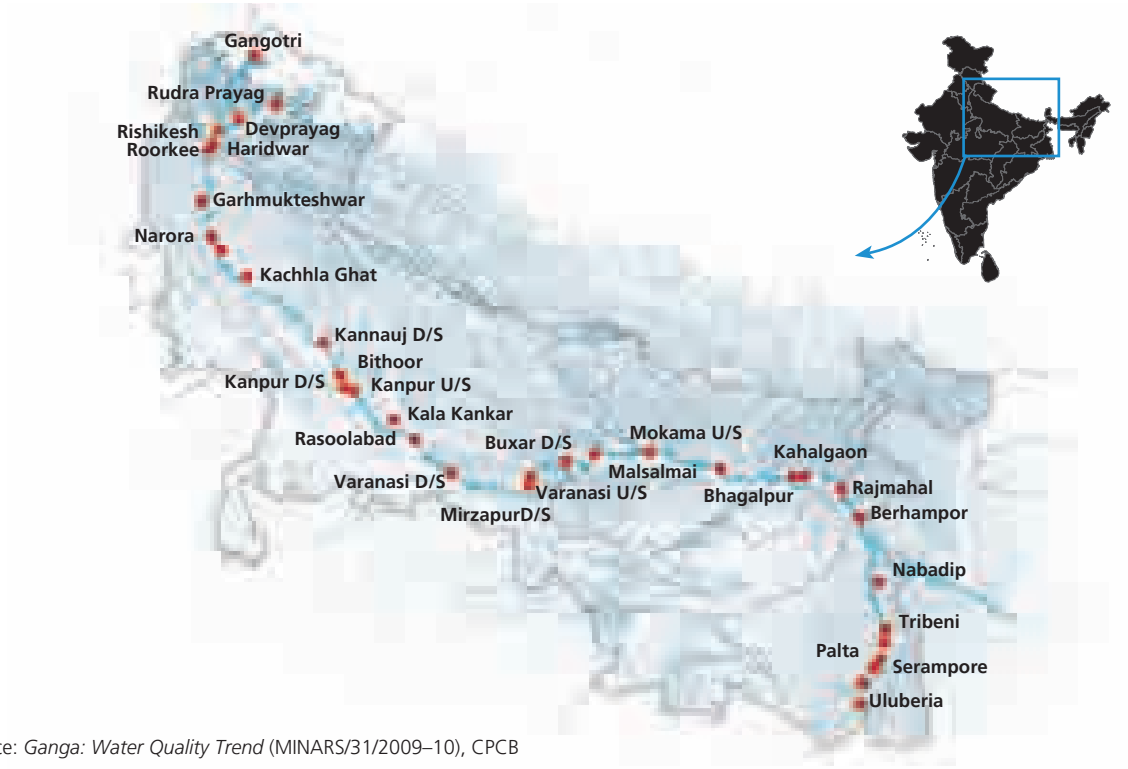
Selection of participatory laboratories shall be guided by three factors:

- Location
- Infrastructure
- Manpower—knowledge and experience

9.2.1 Location of laboratory

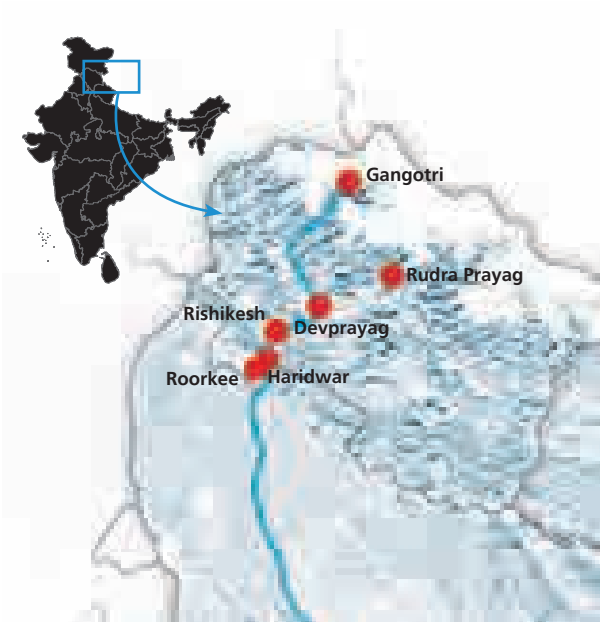
The institution should be located close to the main stream of Ganga. At least nine laboratories are required, with a minimum of three—four samples per month.

Map 1: Ganga—all stations



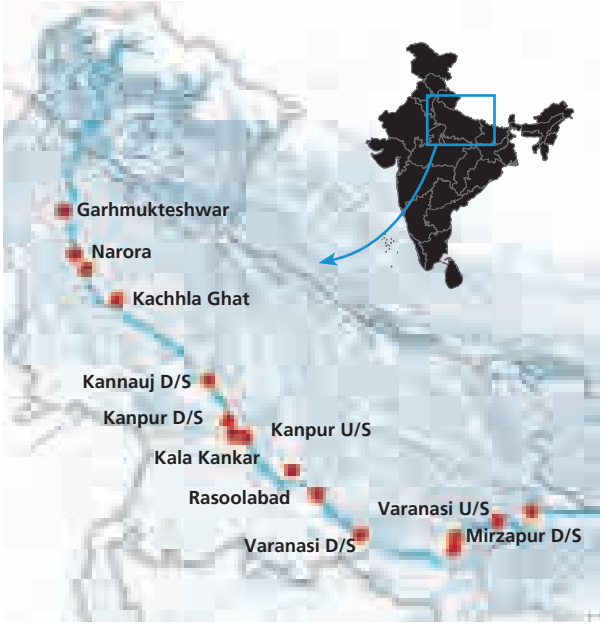
Source: *Ganga: Water Quality Trend* (MINARS/31/2009–10), CPCB

Map 2: Ganga in Uttarakhand



Source: *Ganga: Water Quality Trend* (MINARS/31/2009–10), CPCB

Map 3: Ganga in Uttar Pradesh

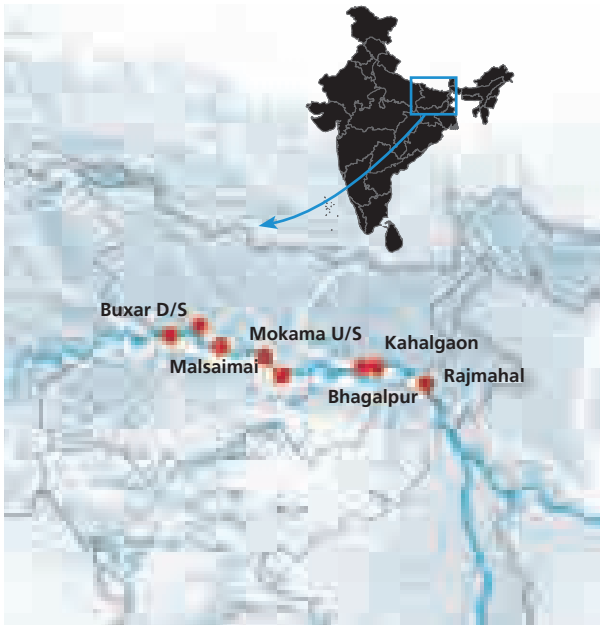


Source: *Ganga: Water Quality Trend* (MINARS/31/2009–10), CPCB

One laboratory is proposed for each of the following stretches:

- Rishikesh to Bijnor
- Anupshahar to Aligarh
- Kanpur
- Allahabad
- Mirzapur to Varanasi
- Buxar to Patna
- Bodhgaya to Muzaffarpur
- Bhagalpur to Katihar
- Palta to Diamond Harbour

Map 4: Ganga in Bihar



Source: *Ganga: Water Quality Trend* (MINARS/31/2009–10), CPCB

Map 5: Ganga in West Bengal

Source: *Ganga: Water Quality Trend* (MINARS/31/2009–10), CPCB

One laboratory is proposed for each of the following stretches:

- Rishikesh to Bijnor
- Anupshahar to Aligarh
- Kanpur
- Allahabad
- Mirzapur to Varanasi
- Buxar to Patna
- Bodhgaya to Muzaffarpur
- Bhagalpur to Katihar
- Palta to Diamond Harbour

9.2.1 Layout plan

In general, the infrastructure of a laboratory comprises of minimum space with a layout plan, power and water supply, including distillation assembly, and some furniture.

The laboratory space must be properly ventilated, with open spaces, laboratory hoods and sinks. Ideally, it should contain a fountain to wash eyes, safety showers, fire-fighting equipment and first aid boxes. A water laboratory must be spread over at least 100–150 sq m. The space should be divided into separate working areas such as analytical laboratory (wet laboratory), instrument room with adequate provision of gas cylinders, balance and microbial rooms, storage for chemicals glassware, field monitoring kits, and office room. A model layout plan is given in *Figure 10: Model layout plan*.

9.2.2 Infrastructure

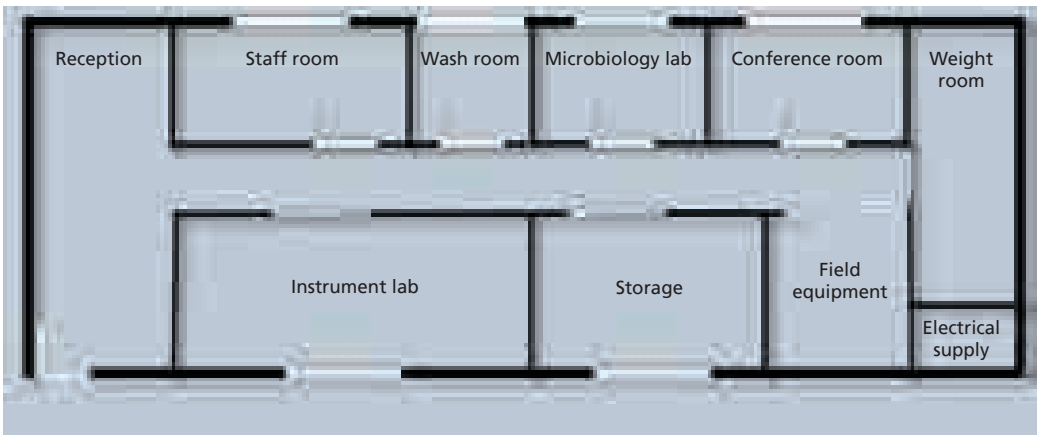
9.2.2.1 Electricity supply and electric services

Regular and stabilized electricity supply (220–230 volts) is essential for smooth functioning of a laboratory and its instruments. Necessary and adequate provisions should be made for continuous supply, constant voltage, adequate load, proper electrical fitting, etc.

Because of the specialized nature of analytical work in a laboratory, the lighting systems need to be tailor-made, according to the requirements of illumination and brightness.

Some sophisticated instruments require constant voltage to maintain stabilized and drift-free operation, regulation of voltage is, therefore, essential and can be achieved through use of voltage stabilizers and uninterrupted power supply (UPS) systems. Since the electric supply for laboratories needs to be continuous, there shall be

Figure 10: Model layout plan



Source: Dr DD Basu/CSE

Table 11: Degree of purity of distilled water

Purity	Maximum conductivity µSiemen/cm	Appropriate concentration of electrolytes (ms/l)
Pure	10	2.5
Very pure	1.0	0.2-0.5
Ultra- or nano-pure	0.1	0.01-0.02
Theoretically pure	0.05	0.00

Source: *Laboratory Analytical Technical Series* (LATS/9/2008-2009), CPCB

additional provision of diesel generator sets to ensure continuous supply of power to equipment like BOD incubators, oven, etc., in case of longish power cuts.

9.2.2.3 Water supply and distilled or de-ionized water

Water is an essential and basic need for laboratory operations such as washing and cleaning. Therefore, laboratories should have provisions for continuous water supply. If possible, dedicated water storage should be made available exclusively for laboratory use. Cleaning of storage tanks after periodic intervals is imperative.

Distilled waste is one of the basic requirement of a laboratory. Many analytical errors are a result of improper quality of distilled water. Generally, distilled water with electrical conductivity of 2.0 microSiemen per centimeter or less is considered reasonably ideal for routine work, the degree of purity of distilled water can be further classified as stated in *Table 11: Degree of purity of distilled water*.

In a water laboratory, for the purpose of water quality monitoring of rivers, pure–very pure quality of distilled water is a minimum requirement.

9.2.2.4 Glassware

Generally, glassware of borosilicate glass, which is relatively inert, is suitable for analytical work. Plastic bottles of polythene (PE) or polypropylene (PP) are suitable for collecting and transporting water samples. Unless instructed otherwise, borosilicate glass bottles may be used to store reagents and standard solutions. Standard solutions of silica, boron and alkali metals should be stored in polyethylene bottles. Whenever necessary, amber- or dark-colored glass bottles must be used for storing photo-reactive chemical solutions.

9.2.2.5 Quality of chemicals or solvents

The quality of chemicals or solvents may become one of the cause for analytical error due to interference of impure material during determination. Thus, selection of chemicals or solvents of an appropriate

Table 12: Checklist for assessment of infrastructure of laboratories

S. no	Assessment	Yes	No	Remarks
1	Is the laboratory space less than minimum space (100–150 sq m)			Acceptable, if not significantly low.
2	Does the laboratory have a proper layout plan with designated space for wet laboratory, balance room, microbiology laboratory, etc.			If no, examine in future if it is possible?
3	Does the laboratory have arrangements for adequate power supply (220–230 volts)?			
4	Is there a provision of UPS system for designated instruments?			
5	Is there a backup power supply system (DG set)?			
6	Is there a system of adequate water supply?			If not, ask them to provide.
7	Is there distilled water-making assembly?			If not, ask, what is the present arrangement?
8	Does the laboratory have a proper illumination and ventilation systems?			If not, ask if it is possible to do so?
9	Is the laboratory's furniture up to the mark?			If not, can it be possible to do so?
10	Is there a sample digestion system?			If not, is there a space to do so?
11	Is the laboratory using AR/GR grade chemicals?			If not, what grade are they using?
12	Is the laboratory using borosil glass wear?			If not, what are they using?
13	Is the laboratory's safety equipment adequate?			Ask for the minimum requirement.

Source: Dr DD Basu/CSE

quality is a very crucial factor in achieving results with desired accuracy.

Generally, laboratories use laboratory grade or analytical grade (AR) or guaranteed grade (GR) chemicals and solvent. For the preparation of standard solutions, AR or GR chemicals are preferred. For calibration, reference material (RM) or certified reference material (CRM) is used.

9.2.2.6 Sample digestion system and hood system

An efficient hood system is necessarily required in laboratories in order to remove various toxic and hazardous fumes generated during the use of organic solvents or during digestion.

9.2.2.7 Laboratory furniture

Laboratory furniture must have ergonomic design. The top of work benches should be acid- and alkali-resistant. Steel or aluminum frames and fittings must be non-corrosive. Stainless steel should be preferred. Storage cupboards shall be made up of clipboard covered with melamine sheets. All furniture is to be designed specifically according to the requirement of the laboratory. The working desks are also to be laminated and non-corrosive.

9.2.2.8 Checklist for assessment of laboratory infrastructure

For a ready-reckoner on laboratory infrastructure, please refer to *Table 12: Checklist for assessment of infrastructure of laboratories*.

The assessor may utilize this checklist and evaluate the grading laboratory as adequate, partially adequate, or not adequate. If it is partially adequate, it should be ensured that efforts are made to make it adequate.

10. Sampling programme

The sampling programme consists of the following components:

- Reconnaissance survey to identify the sampling point
- In situ observation and analysis
- Logistics and field kit

10.1 RECONNAISSANCE SURVEY

Selected institution should be invited for a meeting to identify locations for the sampling programme as laid down in the proposed protocol. A field trip should be arranged in which the participatory institution for a specific stretch of a river, in consultation with the state pollution control board, identifies the exact sampling point, keeping in mind the mixing zone and depth of, and all-weather access to the sampling point. A reconnaissance survey will also identify drains discharging wastewater. It will also observe in situ use of the water in cattle bathing and washing. In addition, the sensitivity of water can be gauged according to the designated best use concept. Organized mass bathing on auspicious occasions should also be recorded. Any other notable observation should also be considered in the reconnaissance survey.

10.2 IN SITU FIELD OBSERVATION, ANALYSIS AND STORAGE

In situ field observations, analysis and storage begins with the observation of weather. Generally, in sunny and hot weather, the chances of encountering dying bacteria are high. When it is drizzling, the chances of surface runoff carrying pollutants to water bodies without much dilution will add to the pollutant load. It is better to avoid sampling in moderate to heavy rain.

Odour and colour are two essential parameters to be observed. Intensity of odour is dependent on temperature and weather. In high temperature and humid weather, the decomposition happens fast, generating an unpleasant odour. Weather is also a factor in the colour of the water. Generally, water bodies with low velocity during fair weather generate some form of colour, which disappears with rain. Temperature, velocity, salinity and DO should be measured, because they are important and interrelated. Data about the container, preservation and treatment of samples should also be reported to the laboratory. For the purpose of Ganga monitoring programme of CSE, *Form II: Sample nomenclature, number and record* provides a good overview of the useful data.

10.3 LOGISTICS AND FIELD KIT

The most important part of the logistics is conveyance. It should accommodate three persons and have space to carry the sampling kits and other accessories. Minimum requirement has already been stated in *Section 2.2.1: Sampling equipment*.

Form II: Sample nomenclature, number and record

Sample code											
Name of observer				Agency							
Date:				Station code							
Time:											
Parameter's code	Container				Preservation				Treatment		
	Glass	PVC	PE	Teflon	None	COD	Acid	Other	None	Decant	Filter
(1) General											
(2) Bacteriology											
(3) BOD											
(4) COD, NH_3, NO_3											
(5) Toxic metals											
(6) Trace organics											

Source of sample			
Water	Point	Approach	Medium
o River o Drain o Canal o Lake / tank / pond	o Main current o Right bank o Left bank	o Bridge o Boat o Wading	o Water
Sample type	o Grab	o Time component o Flow component o Depth integral o Width integral	
Sample device	o Weighted bottle	o Depth sampler	

Field determination			
Temperature °C	pH	EC µMho/cm	DO mg/l

Odour code	(1) Odour-free (2) Rotten eggs (3) Burnt sugar (4) Soapy (5) Fishy (6) Septic (7) Aromatic (8) Chlorinous (9) Alcoholic (10) Unpleasant	Colour code	(1) Light brown (2) Brown (3) Dark brown (4) Light green (5) Green (6) Dark green (7) Clear (8) Other(specify)

Remarks				
Weather	o Sunny	o Cloudy	o Rainy	o Windy
Water velocity	O High (> 0.5 m/s)	O Medium (0.1–0.5 m/s)	O Low (< 0.1 m/s)	O Standing

Source: Dr DD Basu/CSE

11. Development of standard operating procedure for laboratories

A standard operating procedure for laboratories should be developed based on the following components:

- Sample acceptance requirement
- Sample storage conditions and unused sample disposal
- Analytical procedure
- Quality assurance and quality control
- Data validation and management

11.1 SAMPLE ACCEPTANCE REQUIREMENT

The laboratory should maintain written sample acceptance procedures that clearly outline the circumstance under which samples will be accepted for analysis at the laboratory.

The sample acceptance procedure has to necessarily include (but should not be limited to) the following areas of concern:

- Proper and complete documentation to be accompanied with the samples for analysis, which shall include sample identification, the location, date and time of collection, collectors' name, preservation and sample type, and any special remarks concerning the sample.
- Proper sample labelling to include unique identification and labelling system for the samples with requirements concerning the durability of the labels (water resistant) and the use of indelible ink; adhesive cotton tape may be used for labelling.
- Use of appropriate sample containers.
- Adherence to specified holding times for samples before analysis.
- Adequate sample volume. Sufficient sample volume must be available to perform all the necessary tests.

11.2 SAMPLE STORAGE CONDITIONS

The laboratory should maintain documented procedures and appropriate facilities to avoid deterioration, contamination, or damage to the sample during storage, handling, preparation and testing. The samples have to be stored or conditioned under specific environmental conditions, these conditions shall be maintained, monitored and recorded.

Sample should be stored according to the conditions specified by preservation protocol summarized in *Table 13: Collection and preservation of environmental samples*.

Table 13: Collection and preservation of environmental samples

S. no.	Determination	Container	Minimum sample size (ml)	Preservation	Maximum storage recommended	Regulatory
1.	Acidity	P.G.(B)	100	Refrigerate	24 hours	14 days
2.	Alkalinity	P.G.	200	Refrigerate	24 hours	14 days
3.	BOD	P.G	1,000	Refrigerate	6 hours	48 hours
4.	Boron	P.G.(PTFE) orquartz	1,000	HNO_3 to pH < 2	28 days	6 months
5.	Bromide	P.G.	100	Non-required	28 days	28 days

6.	Carbon, organic, total	G.(B)	100	Analyze immediately or refrigerate and add HCl, H_3PO_4or H_2SO_4 top H<2	7 days	28 days
7.	Carbon dioxide	P.G.	100	Analyze immediately	0.25 hours	N.S.
8.	COD	P.G.	100	Analyze as soon as possible or add H_2SO_4 to pH < 2 refrigerate	7 days	28 days
9.	Chloride	P.G.	50	Not required	N.S.	0.28 days
10.	Chlorine (total or residual)	P.G.	500	Analyze immediately	0.25 hours	0.25 hours
11.	Chlorine dioxide	P.G.	500	Analyze immediately	0.25 hours	N.S.
12.	Chlorophyll	P.G.	500	Unfiltered dark–4 °C filtered dark–20 °C (do not store in frost-free freezer)	24–48 hours	–
13.	Colour	P.G.	500	Refrigerate	48h	4h
14.	Specific conductance	P.G.	500	Refrigerate	28h	28d
15.	Cyanide (total)	P.G.	1,000	Add NaOH to pH >12, refrigerate in dark	24h	14 days, 24 hours if sulphide present
16.	Cyanide amenable to chlorination	P.G.	1,000	Add 0.6 g ascorbic acid if chlorine is present and refrigerate	Analyze immediately	14 days, 24 hours if sulphide present
17.	Fluoride	P	100	Not required	28 days	28 days
18.	Hardness	P.G.	100	Add HNO_3 or H_2SO_4 to pH < 2	6 months	6 months
19.	Iodine	P.G.	500	Analyze immediately	0.25 hours	N.S.
20.	Metal (general)	P(A) G(A)	1,000	For dissolved metals filter immediately, add HNO_3 to pH < 2	6 months	6 months
21.	Chromium VI	P(A)G(A)	1,000	Refrigerate	24 hours	24 hours
22.	Mercury	P(A)G(A)	1000	Add HNO_3 to pH < 2, 4 °C refrigerate	28 days	28 days
23.	Nitrogen ammonia	P.G.	500	Analyze as soon as possible or add H_2SO_4 to pH < 2 refrigerate	7 days	28 days
24.	Nitrate	P.G.	100	Analyze as soon as possible, refrigerate	48 hours	48 hours; 28 days for chlorinated samples
25.	Nitrate + nitrite	P.G.	200	Add H_2SO_4 to pH < 2 refrigerate	1–2 days	28 days
26.	Nitrite	P.G.	100	Analyze as soon as possible, refrigerate	None	48 hours
27.	Organic kjehldal	P.G.	500	Refrigerate, add H_2SO_4 to pH < 2	7 days	28 days
28.	Odour	G.	500	Analyze as soon as possible, refrigerate	6 hours	N.S.
29.	Oil and grease	G. (widemouth)	1,000	Add H_2SO_4 to pH < 2 refrigerate	28 days	28 days
30.	Pesticides	G.(S)PTFE–lined cap	1000	Refrigerate add 1,000 mg ascorbic acid per litre, if residual chlorine is present	7 days	7 days until extraction; 40 days after extraction
31.	Phenols	P.G.	500	Refrigerate, add H_2SO_4 to pH < 2	–	28 days until extraction

32.	Oxygen, dissolved electrode method	G.BOD bottle	300	Analyze immediately	0.25 hours	0.25 hours
	Winkler method	G.	1,000	Titration may be delayed after acidification	8 hours	8 hours
33.	pH	P.G.	50	Analyze immediately	0.25 hours	N.S.
34.	Phosphate	G.(A)	100	For dissolved phosphate filter immediately,refrigerate	48 hours	N.S.
35.	Phosphorus (total)	P.G.	100	Add H_2SO_4 to pH < 2 and refrigerate	28 days	
36.	Salinity	G. (waxseal)	240	Analyze immediately or use waxseal	6 months	N.S.
37.	Silica	P. (PTEE) or quartz	200	Refrigerate, do not freeze	28 days	28 days
38.	Sludge digester gas	G. (gas bottle)	–	–	N.S.	
39.	Solids	P.G.	200	Refrigerate	7 days	2–7 days, see cited reference
40.	Sulfate	P.G.	100	Refrigerate	28 days	28 days
41.	Sulfide	P.G.	100	Refrigerate, add 4 drops 2 N zinc acetate/100ml, add NaOH to pH > 9	28 days	28 days
42.	Temperature	P.G.	–	Analyze immediately	0.25 hours	0.25 hours
43.	Turbidity	P.G.	100	Analyze same day, store in dark upto 24 hours, refrigerate	24 hours	48 hours

Remarks:

1. Sample can be collected in an appropriately-sized container instead of performing individual parameter-wise sampling requiring similar containers and preservation.
2. For determinations not listed, glass or plastic containers should be used, preferably refrigerating during storage and analyze as soon as possible.

P. = Plastic (polyethylene or equivalent); G. = Glass; G. (A) or P. (A) = Rinsed with 1+1 HNO_3; G. (B) = Glass borosilicate; G. (S) = Glass, rinsed with organic solvents or baked; Refrigerate = Storage at 4°C ± 2°C in dark; Analyze immediately = Analyze within 15 minutes of sample collection; N.S. = Not specified

Source: *Guidelines for recognition of environmental laboratories under the EPA, 1986* (LATS/9/2008–9).

11.3 UNUSED SAMPLE DISPOSAL

Laboratories should have a standard operating procedure for the disposal of samples, leftover digested sample leachates, and extracts or other sample predation products. Laboratories should maintain appropriate documentation and records demonstrating that samples have been properly disposed of as per the applicable rules, ensuring that no environmental hazard occurs due disposal of sample leftovers.

11.4 ANALYTICAL PROCEDURE

In India, the laboratories generally follow standards developed under APHA (American Public Health Association), BIS (Bureau of Indian Standard) or ASTM (American Society for testing and Materials). CPCB also produced a guide manual titled *Water and Wastewater Analysis*. These standard methods do not vary much on water and wastewater analysis (see *Table 14: Parameter-wise analytical methods and associated equipment or instruments*). A brief summary of the analytical methods is given in *Annexure III*.

11.5 BASIC EQUIPMENT OR INSTRUMENTS

In order to analyze the nine core parameters and 19 general parameters, and the analytical methods, some basic tools are needed, as summarized under *Table 15: Basic equipment required for core and general parameters*.

Table 14: Parameter-wise analytical methods and associated equipment or instruments

S. no.	Parameter	Methods	Equipment or instrument
Physical methods			
1	pH	Electrometric method	pH meter
2	Turbidity	Nephelometry or turbidity meter	Nephelometer
3	Temperature (°C)	–	Thermometer
4	Conductivity (µMho/cm)	Instrumental methods	Conductivity meter
5	DO	Instrumental method	DO meter
Titrimetric methods			
6	DO (mg/l)	Winkler's method, isometric titration	Glass wear (pipette or burette)
7	Acidity or alkalinity (mg/l)	Acid-base titration	Glass wear (pipette or burette)
8	COD (mg/l)	Oxidation–reduction titration	COD digestion assembly + glassware
9	Total hardness (mg/l)	Complexometric (EDTA) titration	Glassware
10	Calcium hardness (mg/l)	Complexometric (EDTA) titration	Glassware
11	Chloride (mg/l)	Argento-metric titration	Glassware
Colourimetric			
12	Nitrate/nitric (mg/l)	–	Spectro–photometer
13	Kjeldhl nitrogen (mg/l)	–	Khjeldahl assembly
14	Ammonia (NH_3) (mg/l)	Lesslerisation method	Spectro–photometer
15	Boron	Curcimine method	Spectro–photometer
16	Phosphate	Stannous chlorice/ ascorbic methods	Spectro–photometer
17	Sulfate	Turbidric method	Nephelometer or Spectro–photometer
18	Fluoride	Ion-selective methods SPAWD methods	Ion meter/ spectro–photometer
Gravimetry			
19	Total dissolved solids (mg/l)	Gravimetry (weight difference at 105°C)	Oven, analytical balance
20	Total fixed dissolved solids (mg/l)	Gravimetry (weight difference at 550°C)	Muffle furnace, analytical balance
21	Total suspended solids (mg/l)	Gravimetry	Oven analytical balance
Flame emission photometry			
22	Sodium (mg/l)	Flame emission measurement	Flame photometer
23	Potassium (mg/l)	Flame emission measurement	Flame photometer
Microbiological test			
24	Total Coliform (MPN/100ml)	• Multiple tube method • Membrane filler method	Special microbial lab
25	Faecal Coliform (MPN/100ml)	• Multiple tube method • Membrane filler method	Special microbial lab

Note: BOD measurement, difference of DO measured at initial slop and after incubation for standard time and temperature.
Source: *Guidelines for recognition of environmental laboratories under the EPA, 1986* (LATS/9/2008–9).

Advance laboratories, which have to analyze metal and pesticide, need atomic absorption spectrophotometers (AAS) and gas chromatographs. AAS should have the required cathode lamp, and the gas chromatograph should be equipped with a detector.

Table 15: Basic equipment required for core and general parameters

List of equipment	List of instruments
• Ice box (2) • Filtration assembly • Heating mantle • Hot air oven • Hot plate • Water bath • Thermometer • Autoclave • BOD incubator • Refrigerator (big size)	• pH meter • Conductivity meter • Spectrophotometer • Flame photometer • Ion selective electrode • DO meter • Analytical balance

Source: *Guidelines for recognition of environmental laboratories under the EPA, 1986* (LATS/9/2008–9).

11.6 SUGGESTED ROUTINE MAINTENANCE FOR COMMON LABORATORY INSTRUMENTS AND EQUIPMENT

Manuals or documents describing the operating procedure of equipment and instruments should preferably be kept in the working area for ready reference by analysts. Each instrument should also have a log-book to record all maintenance issues and corrective action taken.

The maintenance procedure described in the manufacturing instruction manuals must be followed. Analysts or operators are responsible for routine maintenance. Supervisors should review the maintenance register to check whether malfunctions are reported and repairs performed regularly. For a list of common maintenance activities and their frequency (see *Table 16: Suggested routine maintenance activities for common laboratory instruments and equipment*).

11.7 CALIBRATION OF INSTRUMENTS AND EQUIPMENT

Calibration of instruments and equipment can be categorized as:

- Requirements of analytical support equipment
- Requirement for instrument calibration
  a. Initial instrument calibration
  b. Continuing instrument calibration or verification

All information related to calibration of instruments and equipment needs to be fully documented in the appropriate record. Calibration of all devices that may or may not be used in actual testing instruments but are necessary to support operations is necessary. These include balances, ovens, refrigerators, freezers, incubators, water baths, temperature measuring devices, and volumetric dispensing devices, (see *Table 17: Calibration requirements for some of the common laboratory support equipment*).

11.8 MANPOWER

Generally, an environmental laboratory (water, wastewater or air analysis) needs a minimum nine full-time skilled personnel. But in case of water samples with nine core and 19 general parameters, with an average of four samples every day, five full-time skilled personnel are sufficient (see *Table 18: Manpower with qualification and job description*).

11.9 DATA MANAGEMENT

Data management begins with handling of raw data, and its validation, entry and safe storage.

11.9.1 Raw data

Raw data refers to any laboratory worksheets, records, memoranda, notes or exact copies thereof that are the result of original observations and activities of a study. For raw data entries, it is recommended to use laboratory notes for each study. This should be robust, bound and numbered with pages. All entries should be made with indelible ink.

Table16: Suggested routine maintenance activities for common laboratory instruments and equipment

Instrument	Suggested maintenance activity	Frequency	Remarks
pH meter	Clean the electrodes	Daily	
	Refill the electrodes	As needed	
Conductivity	Clean the electrode	Daily	
DO meter	Clean the electrode	Daily	
	Change the electrode	As needed	
Analytical balance	Clean the pan	Daily	
	Replace the light ball	Annually	Contractor
	Adjust the scale deflection	Annually	Contractor
Spectrophotometer	Check the lamp alignment	Weekly	
	Replace the lamp	As needed	
	Clean the windows	Daily	
	Clean the sample compartment	Daily	
	Clean the curvet	After every use	
Refrigerator	Cleanliness	Monthly	
Oven	Check temperature with certified temperature	Annually	
Autoclave	Check the gas kit	Weekly	
	Clean the inverter	Monthly	
	Sterilization indicator tape time mechanism check		
Laminar flow	Cleaning of HEPA filters and pre-filters, general upkeep and maintenance	Twice a year	Contractor
Turbidity meter	Clean the instrument	Monthly	
	Clean the calls	Daily or after use	
Thermometer	Check the cracks and gaps in the mercury	Daily	
Flame photometer	Clean The burner	Weekly	
	Clean or change the sample aspiration tube	Monthly	
	Clean the filter glass	monthly	

Source: *Guidelines for recognition of environmental laboratories under the EPA, 1986* (LATS/9/2008–9).

Table 17: Calibration requirements for some of the common laboratory support equipment

Equipment	Calibration requirement
Balance	Must be serviced and calibrated annually by an approved vendor. Calibration must be checked daily or before the balance is used with weights classified as Class-I by nationally recognized organization
Thermometer	Working glass thermometer must be calibrated against a certified thermometer at least annually
Refrigerator or freezer	Refrigerator temperature acceptance limit between 2°C to 6°C. Freezer acceptance limit < minus 10^0C. Thermometer must be immersed in glycol or mineral oil
Ovens	Temperature of units must be checked daily or before use
Incubators	Thermometer must be used in glycol or mineral oil. Acceptable temperature is 35°C–37°C
Autoclave	Autoclave pressure must be 1.02 ± 0.03 kg/cm^2. Gauge pressure temperature acceptance criteria 120°C ± 2°C
Micropipettes	Calibration are checked gravimetrically as required by the operation-specific SOP
Syringes	All syringes and volumetric glassware must be purchased as Class-A items. Calibration of these items by the laboratory is not required

Source: *Guidelines for recognition of environmental laboratories under the EPA, 1986* (LATS/9/2008–9).

Table 18: Manpower with qualification and job description

S. no.	Qualification	Nature of the job	No. of personnel
1.	High school or intermediate with science	Assistance in sampling and analysis	2
2.	Bachelor degree in science or equivalent master's degree in science	Sampling and analysis	3
3.	Master's degree in science	Sampling and analysis, Supervision of analysis	1

Source: DD Basu/CSE

11.9.2 Data validation

The most important step of validation is checking the data from the raw data notebooks. The supervisor must examine the calculations made by the analyst, like weighing of chemicals and filter value, as well as typing errors.

The supervisor should also check following:

- Is the data within the detection limits of a particular method?
- Is the data within the expected ranges of a parameter?
- Are there too many (or too few) significant digits reported?
- Is the reported data physically or scientifically possible?
- Ensure repeatability. At least three repetitions of each sample being analyzed need to be performed, and the results shall be accepted on the two closest values to ensure precision.

Besides the generality, statistical investigation of parameters may also support a validation programme. Correlation of parameters with the acceptable premises of chemistry may indicate consistency of data. Common interrelated parameters are:

- COD vs BOD
- Total Coliform vs Faecal Coliform
- TDS vs conductivity
- TDS vs FDS
- TDS vs common ions such as K^+, Na^+, Ca^{2+}, Mg^{2+}, CO_3^{2-}, HCO_3^-, Cl^-, SO_4^{2-}

The third approach is the ionic balance in which the summation of cations is close to summation of anions.

$$\Sigma Na^+ + Ca^{2+} + Mg^{2+} \approx \Sigma CO_3^{2-}, HCO_3^- + Cl^- + SO_4^{2-}$$

The ions shall be converted from the unit mg/l to meq/l

Another visual aspect of checking is the greater or smaller values among the correlated parameters, such as

- COD > BOD
- Total iron > Fe^{2+}, Fe^3
- Total Coliform > Faecal Coliform
- Total oxidized nitrogen ≥ nitrate + nitrite
- TS > TDS
- TS > Total suspended solids
- Total hardness = calcium hardness + magnesium hardness
- EC ≥ TDS

'Identification outlier value' is also an important technique for validation of data. Generally, the range of the data with respect to a parameter of a station on the basis of historical database is the criteria of identification of 'outlier'.

11.9.3 Data storage and transmission

Once the data is validated, the participatory laboratories shall enter it in a dedicated format onto a computer (dedicated hard disk) and transmit it to the dedicated CSE server. Besides the server, CSE shall also have an alternative arrangement, in case of any emergency. Participatory laboratories shall also maintain a file or register, to cover the contingency of computer crashes.

12. Capacity building for participatory laboratories

In order to design capacity building of participatory laboratories, assessment of their infrastructure and procedures is necessary. Checklists are a handy tool to asses this. A checklist for infrastructure has already been provided in one of the earlier sections.

12.1 CHECKLIST FOR LABORATORY PROCEDURE AND MANPOWER ASSESSMENT

Table 19: Checklist for assessment of laboratory procedure provides a checklist for laboratory procedure from sampling to data management.

Once such an assessment of infrastructure, laboratory procedure and manpower is completed, the laboratory may be graded as adequate, partially adequate and inadequate. Inadequate laboratories may not be considered for enlisting in the water quality monitoring programme.

The infrastructure and knowledge in adequate and partially adequate laboratories should be augmented. In terms of infrastructure, enlisting new equipment, instruments, glassware, chemicals, and, in some cases, water distillation assembly may be considered (see *Table 20: Suggested training programme*).

Table 19: Checklist for assessment of laboratory procedure

S. no.	Assessment	Yes	No	Remarks
A	Is there any format for reconnaissance survey and sampling programme?			If no, such a format shall be developed as given in Table 12
B	Is there a procedure to be followed in sample storage?			If no, the condition shall be applied as per Table 13
C	Is there a format for sample acceptance requirement?			If yes, check its accuracy
D	Does the laboratory follow established analytical procedure?			If yes, identify the procedure such as BIS, APHA, ASTM
E	Is the analytical procedure available to concerned analysts?			
F	Is the laboratory capable to analyze all the core parameters?			If not, identify the parameter not analyzed
G	Is the laboratory capable to analyze all the general parameters?			If not, identify the parameter not analyzed
H	Does the laboratory have adequate manpower?			If not, can it be strengthened?
I	Does the laboratory personnel have sufficient knowledge of water analysis?			
J	Does the laboratory have adequate equipment and instruments?			
K	Does the laboratory have a preventive maintenance protocol?			If yes, is it adequate?
L	Does the laboratory maintain notebooks and register?			
M	Does the supervisor have the knowledge to validate the data?			If yes, is it practiced?
N	If yes, is it practiced in routine work?			
o	Does the laboratory maintain computer-based data storage systems?			

Source: Dr DD Basu/CSE

Table 20: Suggested training programme

Training programme or workshop	Frequency	Target allowance	Duration
Level-I: Supervision			
Water quality monitoring programme holistic approach (About manual)	One	Supervision, CSE in-house staff (water team + laboratory team)	3 days
Analytical procedure workshop on identification methods and uniform procedure	One	Supervisor or laboratory team	2 days
Laboratory procedure work sheets	One	Supervisor or laboratory team of CSE	2 days
Statistical methods on water quality monitoring (data validation, quality control and interpretation of data)	Two	Supervisor or water and laboratory team	5 days
Quality assurance and quality control	One	Supervisor or water team	2 days
Level-II: Analysis in laboratory			
Analytical methods of core and general parameters	One	Supervisor or laboratory analyst	5 days
Onsite sampling programme, including field exercise	One	Laboratory analyst, field attendant or laboratory team of CSE	5 Days
Laboratory procedure	One	Laboratory team of CSE	5 Days
Quality assurance and control	Two	Laboratory analyst or field attendant	3 Days
Level-III: General laboratory activities			
Laboratory activities, including distillation	One	Laboratory attendants	3 Days
Field activities (including field kit making)	One	Laboratory attendants	3 Days

Source: Dr DD Basu/CSE

13. Quality assurance and quality control

Quality assurance is the definite programme for laboratory operation that specifies the measures required to produce reliable data of known precision and accuracy.

13.1 CONCEPT OF ERROR

No quantitative result is of any value unless it is accompanied by an estimate of error inherent in it. In scientific experimentation, errors are not only mistakes and oversights, but can also be a result of uncertainty. There are three main types of errors:

- Gross error is a result of human mistake or oversight. The can happen during the entry of data.
- Systematic error is measured as the difference between the mean of series of subsequent standards and the true concentration of the standard sample. It is expressed as mean error.

  Mean error = X – TV
  X = Mean TV = True value

  If the mean error is high, corrective measures must be taken. Incorrect weights, volumetric flask or pipette, incorrect calibration of instrument, even parallax (the apparent displacement of an observed object due to a change in the precision of the observer) of the analyst can be a source of systematic error.
- Random error is an imprecise error that is not repeatable. It happens due to drainage error in the volumetric glass wear or calibration in the glassware.

13.2 RELATIONSHIP OF ACCURACY AND PRECISION WITH SYSTEMATIC AND RANDOM ERROR

The relationship between accuracy and precision, and systematic and random error can be described as follows:

- **Accurate value of accuracy:** By definition, accurate value and accuracy is termed as true value or near true value
- **Precision:** If the spread of results of an experiment is small, the result is called precise; if the spread is large, the result is called imprecise
- **Repeatability:** Within a run (batch), precision is called repeatability
- **Reproducibility:** Between runs (batches), precision is called reproducibility

The interrelationship can be illustrated by the following *Figure 11: Interrelationship between accuracy, precision, and systematic and random error*, in which four analysts A, B, C, D produced result of five replicate titration (titer value) of the same batch.

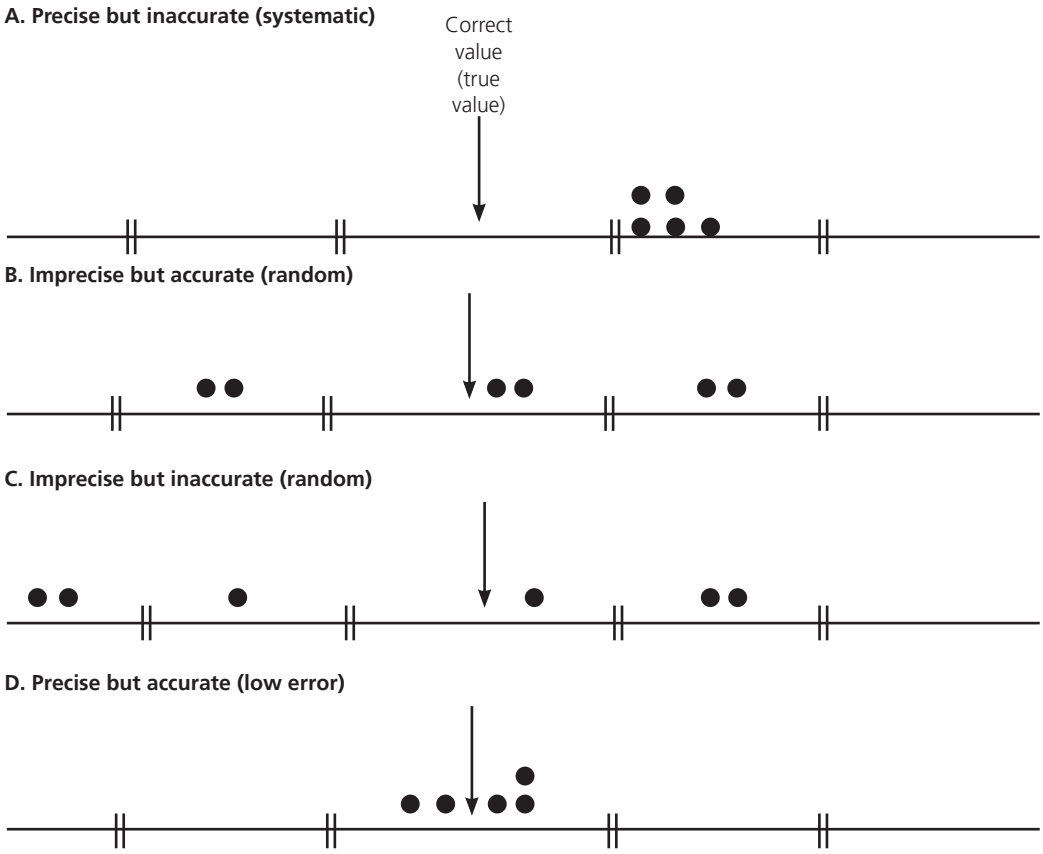
As is clear from the illustration, random error affects precision and is known as indeterminate error, while systematic error is affected by accuracy and is known as determinant error.

13.3 ANALYTICAL QUALITY CONTROL PROGRAMME

Objectives of analytical quality control programme are:

- To assess the status of analytical facilities and capabilities of concerned laboratories
- To identify the serious constraints (random and systematic) in the working environment of laboratories
- To provide necessary assistance to the concerned laboratories in overcoming the shortcomings in the analytical capabilities
- To validate the water quality monitoring data

Figure 11: Interrelationship between accuracy, precision, and systematic and random error



Source: *Statistics for Analytical Chemistry*, J. C. Miller

- 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 laboratories in an organized manner

13.4 BASIC NEEDS OF QUALITY ASSURANCE

In order to assure reliable water laboratory results, the following are required:

- A well-designed sampling programme, which includes sampling, in situ analysis, and sample preservation
- Suitable laboratory facilities
- Up-to-date laboratory instruments, sampling equipment glassware and reagents
- Well-maintained equipment and facilities
- Standardized analytical procedures covering desired variables
- Well-trained laboratory staff
- Adequate filing and reporting system
- A systematic analytical quality control programme

13.5 QUALITY CONTROL CHARTS

Analytical quality can be violated by random and systematic errors during determination. Random errors reduce precision, while systematic errors reduce accuracy. To check both types of errors, quality control charts are made on the assumption that the experimental data has normally distributed errors. Quality control charts should be plotted from the results repeatedly obtained from standard samples of known concentration against time. In order to prepare a quality control chart, the mean and standard deviation are calculated

based on an initial calibration study (analysis of at least 20 replicate standards of realistic concentration). The control chart is then constructed with the calibration mean as its central line. Warning and rejection areas are added at ± two lines and ± three times the standard deviation from the mean respectively. The analysis is performed each day for the same standard. If the analytical result of standard analysis falls outside the ± three standard deviation line, the analysis is said to be out of control and an immediate check is required to know the cause for this gross analytical error. After corrective measures, the analysis should be repeated. The occurrence of an unduly high percentage of results exceeding the warning limits (two standard deviations) is an indication that laboratory precision may not be as good as expected or that the frequency distribution of the results are not normal. The control limit may be recalculated periodically as experience is gained with the technique. Preferably, there should be use of several standards that span a range of concentration to ascertain linearity and to avoid unintentional bias due to familiarity with fixed results.

13.6 LEVEL OF ANALYTICAL QUALITY CONTROL PROGRAMME

The AQC scheme is taken up at two levels which is described in the following paragraphs.

13.6.1 Internal AQC or within-laboratory AQC

It is necessary to check the precision and accuracy of analytical results within laboratory. Internal checking is also a demonstration of the capability of a laboratory's analytical functions. Various sequential stages involved for each parameter are:

- Choosing an analytical method suitably free from bias and ensuring the complete and unabridged description of that method
- Checking that satisfaction precision is obtained with a method
- Establishing a control chart as a continuous check on precision and some source of bias
- Ensuing accuracy of a standard solution

13.6.2 External AQC or between-laboratory AQC

A group of laboratories have to achieve comparability of results by controlling the precision and accuracy of each laboratory. The reasons for AQC tests between laboratories are as follows:

- To test for possible error caused by sources not already checked within the laboratory
- To provide direct evidence that the required compatibility of results between laboratories has been achieved
- Accuracy may deteriorate with time and, hence, subsequent regular tests are required as a continuing check on between-laboratory bias
- The procedure to convert a method to standard status is done through collaborative tests (inter-laboratory studies)

13.6.3 AQC approach of the proposed Ganga monitoring programme at CSE

CSE shall conduct an internal AQC programme for a few parameters, including control charts, and develop a protocol for participatory laboratories. This programme will also organize trainings and encourage participating laboratories to perform internal AQC. Once the participating laboratories are familiar with internal AQC, the inter-laboratory AQC programme may be conducted on continuous basis. Feedback from this programme shall help in developing a time-bound ratification process to minimize the analytical error of core and general parameters.

CSE's own laboratory also conducts internal AQC for pesticide and metal analysis.

13.7 DATA INTERPRETATION

Data interpretation and dissemination is the end product of this programme. Data interpretation shall be done with the help of following statistical tools:

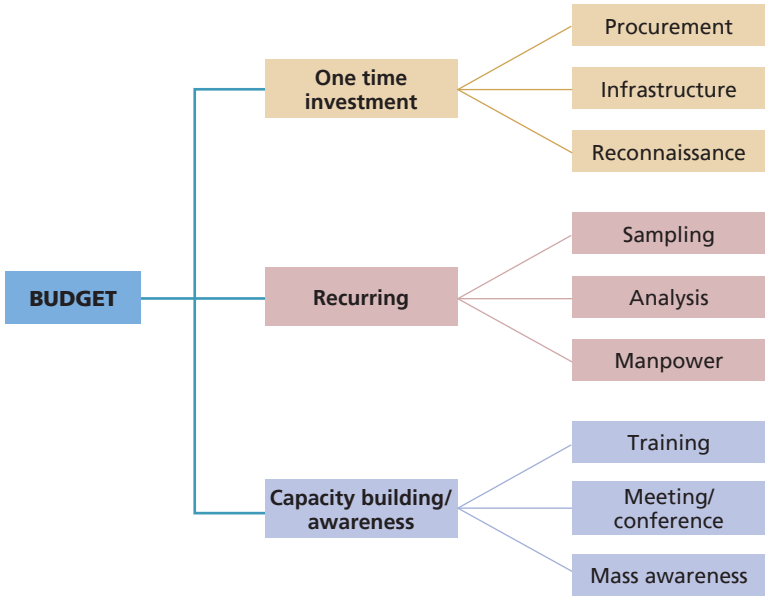
- Control tendencies of data—mean/ median
- Spread of data—percentile value at least 25.50, 90th value
- Temporal trend—non-parametric test and time series analysis
- Spatial trend—interstation correlation and regression analysis
- Exceeding of limits—percentage of data with respect to each parameter
- Interrelation of parameters—correlation and regression

Data analysis will identify a stretch as relatively good, critical and extremely critical with respect to important parameters. The outcomes can be plotted on a map. A water quality index can be developed for this purpose. Box-Wisker plot of water quality index of every station in a map can also indicate spatial and temporal trends. A separate statistical manual can be brought out in due time.

14. Budget

Budget calculation comprise of two parts, the first is one-time investments, including procurement of equipment and instruments, and infrastructure development. The other is recurring cost which involves procurement of glassware, chemicals, cost of manpower, and contingency for field investigation, including sampling. In addition, there is also the cost of capacity building for meetings, conferences and mass awareness programmes. The different components of a budget are given in *Figure 12: Components of budget*.

Figure 12: Components of budget



Source: Dr DD Basu/CSE

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ANNEXURES

Annexure I: Existing monitoring stations under national water quality monitoring programme of Ganga

S. no.	Location	State
1	Bhagirathi at Gangotri	**Uttarakhand**
2	Alkananda B/C Mandakini at Rudraprayag	
3	Mandakini B/C Alkananda at Rudrapryag	
4	Alkananda A/C Mandakini at Rudraprayag	
5	Alkananda B/C To Bhagirathi at Devprayag	
6	Bhagirathi B/C with Alkananda at Devprayag	
7	Alkananda A/C with Bhagirathi at Devprayag	
8	Ganga at Rishiesh U/S	
9	Ganga A/C of River Song NearSatyanarayan Temple D/S Raiwala	
10	Ganga at Haridwar D/S	
11	Upper Ganga River D/S Roorkee	
12	Ganga at Garhmukteshwar	**Uttar Pradesh**
13	Ganga U/S, Anoopshahar	
14	Ganga D/S, Anoopshahar	
15	Ganga at Narora (Bulandshahar)	
16	Ganga at KachhlaGhat, Aligarh	
17	Ganga at Kannauj U/S (Rajghat)	
18	Ganga at Kannauj D/S	
19	Ganga at Bithoor (Kanpur)	
20	Ganga at Kanpur D/S (Ranighat)	
21	Ganga at Kanpur D/S (Jajmau Pumping Station)	
22	Ganga at Dalmau (Rai Bareilly)	
23	Ganga a Kala Kankar, RaeBareli	
24	Ganga at Allahabad (Rasoolabad)	
25	Ganga at Kadaghat, Allahabad	
26	Ganga at Allahabad D/S (Sangam)	
27	Ganga U/S, Vindhyachal, Mirzapur	
28	Ganga D/S, Mirzapur	
29	Ganga at Varanasi U/S (Assighat)	
30	Ganga at Varanasi D/S (Malviya Bridge)	
31	Ganga at Trighat (Ghazipur)	
32	Ganga at Buxar	Bihar

33	Ganga at Buxar, Ramrekhaghat	
34	Ganga at Indrapuri, Dehri on Sone	
35	Ganga at the Confluence of Sone River Doriganj, Chapra	
36	Ganga at Khurji, Patna U/S	
37	Gangs DarbhangaGhat at Patna	
38	Ganga at Patna D/S (Ganga BDG)	
39	Ganga at PunPun, Patna	
40	Ganga at Fatuha	
41	Ganga at Mokama (U/S)	
42	Ganga at Mokama (D/S)	
43	Ganga at Munger	
44	Ganga at Sultanganj	
45	Ganga at Bhagalpur	
46	Ganga at Kahalgaon	
47	Ganga at Rajmahal	Jharkhand
48	Ganga at Baharampore	West Bengal
49	Tribeni on Ganga, Near Burning Ghat	
50	Ganga at Howrah-Shivpur	
51	Ganga at Serampore	
52	Ganga at Dakshineshwar	
53	Nabadip on ganga, Ghoshpara near monipurghat	
54	Ganga at Garden Reach	
55	Ganga at Uluberia	
56	Ganga at Palta	
57	Ganga at Diamond Harbour	

Annexure II: Monitoring station proposed by CSE

Name of the monitoring point (town/city)	State
Ganga at Rishikesh U/S	Uttarakhand
D/S Raiwala	
Ganga at Haridwar D/S	
Ganga at Bijnor	Uttar Pradesh
Ganga D/S, Anoopshahar	
Gangaghat	
Ganga at KachhlaGhat, Aligarh	
Ganga at Bithoor (Kanpur)	
Ganga at Kanpur D/S (Jajmau Pumping Station)	
Ganga at Allahabad (Rasoolabad)	
Ganga at Allahabad D/S (Sangam)	
Ganga D/S, Mirzapur	
Ganga at Chunar	
Ganga at Varanasi U/S (Assighat)	
Ganga at Varanasi D/S (Malviya Bridge)	
Ganga at Buxar	Bihar
Ganga at Buxar, Ramrekhaghat	
Ganga at Khurji, Patna U/S	
Ganga at Patna D/S (Ganga BDG)	
Falgu River U/S, Bodhgaya	
Falgu River D/S, Bodhgaya	
Budhi Ganga U/S, Muzaffarpur	
Budhi Ganga D/S, Muzaffarpur	
Ganga at Bhagalpur	
Ganga KatiharU/S	
Ganga Katihar D/S	
Ganga at Palta	West Bengal
Ganga at Dakshineshwar	
Ganga at Garden Reach	
Ganga at Diamond Harbour	
Bongaon for groundwater monitoring	West Bengal
Bansberia for groundwater monitoring	

Annexure III: Methods of analysis of water quality parameters (a brief outline)

- **pH**

pH scale for an aqueous solution lies between 0 and 14. The determination is usually done by electrometric method. In this method, pH is determined by measurement of the electromotive force (emf) of a cell comprising of an indicator electrode (an electrode responsive to hydrogen ions such as glass electrode) immersed in the test solution and a reference electrode. The emf of this this cell is measured with pH meter.

The pH of a solution is measured as negative logarithm of hydrogen ion concentration. At a given temperature, the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion concentration pH value from 0to 7 are diminishing acidic 7 to 14 increasingly alkaline and 7 is neutral.

- **Colour**

The method is useful in the field by comparing the colour of a sample with a comparator when viewed by transmitted light through a depth of several feet, pure water exhibits a light blue colour which may be altered by the presence of organic matter to greenish blue, green, greenish yellow, yellow or brown. The visual comparison method is applicable to nearby all samples of potable water pollution by certain industrial waste may produce unusual colours that can not be matched. In such cases, an instrumental method is useful. colour expressedin terms of pt/co standard unit total alkalinity (complete neutralization of OH^-, CO_3^-, HCO_3^-)

- **Hardness**

Hardness is determined by ethylene diaminetetra acetic acid (EDTA) method in alkaline condition. EDTA and its sodium salts from a soluble chelated complex with certain metal ions. Calcium and Magnesium ions develop wine red colour with Eriochrome black Tan aqueous solution at pH 10.0 to 1 forms when EDTA is added as a titrant. Calcium and magnesium bivalent ions get complexed, resulting in a change from wine red to blue which indicates end point of titration. Magnesium ion must be present to yield satisfactory point of titration. Hence, a small amount of complex of neutral magnesium salt of EDTA is added to the buffer. The sharpness of the end point increases with increasing pH. However, the specified pH of 10.00.1 is a satisfactory compromise. At a higher pH i.e.at about 12.0 Mg^{++} ions precipitate and only Ca^{++} ions remain in this solution. At this pH meroxide (ammonium purporate) pink colour with Ca^{++} gets complexed resulting in a change from pink to purple which indicates end point of the reaction. To minimize the tendency towards $CaCO_3$ precipated limit in the duration of titration period 5 minutes.

- **Alkalinity**

Alkalinity of sample can be estimated by titrating with standard sulfuric acid (0.02 N) at room temperature using phenolphthalein indicator will indicate complex neutralization of OH^- and $\frac{1}{2}$ CO_3^-, while sharp change from yellow to orange of methyl orange indicator will indicate total alkalinity (complete neutralization of OH^-, CO_3^- , HCO_3^-)

- **Conductivity**

This method is used to measure the conductance generated by various ions in the solution water. Rough estimation of dissolved ionic contents of water sample can be made by multiplying specific conductance (in ms/cm) by an empirical factor which may vary from 0.55 to 0.99 depending on the temperature of measurements.

Conductivity measured gives rapid and practical estimate of the variation in the dissolved mineral contents of water body.

- **Total solids**

Residue left after the evaporation and subsequent drying in oven at specific temperature 103–105°C of a known volume of sample are total solids include "total

suspended solids (TSS)" and "total dissolved solids" (TDS) whereas loss in weight on ignition of the same sample at 550°C in which organic matter is converted to CO_2 volatilization of inorganic matter as much as consistent with complete oxidation of organic matter are volatile solids.

- **Dissolved oxygen**

The Winkler or iodometric method and its modification are the standard procedures for determining dissolved oxygen at the present time. The test depends upon the fact that oxygen oxidize Mn^{+2} to a higher state of valance under alkaline condition and that manganese in higher state of valance is capable of oxidizing I^- to free I_2 under acid condition. Thus the amount of free iodine released is equivalent to the dissolved oxygen originally present. The iodine is measured with standard sodium thiosulphate solution and interpret ends in terms of dissolved oxygen.

The liberated iodine is titrated against $Mn^{+2} + 2OH^- \rightarrow Mn(OH)_2$ (White precipitation)

$$Mn^{+2} + 2OH^- + \frac{1}{2}O_2 \rightarrow MnO_2 + H_2O$$

$$Mn(OH)_2 + \frac{1}{2}O_2 \rightarrow MnO_2 + H_2O$$

$$MnO_2 + 2I^- + 4H^- \rightarrow Mn^{+2} + I_2 + 2H_2O$$

$$2Na_2S_2O_3 5H_2O + I_2 \rightarrow Na_2S_4O_6 + NaCl + 10H_2O$$

nitrite interference may be easily overcome by the use of sodium oxide (NaN_2). It is most convenient to incorporate the azide in alkali- KI reagent, while sulfuric acid is added, the following reaction occurs and NO_3^- is destroyed

$$NaN_2 + H^+ \rightarrow NH_3 + Na^+$$

$$HN_3 + NO_2^- + H^+ \rightarrow N_2 + N_2O + H_2O$$

- **Biochemical oxygen demand**

The test measures the oxygen utilized for the biochemical degradation of organic material (carbonaceous demand) and oxidation of inorganic material such as sulphides and ferrous ions during a specified period. It also measures the oxygen used to oxides reduced forms (nitrogenous demand) unless their oxidation is prevented by an inhibitor. Temperature effects are held constant by performing a test of fixed temperature. The methodology of BOD test is to compare a difference between initial and final DO of the sample incubation. Minimum 1.5L of sample is required for the test DO is estimated by iodometric titration.

Since the test is mainly a bioassay procedures it is necessary to provide standard conditions of temperature, nutrient supply, pH (6.5-7.5), adequate population of microorganisms and absence of microbial-growth inhibiting substance. The low solubility of oxygen in water necessitates strong waste to be diluted to ensure that the demand does not increase the available oxygen. A mixed group of microorganisms should be present in the sample, otherwise the sample has to be seeded. Generally temperature is controlled at 20°C and the test is conducted for three 5 days as 70-80% of the carbonaceous waste are oxidized during this period. However, in India 27°C and 3days incubation period as accepted norms.

- **Chemical oxygen demand**

The open refuse method is suitable for wide range of wastewater with a large sample size. The dichromate refuse method is preferred over procedure using oxidation (e.g. potassium permanganate) because of its superior oxidizing ability, applicability to wide

$$2K_2Cr_2O_7^- + 8H^+ + carboncompound \rightarrow -CO_2 + 8H_2O + Cr_2(SO_4)_3$$

$$6Fe^{(+2)} + Cr_2O_7^- \rightarrow Fe^{+2} + 2Cr^{+3} + 2H_2O$$

Variety of samples and ease of manipulation. Oxidant of mist organic compounds is up to 95-100% of the theoretical value. The organic matter gets oxidized completely by potassium dichromate ($K_2Cr_2O_7$) with silver sulfate as catalyst in presence of concentrated H_2SO_4 to produce $CO_2$and H_2O the excess $K_2Cr_2O_7$ remaining.

After the reacts ion is titrated with ferrous

ammonium sulfate $[Fe(NH_4)_2(SO_4)]$. The dichromate consumed gives the oxygen (O_2) required for oxidation of organic matter.

- **Turbidity**

Turbidity can be measured by its effect on the scattering light which is termed as nephelometery. Turbidimeters can be used for sample with moderate turbidity and nephelometer for sample with low turbidity. Higher the intensity of scattered lights higher the turbidity.

Turbidity is an expression of the optimal property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. This method is usedfor low turbidity value. For that nephelometeric technique is developed. Results from nephelometeric turbidity units (NTU)

- **Sulfate**

The most common technique is used for the determination of sulfate is turbidometric method .this method is used is used for the determination of sulfate ions. sulfate ions (SO_4^-) is precipitated in an acetic acid medium with barium chloride($BaCl_2$) so as to form barium sulfate($BaSO_4$) crystals of uniform size. The reaction involved is given below

$$Ba^{(++)} + SO_4^{--} \rightarrow BaSO_4 (\text{White})$$

Light absorbance of the $BaSO_4$ suspensions is measured by a photometer or the scattering of light by nephelometer

- **Chloride**

The quality of sample for estimation of chloride should be 100ml, or a suitable portion diluted to 100ml. chloride is determined in a neutral or is lightly alkaline solution by titration with standard silver nitrate, using potassium chromate as indicator.

Silver chromate is quantitatively before red silver chromate is formed. The chemical reactions involved in these methods are given below

$$2Ag^+ + Cl^- \rightarrow AgCl \quad (\text{White precipitate})$$

$$2Ag^+ + CrO_4^{2-} \rightarrow Ag_2CrO_2 \quad (\text{Red precipitate})$$

- **Sodium**

Trace amount of sodium can be determined by flame emission photometry at the wavelength of 589nm. The sample is sprayed into a gas flame and excitation is carried out under carefully controlled and reproducible conditions. The desired spectral line is isolated by the use of interference filters or by a suitable slit arrangement in light-dispersing devices such as prisms or gratings. The intensity of light is measured by a phototube potentiometer or other appropriate circuit. The intensity of light at 589nm is approximately proportional to the concentration of the element.

- **Potassium (K)**

Trace amounts of potassium can be determined in either a direct reading of internal standard type of flame photometer at a wavelength of 766.5nm. Because much of information pertaining to sodium applies equally to the potassium determination, carefully study the entire discussion dealing with the flame photometric determination of sodium before making a potassium determination.

- **Ammonia (nesslerisation method)**

Ammonia produce a yellow coloured compound when reacts with alkaline nessler reagent, provided the sample is clarified properly. Pretreatment with $ZnSO_4$ and NaOH precipitates Ca,Fe,Mg and sulphide and removes turbidity and apparent colour. Addition the chemical reaction of the method is given below

$$2Kr_4HgI_4 + NH_3 + 3KOH = (NH_2Hg_210) + 7KI + 2H_2O$$

- **Nitrogen (nitrate) (NO_3^{2-})**
  - **(UV – spectrophotometric method)**

  Nitrate is determined by measuring

the absorbance at 220 nm in sample containing 1ml of hydrochloric acid (1N) in 100ml sample. The concentration is calculated from stand and nitrate solution in range 1-11 mg/l on N.

- **Phenol Disulfonic Acid (PDA)**

Nitrate reacts with phenol disulfonic acid and produces a nitro derivatives which is alkaline solution develops yellow colour due to rearrangement of its structure. The colour produced follow beer's law and is intensely proportional to the concentration of NO_3^- present in the sample.

- **Nitrite**

Nitrite (HO_2^- is determined by through formation of a reddish purple azodye at pH 2.0-2.5 by coupling diazodised sulphanalide with N-Napthyl ethylenediamine dihydrochloride. The colour system follows beer's law up to 180 μg N/L with 1cm path at 543 nm.

- **Phosphate**

In acidic condition, orthophosphate reacts with ammonium molybdate to form molybdophosphoric acid. It is further reduced to molybdenum blue by adding reducing agent such as stannous chloride or ascorbic acid. The blue colour developed after the addition of ammonium molybdate is measured at 690 or 800nm within 10-12 minutes after development of colour by using blank. The concentration is calculated from the standard graph. The intensity of the blue coloured complex is measured which is directly proportional to the concentration of phosphate present in the sample.

- **Fluoride**

Fluoride is measured by two methods

- Ion selective
- Colorimetric methods (SPANDS)

Ion selective method

When the fluoride electrode (ianthanum fluoride crystal) is dipped in a sample whose concentration is to measured , a potential is established by the presence of fluoride ions by any modern pH meter having an expanded millivolt scale.

The fluoride ion selective electrode can be used to measure the acitivity or concentration of fluoride in aqueous sample by use of an appropriate curve. The electrode does not respond to bound or complexed fluoride.

Sodium 2- (parasulphphenylazo) -1, B-dihydroxy-3, 6-napthalene disulphate (SPANDS) method

This method is used for estimation of fluoride in natural water in the concentration range 0-1.4 mg/l.

Under acidic condition fluoride (F^-) react with zirconium-SPANDS-dye-lake, dissociating a portion of it into a colourless complex anion (ZrF_6) and the dye.

As the amount of fluoride increases, the colour produced becomes progressively lighter and hence it obeys Beer's law in reverse manner.

Centre for Science and Environment
41, Tughlakabad Institutional Area, New Delhi 110 062
Phone: 91-11-40616000, Fax: 91-11-29955879
E-mail: cse@cseindia.org
Website: www.cseindia.org