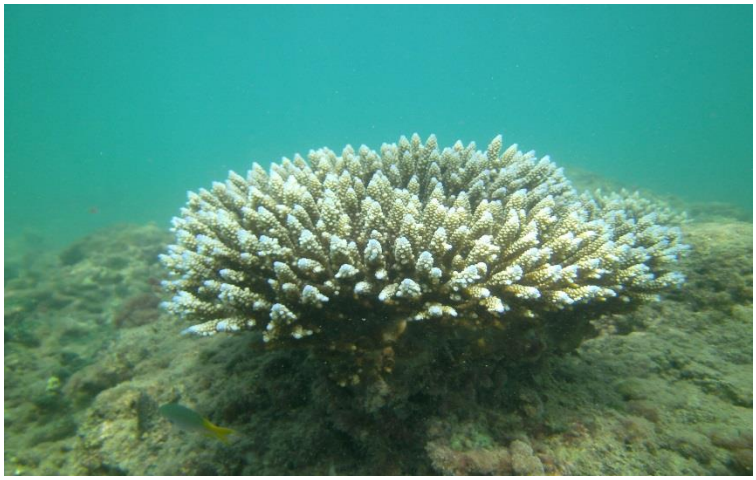
A protocol for joint assessment of the SDG Targets 6.3 and 14.1 on freshwater and marine pollution



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A protocol for joint assessment of the SDG Targets 6.3 and 14.1 on freshwater and marine pollution

Chapter -1 Introduction

1.1.Water sector of Sri Lanka

As currently available statics reveal, Sri Lanka is relatively well enriched with water resources. The estimated annual water supply per capita, is at around 2 329 cubic meters, which is above the standard international threshold of 1 700 cubic meters per person. Annual freshwater withdrawal of Sri Lanka is only about 25 % of its total resources (World Bank). The United Nations water scarcity level is 40 % and accordingly Sri Lanka's water scarcity is far below the 40 % level adopted by the United Nations to mark water scarcity (IWMI, 2017) .

It is estimated that water demand of the country in 2025 will increase of less than 50 % of the water actually withdrawn I991 and this amount will be equal to less than half of the available water resources (IWMI, 2017). According to the Climate Secretariat there are 103 distinct river basins, 309 man-made major irrigation reservoirs 24 and about 12 000 minor irrigation reservoirs (Climate chnage Secretariate , 2010).

Figure 1Map showing major river basins of Sri Lanka

Available statics are evident that this is very noticeable temporal and spatial aspects of water scarcity in the country and this mainly owing to the bimodal pattern of rainfall (IWMI, 2017). It has been alerted that by 2025, most of the districts in the dry zone will face severe seasonal or year-round absolute water scarcity at the current level of irrigation efficiency (Planning, 2013). These are currently recorded for over 75 % of the irrigation withdrawals and have the highest increase in water withdrawals projected for the future. Surface water sources are dominated in water sector of Sri Lanka, whereas groundwater use is largely limited to domestic water supply and small-scale irrigation.

Moreover, increased trends of demand for groundwater is being observed which is facilitated by low-cost drilling and pumping technologies and a government subsidy for groundwater development for small-scale agriculture that was introduced in the early 1990s (IWMI, 2017). A major threat emerging in many areas is the degradation of water quality which can critically lower the water available for potable, agricultural and commercial uses. Especially in rural areas, agricultural pollution is the major source of pollution. This deteriorated water quality has contributed to a serious environmental health crisis which includes; chronic kidney disease, thought to result from contaminated groundwater, is widespread, particularly in the rural areas of the dry zone. The water scarcity will be further increased with climate

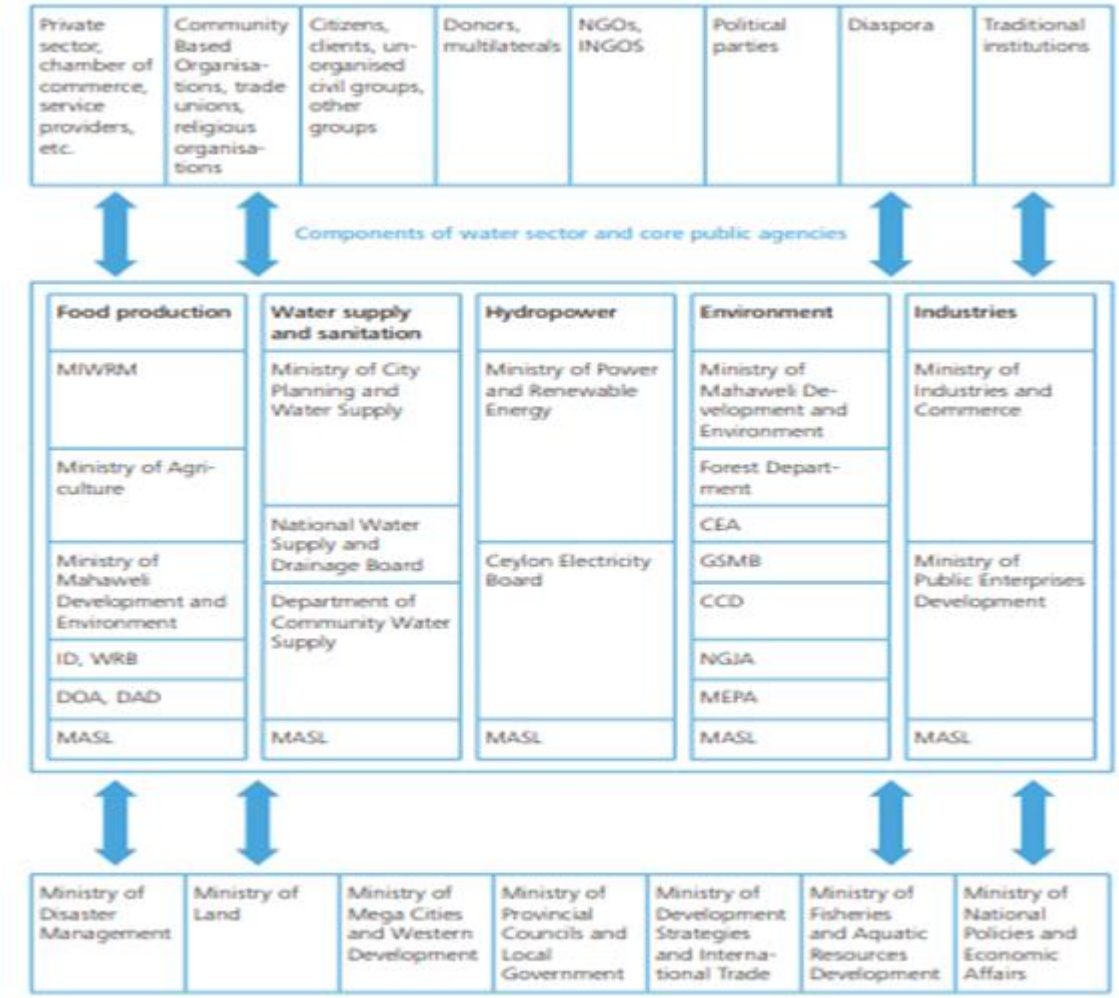
change impact. There is enough evidence that suggests that Sri Lanka's climate has already changed. During the period 1961-1990 air temperature increased by 0.016 °C per year and annual precipitation decreased by 144 millimeters (mm) (7 %) compared to the period 1931-1960 (IWMI, 2017).

The estimated annual total wastewater generation in the country is 273 million cubic meters and a major proportion of this volume is diverted to the sea or surface water bodies ((Jayakodi, Raschid-Sally, Abayawardana, & Najim, 2006). Whereas the amount of wastewater and solid and liquid waste produced by industries located in the major industrial parks is approximately 30 million cubic meters per year. The insufficient capacity of the existing sewage system in the greater Colombo area to properly handle the wastewater and sewerage might lead to poor-quality water bodies and waterways (IWMI, 2017). The status of wastewater as a part of the overall water budget is minimal and precise data on this component of the water balance is not readily available. Annual fresh water withdrawals in Sri Lanka in 2014 is estimated to have been around 13 billion m^3 during the period 1962-2014 (World Bank, 2015). Out of 13 billion $m^{3,}$ 87 % is utilised for agriculture and about 6 % is being utilized for municipal water supply and industry (World Bank, 2015). Paddy, the primary food crop of Sri Lanka, moreover paddy is traditionally cultivated by utilizing surface irrigation schemes. About 560 000 hectares of irrigated land is devoted to paddy cultivation, which produces about two thirds of the total national rice output. Average water duty for paddy cultivation is 6 acre-feet (7 400 m^3), which is much higher than in many other Asian countries (Ministry of Finance and Planning, 2013). Groundwater use in agriculture is mainly for non-paddy crop cultivation.

1.2 Institutions involved in water management

There are a range of agencies involved in water management sector and these agencies can be categorized according to their area of jurisdiction as national institutions and provincial institutions. The institutional set up associated with water sector can be divided into government agencies dealing mainly with

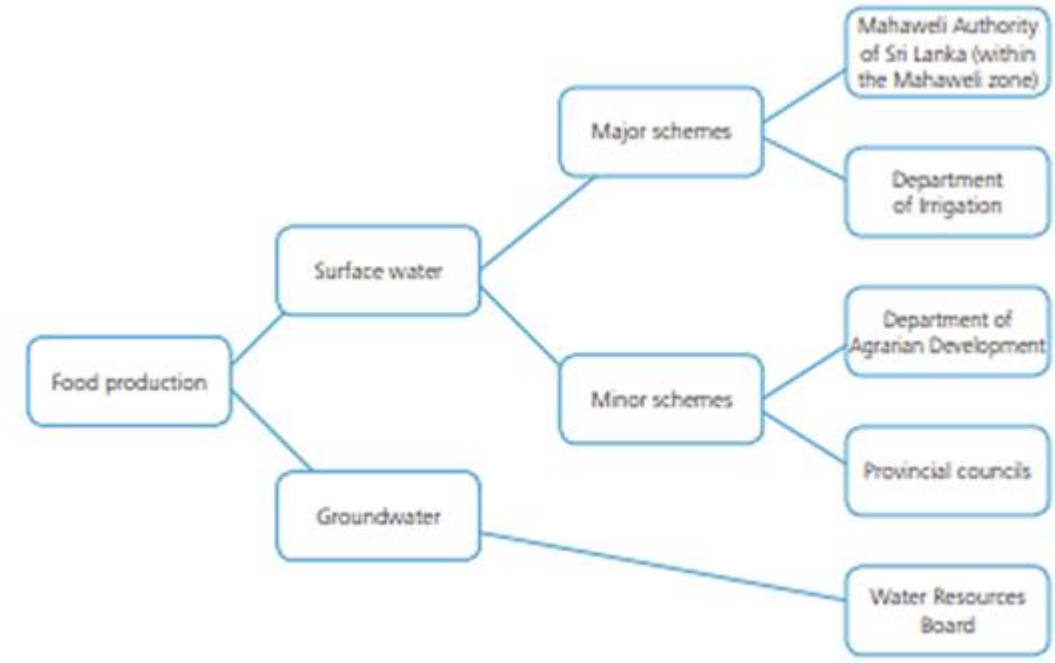
(a) food production; (b) water supply and sanitation; (c) hydropower; and (d) environmental management. In addition, there are several NGOs that are involved with the water sector (IWMI, 2017). While some ministries, agencies and NGOs function almost exclusively within a particular subsector, many have cross-cutting functions. Below diagram shows a schematic representation of Sri Lanka's water sector.



(Source: IWMI, 2015)

Figure 2 Schematic representation of Sri Lanka's water section

Food production is one of the main goals of irrigation and water resources development in Sri Lanka. The institutional landscape of responsible agencies for irrigation is highly complex. The Ministry of Irrigation and Water Management and the Irrigation Department, Ministry of Mahaweli Development and Environment and agencies under its purview are the key organisations responsible for irrigation development policy and the management of all major and medium irrigation schemes. Minor schemes come under the provincial councils. Owing to inadequate technical capacity in most provincial irrigation departments, the Agrarian Development Department continues to manage the minor schemes (IWMI, 2017). There is no single agency responsible for groundwater development and use. The Water Resources Board is responsible for conducting hydrological investigations and policy-oriented research pertaining to groundwater.

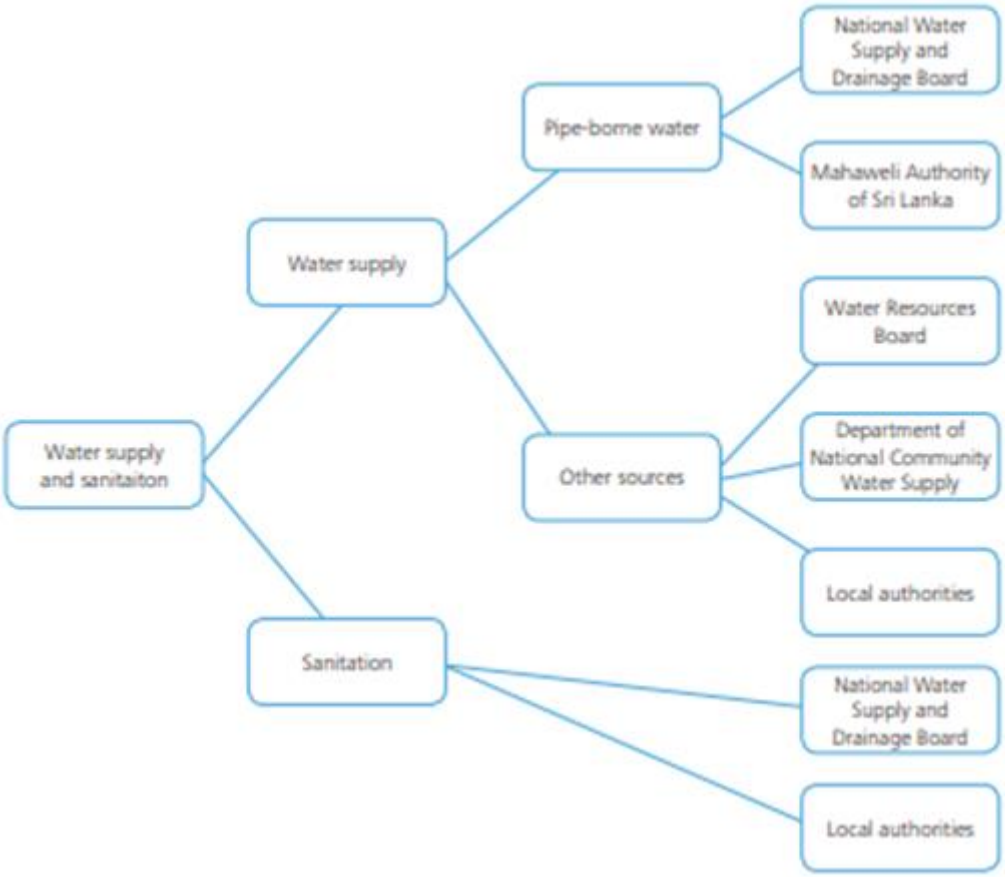


Source: IWMI, 2015

Figure 3 Subsector layout - food production

1.3. Water supply and sanitation

The water supply and sanitation subsector comprise investment by several donors, especially the World Bank, the ADB, the JICA, the AFD and the EU. Figure 4 depicts a schematic representation of the subsector. This includes the provision of pipe-borne water as well as other sources of water extraction together with the provision of sanitation facilities. It is also an area targeted by many organisations for the construction of water supply and sanitation systems, domestic wells and rainwater-harvesting schemes. The current concern over the drinking water quality in certain regions of Sri Lanka, where CKDu is prevailing, has reinforced the urgency to provide access to clean water.

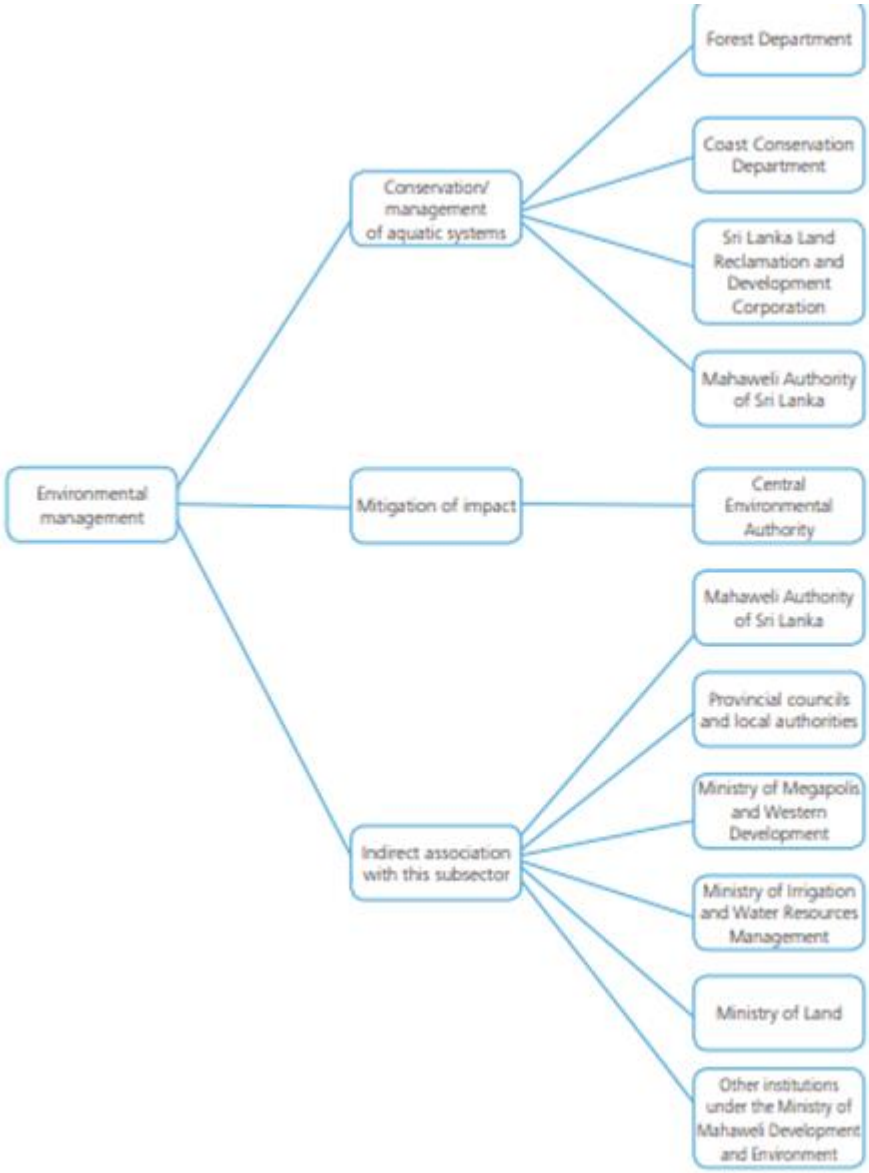


Source: IWMI, 2015

Figure 4 Subsector layout - water supply and sanitation

1.4. Environmental management

This includes government agencies involved in the conservation of aquatic ecosystems that mitigate the impact of developmental activities on water resources and agencies who play a more distant role in both services. A more recent private sector initiative is the business and biodiversity platform. The objective of this initiative is to set up a place where businesses can come together to share experiences and best practices, learn from their peers and voice their needs and concerns to strengthen the link between the business sector and biodiversity conservation The Global Water Partnership (and the Sri Lanka Water Partnership) works towards the advancement of the integrated water resources management (IWRM) strategies, for which environmental management (mitigation of pollution, watershed protection, wetland management and reducing unregulated rivers and mining) are major focus areas. The subsector map is depicted in Figure 5.



Source: IWMI, 2015

Figure 5 ***Subsector layout - Environmental management***

1.5. Legal framework of the water sector

Currently, the number of parliaments acts concerning the water sector, including water supply, water quality, drainage, irrigation and environmental conservation exceeds 50. These laws have been enacted over time to meet specific needs, often with inadequate consideration of existing legislations and future needs. Laws are administered by numerous agencies with a wide range of responsibilities. Common features of water resource management policy in

Sri Lanka are a confusion of policies with overlapping responsibilities and duplication of activities, conflicting jurisdictions and inaction. Sri Lanka's laws from colonial times never reflected any urgency for conservation as there was a general perception of water abundance in the country, though in realistic terms, there is not enough water for all purposes (IWMI, 2017). With its historical and long-standing focus on irrigated agriculture, Sri Lanka has resulted in very strongly irrigation-based institutions. These power domains were reinforced by political imperatives that for very logical reasons at the time provided for free infrastructure support and services in irrigation (Ratnayake, 2015). A mutually dependent nexus developed between politicians seeking political rent from such investment and services to promote their own visibility and at the same time enable agencies to feel secure, despite the management and operational inefficiencies and failures (Ratnayake, 2015). The provision of free water and services held benefits for both agency staff and politicians. The ID, established in 1900, is responsible for managing major irrigation and interprovincial schemes. It is also responsible for administering the Irrigation Ordinance. MASL is in charge of managing water resources under its purview, as specified in the MASL Act No 23 of 1979 (the Mahaweli River Basin as well as several other hydrologically connected basins and special areas). The MASL act provides power to apply a holistic perspective and a comprehensive approach to resource-based social and economic development, including irrigation and water management, land development and settlement, agricultural development, post-settlement activities, watershed management and environmental conservation.

The NWSDB Act No 2 of 1974 and its subsequent amendments mandated to the NWSDB to provide safe water supply to domestic, commercial and industrial premises and to provide a safe sewerage system. The Ceylon Electricity Board Act No 20 of 2009 and its amendment provide rights to the Ceylon Electricity Board to use water for electricity generation.

The Water Resources Board was established under the Water Resources Board Act No 29 of 1964 with the broad mandate of advising various aspects of water resource management to the relevant subject minister and, more importantly, to play a coordinating role of various line agencies. However, the functions of the board are limited to the development of groundwater resources.

The Central Environment Authority (CEA) was formed under the National Environmental Act No 47 of 1980 with the mandate of protecting and managing the environment. The

authority was given wider regulatory powers for pollution control (including water) by the amended Acts No 56 of 1988 and No 53 of 2000. The major problem with the current institutional arrangements for water quality management is uncoordinated efforts of the agencies handling the management of water quantity and quality. Lack of coordination between land-use activities and water management is also an issue, even though the CEA has been active in controlling industrial pollution through various monitoring activities of industries after the licenses awarded are considered to be inadequate (Climate chnage Secretariate , 2010).

Water Pollution Control:

Water quality in Sri Lanka is arguably an even more serious problem than water shortage. In rural areas, where less than half the population has access to purified water, agricultural runoff is the dominant pollution source, while in urban areas human and industrial waste is left largely untreated, contaminating both surface water and underground water supplies. This crisis of water quality has contributed to serious environmental health crisis.

Chronic kidney disease, considered to be contaminated groundwater, is now widespread and is a major concern that has attracted the attention of the authorities at the highest political level. Legislation to control water pollution is inadequate. The State Lands Ordinance (as amended) recognises that the right to the use, flow, management and control of the water in any public lake or stream is vested in the state. In the exercise of such a right, the state may enter any land and take measures for the conservation and supply of such water for its more equal distribution, beneficial use and protection from pollution.

The Mines and Minerals Act (No 33 of 1992), empowers an owner or occupier of any land or a licensee authorised in terms of the act to produce and consume mineral water in or from such land for his or her personal use. The WRB established in terms of the Water Resources Board Act is given the mandate of advising the minister regarding the preparation of plans for the conservation, utilisation, control and development of groundwater.

1.6. Water quality monitoring programme and responsible agencies

1.6.1. Existing water quality monitoring protocol in the country and within the watershed

Presently, there is no fixed long-term programme to monitor qualities of water bodies including inland and sea water in Sri Lanka. However, several government agencies have

mandate to monitor water quality in public water bodies and take remedial action. The importance of the water quality monitoring and management has given priority due to recent health issues such as spreading of the chronic kidney disease of unknown aetiology.

The water quality of the public water bodies, including coastal and marine areas is monitored by different interested groups to ascertain changes of water quality, identify water quality problems, and gather information for pollution assessment and management. Following agencies are involved in water quality monitoring in public water bodies with different objectives.

Central Environment Authority

National Water Supply and Drainage Board

Irrigation Department

National Aquatic Resources development and research agency

Coast Conservation Department

Marine Environment Protection Authority

Other research agencies such as Industrial technology Institute

1.6.2. Responsibilities of the stakeholder's agencies

- Central Environmental Authority (CEA) under the Ministry of Environment - responsible for preventing inland water pollution
- National Water Supply and Drainage Board (NWS&DB) - responsible for potable water supply and domestic sewerage treatment and management in the country.
- Dept. of Irrigation - for irrigation water supply and management
- Water Resources Board - for groundwater management
- Mahaweli Development Authority - for Managing specific water resources diversion and development projects.
- Board of Investment – industrial wastewater treatment
- Marine Environment Protection Authority
- Coastal Conservation and Coastal Resources Management Department

Chapter 2

2. Water quality monitoring requirement as per SDG for Maduru oya watershed

2.1 Introduction about Maduru oya watershed and Kayankerni and Pasikuadah coral reef

Kayankerni and Paskudah reef systems are ecologically diverse and congregate a diverse array of corals and other vibrant plant and animal life that includes just over 200 species of fish. (Weerakkody, , Subhashana, , & Lakmal, 2012). Sedimentation, decreased salinity resulted by changes in flow patterns, and agricultural runoff have contributed to significant degradation of nearshore reefs in the area, particularly within Pasikudah Bay (Allepola, Harishchnadra, Dhanushkka, & Ranawana, 2015). The influx of land-based pollution comes from the adjacent Maduru Oya river basin discharged via the Valachchenai estuary. The Maduru Oya is a major river system in the North Central Province of Sri Lanka, with the main channel traversing approximately 135 km, in a general south to north orientation with its headwaters in the vicinity of Bibile and Rideemaliyadda. The river intersects the Maduru Oya National Park and drains into a large estuarine environment around Valaichchenai Harbour at the coast. The basin area is some 1,541 square kilometers and receives an estimated 3,060 million cubic meters of rain per year, where approximately 26 percent of the water reaches the sea (FAO, 2019).

The main coastal towns of Oddamavadi and Valaichchenai are situated along the coastal estuary of the Maduru Oya River, north of Pasikuadah Bay and south of Kayankerni. According to the Sri Lanka Department of Census and Statistics (2007) the Batticaloa District had a population of 515,85719. The main economic activities of these coastal communities are fishing, agriculture and trade. There is an extensive coastal fishery using gill nets, drift nets, traps and lines for reef-associated species and small pelagics. Collection of lobsters, sea cucumber, chanks, and ornamental species by scuba diving is also carried out. The Valachchenai estuary and fisheries harbor provides anchorage for around 250 multi-day fishing boats engaged in offshore fisheries (FAO, 2019). The use of illegal and destructive fishing methods such as bottom set nets and dynamite fishing are prevalent in the area and constitute significant threats to coral reefs.

Agriculture consists of rice farming, fruit and vegetable cultivation and cashew cultivation, as well as extensive livestock. There have also been efforts to expand aquaculture, with a large prawn farm established near Kayankerni by the National Aquaculture Development Authority. The interior upland areas of the Maduru Oya watershed is dominated by a mix of agricultural and pastoral land, homesteads, and dry zone forest. The main agricultural crops include rice, corn, and vegetables. Recreational tourism has been generating modest revenue to coastal communities and can be expected. to grow significantly in terms of total revenue and relative importance over the next decade. Pasikudah has been identified as a major tourism development zone by the government and more than ten new resorts have been established in the last five years, along with a growth in locally owned budget accommodation and auxiliary services such as tours, excursions, eateries and shops. Tourism activities that are directly dependent on the coral reef such as scuba diving and snorkelling have also seen a growth in recent years.

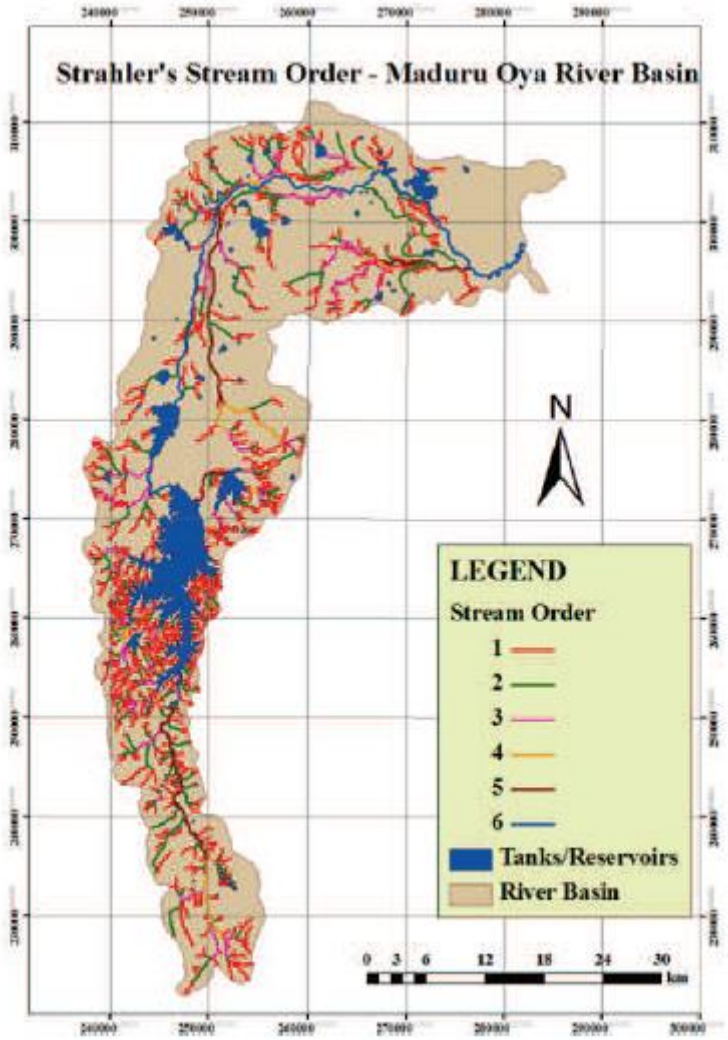


Figure 6 Strahler's Stream Order applied to Maduru oya river basin

2.1.2. Present issues related to watershed pollution load and impact on coral reef

Reef communities at particular locations in the country have demonstrated resilience to recent bleaching events, signalling possibly a higher chance of being less impacted by climate change in the coming decades. Kayankerni and Pssikuda coral reefs are located at near to the malwathu oya meets the sea. Therefore, there are close link between coral reef and freshwater and other pollutant discharge by Maduruoya the sea area. Maduruoya and its watershed area are highly used for agriculture and there also urban areas in this watershed. Sri Lanka is among the countries which use highest amount of inorganic fertilizer for hectare of land area. The main reason for the use of excessive amount of fertilizer is availability of fertilizer subsidies for farmers and unavailability of good agriculture extension services. The most of the fertilizer and agrochemical residues finally end of with the sea areas close to Kayankerni

and Pasikuda coral reefs. The large amount nutrient and other type of pollutant enters into Maduruoya river and finally end up with the sea area close it including coral reef. Therefore, there are impact on coral reef due to discharges of Maduruoya especially fresh water. Recent study shows that the excessive of fresh water carries through Maduruoya and its watershed area has direct impact on the coral reef (Allepola, Harishchnadra, Dhanushkka, & Ranawana, 2015). However so far, no studies were carried out to impact on nutrient input ot the sea areas and its impact on coral reefs. This makes a good case for their protection from anthropogenic stressors where these reefs may be used in the future for restorative work in other locations.

2.2. Sustainable Development Goal 6 and Sustainable Development Goal 14 Linkage between SDG goal 6.3 and SDG goal 14.1

SDG 6: Clean water and sanitation

Mainly focus on fresh water and fresh water management directly this also related to human health. Also target 6.3 mainly focus on the water quality and reduction of fresh water pollution eventually reduce the pollution load carried to sea by land. The achievement following six targets is essential to achieve SDG 6.

6.1 By 2030, achieve universal and equitable access to safe and affordable drinking water for all.

6.2 By 2030, achieve access to adequate and equitable sanitation and hygiene for all and end open defecation, paying special attention to the needs of women and girls and those in vulnerable situations

6.3 By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally.

6.4 By 2030, substantially increase water-use efficiency across all sectors and ensure sustainable withdrawals and supply of freshwater to address water scarcity and substantially reduce the number of people suffering from water scarcity.

6.5 By 2030, implement integrated water resources management at all levels, including through transboundary cooperation as appropriate

6.6 By 2020, protect and restore water-related ecosystems, including mountains, forests, wetlands, rivers, aquifers and lakes

6.A By 2030, expand international cooperation and capacity-building support to developing countries in water- and sanitation-related activities and programmes, including water harvesting, desalination, water efficiency, wastewater treatment, recycling and reuse technologies.

6.B Support and strengthen the participation of local communities in improving water and sanitation management

The third target of the SDG (6.3.) is "By 2030, improve water quality by reducing pollution, eliminating dumping and minimizing release of hazardous chemicals and materials, halving the proportion of untreated wastewater and substantially increasing recycling and safe reuse globally". The target 6.3 divided into two indicators. There are two proposed indicators to measure the achievement of target.

The first indicator: 6.3.1 "Proportion of wastewater safely treated" addresses the latter part of the target that calls for a halving of the proportion of untreated wastewater. The second indicator 6.3.2: "Proportion of bodies of water with good ambient water quality" aims to cover freshwater quality more generally by assessing the proportion of freshwater bodies with good ambient water quality.

Sustainable Development Goal 14: "Conserve and sustainably use the oceans, seas and marine resources for sustainable development". There are following seven targets.

Target 14.1: By 2025, prevent and significantly reduce marine pollution of all kinds, in particular from land-based activities, including marine debris and nutrient pollution.

Target 14.2: By 2020, sustainably manage and protect marine and coastal ecosystems to avoid significant adverse impacts, including by strengthening their resilience, and take action for their restoration in order to achieve healthy and productive oceans.

Target 14.3: Minimize and address the impacts of ocean acidification, including through enhanced scientific cooperation at all levels.

Target 14.5: By 2020, conserve at least 10 per cent of coastal and marine areas, consistent with national and international law and based on the best available scientific information

Target 14.6: By 2020, prohibit certain forms of fisheries subsidies which contribute to overcapacity and overfishing, eliminate subsidies that contribute to illegal, unreported and unregulated fishing and refrain from introducing new such subsidies, recognizing that appropriate and effective special and differential treatment for developing and least developed countries should be an integral part of the World Trade Organization fisheries subsidies negotiation.

Target 14.7: By 2030, increase the economic benefits to small island developing States and least developed countries from the sustainable use of marine resources, including through sustainable management of fisheries, aquaculture and tourism.

Among the above target 14.1 directly related to marine pollution and specially land based pollution and marine litter pollution. The proposed indicator for the 14.1 target is Index of coastal eutrophication and floating plastic debris density (Vitro R. , 2017).

2.3 Linkage between SDG goal 6.3 and SDG goal 14.1

The proposed indicator of 6.3.1 is 6.3.1 “Proportion of wastewater safely treated. This indicator designed to cover all wastewater, with focus on households and effluent from hazardous industries. The large amount of domestic waste water and industrial waste water discharge into water stream or rivers and finally end up with the sea. A halving of the proportion of untreated wastewater as defined and measured by indicator 6.3.1 is likely to receive fresh and marine water recipients of a significant part of the (Biochemical oxygen demand BOD) and nutrient loads and greatly contribute to reducing marine pollution (UN Environment , 2018). It would also contribute significantly to reducing adverse impacts on the marine and coastal environments and allow for their restoration. It can be argued that

reducing the nutrient load through the increase of proportion of waste water safely treated can be reduced marine pollution and therefore there is very good link among two indicators (Berggren,Liss Lymer, B & Liss Lymer, 2016).

In addition, Indicator 6.3.2 shall measure the areal proportion of water bodies in a country with good ambient water quality compared to all water bodies in the country. The word "Good" is defined as an ambient water quality that does not damage ecosystem function and human health. Rivers and other water bodies connected to the sea and all drains coming through the catchment finally end up with the sea (Berggren,Liss Lymer, B & Liss Lymer, 2016). If the water bodies water quality can remain as a good condition, the pollution load coming from land base rivers and water bodies can be reduced. Especially nutrients release from agriculture, aquaculture, municipal etc should be reduced to maintain water bodies in a good water quality condition. Eventually this finally reduce the pollution load. Therefore, it is very clear that SDG goal 6.3 and 14.1 has very strong link and the achievement of 6.3 target eventually helpful to achieve the target of SDG 14.1.

"Index of coastal eutrophication and floating plastic debris density. The main cause of hypoxic conditions, is excessive nutrient pollution from land-based human activities. The proportion of floating plastic debris that enters the marine environment through rivers seems not to have been quantified but significant amount plastic litter entered to the sea by rivers is probably significant.

Oceans and seas are major sources of water in the hydrological cycle and therefore require sustainable management through integrated water management that addresses the multiplicity and diversity of water actors. Ocean sustainability directly links to sustainable water management. Preventing marine pollution contributes to improving water quality and vice versa. Conservation of marine and coastal areas can support integrated water resource management and contribute to protecting and restoring water-related ecosystems. Sustainable aquaculture can contribute to water-use efficiency and local water and sanitation management. In return, increasing water-use efficiency may have positive feedbacks on marine and coastal ecosystems and support their conservation and sustainable use. For example, replacing open by closed recirculation systems to reduce water demand would also limit waste water flow to the environment. A potential negative side effect of strengthening

coastal tourism or aquaculture as part of blue growth might be the resulting impact on water quality and availability.

2.4. Measurement and monitoring of SDG 6.3 and 14.1 Indicators.

It is necessary to have a systematic approach to measure and monitor indicators through this evaluation can be done to understand the level of achievement of each target.

As per the GEMS guideline using the target values, a simple index based on the compliance of the monitoring data with the selected target values is used to classify the quality of individual water bodies. The monitoring values of the water body in all locations of the water body are compared with the target values. The index is defined as the percentage of monitoring values that complies with the target values (GEMS, 2018).

$$C_{wq} = \frac{n_c}{n_m} \times 100$$

Where

C_{wq} is the percentage compliance [%];
n_c is the number of monitoring values in compliance with the target values;
n_m is the total number of monitoring values.

The result of the classification of individual water bodies can be aggregated to the national level by calculating the proportion of classified water classified as having a good quality status to the total number of classified water bodies expressed in percentage (GEMS, 2018).

$$WBGQ = \frac{n_g}{n_t} \times 100$$

Where

$WBGQ$ is the percentage of water bodies classified as having a good quality status;
n_g is the number of classified water bodies classified as having a good quality status;
n_t is the total number of monitored and classified water bodies

Water quality parameter which can be sued to measure the above indicator.

Dissolved oxygen

Biological oxygen demand,

Chemical oxygen demand

Salinity

Electrical conductivity

Total dissolved solids

Total nitrogen Nitrogen* Total oxidised nitrogen, Nitrite, Ammoniacal nitrogen

Nitrate

Phosphorous

Total phosphorous

Acidification pH

2.5. Methodology for monitoring of 14.1 indicators

There is no internationally accepted methodology to assess the proposed indicator of the Index of coastal eutrophication potential (ICEP) However, there are proposed method and following can be adopted to measure the indicator.

$$ICEP = [NFlx/(14*16) - SiFlx/(28*20)]*106*12 \quad \text{if } N/P<16 \text{ (N limiting)}$$

$$ICEP = [PFlx/31 - SiFlx/(28*20)]*106*12 \quad \text{if } N/P>16 \text{ (P limiting)}$$

NFlux = DINFlux + DONFlux + PNFlux, and

PFlux = DIPFlux + DOPFlux + PPFlux,

Where;

- DON = dissolved organic nitrogen; PN = particulate nitrogen; DIP = dissolved inorganic phosphorus; DOP = dissolved organic phosphorus; and PP = particulate phosphorus
- Si- Reactive Silica

This indicator is developed based on the non-siliceous algae considering the fact that siliceous algae are not harmful to the ecosystem and this indicator varies from -5to 5 and if the indicator value is -5 obtained the coastal water is considered to be oligotrophic whereas +5 indicate eutrophic coastal waters (Gilles & Josette , 2007).

Water quality parameters required to measure the above equation

Dissolved organic nitrogen

Particulate nitrogen

Dissolved inorganic nitrogen

Dissolved organic phosphorus

Particulate phosphorus

Total Prosperous

Reactive Slica

As per the above equation this indicator calculates the fluxes of nitrogen and phosphorus and finally it diverted carbon Kg per square Km per day. Hence this can be use only rivers and stream which flows to the sea. Based on that eutrophication potential can be decided. However actual eutrophication potential of the selected sea area cannot measure using the above indicator. It is essential to obtain the sea areas actual eutrophication level based on the nutrient load. Therefore, we proposed to use TRIX (tropic index) which can use to measure eutrophication level of selected coastal areas (Vollenweider, Glovanard, Montanari, & Rinaldi, 1998).

The value comes out from the integration of more factors indicating the trophic level; it eliminates the subjective estimations based on the singular parameters.
It reduces the complexity of coastal system; and it distinguishes among different spatio-temporal situations, thus allowing a quantitative comparison.

$$TRIX = \left(\frac{k}{n}\right) \sum i = n \ ((\log M - \log L)/(logU - logL))_i$$

Where;

- n = number of the variables (in our case five),
- M = measured value of the variable,

- U = upper limit,
- L = lower limit.

  K= Constant

$$\text{TROPHIC INDEX} = (\text{LOG}[\text{Ch}^{*}\text{aD}\%)\text{O}^{*}\text{N}^{*}\text{P}] - [-1{\cdot}5])/1{\cdot}2$$

Table 1 Table showing TRIX units and corresponding trophic state

Conditions	TRIX units	Trophic state	Water quality condition
Oligotrophic	**< 4**	**Elevated**	**Scarcely productive water**
Mesotrophic	**4 << 5**	**Good**	**Moderately productive water**
	5 << 6	**Mediocre**	**Very productive waters**
Eutrophic	**> 6**	**Bad**	**Strongly productive water**

Water quality monitoring parameters which can be used calculate the above TRIX index.

- Chlorophyll- a (µg/L)
- Oxygen as absolute % deviation from saturation (100-O%)
- Total nitrogen (µM)
- Total phosphorous (µM)
- Reactive silicate (µM)

The above details clearly show that the integrated assessment methodology can be adopted to measure the indicators of SDG 6.3. and 14.1.

Chapter 3

3.The proposed protocol for a joint assessment of the SDG targets 6.3 and 14.1 Source to seawater quality monitoring protocol

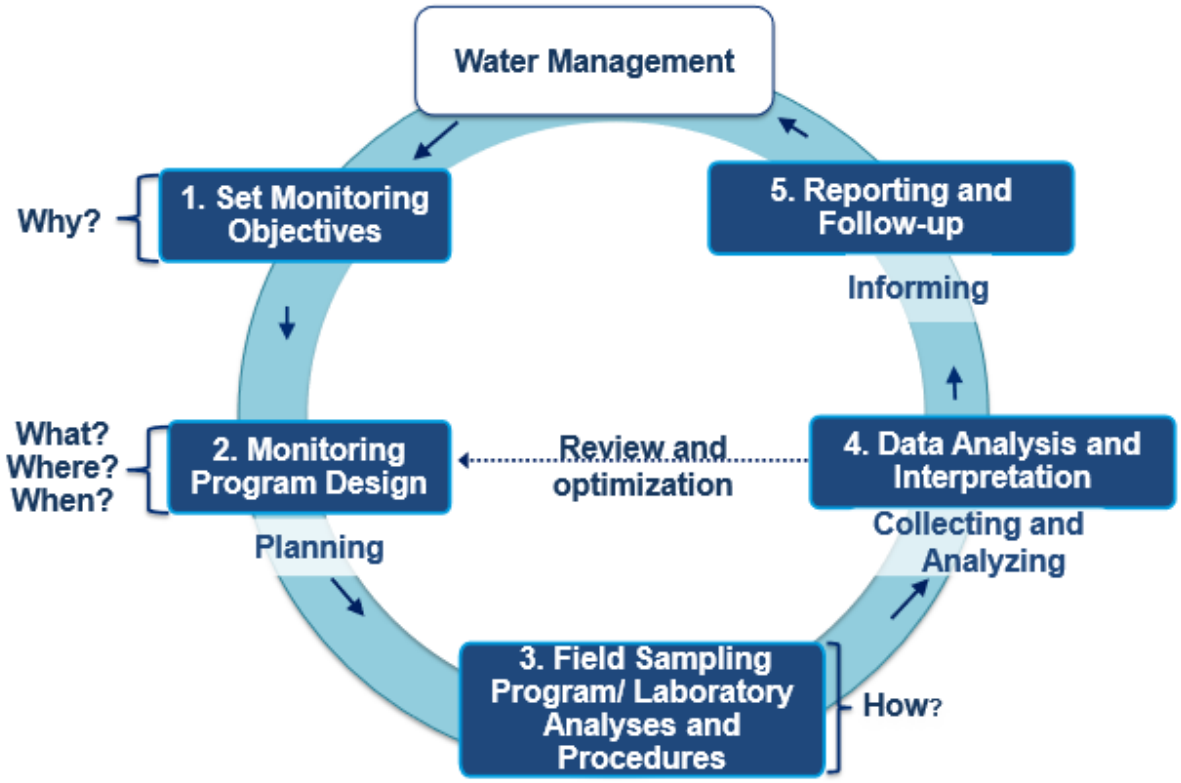
3.1.Preamble

The vision formulated in the 2030 Agenda for Sustainable Development1 paints the picture of a world free from poverty and hunger where citizens have universal and equitable access to education, health care, food, water, sanitation and energy, enjoy equal rights and opportunities and where each country enjoys sustained, inclusive and sustainable economic growth. An integral part of that vision is the recognition of the need to sustainably manage the planet's natural resources to be able to achieve and sustain the social and economic development required to achieve the ambitious set of goals by 2030. The adopted 17 goals and 169 associated targets are "integrated and indivisible" Ibid balancing complex economic, social and environmental dimensions of sustainable development. The formulation of the goals and targets captures several cross-disciplinary connections, but it has not been able to encompass all actual systemic linkages.. In order to maximize synergies and balance potential trade-offs in the delivery of different targets it will be important to understand both explicit and implicit interlinkages. A central challenge in the effort to achieve a sustainable development concerns how to balance competing uses of water in an equitable manner while maintaining water quality and ensuring healthy and diverse ecosystems from "source" to "sea". Access to water is a pre-requisite for human well-being and for much of the food, energy and industrial production that is necessary to achieve a sustainable economic growth. At the same time, such activities may also significantly alter a number of water-related flows that connect land and urban areas with freshwater systems, deltas, coasts and oceans3. The dynamic interface between land and oceans captures a key development and environmental challenge of our time. Marine and coastal resources represent enormous assets and opportunities for local and global economy, but they may be jeopardized by upstream activities on land and along rivers. A third of the total annual economic value of the oceans is dependent on healthy ocean ecosystems.

3.2. Step by step of protocol for joint assessment of the SDG Targets 6.3 and 14.1 on freshwater and marine pollution

Water quality monitoring should be carried out to measure the SDG indicators of SDG 6.3 and SDG 14.1 and it will help to decide the level of achievement of relevant SDG. Any water quality monitoring programme should be designed to achieve the relevant objectives. The developing of water quality monitoring involve several processes. The key processes involved in designing a water quality monitoring program are to determine why to monitor, what to monitor, and where, when and how to monitor (CCME, 2015).

The different activities are involved in designing water programes and figure 7 summarizes the different activities involved in designing water quality monitoring programs.



Source : CEMC, 2015

Figure 7: Generic water quality programme design considerations

Steps for water quality monitoring programs include:

Step 1-defining the monitoring goal and objectives;

Step 2-the selection of monitoring variables, station selection and temporal frequencies

Step 3- the development of sampling protocols, the choice of sampling equipment and the selection of appropriate laboratory analysis and data verification procedures;

Step 4; data analysis and interpretation

Step 5; and reporting

Steps 1 and 2 are related to the planning component, Steps 3 and 4 to data collection and analyses activities, and Step 5 to communication and reporting.

SDG target 6.3 can be measured the proportion of classified water classified as having a good quality status percentage as indicator. The water quality programme design to measure the above indicator should be long term status and trend monitoring programme. SDG 14.1 can be measured using index of coastal eutrophication potential. However it is not sufficient to measure the pollution impact to the coastal area and therefore TRIX (Tropic index) need to be measured in coastal areas to identify whether nutrient fluxes carried to the sea have a significant changes of tropic level of coastal areas. The water quality monitoring programme to measure the above indicator also should be long term status and trend monitoring progrmmae. The main goal of water quality monitoring programme is to assess the fresh and coastal water conditions to measure SDG target achievement while the objectives of the monitoring programme is provide all necessary water quality data to measure the above indicators.

Following water quality variables should be monitored to the measure the above indicators

SDG 6.3 Indicator

Dissolved oxygen

Biological oxygen demand,

Chemical oxygen demand

Salinity

Electrical conductivity

Total dissolved solids

Total nitrogen Nitrogen* Total oxidised nitrogen, Nitrite, Ammoniacal nitrogen

Nitrate

Phosphorous

Total phosphorous

Acidification pH

SDG 14.1 Indicator

Dissolved organic nitrogen

Particulate nitrogen

Dissolved inorganic nitrogen

Dissolved organic phosphorus

Particulate phosphorus

Total Prosperous

Reactive Slica

TRIX

Chlorophyll- a (µg/L)

Oxygen as absolute % deviation from saturation (100-O%)

Total nitrogen (µM)

Total phosphorous (µM)

Reactive silicate (µM)

3.3. Field sampling programme/ laboratory analyses procedure.

3.3.1. Site selection

The location of a water-quality monitoring site is directly related to the purpose of monitoring and the data-quality objectives. Stream characteristics, location of the site, and other data-quality objectives determine sampling point.

Following factors have to be considered when sampling sites are being selected;

- Representative of cross-sectional variability
- Constraints of channel configuration
- Velocity of streamflow

- Turbulence
- Range of values for water-quality physical properties
- Safety hazards

Sufficient cross-section measurements must be made at the site to determine if a prospective site is sufficiently well mixed and to ensure that the site will not be subject to significant difference in a cross section. If significant horizontal or vertical variability is determined, consideration must be given to choosing another site or using a different approach to meet the data-quality objectives.

To assess water quality in the watershed, streams with higher stream order representing various land uses have to be inspected. Large streams and rivers may be monitored best from the downstream side of bridge abutments.

3.3.2. Determining in situ parameters

4.2.1 Dissolved oxygen

4.2.2 Salinity

4.2.3 Electrical conductivity

4.2.4 pH

Above parameters can be determined in situ by using a handheld multipara-meter meter

Meter Calibration

Measurements that compare field meter physical property values with the continuous monitor readings should be made before, during, and after servicing the monitor to document any environmental changes during the service interval. Measurements are made at the monitoring site by using calibrated field instruments as close to the sensor as possible and within 5-minute intervals. Before site visits, all support field meters should be checked for operation and accuracy. Minimum calibration frequency is detailed by Wilde and Radtke (1998) for each type of meter, and all calibrations are recorded in the corresponding instrument log books (UNEP/WHO, 1996).

Calibration and adjustments for multi parameter sensor systems are found in the manufacturer's service manuals. Accuracy of field pH meters should be at least + 0.1 pH unit. Two standard buffers bracketing the expected range of environmental values are used to calibrate a pH electrode, and a third is used as a check for linearity. The pH-7 buffer is used

to establish the null point, and a pH-4 or pH-10 buffer is used to establish the slope of the calibration line at the temperature of the solution. The slope of a pH electrode is temperature sensitive, but modern sensors can adjust the pH slope to the observed temperatures through manual or automatic temperature

3.3.3. Determining ex situ parameters

BOD (Biochemical Oxygen Demand)

The test should be carried out as soon as possible after samples have been taken. If samples are kept at room temperature for several hours, the BOD may change significantly, depending on the character of the samples. In some instances, it may decrease and in others it may increase. The decrease at room temperature has occasionally been found to be as much as 40 per cent during the first 8 hours of storage. If samples cannot be dealt with at once they should, whenever practicable, be stored at about 5 °C. In the case of individual samples collected over a long period, it is desirable to keep all the samples at about 5 °C until the composite sample can be made up for the BOD determination. Samples must be free from all added preservatives and stored in glass bottles. It is necessary that excess dissolved oxygen be present during the whole period of incubation, and desirable that at least 30 per cent of the saturation value remains after 5 days. Since the solubility of atmospheric oxygen at the temperature of incubation is only 9 mg l^{-1}, samples that absorb more than about 6 mg l-1 during incubation for 5 days will not fulfil this condition. This is the case with sewage, nearly all sewage effluents, and many other waste liquids. The additional oxygen is supplied by diluting the sample with clean, well aerated water. The amount of dilution depends upon the nature of the sample.

Interferences

If the pH of the sample is not between 6.5 and 8.5, add sufficient alkali or acid to bring it within that range. Determine the amount of acid and alkali to be added by neutralizing a separate portion of the sample to about pH 7.0 with a 1 mol l^{-1} solution of acid or alkali, using an appropriate indicator (e.g. bromothymol blue), or pH meter. Add a calculated aliquot volume of acid or alkali to the sample for the BOD test (UNEP/WHO, 1996).

Some samples may be sterile, and will need seeding. The purpose of seeding is to introduce into the sample a biological population capable of oxidising the organic matter in the

wastewater. Where such micro-organisms are already present, as in domestic sewage or unchlorinated effluents and surface waters, seeding is unnecessary and should not be carried out. When there is reason to believe that the sample contains very few micro-organisms, for example as a result of chlorination, high temperature, extreme pH or the specific composition of some industrial wastes, the dilution water should be seeded.

For seeding, to each liter of dilution water add 5 ml of a fresh sewage effluent of good quality obtained from a settling tank following an aerobic biological process of purification. If necessary, settle (not filter) the effluent in a glass cylinder for about 30 minutes.

If such effluent is not available, use settled domestic sewage that has been stored at 20 °C for 24 hours; for seeding, add 1-2 ml of the supernatant to each liter of dilution water.

The special difficulties in choosing a seed for industrial effluents that are toxic, or that are not broken down by sewage bacteria, are dealt with in the following sub-section on "Seeding samples of industrial effluents". If the samples are analyzed in different laboratories, better agreement between test results will be achieved by using the same type of seed or, preferably, the same seed.

Some samples may be supersaturated with dissolved oxygen, especially waters containing algae. If such samples are to be incubated without dilution, the dissolved oxygen concentration should be lowered to saturation to prevent loss of oxygen during incubation.

The sample should be brought to about 20 °C in a partly filled bottle and well shaken.

A few sewage effluents and certain industrial effluents contain either residual chlorine or the products of the action of chlorine on certain constituents. Such liquids cannot be used directly for the determination of BOD because of the bactericidal effect of the chlorine or of its products and also because chlorine would introduce an error into the determination of dissolved oxygen. If the samples are allowed to stand for 1 to 2 hours, the residual chlorine will often be dissipated. Dilutions for BOD can then be prepared with properly seeded standard dilution water.

Higher concentrations of chlorine, and of many compounds containing available chlorine, may be removed by treating a portion of the sample with sodium bisulphite. The treated portion is then used for the BOD test. This procedure will probably give reasonably good results for domestic sewage effluents that have been chlorinated, since the chlorine will be present chiefly as chloramines formed by combination of chlorine with the ammonia present.

However, in the case of other effluents consisting of, or containing, industrial wastes, the chlorine may have combined with organic compounds present to produce substances which, although giving no reaction for chlorine with the starch-iodide test described below, are

inhibitory to biochemical oxidation or are even bactericidal. The BOD, as determined in these circumstances, is generally lower than would be expected for the organic content as measured by other tests.

Should a value for BOD of a chlorinated effluent be required, notwithstanding the uncertainty of the interpretation of the test, the following procedure should be used:

1. If the sample is alkaline to phenolphthalein bring it to a pH of 5.0 by the addition of dilute sulphuric acid. Add a crystal of potassium iodide to a convenient measured volume of sample (e.g. 100 ml) and titrate it with approximately 0.0l25 mol l^{-1} or 0.025 mol l-1 sodium bisulphite (or sulphite) solution, using a few drops of starch solution as an indicator.

2. To another portion of sample, sufficient to carry out the BOD test, add the requisite amount of dilute sulphuric acid to adjust the pH to 5.0, followed by the volume of sodium bisulphite solution determined by the previous titration. After thorough mixing allow to stand for several minutes, then check the absence of chlorine by testing a small portion of the treated sample with neutral starch-iodide.

3. Confirm the absence or excess of bisulphite on another portion by means of starch solution and a drop of 0.0125 mol l-1 iodine, which should develop a blue colour. Adjust the pH to about 7.3 before proceeding with the test.

4. Make up the dilution with seeded dilution water and proceed as for unchlorinated samples.

Note: Some wastewaters contain substances reacting with iodine, which precludes the determination of dissolved oxygen by iodometric titration. An instrumental method should be used.

Seeding samples of industrial effluents

A seed of sewage effluent, as described above, is satisfactory for many industrial effluents. However, if the BOD of such effluents as found by the standard test is substantially less than the chemical oxygen demand (COD) it may be for one of the following reasons:

(i) The sample contains compounds resistant to biochemical breakdown,
(ii) The seeding organisms are of an unsuitable type or require acclimatization, or
(iii) Toxic or bacteriostatic compounds are present, exerting an inhibiting effect at the concentration employed for the test.

Compounds constitutionally resistant to breakdown will not exert an oxygen demand on the receiving waters, but substances amenable to breakdown will generally contribute to the pollution load, even if the BOD test fails for reasons (ii) and (iii) above. Before embarking on the tedious, and sometimes impossible, task of preparing a seed by the method described below, the analyst should decide whether sufficient information about the sample may be given by alternative methods such as determinations of COD and organic carbon (UNEP/WHO, 1996).
Sometimes, if the difficulty is the result of condition (iii), it is possible to obtain reliable BOD values merely by increasing the dilution until the toxic constituents of the sample are below the inhibitory threshold concentrations. If this procedure fails, or if condition (ii) applies, the following method should be used:

1. Neutralize the sample if necessary, then add about 10 per cent of the threshold toxic concentration of the sample (if known; otherwise add a concentration that is thought unlikely to kill activated sludge organisms) to a mixture of settled sewage and activated sludge (2,000mg l^{-1} suspended solids) and aerate by diffused air or by stirring.

2. After one day, allow the sludge to settle and decant the supernatant liquid, top up to the same volume with sewage and sample as before. Repeat daily. After 3 or 4 days measure the BOD of the sample using dilution water seeded with the settled mixture, then increase the proportion of sample in the mixture by a factor of 2.

3. Continue the procedure, doubling the proportion in 3- or 4-day intervals, until a maximum BOD has been reached.

If a laboratory-scale, continuously-fed, activated sludge unit is available, this can be used in a similar way to produce a seed acclimatized to the sample. Sometimes, adapted seed is available from the effluent of a biological treatment process receiving the waste in question,

or the seed might be developed from the receiving water below the point of discharge of this waste, if it is not being treated.

Apparatus

- Incubation bottles.

It is recommended that narrow-mouthed, glass-stoppered bottles of a nominal capacity of 250 ml be used, and it is essential that the bottles are clean. New bottles should be cleaned with either 5 mol l^{-1} hydrochloric or sulphuric acid and thoroughly rinsed. In normal use, bottles are kept clean by the acidic iodine solution of the Winkler procedure and require no treatment apart from thorough rinsing with tap water and distilled water. Special cleaning may be necessary in some cases, but the use of chromic acid is not recommended because traces of chromium may remain in the bottle.

Some analysts prefer to use bottles of about 125 ml capacity, thus reducing the incubator space required. There is evidence, however, that with samples of some types the size of bottles (i.e. the ratio of the glass surface to the volume of liquid) may influence the result. The analyst wishing to use small bottles must, therefore, be satisfied that such a procedure gives results similar to those obtained by use of bottles of standard size.

As a precaution against drawing air into the dilution bottle during incubation, a water seal is recommended. Satisfactory water seals are obtained by inverting the bottles in a water-bath or adding water to the flared mouth of special BOD bottles.

- Incubator or water-bath.

The temperature of incubation should be 20 ± 0.5 °C. A water bath, or constant temperature room is usually employed. Incubation must be carried out in the dark. Some samples may contain algae which, if incubated in the light, would give off oxygen by photosynthetic action, and thus interfere with the BOD determination.

Reagents

- Dilution water.

The logical diluent for a sewage effluent is the river water into which the effluent is discharged, but this method can be adopted only in special cases and is obviously unsuitable where effluents from widely differing localities are dealt with in one laboratory. Moreover,

the river water may itself have a considerable BOD. Distilled water alone is unsatisfactory as a diluent, and it is recommended that a synthetic dilution water be employed. This is prepared by adding reagents to good quality distilled water. Water from copper stills should not be used since copper inhibits biochemical oxidation (0.01 mg l^{-1} is the maximum safe concentration). Some commercial vapour compression stills have also been shown to produce water containing copper. Deionized water produced in some commercial units has been found satisfactory, but deionizing columns in hard-water areas require frequent regeneration. It may be convenient, however, to run two deionizing columns in series, or to deionize the water from a vapour compression still. Water from a new or freshly regenerated column should always be shown to give similar BOD values to distilled water, bearing in mind that the resins may introduce or fail to remove undesirable organic matter.

Stock solutions of the following pure chemicals are required; any solutions showing signs of precipitates or growths should be discarded.

- Ferric chloride solution:

Dissolve 0.125 g ferric chloride, $FeCl_3.6H_2O$, in 1 liter water.

- Calcium chloride solution:

Dissolve 27.5 g anhydrous calcium chloride, CaCl2, (or equivalent if hydrated calcium chloride is used), in 1 liter water.

- Magnesium sulphate solution:

Dissolve 25 g magnesium sulphate, $MgSO_4.7H_2O$, in 1-liter water.

- Phosphate buffer stock solution:

Dissolve 42.5 g potassium dihydrogen phosphate, KH_2PO_4, in 700 ml water and add 8.8 g sodium hydroxide. This should give a solution of pH 7.2 which should be checked. Add 2 g ammonium sulphate, and dilute to 1 liter. Add 1 ml of each reagent to each liter of freshly distilled (or deionized) water. Bring the water to incubation temperature 20 ± 1 °C and saturate with oxygen by bubbling air through it or by shaking the partially filled bottle, and use as soon as possible. Discard any dilution water remaining unused and clean the bottle, preferably with a sterilizing agent. Thoroughly wash and rinse free from residual traces of the agent, and store out of direct sunlight. Stocks of dilution water should never be “topped up”

with fresh solution. A satisfactory dilution water, when incubated with or without a seed under standard conditions should not absorb more than 0.2 mg l-1 of oxygen, and in any case must not absorb more than 0.5 mg l^{-1}. A high oxygen uptake may sometimes be associated with the presence of water-soluble organic vapors in the laboratory atmosphere. Water for dilution should therefore be distilled (or deionized) and used in a room from which volatile organic compounds are excluded. Air used for aeration must be as clean as possible (UNEP/WHO, 1996).

Procedure

1. Pretreatment of dilution water by seeding is sometimes necessary (see above). Pretreatment of sample (see "Interferences") is needed if the sample is supersaturated with oxygen or if the sample contains residual chlorine. If the pH of the sample is not between 6.5 and 8.5, it should be brought within this range.

2. Samples that have been stored in a refrigerator should be allowed to reach room temperature before dilutions are made. All samples must be well mixed just before dilution.

3. In some wastes, suspended matter may cause difficulty because the distribution of the solids may be uneven when the sample is made up into dilutions. This may cause discrepancies in the results from different dilutions or duplicate dilutions. In such cases, shake the sample vigorously immediately before the dilutions are made. Artificial homogenizing procedures may cause an increased oxygen demand, and cannot be recommended.

4. Sometimes, the BOD determination in settled or filtered samples is needed. In such cases a settling time of 30 minutes is usually applied. For the BOD test of filterable substances, membrane filter, glass-fibre filter or paper filter may be used. The type of filter should be indicated in reporting the result. If determinations other than the BOD test are carried out on the filtered sample (e.g. residue, COD), it is recommended that filters of the same type and porosity be used for all of those procedures.

Dilution

5. Unless the approximate BOD of the sample is already known, the required degree of dilution will not be known and more than one dilution will have to be made. Recommended dilutions are given in Table 2 With experience, the analyst will often be able to use the COD as a guide to the dilution required. As low a dilution as possible should be used consistent with at least 30 per cent of the oxygen remaining after 5 days. It should be noted that some metals, e.g. copper, chromium, lead, will partially inhibit oxygen consumption.

6. In preparing dilutions for the BOD test, siphon or pour carefully the standard dilution water (seeded if necessary) into a graduated cylinder of capacity 1,000-2,000 ml, filling the cylinder half-way without entrainment of air. Add the quantity of carefully mixed sample to make the desired dilution and dilute to the desired level with dilution water. Mix well. Each analyst will have a preferred detailed procedure for preparing dilutions. Nevertheless, the following principles must be strictly adhered to:

(i) The sample and dilution water must be mixed thoroughly, but violent agitation leading to the formation of minute air bubbles must be avoided. Mixing may be accomplished by careful repeated inversion of a bottle or stoppered measuring cylinder containing the sample and dilution water, or by use of a magnetic stirrer in a completely filled bottle.

(ii) Dilutions involving the measurement of less than 5 ml of sample should be made by first diluting the sample in a volumetric flask (e.g. 10 dilution) and then using the appropriate volume of this mixture for final dilution to the required strength.

(iii) The diluted mixture is transferred to two incubation bottles (more if replicate results are required) by siphoning or by careful pouring. If a siphon is used, at least 50 ml of mixture must be discarded before the first bottle is filled. Bottles must be filled completely, allowed to stand for a few minutes and then tapped gently to remove bubbles. The stoppers are then inserted firmly without trapping air bubbles in the bottle.

(iv) On any one occasion, exactly the same mixing and transfer techniques must be used for all dilutions and samples.

(v) Bottles of the dilution water used in the test must be prepared at the same time as the sample dilutions to permit a determination of the blank.

Table 2 Recommended dilutions for the BOD test

Range of BOD values to be determined (mg l^{-1})	Sample volume (ml)	Dilution water volume (ml)	Dilution factor "d"	Report to nearest mg l^{-1}	Source of sample
0 to 6	undiluted	0	1	0.1	R
4 to 12	500	500	2	0.2	R, E
10 to 30	200	800	5	0.5	R, E
20 to 60	100	900	10	1	E, S
40 to 120	50	950	20	2	S
100 to 300	20	980	50	5	S, C
200 to 600	10	990	100	10	S, C
400 to 1,200	5	995	200	20	I, C
1,000 to 3,000	2	998	500	50	I
2,000 to 6,000	1	999	1,000	100	I

R River water

E Biologically purified sewage effluent

S Settled sewage or weak industrial wastewater

C Crude (raw) sewage

I Strong industrial wastewater

Determination of dissolved oxygen and incubation

7. Determine the initial concentration of dissolved oxygen in one bottle of the mixture of sample and dilution water, and in one of the bottles containing only dilution water. Place the other bottles in the incubator (those containing the sample, or the mixture of sample and dilution water, and that containing the plain dilution water to act as a blank, unseeded or seeded in accord with previous steps).

8. Incubate the blank dilution water and the diluted samples for 5 days in the dark at 20°C.The BOD bottles should be water-sealed by inversion in a tray of water in the incubator or by use of a special water-seal bottle. Although it is known that the BOD

of some samples is increased if the liquid is agitated during the incubation, it is not at present suggested that agitation should be provided (UNEP/WHO, 1996).

9. After 5 days determine the dissolved oxygen in the diluted samples and the blank using the azide modification of the iodometric method or an electrometric method. Those dilutions showing a residual dissolved oxygen of at least 30 per cent of the initial value and a depletion of at least 2 mg l-1 should be considered the most reliable.

Independent check of the technique

10. It might be thought desirable, from time to time, to check the technique. For this purpose, pure organic compounds of known or determinable BOD are used. If a particular organic compound is known to be present in a given waste, it may well serve as a control on the seed used. A number of organic compounds have been proposed, such as glucose and glutamic acid. In exceptional cases, a given component of a particular waste may be the best choice to test the efficacy of a particular seed. For general use, a mixture of glucose and glutamic acid has certain advantages. Glucose has an exceptionally high and variable oxidation rate with relatively simple seeds. When glucose is used with glutamic acid, the oxidation rate is stabilized and is similar to that obtained with many municipal wastes.

11. For the check, dissolve 150 mg each of glucose and glutamic acid (both dried at 103°C for 1 hour) in 1 liter of water. This solution should be freshly prepared.

12. Make up a 1 in 50 dilution using seeded dilution water and determine the BOD in the usual way. The BOD should be approximately 220 mgl^{-1}.If the result obtained is less than 200 mg l-1 or more than 240 mg l-1, some defect in the seed, dilution water or experimental techniques should be suspected.

Immediate dissolved oxygen demand

Substances ox disable by molecular oxygen, such as ferrous iron, sulphite, sulphide and aldehyde, impose a load on the receiving water and must be taken into consideration. The

total oxygen demand of such a substrate may be determined by using a calculated initial dissolved oxygen (DO) or by using the sum of the immediate dissolved oxygen demand (IDOD) and the 5-day BOD. Where a differentiation of the two components is desired, the IDOD should be determined. It should be understood that the IDOD does not necessarily represent the immediate oxidation by molecular dissolved oxygen, but may represent an oxidation by the iodine liberated in the acidification step of the iodometric method.

The depletion of dissolved oxygen in a standard water dilution of the sample in 15 minutes has been arbitrarily selected as the IDOD. To determine the IDOD, the dissolved oxygen of the sample (which in most cases is zero) and of the dilution water is determined separately. An appropriate dilution of the sample and dilution water is prepared, and the dissolved oxygen of the sample dilution minus the observed dissolved oxygen after 15 minutes is the IDOD (mg l-1) of the sample dilution (UNEP/WHO, 1996).

Calculation

(1) When BOD has been determined in an undiluted sample

BOD (mg l-1) = DO before incubation (mg l-1) - DO after incubation (mg l-1)

(2) When BOD has been determined in a diluted sample

A. Without correction for blank (i.e. for the BOD of the dilution water itself)

When seeding is not required:

$$BOD = \frac{D_1 - D_2}{P} \text{ mg } l^{-1}$$

When using seeded dilution water:

$$BOD = \frac{(D_1 - D_2) - (B_1 - B_2)f}{P}$$

Including IDOD if small or not determined:

$$BOD = \frac{D_c - D_2}{P} \text{ mg } l^{-1}$$

$$IDOD = \frac{D_c - D_1}{P} \text{ mg } l^{-1}$$

Where:

D0 = DO of original dilution water

D1 = DO of diluted sample immediately after preparation (mg l-1)

D2 = DO of diluted sample after 5 days' incubation

Dc = DO available in dilution at zero time = *Dop + DsP*

Ds = DO of original undiluted sample

p = decimal fraction of dilution water used

P = decimal fraction of sample used: (*P + p* = 1.00)

B1 = DO of dilution of seed control* before incubation;

B2 = DO of dilution of seed control* after incubation;

$$f = \frac{\%\ \text{of seed in } D_1}{\%\ \text{of seed in } B_1}$$

$$\text{Seed correction} = (B_1 - B_2)f$$

B. With correction for the BOD of the dilution water

If the BOD of the dilution water reaches the limit of 0.5 mg l-1 or approaches it, the correction may be of importance, especially for samples of water having a low BOD but requiring a dilution. In such cases, correction for BOD may be used. The calculation is then:

$$BOD = \frac{1{,}000}{V} \times (BOD_m - BOD_d) + BOD_d \text{ mg } l^{-1}$$

$$BOD = \frac{1{,}000}{V}[(S_m - S_t) - (D_m - D_t)] \text{mg } l^{-1}$$

COD (chemical Oxygen Demand)

Sample Handling

Preferably collect samples in glass bottles. Test unstable samples without delay. If delay before analysis is unavoidable, preserve sample by acidification to pH≤2 using concentrated H_2SO_4. Blend samples containing settleable solids with a homogenizer to permit representative sampling. Make preliminary dilutions for wastes containing a high COD to reduce the error inherent in measuring small sample volumes.

Methods

The dichromate method is the reference procedure for COD determinations. In this, a sample is refluxed in strongly acid solution with a known excess of potassium dichromate. Most

types or organic matter are oxidized in the boiling mixture of chromic and sulphuric add. After digestion, the remaining unreduced $K_2Cr_2O_7$ is titrated with ferrous ammonium sulphate to determine the amount of $K_2Cr_2O_7$ consumed and the oxidizable organic matter is calculated in terms of oxygen equivalent

Interferences

Straight-chain aliphatic compounds, aromatic hydrocarbons and pyridine are not oxidized to any appreciable extent, although this method gives more nearly complete oxidation than a permanganate method. The straight-chain compounds are more effectively oxidized when silver sulphate is added as a catalyst. However, silver sulphate reacts with chlorides, bromides or iodides to produce precipitates that are only partially oxidised. There is no advantage in using the catalyst in the oxidation of aromatic hydrocarbons, but it is essential to the oxidation of straight-chain alcohols and acids. The oxidation and other difficulties caused by the presence of chlorides in the sample may be overcome by adding mercuric sulphate before refluxing, in order to bind the chloride ion as a soluble mercuric chloride complex, which greatly reduces its ability to react further (UNEP/WHO, 1996).

Nitrite nitrogen exerts a COD of 1.14 mg mg-1 of nitrite nitrogen. To eliminate significant interference due to nitrites, 10 mg of sulphamic acid for every 1 mg of nitrite nitrogen in the refluxing flask may be added. If a series of samples containing nitrite is analysed, the sulphamic acid may be added to the standard dichromate solution, since it must be included in the distilled water blank. Thus, 120 mg of sulphamic acid per liter of dichromate solution will eliminate the interference of up to 6 mg of nitrite nitrogen per liter in the sample if a 20-ml sample is used. An aliquot volume of the sample diluted to 20 ml should be used to eliminate the interference of higher concentrations of nitrite.

Ferrous iron and hydrogen sulphide exert COD of 0.14 mg mg-1 Fe^{2+} and 0.47 mg mg^{-1} H_2S respectively. Appropriate corrections can be calculated and subtracted from the result or both interferences can be removed by bubbling air through the sample, if easily volatile organic matter is not present.

The procedure can be used to determine COD values of 50 mg l^{-1} with the standard dichromate solution (0.0417 mol l^{-1}). With the dilute dichromate, values are less accurate, especially below 10 mg l^{-1}, but may be used to indicate an order of magnitude.

Apparatus

- A reflux apparatus consisting of a 250-ml Erlenmeyer flask (500 ml if large samples are used) with ground-glass neck, and a 300-mm double surface condenser (Liebig, Friedrichs, West or equivalent) with a ground-glass joint. Since absolute cleanliness is essential, flasks and condensers should be protected from dust by inverted cups when not in use. The glassware must be used exclusively for COD determinations.
- A heating mantle or hotplate.
- A hotplate producing at least 1.5 W cm^{-2} of heating surface to ensure adequate boiling of the liquid in the flask. Heating mantles are preferred because they prevent the problem of overheating.

Reagents

- Sulphuric acid (*d* =1.84).
- Standard potassium dichromate solution, 0.0417 mol l^{-1} Dissolve 12.259 g of K2Cr2O7 primary standard grade, dried at 103 °C for 2 hours, in distilled water and dilute to 1.000 liter.
- Dilute standard potassium dichromate solution, 0.00417 mol l^{-1}Dilute 100 ml of the standard potassium dichromate solution to 1.000 liter.
- Standard ferrous ammonium sulphate solution, 0.250 mol l^{-1} Dissolve 98 g of $Fe(NH_4)_2(SO_4)_2.6H_2O$ analytical grade crystals in distilled water. Add 20 ml of H2SO4 (*d* =1.84), cool and dilute to 1.000 litre. This solution may be standardised against the standard potassium dichromate solution as follows:
- Dilute 10.0 ml of standard potassium dichromate solution, 0.0417 mol l-1, to about 100 ml. Add 30 ml H_2SO_4 (*d* = 1.84) and allow to cool. Titrate with the ferrous ammonium titrant, using 2 or 3 drops of ferroin indicator.

$$\text{Concentration (mol } l^{-1}) = \frac{V_1 \times 0.25}{V_2}$$

Where:

*V*1 = volume (ml) of $K_2Cr_2O_7$

*V*2 = volume (ml) of $Fe(NH_4)_2(SO_4)_2$

- Dilute standard ferrous ammonium sulphate solution, 0.025 mol l-1 Dilute 100 ml of the standard ferrous ammonium sulphate solution to 1.000 litre. Standardize daily against the dilute standard potassium dichromate, 0.00417 mol l^{-1}
- Silver sulphate, reagent powder. This reagent may be used either directly in powder form or in saturated solution, or it may be added to the sulphuric acid (about 5 g of Ag_2SO_4 to 1 litre of H_2SO_4; 1-2 days are required for dissolution).
- Mercuric sulphate, analytical grade crystals.
- Ferroin indicator solution. Dissolve 0.695 g of ferrous sulphate, $FeSO_4.7H_2O$, in water. Add 1.485 g of 1, 10-phenanthroline monohydrate, shaking until dissolved. Dilute to 100 ml. This solution is also commercially available.
- Sulphamic acid, analytical grade (required only if the interference of nitrites is to be eliminated).
- Anti-bumping granules that have been previously heated to 600°C for 1 hour.

Procedure

Initial dilutions in volumetric flasks should be made on waste with a high COD value to reduce the error that is inherent in measuring small samples.

A. Samples with low chloride concentrations

If the sample contains less than 100 mg l^{-1} chloride after evaporation, proceed as follows:

1. Place in an Erlenmeyer flask 20.0 ml of the sample or an aliquot diluted to 20.0 ml with distilled water.
2. Add 10.0 ml of standard potassium dichromate solution, 0.0417 mol l^{-1}, and a few antibumping granules. Mix well.
3. Add slowly, with caution, 30 ml of concentrated H_2SO_4 containing silver sulphate, mixing thoroughly by swirling while adding the acid. If H2SO4 containing silver sulphate is not used, add 0.15 g of dry silver sulphate and then, slowly, 30 ml of concentrated H_2SO_4

Note: If the liquid has not been well mixed local heating may occur on the bottom of the flask and the mixture may be blown out of the flask.

4. Attach the condenser to the flask and reflux the mixture for 2 hours. Allow to cool and then wash the condenser with distilled water.

5. Dilute the mixture to about 150 ml with distilled water, cool to room temperature, and titrate the excess dichromate with standard ammonium ferrous sulphate using 2-3 drops of ferroin indicator. Although the quantity of ferroin is not critical, do not vary it among different samples even when analysed at different times. The end-point is when the colour changes sharply from blue-green to reddish-brown, even though the blue-green may reappear within several minutes.
6. Reflux in the same manner a blank consisting of 20 ml of distilled water together with the reagents and titrate as in step 5, above.

B. Samples with high chloride concentration

If the sample contains more than 100 mg l-1 chloride after evaporation or dilution, proceed as follows: To 20.0 ml of sample or aliquot in the flask add 0.5 g of mercuric sulphate and shake thoroughly. This addition is sufficient to complex 40 mg of chloride ion or 2000 mg l-1 when 20.0 ml of sample are used. If more chloride is present, add more HgSO4 to maintain a $HgSO_4$: Cl^- ratio of 10:1. It is not important if a slight precipitate develops because it will not affect the determination. Continue with steps 2 to 6, as above.

Adjustments for other sample sizes

If a water is expected to have a higher or lower than normal COD, a sample ranging in size from 10.0 ml to 50.0 ml may be used with the volumes, weights and concentrations adjusted accordingly. Table 3 gives the appropriate reagent quantities for different sample sizes.

Use these quantities when following the procedure given above. When using large samples, increase the size of the Erlenmeyer flask to 500 ml to permit titration within the refluxing flask.

C. Samples with low COD

Follow one of the procedures given above for high and low chloride concentrations with the following differences:

1. Use dilute standard potassium dichromate, 0.00417 mol l^{-1}
2. Perform the back titration with either 0.025 mol l-1 or 0.01 mol l-1 ferrous ammonium sulphate.
3. Use redistilled water for the preparation of all reagents and blanks.

Exercise extreme care with this procedure because a trace of organic matter in the glassware or the atmosphere may cause a gross error. If a further increase in sensitivity is required, reduce a larger sample to 20 ml (final total volume 60 ml) by boiling in the refluxing flask on a hotplate in the presence of all the reagents. Carry a blank through the same procedure. The ratio of water to sulphuric acid must not fall much below 1.0 or a high blank will result because of the thermal decomposition of potassium dichromate. This technique has the advantage of concentrating without significant loss of easily digested volatile materials. Hard-to-digest volatile materials, such as volatile acids, are lost but an improvement is gained over ordinary evaporative concentration methods. Moreover, as sample volume increases, correspondingly lower concentrations of chlorides will be complexed by 0.4 g of $HgSO_4$.

Table 2 Reagent quantities for different s

Sample size (ml)	Standard potassium dichromate (ml)	H_2SO_4 with Ag_2SO_4 (ml)	$HgSO_4$ (g)	Ferrous ammonium sulphate (mol l^{-1})	Final volume before titration (ml)
10.0	5.0	15	0.2	0.05	70
20.0	10.0	30	0.4	0.10	140
30.0	15.0	45	0.6	0.15	210
40.0	20.0	60	0.8	0.20	280
50.0	25.0	75	1.0	0.25	350

Calculation

$$\text{Concentration of COD} = \frac{(a-b)\times c \times 8{,}000}{V}\ \text{mg l}^{-1}$$

Where:

a = ferrous ammonium sulphate (ml) used for blank

b = ferrous ammonium sulphate (ml) used for sample

c = molarity (mol l-1) of ferrous ammonium sulphate

v = volume of sample (ml)

Ammoniacal Nitrogen

When nitrogenous organic matter is destroyed by microbiological activity, ammonia is produced and is therefore found in many surface and groundwaters. Higher concentrations occur in water polluted by sewage, fertilisers, agricultural wastes or industrial wastes containing organic nitrogen, free ammonia or ammonium salts.

Certain aerobic bacteria convert ammonia into nitrites and then into nitrates. Nitrogen compounds, as nutrients for aquatic micro-organisms, may be partially responsible for the eutrophication of lakes and rivers. Ammonia can result from natural reduction processes under anaerobic conditions. The proportions of the two forms of ammonia nitrogen, i.e. free ammonia and ammonium ions, depend on the pH:

Sample handling

The preferred procedure is to remove ammonia from the sample by distillation. The ammonia may then be determined either by titration or colorimetrically using Nessler's reagent. Direct nesslerisation of the sample is quicker but is subject to considerable interference. The procedure given is the distillation and titration method.

If it is not possible to carry out the determination very soon after sampling, the sample should be refrigerated at 4 °C. Chemical preservation may be achieved by adding either 20-40 mg HgCl2 or 1 ml H2SO4 to 1 litre of sample (UNEP/WHO, 1996).

Principle

Ammonia can be quantitatively recovered from a sample by distillation under alkaline conditions into a solution of boric acid followed by titration with standard acid. The method is particularly suitable for the analysis of polluted surface and ground waters that contain sufficient ammonia to neutralise at least 1 ml of 0.00714 mol l-1 HCl.

Interferences

Volatile amines, if present, interfere with the acid titration. Generally, however, this method is less subject to interferences than other methods.

Apparatus

Distillation apparatus, consisting of a 1-litre, round-bottomed, heat-resistant glass flask fitted with a splash head, together with a suitable vertical condenser of either the spiral tube or double surface type. The condenser must be arranged so that the outlet tip can be submerged in the liquid in the receiv**er.**

Usual laboratory glassware.

Reagents

Ammonia-free water. This should be prepared fresh for each batch of samples, since it is virtually impossible to store ammonia-free water in the laboratory without contamination from ammonia fumes.

(i) Distillation. To each litre of tap water add 2 ml of a solution of ferrous sulphate (100 g l-1 $FeSO_4.7H_2O$) and sufficient sulphuric acid to give a slight acid reaction to methyl orange. Distil with care, preferably in an all-glass distillation apparatus provided with a splash head. Reject the first 50 ml of distillate and then proceed until three- quarters of the volume of water has distilled over. Test for the absence of ammonia in the distillate with Nessler's reagent in the manner described below**.**

(ii) Ion exchange. As an alternative, ammonia may be removed from distilled water by the use of a strongly acidic cation exchange resin (hydrogen form). If only a small quantity of ammonia-free water is needed, add about 3 g of the cation exchange resin to each litre of distilled water and shake for a few minutes. If a regular supply of ammonia-free distilled water is needed, it is convenient to pass distilled water slowly down a column of the resin enclosed in a glass tube (250 mm long and about 25 mm in diameter is suitable). In either case, check that the water is free from ammonia by testing with Nessler's reagent.

Light magnesium oxide.

Indicating boric acid solution. Dissolve 20 g pure boric acid, H_3BO_3, in warm water and dilute to approximately 1 litre. Add 20 ml methyl red solution (0.5 g l-1) and 0.4 ml methylene blue solution (15 g l-1) and mix well. One drop of 0.1 mol l-1 NaOH should change the colour of 20 ml of the solution from purple to green. The solution is stable for several months.

of hydrochloric acid (d = 1.18) to 1 litre. Standardise by a suitable method and dilute with water to give a solution of the required strength.

Procedure 1. Before assembling the apparatus, thoroughly clean the distillation flask, splash head and condenser. In order to free the apparatus from possible contamination by ammonia, add to the flask about 350 ml water (preferably ammonia-free) and distil until the distillate is shown to be ammonia-free by testing with Nessler's reagent. Empty the distillation flask and allow it to cool.

2. Place a suitable volume of the sample in the flask; 100 ml should be sufficient for a purified effluent, while 200 to 400 ml of surface water may be necessary to give a final titration of reasonable magnitude. Use a 400-ml beaker as a receiver and keep the lower end of the delivery tube from the condenser below the surface of the absorbent liquid throughout the distillation.

3. Neutralise the measured volume of sample with NaOH, if necessary.

4. Dilute the measured volume of sample, if necessary, to 400 ml with ammonia-free water in the distillation flask and add about 0.25 g magnesium oxide.

5. Place 50 ml of the indicating H3BO3 solution in the 400-ml receiving beaker.

6. Distil at a rate of about 10 ml per minute. As the indicating H3BO3 solution changes colour, titrate with 0.00714 mol l-1 HCl, continuing the distillation until the addition of one drop of the standard acid produces a permanent pink colour in the solution.

7. At the completion of the titration, remove the receiver from the apparatus before the source of heat is withdrawn.

8. Carry out a blank determination and correct the final titration values for samples to compensate for any.

$$\text{Ammonia nitrogen (as N)} = \frac{100V_2}{V_1}\ \text{mg l}^{-1}$$

where

V_1 = volume of sample taken (ml)
V_2 = volume of 0.00714 mol l^{-1} acid used (ml).

Nitrate

Nitrate, the most highly oxidized form of nitrogen compounds, is commonly present in surface and ground waters, because it is the end product of the aerobic decomposition of organic nitrogenous matter. Significant sources of nitrate are chemical fertilisers from cultivated land and drainage from livestock feedlots, as well as domestic and some industrial waters.

The determination of nitrate helps the assessment of the character and degree of oxidation in surface waters, in groundwater penetrating through soil layers, in biological processes and in the advanced treatment of wastewater.

Unpolluted natural waters usually contain only minute amounts of nitrate. In surface water, nitrate is a nutrient taken up by plants and assimilated into cell protein. Stimulation of plant growth, especially of algae, may cause water quality problems associated with eutrophication. The subsequent death and decay of algae produces secondary effects on water quality, which may also be undesirable. High concentrations of nitrate in drinking water

may present a risk to bottle-fed babies under three months of age because the low acidity of their stomachs favours the reduction of nitrates to nitrites by microbial action. Nitrite is readily absorbed into the blood where it combines irreversibly with haemoglobin to form methaemoglobin, which is ineffective as an oxygen carrier in the blood. In severe cases a condition known as infantile methaemoglobinaemia may occur which can be fatal for young babies.

The determination of nitrate in water is difficult because of interferences, and much more difficult in wastewaters because of higher concentrations of numerous interfering substances.

The first method given here, Devarda's alloy method, involves oxidation, distillation and titration. One of its attractive features is that it can be performed on the residue remaining in the flask after the distillation process required in the determination of ammonia nitrogen. The distillation step in the method also eliminates many interferences and is often used for the analysis of wastewater samples..

Sample handling

To prevent any change in the nitrogen balance through biological activity, the nitrate determination should be started as soon as possible after sampling. If storage is necessary, samples should be kept at a temperature just above the freezing point, with or without preservatives, such as 0.8 ml of concentrated sulphuric acid (d = 1.84) or 40 mg of mercury (as mercuric chloride) per litre of sample. If acid preservation is employed, the sample should be neutralised to about pH 7 immediately before the analysis is begun.

Devarda's alloy method (reduction to ammonia)

Principle

This method is suitable for nitrate concentrations exceeding 1 mg l-1, especially for wastewater and polluted surface water. The analysis may be carried out either on the original sample or on the residue from the determination of ammonia.

Nitrate is reduced to ammonia by nascent hydrogen, by the use of Devarda's alloy (59 per cent Al, 39 per cent Cu, 2 per cent Zn). The resulting ammonia is distilled and its concentration determined by titration.

Nitrites are also reduced by Devarda's alloy and their separate determination can be carried out rapidly and readily. The nitrate concentration can therefore be satisfactorily determined by subtracting the nitrite fraction from the total oxidised nitrogen.

Sometimes, especially when the proportion of nitrogen present as nitrite is small, the report of the analysis is confined to total oxidised nitrogen.

Interferences

Ammonia must be removed from the sample before the main procedure is started. This is achieved either by pretreatment or by using the distillation residue from the determination of ammonia. The air in the laboratory and the distilled water used for solutions and during the procedure should be free of ammonia. If the sample or any reagent needs to be filtered, only nitrogen-free filters should be used. Nitrite is determined separately and subtracted from the result.

Apparatus

√ The same glassware and distilling apparatus as for the ammonia nitrogen determination (see section 7.14). Reagents

The following reagents are required in addition to those used for the ammonia nitrogen determination:

√ Devarda's alloy, powdered. If fine powder is not available, the material should be ground to pass through a 0.07-0.1 mm sieve (200-140 mesh). It should be as free as possible from nitrogen. It can be purchased as such but a blank determination of its nitrogen content should always be carried out under the conditions of the test.

√ Sodium hydroxide, 10 mol l-1 (needed only if an original sample is used - see procedure).

Procedure

Determination on an original sample

1. Before assembling the apparatus, thoroughly clean the distillation flask, splash head and condenser. In order to free the apparatus from possible contamination by ammonia, add to the flask about 350 ml water, preferably ammonia-free, and distil until the distillate is shown to be free from ammonia by testing with Nessler's reagent. Empty the distillation flask and allow it to cool.

2. Measure 200 ml of the sample into the flask.

3. Add 10 ml of 10 mol l-1 sodium hydroxide. Evaporate in the distillation flask to 100 ml. Allow the residue to cool.

4. Continue as indicated in step 6, below.

Determination on the residue from the analysis for ammonia 5. At the end of the distillation procedure for the analysis for ammonia, allow the residue to cool.

6. To the cooled residue add sufficient ammonia-free water to bring the volume in the distillation flask to about 350 ml. Add 1 g Devarda's alloy, and immediately connect the flask to the condenser.

7. After some minutes, start the distillation, keeping the lower end of the delivery tube from the condenser below the surface of the liquid in the receiver throughout the distillation.

8. Place 50 ml of the indicating boric acid solution in the receiver and distil at a rate of about 10 ml per minute.

9. As the absorbent solution changes colour, titrate with 0.00714 mol l-1 hydrochloric acid, continuing the distillation until the addition of one drop of the standard acid produces a permanent pink colour in the solution.

10. At the completion of the titration, remove the receiver from the apparatus before the source of heat is withdrawn.

11. Carry out blank determinations as appropriate. For each sample, correct the final titration figure for any ammonia in the reagent used.

Calculation

$$\text{Nitrate nitrogen (as N)} = \frac{(a-b)\times 100}{V} - n \text{ mg l}^{-1}$$

where

a = volume of 0.00714 mol l^{-1} acid used for titration of the distillate of the sample (ml)
b = volume of 0.00714 mol l^{-1} acid used for titration of the distillate of the blank (ml)
V = volume of the undiluted sample (ml)
n = concentration of nitrite nitrogen in mg l^{-1} N, determined separately

Nitrite

Nitrite is an unstable, intermediate stage in the nitrogen cycle and is formed in water either by the oxidation of ammonia or by the reduction of nitrate. Thus, biochemical processes can cause a rapid change in the nitrite concentration in a water sample. In natural waters nitrite is normally present only in low concentrations (a few tenths of a milligram per litre). Higher concentrations may be present in sewage and industrial wastes, in treated sewage effluents and in polluted waters.

Sample handling

The determination should be made promptly on fresh samples to prevent bacterial conversion of the nitrite to nitrate or ammonia. In no case should acid preservation be used for samples to be analysed for nitrite. Short-term preservation for 1 to 2 days is possible by the addition of 40 mg mercuric ion as HgCl2 per litre of sample, with storage at 4 C.

Principle

Nitrite reacts, in strongly acid medium, with sulphanilamide. The resulting diazo compound is coupled with N-(1-naphthyl)-ethylenediamine dihydrochloride to form an intensely redcoloured azo-compound. The absorbance of the dye is proportional to the concentration of nitrite present.

The method is applicable in the range of 0.01-1.0 mg l-1 nitrite nitrogen. Samples containing higher concentrations must be diluted.

Interferences

There are very few known interferences at concentrations less than 1,000 times that of the nitrite. However, the presence of strong oxidants or reductants in the samples will readily affect the nitrite concentrations. High alkalinity (>600 mg l-1 as CaCO3) will give low results owing to a shift in pH.

Apparatus

Spectrophotometer equipped with 10-mm or larger cells for use at 540 nm. √ Nessler tubes, 50 ml, or volumetric flasks, 50 ml.

Reagents Hydrochloric acid, 3 mol l-1 Combine 1 part concentrated HCl with 3 parts distilled water.

Nitrite- and nitrate-free distilled water. Add 1 ml of concentrated sulphuric acid and 0.2 ml manganous sulphate (MnSO4) solution to 1 litre of distilled water and make it pink with 1-3 ml potassium permanganate solution (440 mg KMnO4 in 100 ml distilled water). Redistil in an all borosilicate glass still. Discard the first 50 ml of distillate. Test each subsequent 100 ml fraction of distillate by the addition of DPD indicator, discarding those with a reddish colour that indicates the presence of permanganate.

DPD indicator solution. Dissolve 1 g of DPD oxalate or 1.5 g of p-amino-N, N-diethyl-aniline sulphate in chlorine-free distilled water containing 8 ml of H2SO4, 18 mol l-1, and 200 mg of disodium ethylenediaminetetraacetate dihydrate (EDTA). Make up to 1 litre and store in a brown bottle and discard the solution when it becomes discoloured.

Note: DPD indicator solution is commercially available.

Buffer-colour reagent. Distilled water free of nitrite and nitrate must be used in the preparation of this reagent. To 250 ml of distilled water add 105 ml concentrated hydrochloric acid, 5.0 g sulphanilamide and 0.5 g N-(1-naphthyl)-ethylenediamine dihydrochloride. Stir until dissolved. Add 136 g of sodium acetate (CH3COONa.3H2O) and again stir until dissolved. Dilute to 500 ml with distilled water. This solution is stable for several weeks if stored in the dark.

Stock nitrite solution. Distilled water free of nitrite and nitrate must be used in the preparation of this solution. Dissolve 0.4926 g of dried anhydrous sodium nitrite (24 hours in desiccator) in distilled water and dilute to 1 litre. Preserve with 2 ml chloroform per litre (1.0 ml (100 µg nitrite N).

Working nitrite solution. Distilled water free of nitrite and nitrate must be used in the preparation of this solution. Dilute 10.0 ml of the stock solution to 1 litre (1.0 ml (1.0 µg nitrite N).

Procedure 1 . If the sample has a pH greater than 10 or a total alkalinity in excess of 600 mg l-1 (expressed as CaCO3), adjust to approximately pH 6 with 3 mol l-1 HCl.

2. If necessary, pass the sample through a filter of pore size 0.45 µm, using the first portion of filtrate to rinse the filter flask.

3. Place 50 ml of sample, or an aliquot diluted to 50 ml, in a 50-ml Nessler tube and set aside until preparation of standards is completed. At the same time, prepare a series of standards in 50-ml Nessler tubes as follows

Volume of working nitrate solution (ml)	Concentration when diluted to 50 ml (mg l^{-1} of NO_2-N)
0.0 (blank)	0.0
0.5	0.01
1.0	0.02
1.5	0.03
2.0	0.04
3.0	0.06
4.0	0.08
5.0	0.10
10.0	0.20

4. Add 2 ml of buffer-colour reagent to each standard and sample, mix, and allow colour to develop for at least 15 minutes. The pH values of the solutions at this stage should be between 1.5 and 2.0.

5. Measure the absorbance of the standards and samples at 540 nm. Prepare a standard curve by plotting the absorbance of the standards against the concentration of NO2-N.

Calculation

Read the concentration of NO2-N in samples directly from the calibration curve. If less than 50 ml of sample is taken, calculate the concentrations as follows:

$$\text{Nitrite nitrogen (as N)} = \frac{\text{mg l}^{-1} \text{ from standard curve} \times 50}{\text{ml sample}}$$

Total phosphorous

Phosphorus compounds are present in fertilisers and in many detergents. Consequently, they are carried into both ground and surface waters with sewage, industrial wastes and storm run-off. High concentrations of phosphorus compounds may produce a secondary problem in water bodies where algal growth is normally limited by phosphorus. In such situations the presence of additional phosphorus compounds can stimulate algal productivity and enhance eutrophication processes.

Principle

Organically combined phosphorus and all phosphates are first converted to orthophosphate. To release phosphorus from combination with organic matter, a digestion or wet oxidation technique is necessary. The least tedious method, wet oxidation with potassium peroxydisulphate, is recommended.

Orthophosphate reacts with ammonium molybdate to form molybdophosphoric acid. This is transformed by reductants to the intensely coloured complex known as molybdenum blue. The method based on reduction with ascorbic acid is preferable. Addition of potassium antimonyl tartrate increases the coloration and the reaction velocity at room temperature.

For concentrations of phosphate below 20 µg l-1, the recommended procedure involves extraction of the molybdenum blue complex from up to 200 ml of water into a relatively small volume of hexanol, so that a considerable increase in sensitivity is obtained.

Interferences

The method is relatively free from interferences. Changes in temperature of ± 10 °C do not affect the result.

Apparatus

- Heating equipment. One of the following is required:
- Hotplate, a 30 cm × 50 cm heating surface is adequate.
- Autoclave. An autoclave or pressure-cooker capable of developing 1.1-1.4 kPa cm^{-2} may be used in place of a hotplate.

- Colorimetric equipment. One of the following is required:
- Spectrophotometer, with infrared phototube, for use at 880 nm, providing a light path of 40 mm or longer. If this wavelength is not obtainable on the spectrophotometer, a wavelength of 710 nm may be used but there will be some loss of sensitivity.
- Absorptiometer, equipped with a red colour filter and a light path of 40 mm or longer.
- Acid-washed glassware. The glassware used, including sample bottles, should be reserved for the determination of phosphate, should not be used for any other purpose and should be left full of sulphuric acid (4.5 mol l^{-1}
-) until required for use. If necessary, glassware may be cleaned with chromic acid, equal mixtures of nitric and hydrochloric acids, or pure sulphuric acid. Detergents containing phosphate compounds must not be used.

Reagents

- Phenolphthalein indicator solution. Dissolve 0.5 g of phenolphthalein in 50 ml of 95 percent ethyl alcohol, and add 50 ml of distilled water. Add a dilute (e.g. 0.01 or 0.05 mol l^{-1}) carbon dioxide-free solution of sodium hydroxide, a drop at a time, until the indicator turns faintly pink.
- Potassium peroxydisulphate solution. Dissolve 5 g $K_2S_2O_8$ in 100 ml distilled water. Prepare daily.
- Phosphate stock solution. Dissolve 4.390 g potassium dihydrogen phosphate, KH_2PO_4, in 1 litre of water. Add one or two drops of toluene as a preservative (1.0 ml stock solution is equivalent to 1.0 mg P).
- Phosphate working solution. Dilute 10 ml of stock solution to 100 ml with distilled water and mix well. Then dilute 10 ml of this solution to 1 litre and mix. The dilute solution thus obtained will not keep very long and should be freshly prepared when required (1.0 ml working solution is equivalent to 1.0 μg P).
- Ammonium molybdate tetrahydrate solution, 40 g l^{-1}
- Sodium hydroxide, approximately 5 mol l^{-1}
- Sulphuric acid, approximately 2.5 mol l^{-1} Add carefully, with mixing, 140 ml sulphuric acid (d = 1.84) to water, cool and make up to 1 litre.
- Potassium antimonyl tartrate solution. Dissolve 2.7 g potassium antimonyl tartrate in water and make up to 1 litre.

- Reducing agent. Mix together 250 ml of 2.5 mol l^{-1} sulphuric acid, 75 ml ammonium molybdate solution and 150 ml distilled water. Add 25 ml potassium antimonyl tartrate solution and again mix well. The solution should be kept in a refrigerator and is stable for several weeks. Immediately before use of the reagent in step 9 of the procedure, pour an aliquot into an Erlenmeyer flask and add 1.73 g ascorbic acid for each 100 ml of reagent. After the addition of ascorbic acid the solution is unstable and cannot be stored. For each standard and each sample, 8 ml of solution is required.

Procedure

1. Take 100 ml of thoroughly mixed sample.
2. Add 1 drop (0.05 ml) of phenolphthalein indicator solution. If a red colour develops, add sulphuric acid solution drop by drop to just discharge the colour.
3. Add 2 ml sulphuric acid solution and 15 ml potassium peroxydisulphate solution.
4. Boil gently for at least 90 minutes, adding distilled water to keep the volume between 25 and 50 ml. Alternatively, heat for 30 minutes in an autoclave or pressure-cooker at 1.1-1.4 kPa cm^{-2}
5. Cool, add 1 drop (0.05 ml) phenolphthalein indicator solution, and neutralize to a faint pink colour with sodium hydroxide solution.
6. Restore the volume to 100 ml with distilled water and set aside.
7. Prepare a series of standards in 50-ml volumetric flasks as follows:

Volume of working phosphate solution (ml)	Concentration, when diluted to 40 ml (µg l^{-1} of phosphorus)
0.0 (blank)	0
1.0	25
2.0	50
3.0	75
4.0	100
8.0	200
12.0	300
16.0	400

8. Place 40 ml of sample in a stoppered 50-ml volumetric flask.

9. Add 8 ml of the mixed reducing agent to the standards and samples, make up to 50 ml with distilled water and mix. Allow to stand for 10 minutes.
10. Measure the absorbance of the blank and each of the standards. Prepare a calibration graph by plotting absorbance against the concentration of phosphorus in μg l^{-1}
11. Measure the absorbance of the samples and, from the calibration graph, read the number of μg $l^{-1}$of phosphorus in the samples.

Chlorophyll-a

Analysis of the photosynthetic chlorophyll pigment present in aquatic algae is an important biological measurement which is commonly used to assess the total biomass of algae present in water samples.

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Sampling

Samples should be taken with an appropriate sampler, such as a depth or grab sampler, a submersible pump or a hose-pipe sampler (see section 5.2.1). For nutrient poor (high transparency) water up to 6 liters will be required. For eutrophic waters, 1-2 liters are usually adequate (UNEP/WHO, 1996).

Principle

Three types of chlorophyll (chlorophyll *a*, *b*, and *c*) are found in phytoplankton and may be extracted with acetone. Each type has a characteristic light absorption spectrum with a particular peak absorbance. The acetone extract is analyzed in a spectrophotometer at these peaks. The peak height indicates chlorophyll concentration.

When samples are concentrated by filtration for the purposes of analysis, the phytoplankton cells die. Consequently, the chlorophyll immediately starts to degrade and its concentration is thus reduced. The degradation product of chlorophyll *a*, phaeophytin *a*, fluoresces in the same spectral region, and this can lead to errors in results. It is therefore essential to measure the concentration of phaeophytin-*a* and to make appropriate corrections to analytical results.

Apparatus

- Spectrophotometer, with a spectral band width between 0.5 and 2 nm.
- Cuvettes, 1 cm; longer path-length cuvettes may be used (usually 4 cm or 10 cm).

- Centrifuge.
- Tissue-grinder.
- Centrifuge tubes, 15 ml, graduated, screw-tops.
- Filters, glass fiber GF/C, 4.7 cm diameter.
- Filtration cup and pump.

Note: As far as possible, all apparatus should be acid- and alkali-free.

Reagents

- Magnesium carbonate suspension, 1.0 g $MgCO_3$ in 100 ml distilled water. Shake before use.
- Acetone solution, 90 per cent acetone.
- Hydrochloric acid, 1 mol l^{-1}

Procedure

1. After recording the initial water volume, separate the cells from the water by filtration. Filter continuously and do not allow the filter to dry during filtration of a single sample. As filtration ends, add 0.2 ml of $MgCO_3$ suspension to the final few millilitres of water in the filter cup. If extraction is delayed at this point, filters should be placed in individual labelled bags or plastic Petri dishes and stored at -20 °C in darkness. Samples may be transported in this form.
2. Place the filter in the tissue-grinder, add 2-3 ml of 90 per cent acetone, and grind until the filter fibers are separated. Pour the acetone and ground filter into a centrifuge tube; rinse out the grinding tube with another 2 ml of 90 percent acetone and add this to the centrifuge tube. Make up the total volume in the centrifuge tube to 10 ml with 90 per cent acetone. Place top on tube, label, and store in darkness at 4 °C for 10-12 hours. Samples may also be transported in this form.
3. Centrifuge closed tubes for 15 minutes at 3,000 rev/min to clarify samples. Decant the clear supernatant into a clean centrifuge tube and record the volume.
4. Fill a cuvette with 90 per cent acetone. Record absorbance on the spectrophotometer at 750 nm and 663 nm. Zero on this blank if possible; otherwise record the absorbance and subtract it from sample readings.

5. Place sample in the cuvette and record absorbance at 750 nm and 663 nm (750a and 663a).
6. Add two drops of 1 mol l^{-1} HCl to sample in 1-cm cuvette (increase acid in proportion to volume for larger cuvettes). Agitate gently for 1 minute and record absorbance at 750 nm and 665 nm (750b and 665b).
7. Repeat the procedure for all samples. Some preliminary samples may need to be taken to assess the best sample volume.

Calculation

1. Subtract absorbance:

663a - 750a = corrected 663a absorbance
665b - 750b = corrected 665b absorbance

2. Use these corrected 663a and 665b absorbances to calculate:

$$\text{Chlorophyll a} = \frac{26.73(663a - 665b) \times V_e}{V_s \times l} \text{ mg m}^{-3}$$

$$\text{Phaeophytin a} = \frac{26.73[1.7(665_b) - 663_a] \times V_e}{V_s \times l} \text{ mg m}^{-3}$$

Determination of reactive silicate

After oxygen, silicon is the most abundant element in the earth's crust. It is a major constituent of igneous and metamorphic rocks, of clay minerals such as kaolin, and of feldspars and quartz. Although crystalline silica is a major constituent of many igneous rocks and sandstones, it has low solubility and is therefore of limited importance as a source of silica in water. It is likely that most of the dissolved silica in water originates from the chemical breakdown of silicates in the processes of metamorphism or weathering.
The concentration of silica in most natural waters is in the range 1-30 mg l-1 Up to 100 mg l-1 is not uncommon. Over 100 mg l-1 is relatively rare, although more than 1,000 mg l-1 isoccasionally found in some brackish waters and brines.

Sample handling

Samples should be stored in plastic bottles to prevent leaching of silica from glass. Samples should be passed through a membrane filter of 0.45 μm pore size as soon as possible after sample collection and should be stored at 4 °C without preservatives. Analysis should be performed within 1 week of sample collection.

Interferences

Both the apparatus and the reagents may contribute silica. The use of glassware should be avoided as far as possible and only reagents low in silica should be used. A blank determination should be carried out to correct for silica introduced from these sources.

Tannin, large amounts of iron, colour, turbidity, sulphide and phosphate are potential sources of interference. The treatment with oxalic acid eliminates the interference from phosphate and decreases the interference from tannin. Photometric compensation may be used to cancel interference from colour or turbidity in the sample (UNEP/WHO, 1996).

Apparatus

- Colorimetric equipment. One of the following is required:
  - Spectrophotometer for measurement at 815 nm, providing a light path of at least 1 cm.
  - Absorptiometer for measurement at a wavelength of 815 nm.

Note: If no instrument is available for measurement at this wavelength, an instrument capable of measuring at 650 nm can be used, but this leads to a decrease in sensitivity.

Reagents

- Hydrochloric acid, 6 mol l-1 Combine 1 volume of concentrated HCl with an equal volume of water.
- Ammonium molybdate reagent. Dissolve 10 g of ammonium molybdate tetrahydrate, (NH4)6Mo7O24.4H2O, in distilled water, with stirring and gentle warming, and dilute to 100 ml. Filter if necessary. Adjust to pH 7-8 with silica-free NH4OH or NaOH and store in a polyethylene bottle. If the pH is not adjusted, a precipitate gradually forms. If the solution is stored in glass, silica may leach out, causing high

blanks. If necessary, prepare silica-free NH_4OH by passing gaseous NH_3 into distilled water contained in a plastic bottle.

- Oxalic acid solution. Dissolve 10 g of oxalic acid dihydrate, $H_2C_2O_4.2H2O$, in distilled water and dilute to 100 ml.
- Reducing agent. Dissolve 0.5 g of 1-amino-2-naphthol-4-sulphonic acid and 1 g of Na2SO3 in 50 ml of distilled water, with gentle warming if necessary. Add this solution to a solution of 30 g of NaHSO3 in 150 ml of distilled water. Filter into a plastic bottle and store in a refrigerator away from light. Discard the solution when it becomes dark. Do not use aminonaphtholsulphonic acid that is incompletely soluble or that produces reagents that are dark even when freshly prepared; such material is not suitable for silica determinations.
- Silica standard stock solution. Dissolve 313.0 mg of sodium hexafluorosilicate, Na2SiF6, in 1,000 ml of distilled water (1 ml (0.1 mg SiO2). Silica standard working solution. Dilute 100 ml of standard stock solution to 1,000 ml (1 ml (10 µg SiO2).

Procedure

1. Prepare standards and a blank by pipetting portions of the silica working standard into tall-form 50-ml Nessler tubes and make up to 50 ml with distilled water. If measurement is to be made at 650 nm, use portions of 0-30 ml (giving 0-300 µg l^{-1} concentrations in the Nessler tubes); if measurement is to be made at 815 nm use portions of 0-10 ml (0-100 µg l^{-1}). If cells with a light path longer than 1 cm are to be used, the silica concentrations should be proportionally reduced.

Note: Reduction by aminonaphtholsulphonic acid is temperature-dependent. The best results will be obtained if tubes are immersed in a water-bath, thermostatically controlled at a temperature near 25 or 30 °C.

2. To each standard add, in rapid succession, 1.0 ml of HCl, 6 mol l^{-1}, and 2.0 ml of ammonium molybdate reagent. Mix by inverting the tubes at least six times.
3. Add 1.5 ml of oxalic acid solution and mix thoroughly. At least 2 minutes, but less than 15 minutes, after addition of the oxalic acid, add 2.0 ml of reducing agent and mix thoroughly.
4. After 5 minutes, measure the absorbance at 650 or 815 nm.

5. Subtract the absorbance of the blank from the absorbances of the standards to obtain the net absorbances.
6. Prepare a calibration graph relating the net absorbance to the amount of silica (SiO_2).
7. Measure 50 ml of sample into a tall-form Nessler tube and add, in rapid succession, 1.0 ml of HCl, 6 mol l^{-1}, and 2.0 ml of ammonium molybdate reagent. Mix by inverting the tube at least six times.
8. Add 1.5 ml of oxalic acid solution and mix thoroughly. At least 2 minutes, but less than 15 minutes, after addition of the oxalic acid, add 2.0 ml of reducing agent and mix thoroughly.
9. After 5 minutes, measure the absorbance at 650 or 815 nm.
10. Subtract the absorbance of the blank from the absorbance of the sample to obtain the net absorbance.

Calculation

Determine the amount of silica (SiO_2) equivalent to the net absorbance from the calibration graph and divide by the volume of the sample (ml) to obtain the concentration of SiO2 in mg l^{-1}.

$$\text{Concentration of silica} = \frac{SiO_2 \text{ (from graph)}}{\text{ml of sample}} \text{mg } l^{-1}$$

Determining Flow Rate Velocity-Area Method with Current-meter

Principle

Discharge is obtained by calculating the integral of the stream velocity v over the cross-section area of the flow A, where v is measured perpendicular to the cross-section:

$$Q = \int v dA$$

The velocity v can be measured in discrete intervals along the cross-section by means of a current-meter. A current-meter consists of a small propeller mounted on a pole that is

connected to a device which measures the frequency of the propeller rotation. This information can be converted into a stream velocity using the provided look-up tables, which were established during calibration experiments. If we assume a purely laminar flow, the theory of fluid mechanics states that the stream velocity is expected to vary vertically following a parabolic function because of the zero velocity (no-slip condition) at the bottom of the stream bed. In case of a turbulent flow, we would get a logarithmic function. For this reason, velocity should ideally be measured at several depths for each interval along the river cross section. Alternatively, a single measurement is best taken at 40% of the local depth (see Figure 2), which is generally the depth with the mean velocity. Errors in the measurements can be introduced by random occurrences of turbulent eddies during the establishment of the profile, by changes in water height or width of the stream. During the experiment you should also take care to estimate the uncertainty of your measurements.

1) Select an appropriate cross-section: ideally there should be no plants, no big stones and the channel should be clearly defined.

2) Establish a point near the selected cross-section where the water level can be monitored during the measurements.

3) Inspect and measure the cross-section. Make a clear graphical sketch of the profile.

4) Plan the measurement points and protocol based on the sketch of the profile (see Figure 2).

5) Perform the velocity measurements at the planned points. To do so, one should select a propeller adapted to the stream velocity. Report the water level immediately before and after each measurement, as well as any problems or noteworthy particularities encountered during the measurements.

6) Repeat measurements several times.

7) Work out the measurements to obtain total discharge Q.

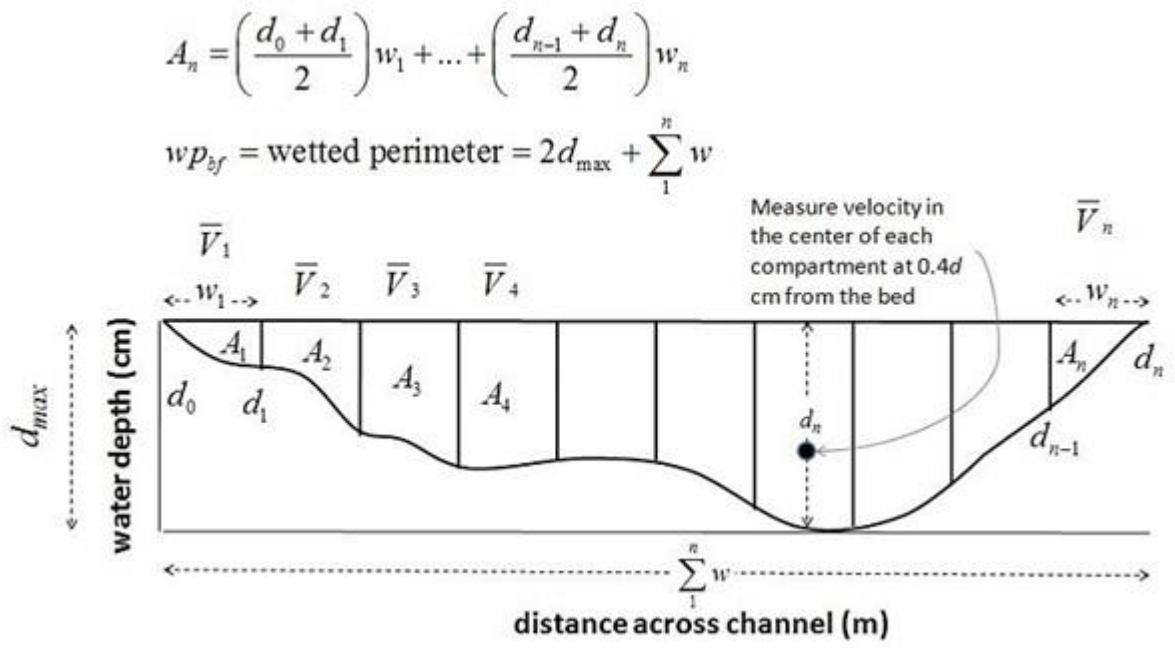


Figure 8: River Corss section and illustration of the compartments

Source:(https://www.ethz.ch/content/dam/ethz/special-interest/usys/iac/iac-dam/documents/edu/courses/climatological_and_hydrological_field_work/Discharge.pdf)

3.4.Determination of floating plastic density

3.4.1. Regional considerations

Monitoring of floating plastic should represent all areas including;

- Areas that are known to generate or accumulate (convergence zones) marine litter such as major shipping lanes, or areas with concentrated fisheries or similar commercial activities.
- Will not impact on endangered or protected species such as sea turtles, sea/shore birds or marine mammals;

Sampling units should be stratified relative to sources within a region such that there are samples obtained from:

- Urban coasts (i.e. mostly terrestrial inputs);
- Rural coasts (i.e. mostly oceanic inputs);
- Within close distance to major riverine inputs;

3.4.2. Overview of potential methods

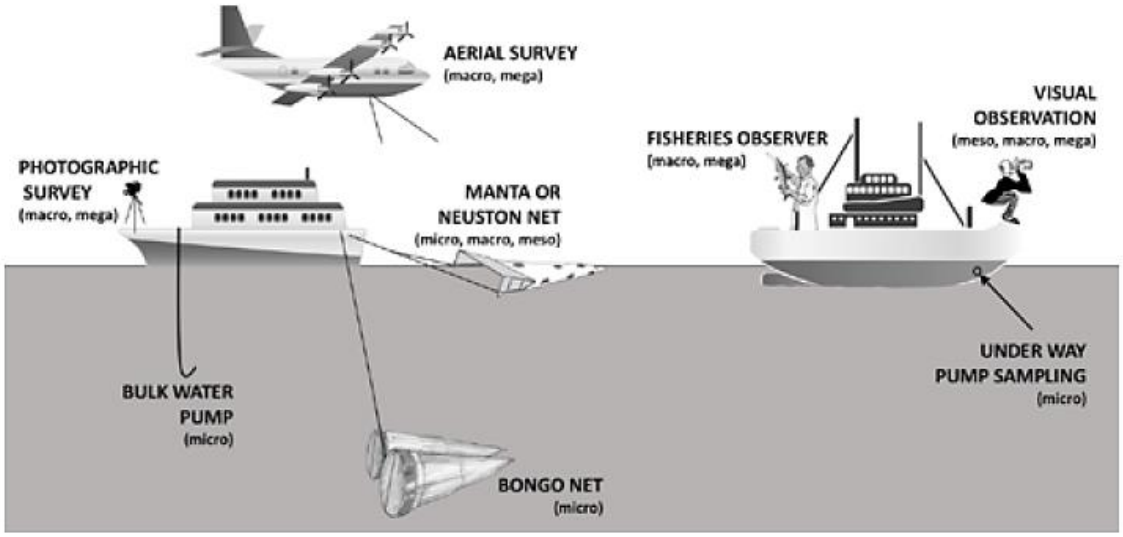


Figure 9 Schematic of possible methods used for sampling the sea surface and water column

The most common is the surface net tow, using a neuston net, manta trawl or mega trawl, to collect floating micro-, meso-and (to a limited extent) macro-plastic items (UNEP/IOC, 2009). To determine the floating plastic density using a manta trawl is highly recommended with a mesh of 300 µm to exclude the smaller microplastics (Smaller than 300 µm) to avoid

complications in counting. If a smaller mesh size is used, a step of digestion is required to remove the resembling organic materials prior to counting of plastics.

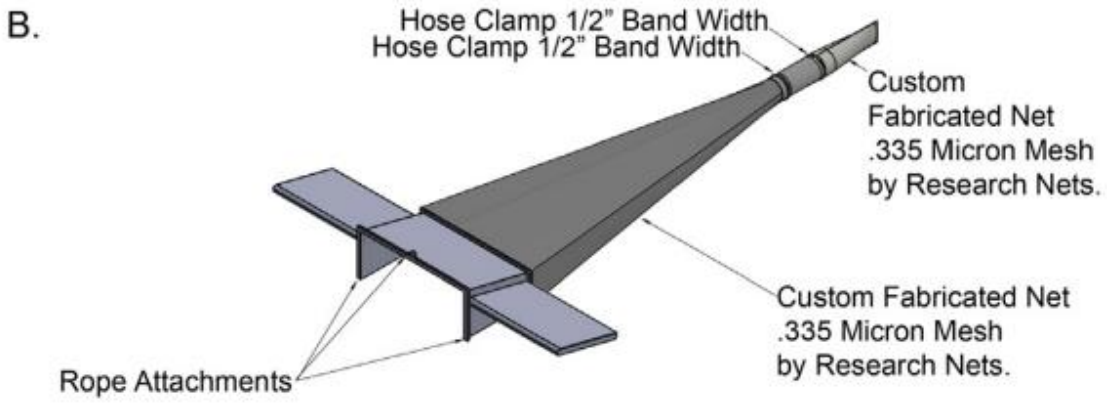


Figure 10 Image of an Manta net (Image curtesy: Microplastic sampling with the AVANI trawl compared to two neuston trawls in the Bay of Bengal and South Pacific)

Table 3 Overview of potential methods (adopted from GUIDELINES FOR THE MONITORING AND ASSESSMENT OF PLASTIC LITTER IN THE OCEAN)

Method	Explanation	Advantages	Limitations
Net tows (manta trawl, neuston net)	Fine-mesh net attached to a large rectangular frame (e.g. 0.5 to 1.0 m wide and 0.4m high) developed for sampling surface and water column waters for plankton, insects and other small biota. Manta trawl with floating wings to keep it on the surface. Net length typically 1-8 m. Mesh size typically 200- 333 µm Standard deployment configured with long side parallel to water surface	Can be deployed from small to large vessels. Underway sampling Use of flow meter to estimate volume.	Use is weather dependant Care needed to minimize contamination from sampling vessel and tow ropes. Can only estimate volume of water filtered when flow meter is used and the frame completely immersed Towing speed and time must be limited to avoid clogging the net and under-sampling surface waters; vessel speed may need to be restricted Under-samples material smaller than mesh size.
Mega net	Large net, up to 4 m wide for sampling larger litter than with a standard manta or neuston net	Captures a macro and meso litter	Use is weather dependent Infrastructure needs to store, deploy and retrieve are great
Bulk water sample	Sampling large volume of water and volume reducing	Known volume sampled Can sample from vessels of opportunity	Limited volume can be processed, restricting it to smallest litter fractions Volume reducing sample on a working deck may exposure sample to contamination
Visual observations from a ship	Visual survey of floating marine litter from the surface of a vessel at sea Use either fixed width transects (assumes all items seen) or distance sampling (corrects for decrease in detection probability with distance from the vessel)	Easy to do from vessels of opportunity Low cost, needs only binoculars (but ideally also a good quality digital SLR camera and telephoto lens)	Limited to waters adjacent to the ship (up to 50 m typically) Bias against dark items and sub-surface items; white and buoyant items easier to spot Report start/stop observation times, observer effort, etc. to be useful.
Photographic and aerial surveys	Visual survey of floating marine litter from an airplane or drone	Cover large areas; ideal for mega-litter	High cost to charter, expensive photography equipment Limited to macro and mega-plastic, with one study (Lebreton *et al.* 2018) observing items as small as 10-cm Bias against dark items and sub-surface items

3.4.3. Sampling units

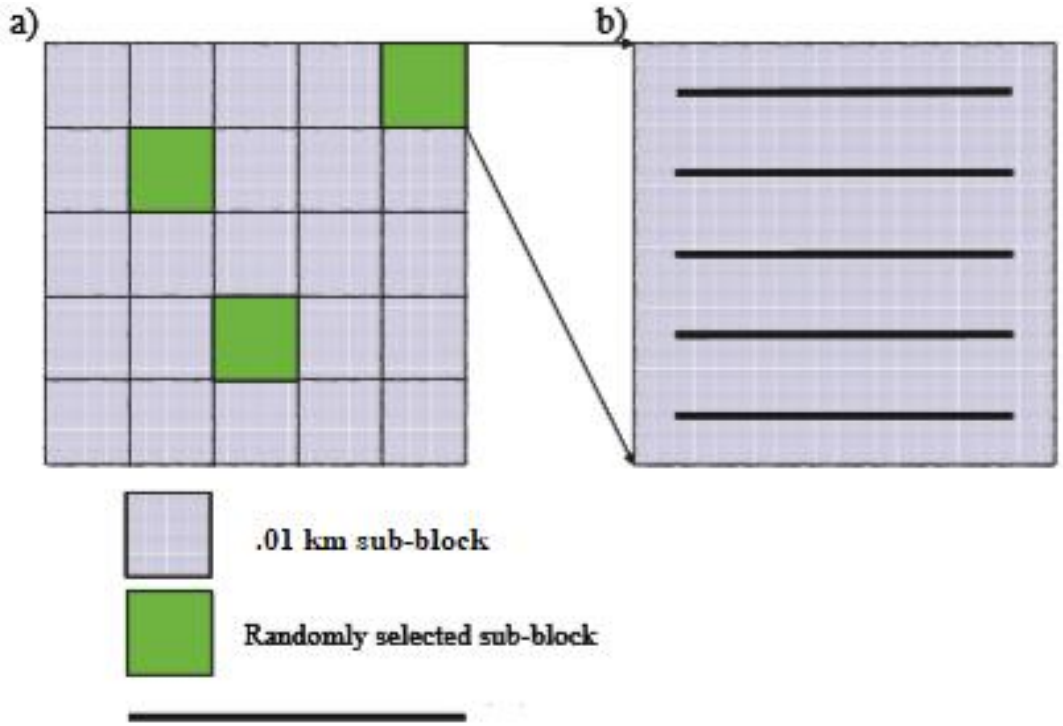
The basic sampling unit for a visual survey will comprise a transect represented by an imaginary line over the surface of the coast which is either travelled by a vessel or aircraft. The line does not need to be straight although it is easier if it is. The observer will record all litter within a fixed distance on one or both sides of the line. The width of the field of view should be recorded along with data about the distance travelled and the litter observed. Visual Transects should be established by monitoring the time employed by observers rather than attempting to identify fixed length units. Ideally location should be mapped using route plotters connected to on-board GPS systems that can record changes in vessel direction and therefore can be used to quantify the size and geographical location of the area surveyed. This approach assumes there will be differences in vessel speed and changes in direction that are beyond the control of the litter observers. Limiting observations to a fixed time period (typically two hours) will help avoid apathy and fatigue while at the same time allow large areas to be surveyed (even at slow speed). Transects of varying length are consistent with the methods employed by Shiomoto and Kameda (2005) in their floating litter survey around Japan. Litter should be measured as per the methods outlined in Ribic et al. (1992) and employed in Shiomoto and Kameda (2005) for strip transects, wherein all litter are recorded within a fixed distance of the direction of travel by the vessel (typically a distance of 50 or 100 m either or both sides of the vessel). The decision about whether to survey both sides of the vessel depends on sea-state, and the field of view of the observer which may differ between vessels. A minimum distance between transects of 1 km should prevent overlap. At least 20 sampling units should be randomly allocated within each region (note the stratification recommended above and that a level of redundancy in sampling units within each region is highly recommended).

3.4.4. Sampling frequency

The minimum sampling frequency for any site should be annually. Ideally it is recommended that locations be surveyed every three months (allowing an interpretation of results in terms of seasonal changes). Quarterly sampling is consistent with the recommendations for comprehensive beach litter assessments. Some consideration should be given to tropical regions where there are essentially only.

3.4.5. Sampling procedure (source: Microplastic sampling with the AVANI trawl compared to two neuston trawls in the Bay of Bengal and South Pacific)

1. Deploy the manta net from the side of the vessel using a spinnaker boom or »A-frame« using lines and karabiners.
2. Deploy the manta net out of the wake zone (approx. 3 - 4 m distance from the boat) in order to prevent collecting water affected by turbulence inside the wake zone.
3. Write down the initial GPS coordinates and initial time in the data sheet.
4. Start to move in straight direction as specified in figure x with a speed of approx. 2 - 3 knots for 30 min and begin the time measurement.
5. At the end of the sampling block stop the boat and write down final GPS coordinates, the length of the route (the most correct way is to calculate the length from the GPS coordinates) and the average boat speed into the data sheet provided and lift the manta net out of the water.
6. Rinse the manta net thoroughly from the outside of the net with seawater using a submersible pump or water from the boat water reservoir. Rinse in the direction from the manta mouth to the cod end in order to concentrate all particles adhered to the net into the cod end. Note: Never rinse the sample through the opening of the net in order to prevent contamination.
7. Safely remove the cod end and sieve the sample in the cod end through a 300 µm mesh size sieve.
8. Rinse the cod end thoroughly from the outside and pour the rest of the sample through the sieve. Repeat this step until there are no longer any particles inside the cod end.
9. Concentrate all material on the sieve in one part of the sieve.
10. With the use of a funnel, rinse the sieve into a glass jar or plastic bottle.
11. Close the bottle, wipe it with paper towels and label the lid and outside of the jar with the sample name and date with waterproof marker (you should also put a second label written with a pencil on velum paper in a jar to avoid the possible loss of the sample name due to the erased label on the jar).



Trawl sub-samples once the three sub-blocks have been selected each can then be trawled. Trawl operations should be conducted such that:

- Ship speed should be restricted to 3-4 knots;
- Each sub-block should be trawled using five parallel trawl shots up to maximum of 100 m long;
- Trawl shots should be separated by a minimum of 10 m.
- The ship should proceed in a straight line against the current, so that trawl net is positioned in a line astern.

Data on all litter collected should be aggregated (summed) across all trawl shots and across all 3 sub blocks. Data should be reported per unit length. The width of the trawl net (when set) needs to be incorporated to provide a measurement of area of sea surface trawled (distance in meters multiplied by width of trawl net) and the data will then be reported **as kg of plastic litter per square meter of sea surface**.

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Annex-I

Summary of Beach Clean-up and Awareness Program along with Technical Professionals on 12-11th April 2019

The Marine Environment Protection Agency (MEPA) conducted a beach clean-up and awareness program in Kayankerni on April 11th, 2019. The aim of the program was to conduct a clean-up of accumulated solid waste along Kayankerni beach with the support of local communities, to promote awareness about solid waste pollution among local fisheries communities and provide the necessary trainings to MEPA professionals about the Water Quality Indications. Several members from low income families have been employed to support clean-up activities as a long term initiative that promotes a cleaner coastal environment and to support livelihoods. With the declaration of the Kayankerni reef as a Marine Sanctuary such efforts are expected to support increased awareness among local communities and promote best practices among fishers, especially with regard to disposal of solid waste. Indiscriminate disposal of solid waste from fisheries activities is accurately a major issue in nearshore coastal environments. Around 40 members of the local community participated in the program along with members of the local fisheries society, MEPA staffs and staff from Blue Resources Trust.