NATIONAL OPEN UNIVERSITY OF NIGERIA

SCHOOL OF SCIENCE AND TECHNOLOGY

COURSE CODE: CHM314

COURSE TITLE: ENVIRONMENTAL CHEMISTRY

COURSE GUIDE

CHM314
ENVIRONMENTAL CHEMISTRY

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CONTENTS PAGE

Introduction

This course guide tells you briefly about the course, the course materials available, how to work with them and maximise your learning through effective time management. Environmental Chemistry is a first semester two-unit degree course for all students offering Bachelor of Science (B.Sc.) Chemistry.

Without a clear scientific understanding and an accurate interpretation of the interactions going on among the chemical species in our environment (in relationship to plants, animals and humans) chemistry, more or less, becomes irrelevant both to the specialist, environmental engineer, health workers, decision makers and the general populace. The price to pay for such ignorance is huge in terms of environmental degradation and the attendant health problems, many of which are often catastrophic and irreversible. It is thus important to approach the study with a mind-set not only of a willing student but also of a determined learner who will obtain high scores and apply the knowledge to solving environmental problems in real life situations, whenever the need arises.

What You Will Learn in this Course

In this course, you will learn about important chemical phenomena in the three environmental compartments: air, water and soil. You will be familiar especially with how such chemical phenomena are relevant to the study and monitoring of environmental pollution, and possible means of averting associated hazards. Certainly, the interconnection of chemistry with such fields as engineering, agriculture, geography, and so on will be better appreciated in the process of going through this course.

The Course Aims

Broadly, the course is aimed at helping every student to have an introductory, and indepth knowledge of important chemical interactions going on in the environment. It is also aimed at preparing students to proffer solutions to issues of environmental problems arising from natural and anthropogenic sources.

The Course Objectives

To achieve the aims set out you should be able to:

explain vividly the central concepts involved in each unit of study
use chemical equations, where necessary, to explain changes going on in a given environmental compartment and
apply the knowledge gained to practically tackle environmental and/or health related issues.

Working through this Course

Each unit has specific learning objectives at the beginning. Endeavour to read these objectives before you study the unit. Again, go through the objectives after completing the unit to see whether you have internalised the concepts treated in the unit.

Read the textbooks and other materials which may be provided by the National Open University of Nigeria. Go through the self assessment exercises and ensure that you answer the questions. At certain points in this course, you would be asked to submit assignments for assessment purposes.

The course should take you about 15 weeks to complete. Read each unit with full concentration. You must attend the tutorial sessions so that you can avail yourself the opportunity of comparing notes and ideas. At the end of this course, there will be a final examination based on what you have learnt; every unit is important, please.

The Course Materials

The main components of the course are:

1. The Course Guide
2. Study Units
3. Self Assessment Exercises
4. Tutor-Marked Assignments
5. Presentation Schedule
6. References/Further Reading

Study Units

Module 1 Natural Cycles and Atmospheric Chemistry

Unit 1	Concepts of Elementary Cycles
Unit 2	Characteristics of the Atmosphere

Module 2 Sources, Types and Effects of Environmental Pollution

Unit 1	Water Pollution
Unit 2	Air Pollution
Unit 3	Soil Pollution

Module 3 Waste Management

Unit 1	Waste water Treatment
Unit 2	Composition of Solid Wastes

Module 4 Water Chemistry and Analysis

Unit 1	Physical Parameters Relevant to Water Analysis
Unit 2	Important Chemical Parameters in Water Chemistry and Analysis
Unit 3	Biochemical Parameters in Water Chemistry and Analysis
Unit 4	Anions and Other Constituents of Concern in Water Chemistry and Analysis

Module 5 Chemical and Physical Instrumentation in Environmental Sciences

Unit 1	Chemical Instrumentation in Environmental Sciences
Unit 2	Physical Instrumentation in Environmental Sciences

There are **five modules** comprising 2, 3,2,4 and 2 units for modules 1,2, 3, 4 and 5 respectively. Thus, this course is made up of 13 units.

In Unit 1 of Module 1, we treat elementary (biogeochemical) cycles: carbon, nitrogen, sulfur and water cycles while in Unit 2 we deal with the characteristics of the atmosphere with emphasis on environmentally relevant chemical reactions taking place in the troposphere, stratosphere, mesosphere, thermosphere and exosphere. In the three units of Module 2, we examine the sources, types and effects of environmental pollution in the air, water and soil compartments. In Module 3, Unit 1 deals with wastewater treatment while Unit 2 deals with the composition of solid (municipal, industrial and hazardous) wastes. The 4 units of module four focus on water chemistry and analysis with emphasis on physical, chemical and biochemical parameters, and anions and other constituents of concern relevant to water chemistry. In module 5 we are concerned with chemical and physical instrumentation in environmental sciences treated in the unit.

Each unit is designed for a duration of one week, for an effective study. That is, covering the entire course should last about 13 weeks. It is expected that two extra weeks would be used for intensive personal revision of the whole course units before the examination commences. Each unit consists of introduction, objectives, reading materials, exercises, conclusion, summary, tutor-marked assignment (TMA), further reading and references.

The exercises with TMAs help you to achieve the stated objectives and to evaluate your progress in the process of mastering the concepts in the material.

Presentation Schedule

Your course materials have important dates for the early and timely completion and submission of your TMAs and attendance of tutorials. You are required, as a matter of compulsion, to submit all your assignments by the stipulated time and date. It is suggested that you have a personal study time-table to ensure that each unit is completed on schedule. Having accumulated study schedule or unsolved exercises is unhealthy and capable of truncating your success. Avoid it.

Assessment

There are three aspects to the assessment of this course: Self Assessment Exercises (SAEs), Tutor-Marked Assignments (TMAs) and End of Course Examination (ECE) and subsequent grading by the facilitator. Each SAE is designed to help you assess your personal understanding of a particular unit. The TMA for a unit must be written for assessment by the course facilitator. The ECE at the end of the course is meant to last between two and three hours.

Tutor-Marked Assignment (TMA)

The TMA is a continuous assessment component of the course. It accounts for 30percent of the total score. You are expected to answer at least four (at most six) of all the TMAs as condition for the end of course examination.

Return a completed TMA schedule to your facilitator. Each TMA is contained in the assignment file. You will certainly be able to complete your assignment from the information and material contained in your reading and references especially as you research more into your references to acquire a wider view point and deeper understanding of the subject matter. Your TMA will be graded by the facilitator and returned to you as soon as possible.

If for any reason you cannot complete and submit your assignment on schedule, contact your facilitator beforehand to discuss the possibility of an extension. This is not automatic, however.

Final Examination and Grading

The end of course examination will have two sections: Section A and Section B. Section A consists of short-structured questions counting for 25per cent of the total marks and lasting one hour, while Section B will be made up of four essay questions of 15 marks each lasting one and half hours. A candidate will be required to answer only three of those questions in Section B counting for a maximum of 45per cent. Thus, the end of course examination counts for 70percent of the total assessment. The breakdown of the assessment is given below:

TMAs equal 30per cent
End of course Examination (ECE)
Section A = 25%
Section B = 45%
Total = 70%

Overall Total = **TMA** + **ECE** = 30 + 70 = **100%**

Facilitators/ Tutors and Tutorials

There are five contact periods of tutorial classes in support of this course. Each contact period is made up of two hours. Each period is a time of face-face interaction between the facilitator and the students on one hand, and among all the participants on the other hand. It is a time to discuss individual problems encountered in the course of his/her study.

You will be notified of the dates, times and location of these tutorials as well as the name, phone number and e-mail address of your facilitator as soon as you are allocated a tutorial group. Do not hesitate to contact your facilitator by telephone or e-mail if you need an **academic** assistance.

Endeavour to attend the tutorials; it is the only chance you have for effective interaction that enhances effective learning. Various challenges you will encounter as you study Environmental Chemistry as a course will be passionately reviewed during these sessions. Prepare your questions and bring them for class discussion. Even when you think you have known everything, come and listen to the problems of others; you will certainly benefit from them.

Summary

Environmental Chemistry as a course, deals with chemical interactions that have serious impacts on the air, water and soil compartments of the environment. It helps a candidate to appreciate the fact that when we talk about environmental contamination or pollution, the species involved know no boundary. It also brings into sharp focus the possible roles of a chemist, in conjunction with other stakeholders in environmental sciences and engineering generally, in solving pollution problems that may appear intractable ordinarily.

By and large, environmental chemistry study helps an individual to be conscious of the need to preserve the environment by judicious use and disposal of resources available to us so as not to embark on a journey of self-elimination or extermination.

While I wish you a resounding success in this course, I sincerely wish that your targets be two-fold: passing your examination well and also applying your knowledge to cause a positive change in our environment.

Course Code	CHM319
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CONTENTS **PAGE**

MODULE 1 NATURAL CYCLES AND ATMOSPHERIC CHEMISTRY

UNIT 1 CONCEPTS OF ELEMENTARY CYCLES

CONTENTS

1.0 INTRODUCTION

Environmental Chemistry is the study of chemical processes occurring in the environment which are impacted by humankind’s activities. These impacts may be felt on a local scale, through the presence of urban air pollutants or toxic substances arising from a chemical waste site, or on a global scale, through depletion of stratospheric ozone or global warming. The focus in our courses and research activities is upon developing a fundamental understanding of the nature of these chemical processes, so that humankind's activities can be accurately evaluated.

The field of environmental chemistry is both very broad and highly interdisciplinary. Within the Department of Chemistry we have a core group of faculty whose research interests are in atmospheric and aquatic chemistry, photochemistry, and the chemistry and transport of long-lived pollutants. We interact with other chemists in the department, with numerous other researchers at the university who have related interests, and with nearby government agencies. Indeed, the setting for the study of environmental chemistry is ideal.

Our graduate programme consists of graduate courses which stress the fundamental photochemical, kinetic, analytical and transport aspects of environmental phenomena, regular seminars, and close interactions between the different research groups. We emphasise the need for students to be able to put their own research into a global context.
Environmental Chemistry is rapidly expanding, and excellent employment opportunities exist in the academic, government, industrial and public policy sectors.

Cycles are sequences of events that repeat themselves in a particular pattern. In environmental chemistry, our concern is basically with **biogeochemical cycles**. Precisely, biogeochemical cycles are interconnected complex processes by which matter or elements that make up the biotic and abiotic systems are used over and over again between the living and non-living things. Some of the very important natural biogeochemical cycles include: **Carbon Cycle, Nitrogen Cycle**, **Sulphure Cycle,** and **Hydrological (Water) Cycle.**

2.0 OBJECTIVES

At the end of this unit, you should be able to:

define biogeochemical cycles
name specific examples of biogeochemical cycles
explain the basic transformations that go on in a named biogeochemical cycle.

3.0 MAIN CONTENT

3.1 Some Biogeochemical Cycles

3.1.1 The Carbon Cycle

The carbon cycle is the series of interconnected changes by which carbon is being continuously circulated among the natural compartments of atmosphere, biosphere, hydrosphere, geosphere and pedosphere. There are four major reservoirs involved in the carbon cycle. These are the plants, the terrestrial biosphere (fresh water systems and non-living organic material), the oceans (where we have dissolved inorganic carbon and living and non-living marine biota), and the sediments (including fossil fuels).

Living organisms are mainly composed of water and various carbon compounds hence the cycling of carbon is of prime importance to the support of life. The concentration of carbon in living matter (18per cent) is about 100 times greater than its concentration in the earth (0.19per cent). Carbon exists as carbon dioxide (CO_2) in the atmosphere, bicarbonate ion (HCO_3^-) in water and calcium carbonate ($CaCO_3$) in carbonate rocks (limestone, chalk, coral). It is the major part of hydrocarbon molecules in petroleum and natural gas; and the main constituent of coal and dead organic matters.

In the Earth's atmosphere, carbon exists as carbon dioxide in 0.03per cent level by volume. This level is currently being shifted towards excess due to imbalance of anthropogenic activities (human-induced) such as excessive combustion of fossil fuels and deforestation. In 1850, atmospheric CO_2 was about 280 ppm and by 2007, it had increased to about 383 ppm.

3.1.1 Ways by which CO_2 is released into the Atmosphere

Some of the ways by which CO_2 is released into the atmosphere are:
Respiration of plants and animals: This is an exothermic reaction involving the breaking down of organic molecules, e.g. glucose, into carbon dioxide and water

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + \text{energy.}$$

Decay of plants and animals: Fungi and bacteria breakdown the carbon compounds i.e. carbohydrates, proteins and lipids in dead plants and animals, and convert the carbon to carbon dioxide in the presence of oxygen or carbon dioxide and methane (CH_4) in the absence of oxygen e.g.

$$C_6H_{12}O_6 \xrightarrow{\text{Methanogens}} 3CO_{2(g)} + 3CH_{4(g)}$$

Fermentation of carbohydrates: The enzymatic decomposition of carbohydrates produces CO_2 as a by-product

$$C_6H_{12}O_{6(aq)} \xrightarrow{\text{Zymase}} 2C_2H_5OH_{(aq)} + 2CO_{2(g)}$$

Burning of fossil and agro fuels: Combustion of fossil fuels like petroleum products, coal, natural gas and agro fuels releases CO_2 (and water vapour) into the atmosphere.

$$C_5H_{12} + 8O_2 \longrightarrow 6H_2O + 5CO_2$$

Thermal decomposition of carbonate rocks or limestone: When limestone soils are heated up or during the production of cement, CO_2 is released into the atmosphere.

$$CaCO_{3(s)} \xrightarrow{\text{heat}} CaO_{(s)} + CO_{2(g)}$$

Warming of surface waters: This leads to the releasing of dissolved CO_2 back into the atmosphere.

Volcanic eruptions: During volcanic eruptions, the volcanic gases released into the atmosphere include water vapour, CO_2 and SO_2.

3.1.2 Ways by which CO_2 is removed from the Atmosphere

Photosynthesis: Primarily, photoautotrophs (plants and algae) use light energy to convert CO_2 and water to organic molecules like glucose and other carbohydrates. To a less extent, chemoautotrophs (bacteria and archaea) convert CO_2 and water to organic matter using energy derived from the oxidation of molecules of their substrates.

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

Formation of carbonic acid: Carbon dioxide dissolves in rain water and droplets pass through the atmosphere. Also, at the surface of the oceans towards the poles where sea water becomes cooler, carbon dioxide dissolves in water to from carbonic acid. Carbonic acid reacts with weathered silicate rocks to produce bicarbonate ions which are used to make marine carbonates.

Conversion of carbon to tissues and shells: Organisms in upper ocean areas of high biological productivity convert reduced carbon to tissues or shells.

In the oceans, the major carbon reservoir is the inorganic carbon: When CO_2 dissolves in water, a hydrated CO_2 molecule is produced which then forms an equilibrium mixture containing bicarbonate (HCO_3^-) and carbonate (CO_3^{2-}) ions. At pH_s lower than those found in sea water, carbonic acid (H_2CO_3) will also be present. This can be summarized as:

$$CO_{2(g)} = CO_2\,(aq)$$

$$H_2O(\ell) + CO_2(aq) = H_2CO_{3(aq)}$$

$$H_2CO_{3(aq)} = H^+_{(aq)} + HCO^-_{3(aq)}$$

$$HCO^-_{3(aq)} = H^+_{(aq)} + CO^{2-}_{3\,(aq)}$$

However, due to the reactions

$$HCO_{3(aq)}^{-} = CO_{2(aq)} + OH_{(aq)}^{-} \text{ and } CO_{3(aq)}^{2-} + H_2O(\ell) = HCO_{3(aq)}^{-} + OH_{(aq)}^{-}$$

Most ocean waters have a pH in the range 8 to 8.3 as they contain more $0H^-$ ions than H^+ ions.

The overall reaction that takes place when CO_2 dissolves in sea water can be summarised as:

$$CO_{2(aq)} + H_2O_{(\ell)} + CO_{3(aq)}^{2-} = 2HCO_3^{-}.$$

The carbon cycle shown in Fig 1 summarises all the processes so far itemised.

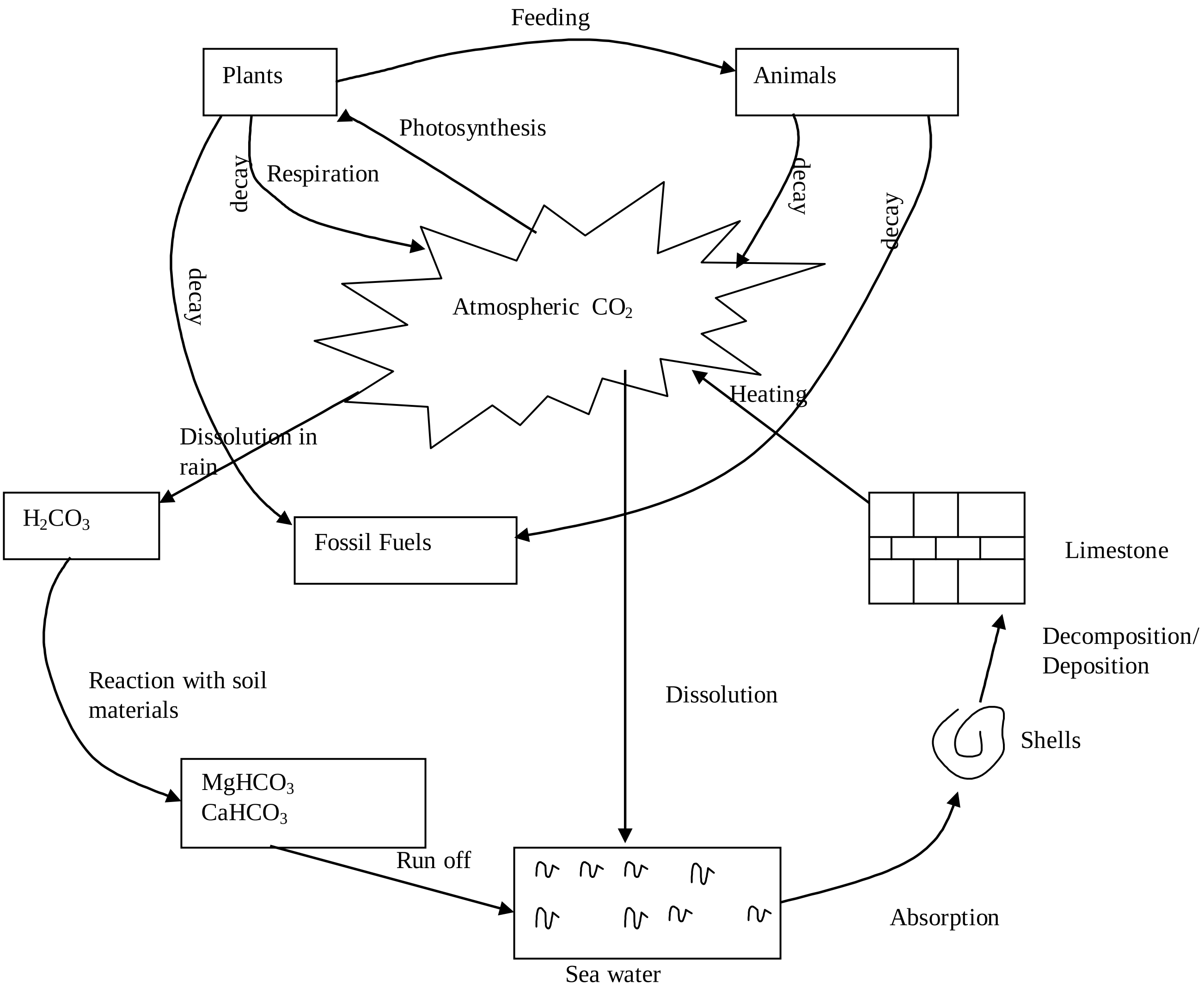


Fig. 1: The Carbon Cycle
Source: O.Y. Ababio, 2002 (modified).

SELF ASSESSMENT EXERCISE 1

1. State the form(s) in which carbon exists in (a) the atmosphere, (b) water, and (c) rocks.
2. List two processes in each case that lead to the (a) addition and (b) removal of $C0_2$ to and from the atmosphere respectively.
3. Is the atmospheric level of CO_2 on a decreasing or an increasing trend currently? Explain.
4. Most ocean waters have a pH in the range 8 to 8.3. Briefly explain this observation using appropriate chemical equations.

3.2 The Nitrogen Cycle

The nitrogen cycle is the biogeochemical cycle that describes the gradual transformation of nitrogen and nitrogen-containing compounds in nature. It is the means by which the supply of nitrogen is distributed in nature.

The Earth's atmosphere, containing about 79percent nitrogen, constitutes the largest pool of nitrogen. Nitrogen is crucial to all life processes on earth. It is present in all amino acids, proteins and nucleic acids (RNA and DNA). Although nitrogen is abundant in the atmosphere and the majority of the air we breathe in is nitrogen (oxygen constitutes only 21percent of the air we breathe in), nitrogen is not readily available for cellular utilisation. This is because the strong triple covalent bonds between the N atoms in N_2 molecules make it relatively inert. By implication, biochemically available nitrogen is in short supply in natural ecosystems. Hence, plant growth and biomass accumulation are limited.

In order for plants and animals to use nitrogen for their metabolic processes, N_2 gas must be converted to a chemically available form such as ammonium (NH_4^+), nitrate (NO_3^-) or organic nitrogen such as urea, $(NH_2)CO$. The nitrogen cycle shown in Figure 2 describes the movement of nitrogen among the atmosphere, biosphere and geosphere in different forms.

3.2.1 Basic Processes of the Nitrogen Cycle

(a) **Nitrogen Fixation**: This is the process by which the atmospheric nitrogen is converted into a form that is readily available to plants and subsequently to animals and humans. There are four ways of converting atmospheric nitrogen (N_2) into more biochemically available forms.

(i) **Biological Fixation:** Symbiotic bacteria, e.g. *Rhizobium*, associated with the root nodules of leguminous plants and some free-living bacteria, e.g. *Azotobacter*, are able to covert (fix) free nitrogen to organic nitrogen.

(ii) **Industrial Fixation:** In the industrial Haber-Bosch process, atmospheric nitrogen and hydrogen (obtained from natural gas or petroleum) are combined to form ammonia, NH_3

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}$$

The ammonia produced can be used to make fertilizers and explosives.

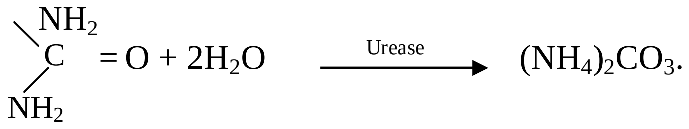
$$2NH_{3(g)} + H_2SO_{4(aq)} \xrightarrow[450\text{-}600^{o}C \\ 200atm]{\text{Iron catalyst}} (NH_4)_2\,SO_4\,(s)$$

(iii) **Combustion of fossil fuels:** The exhaust fumes from internal combustion engines are made up of volatile matters including oxides of nitrogen.

(iv) **Electrical storms (lightning) and photolysis:** During electrical storms, nitrogen is oxidised to NO, which is oxidised by ozone in the atmosphere to form NO_2. NO_2 in turn is reduced back to NO by photolysis. These reactions are important aspects of atmospheric chemistry, but they are inadequate for both terrestrial and aquatic nitrogen turnover.

(a) **Assimilation:** Plants can absorb NO_3^{-} or NH_4^{+} ions from the soil (Nitrogen uptake) through their roots. Absorbed nitrate is first reduced to nitrite ions and then ammonium ions for subsequent incorporation into amino acids, nucleic acids and chlorophyll. In leguminous plants with root nodules, nitrogen in the form of ammonium ions can readily be assimilated. Animals and human beings are incapable of utilising nitrogen from the atmosphere or inorganic compounds hence, they depend on plants or other animals (except ruminants) that feed on plants, for their protein.

(b) **Ammonification:** At death, the proteins stored in the body of plants and animals become waste materials. Urine contains the nitrogen resulting from the metabolic breakdown of proteins in form of urea, $(NH_2)_2CO$. Urea is rapidly hydrolysed by the enzyme to ammonium carbonate, $(NH_4)_2CO_3$.



$$(NH_2)_2C{=}O + 2H_2O \xrightarrow{\text{Urease}} (NH_4)_2CO_3.$$

(c) **Nitrification:** The excess ammonia released by bacterial action on urea and proteins that are not used by plants is oxidised by the autotrophic nitrifying bacteria-Nitrosomonas and Nitrobacter. Under aerobic conditions, Nitrosomonas convert ammonia to nitrite while nitrite is further oxidised to nitrate by Nitrobacter.

$$2NH_3 + 3O_2 \xrightarrow{\text{Nitrobacter}} 2NO_2^- + 2H^+ + 2H_2O$$
$$2NO_2^- + O_2 \xrightarrow{\text{Nitrosomonas}} 2NO_3^-$$

The bacteria derive energy from the oxidation processes. Some of the nitrate formed is used by plants while the excess is carried away in water percolating through the soil because the soil does not have the ability to hold nitrate for long. It is important for the nitrite ions to be converted to nitrate ions because accumlulated nitrites are toxic to plant life.

(d) **Denitrification:** Nitrate and nitrite are reduced under anaerobic conditions by pseudomonas and clostridium bacteria. Nitrate is reduced to nitrite while nitrite is reduced to ammonia. Most of the nitrate is later reduced to nitrogen thus, completing the nitrogen cycle. This constitutes a serious loss of fertilizing matter in soil when anaerobic conditions develop. Also, some denitrifying bacteria produce $N_2$0 from nitrate reduction. The $N_2$0 produced enters the atmosphere and is reduced through photolysis to produce N_2 and an excited state of oxygen, which oxidises N_2O to NO.

$$NO_3^- \longrightarrow N_2 + N_2O$$
$$NO_3^- \longrightarrow NO_2^- \longrightarrow NO \longrightarrow N_2O \longrightarrow N_2$$

SELF ASSESSMENT EXERCISE 2

1(a) What are the basic processes of nitrogen cycle?
(b) Discuss fully anyone of the processes named in 1(a) above.

2. List and discuss the four ways by which atmospheric nitrogen can be converted into more biochemically available forms.
3. In not more than two sentences, discuss the reason(s) why atmospheric nitrogen is not readily available for plants and animals metabolism despite its large atmospheric reservoir.
4. Ground waters in most of the agricultural soils are noted for very high nitrate content. Briefly explain this observation.

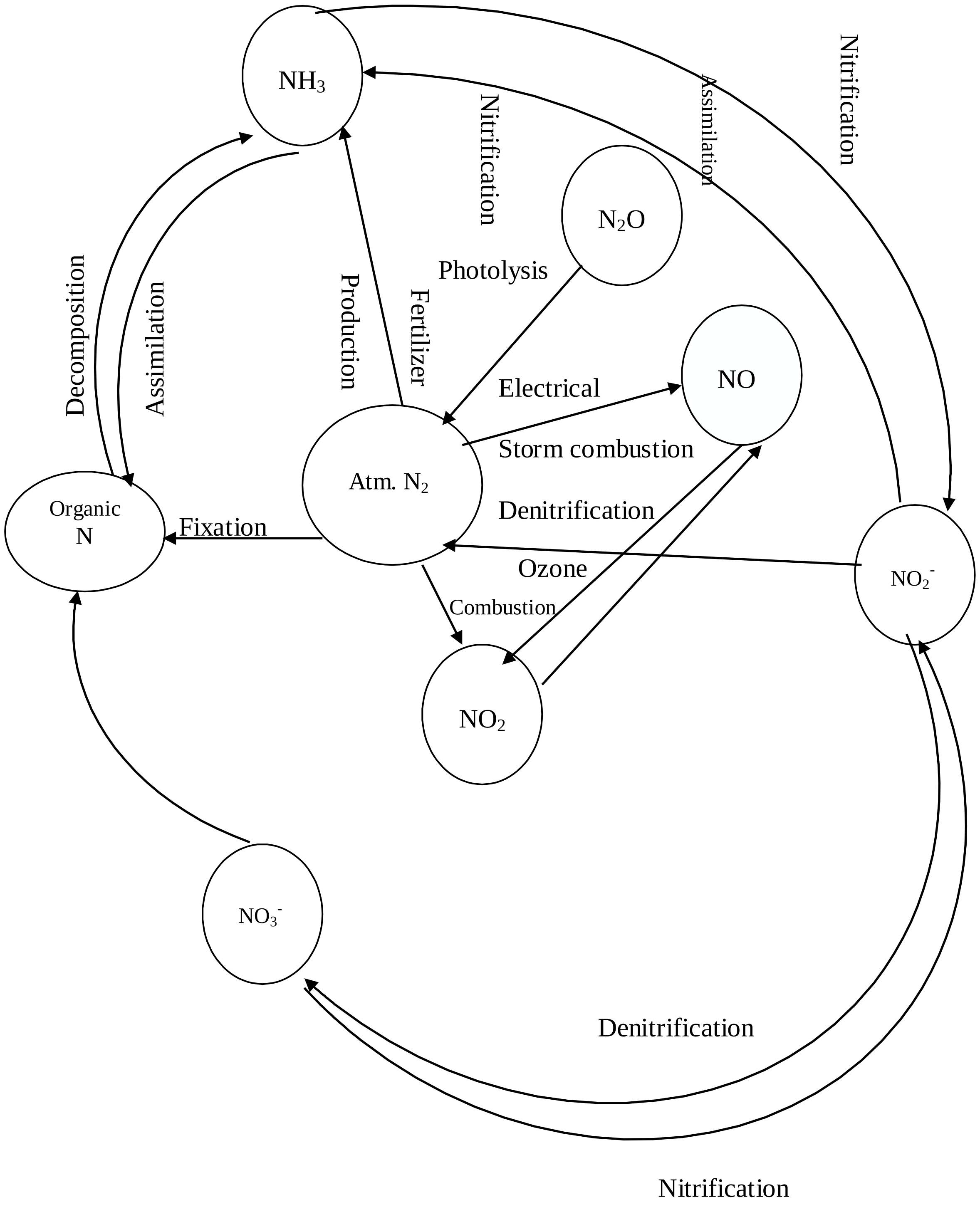


Fig.2: **The Nitrogen Cycle**
Source: **C.N. Sawyer *et al.*, 2006**

3.3 The Sulphur Cycle

On the earth surface sulphur exists as elemental sulphur, sulphur dioxide, sulphuric acid, salts of sulphate, hydrogen sulphide, sulphur trioxide, organic sulphur compounds (such as dimethylsulphide) and amino acids (cysteine and methionine). The biogeochemical transformations of these sulphur species among the atmosphere, biosphere, hydrosphere and geosphere is called the **sulphur cycle**. Most on the sulphur earth is tied up in rocks and salts or buried deep in the ocean in oceanic sediments. Sulphur enters the atmosphere through sources that are both natural (e.g. volcanic eruptions, bacterial processes, evaporation from water or decaying organisms) and human (e.g. wide-scale industrial emission of SO_2 and H_2S).

The major reservoir for sulphur is the crust, with a small, but potentially damaging proportion in the atmosphere. In the air, sulphur is usually oxidised from organic sulphur or elemental sulphur to SO_2 and SO_3 ending up as sulphate (SO_4^{2-}) in sulphate salts or sulphuric acid. The sulphate compounds dissolve in rain water and get precipitated (as rainfall) either as salts or acid rain. In the atmosphere, the oxidation of reduced forms of sulphur by dioxygen occurs without biological control; but can also occur through the actions of microorganisms in the soil, sediment and water column.

O_2 O_2

$$H_2S \longrightarrow (S) \longrightarrow SO_2 \longrightarrow SO_3 \longrightarrow SO_4^{2-}$$

Microorganisms in the soil or water act upon the SO_4^{2-} in the presence of carbohydrates to finally liberate H_2S

$$SO_4^{2-} + H^+ + 2CH_2O \longrightarrow HS^- + 2H_2O + 2CO_2 \longrightarrow HS^- + H^+ \longrightarrow H_2S$$

The formation of H_2S is a characteristics feature of anaerobic marine sediments. In the oceanic surface waters, dimethyl sulphide is formed much more commonly than H_2S because of the presence of the compound dimethylsulphonopropionate produced by some species of phytoplankton.

$$SO_4^{2-} \xrightarrow[\text{hydrosulphide}]{\text{organic}} H_2S + \text{organic sulphides} + [S] \xrightarrow[\text{compound}]{\text{organic}} H_2S + (CH_3)_2S.$$

When organic sulphur compounds are decomposed by bacteria, the initial sulphur product is usually H_2S.

$$R\text{-}SH \xrightarrow{\text{bacteria}} H_2S + RH$$

The hydrogen sulphide produced may be released as a gas to the atmosphere, where it is oxidised, or it may react with metal ions in the sediments or water columns to form insoluble sulphides.

$$H_2S + [S] \longrightarrow Fe^{2+} \longrightarrow FeS + FeS_2$$

or $$2Fe(OH)_3 + 3H_2S \longrightarrow 2FeS + S + 6H_2O$$

$$FeS + S \xrightarrow{Fe^{3+}} FeS_2$$

Many marine phytoplankton produce compounds that breakdown to produce dimethylsulphide, $(CH_3)_2S$, a compound thought to be the major biogenically produced sulphur compound released from oceans. Dimethyl sulphide is rapidly oxidised to form SO_2 and ultimately, SO_4^{2-}. Some microorganisms in muds can generate elemental sulphur from sulphur compounds.

The black colour of many sediments is partially due to the presence of iron sulphides as well as organic matter. Oxidation of the sulphides when exposed to the surface leads to the formation of sulphuric acid:

$$2FeS_2 + 2H_2O + 7O_2 \longrightarrow 2FeSO_4 + 2H_2SO_4.$$

This redox reaction occurs rapidly in the presence of water and dioxygen particularly when microorganisms are involved.

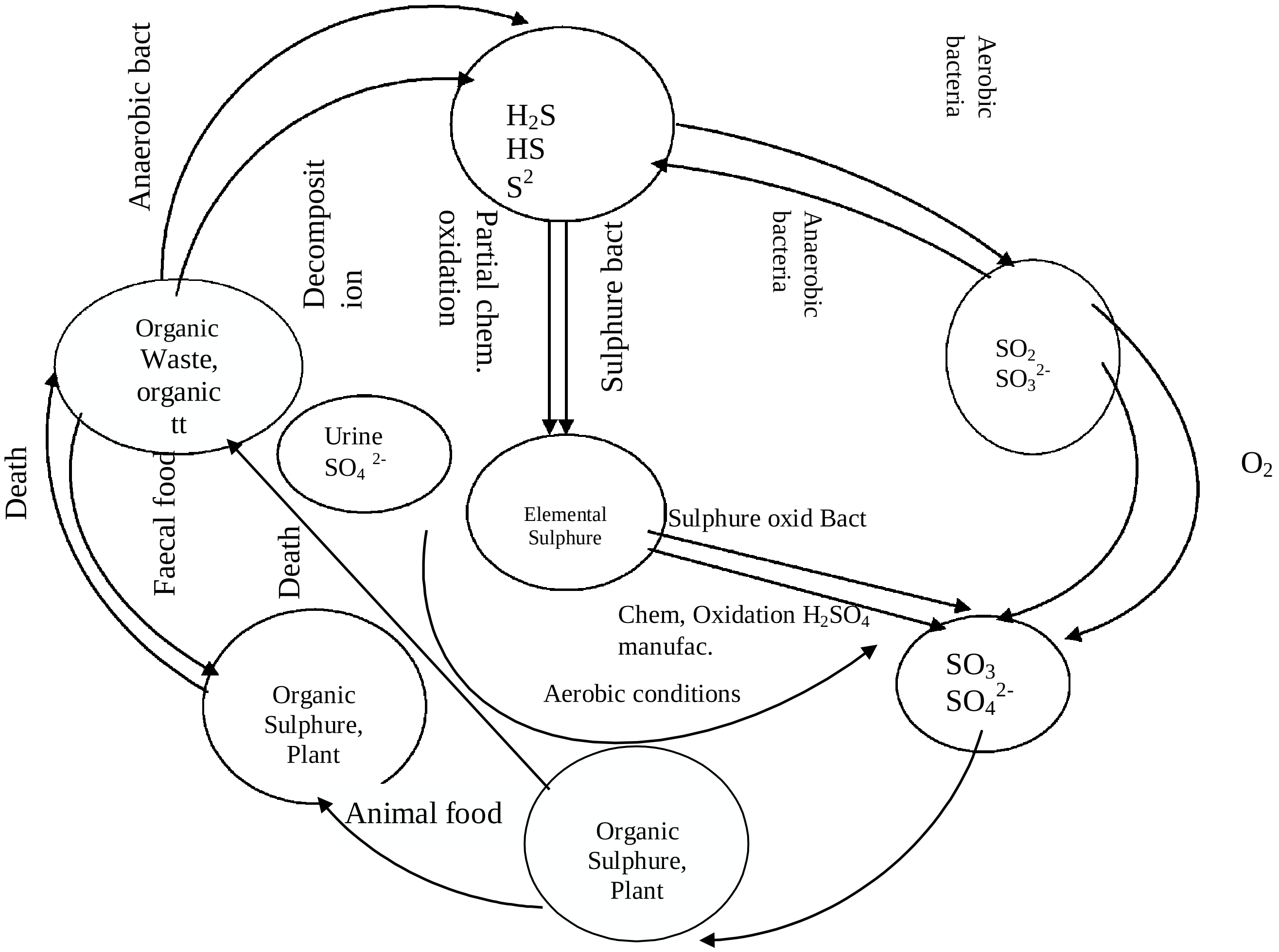


Fig. 3: The Sulphur Cycle
Source: C.N. Sawyer, P.L. McCarty and G.F. Parkin, 2006

3.4 The Water Cycle

Movement of water in its physical states through and around our planet is accomplished by the **water cycle**. Through evaporation, water from the ocean and soil goes as water vapour into the atmosphere; and by transpiration, plants release water into the atmosphere.

In the atmosphere, as the temperature decreases, water vapour condenses into water droplets to form the clouds that precipitate as rainfall. A large proportion of this goes directly into the ocean or indirectly through run-off. Part of the water on the soil sinks down by percolation to form groundwater. The groundwater is pulled through the roots of plants and is transpired back into the atmosphere. Most of the rain and snow that fall on the continents come from plant transpiration than from ocean evaporation.

The water cycle transfers sun's heat energy to various places of the Earth; It also moves contamination or pollution round the planet. Every living thing is directly connected to the water cycle.

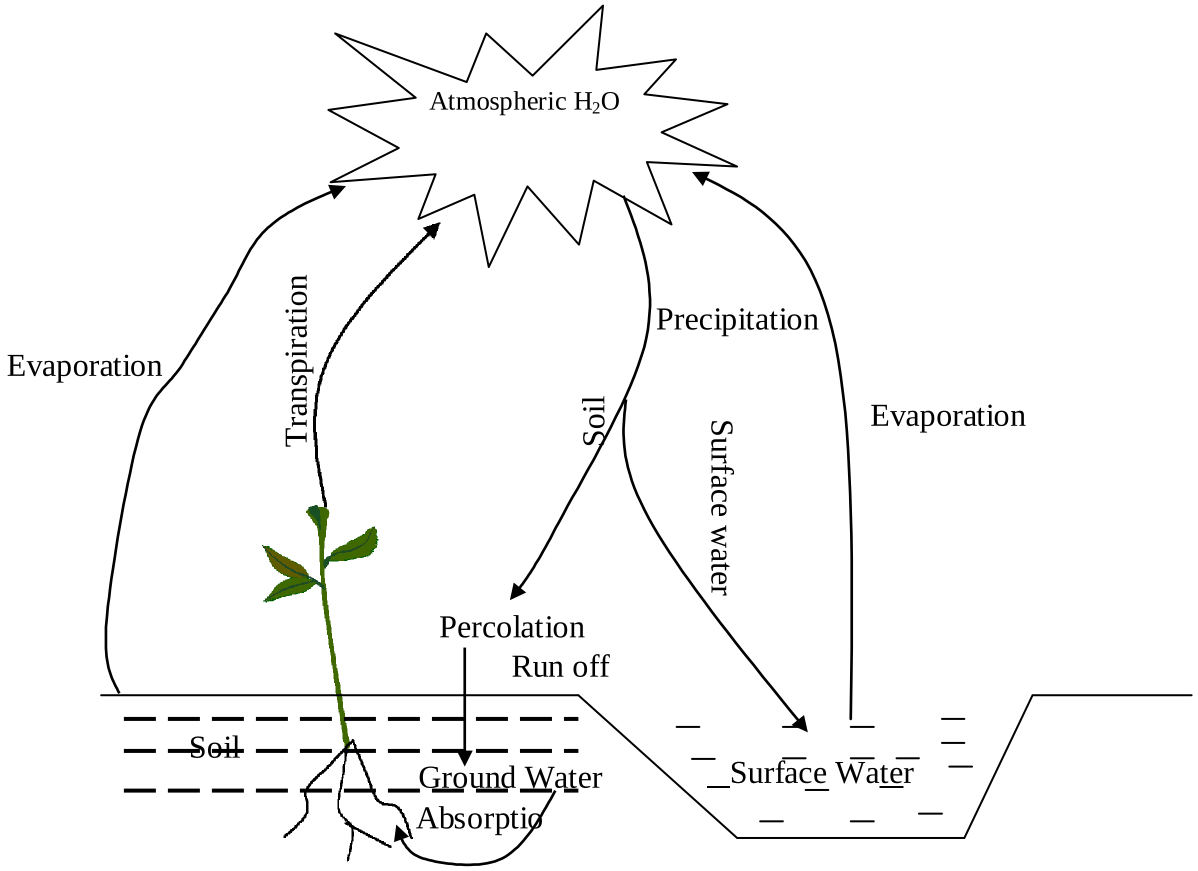


Fig. 4: The Water Cycle

SELF ASSESSMENT EXERCISE 3

Briefly explain (i) how elemental sulphur can be converted to a sulphite or a sulphate, (ii) the microbial transformation process of H_2S to SO_4^{2-}.

4.0 CONCLUSION

Available elements and compounds in the earth continuously undergo transformations that are vital for the preservation of both the activities and the quality of life on Earth. Both living and non-living things of the Earth must interact to effect these transformations.

5.0 SUMMARY

In this unit, you have learnt that:

i. there are various biogeochemical cycles such as the carbon cycle, the nitrogen cycle; the sulphur cycle; and the water cycle;
ii. each biogeochemical cycle is a model that describes the complex movement of a chemical element or its species among matters usually near the Earth's surface;
iii. there are different reservoirs for the recycled elements e.g. for nitrogen, the reservoir is the atmosphere; while for sulphur, it is the crust.
iv. both anthropogenic and natural processes/activities add elements to or remove elements from the environmental compartments.

6.0 TUTOR-MARKED ASSIGNMENT

(a) Explain briefly the roles of bacteria in the biogeochemical cycles of carbon, nitrogen and sulphur.
(b) Using a simplified illustrative diagram, explain briefly either the nitrogen or carbon or sulphur cycle.

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UNIT 2 CHARACTERISTICS OF THE ATMOSPHERE

CONTENTS

1.0 INTRODUCTION

The atmosphere is a layer of air (mixture of gases) that extends up to 700 kilometres above the Earth's surface. The atmosphere is a complex and rapidly changing part of the earth. The fluid nature of the atmosphere causes it to be the most changeable part of the Earth. The atmosphere is constantly under the influence of gravity, earth's rotation and differential heating by solar radiation. The atmosphere drives the **weather** (atmospheric variables that change rapidly-air temperature, humidity, percentage of cloudiness, type and amount of precipitation, air pressure and wind velocity) and the **climate** (the average weather condition in a region over a long period of time).

The gases in the air directly or indirectly support life on the Earth; during respiration, living things consume oxygen and release carbon dioxide; plants absorb carbon dioxide during photosynthesis and release oxygen; nitrogen is converted to useful nutrients to support plant growth and hence, that of the animals that depend on plants for survival.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- name the stratified layers of the atmosphere
- identify the characteristics of each layer that differentiate it from the others and
- discuss atmospheric reactions of notable environmental implications.

3.0 MAIN CONTENT

3.1 General Composition of the Atmosphere

A greater percentage of the air in the atmosphere is made up of clear and odourless gases-nitrogen and oxygen. These two gases are called the **primary** or "**permanent**" gases. According to their relative volumes, average composition of the dry unpolluted atmosphere is given in Table 1. Varying amounts of most of these gases may be found in each of the layers of the atmosphere.

Some of the concentrations are uncertain because (i) analytical procedures for some components have only recently reached the stage where good data can be obtained; (ii) some components such as CH_4, N_2O and CO_2 are known to be increasing in concentration at an appreciable rate; and (iii) it is questionable whether any parts of the atmosphere can be considered entirely free of pollutants or not.

The primary gases do not affect the weather unlike the trace gases. The lower atmosphere contains varying amounts of water vapour which determines its humidity. Water vapour (and to a lesser degree, CO_2) is of great importance in radiative transfer because it absorbs and emits strongly the infra-red (IR), the region of the spectrum at which earth radiates energy back to space. Carbon dioxide plays a major role in the greenhouse effect and the attendant temperature attenuation of the earth. Various gaseous and solid impurities such as Chlorofluorocarbons (CFCs) in the atmosphere resulting from human activities contribute to the ozone layer depletion. The air also carries many kinds of dust of meteorite and terrestrial origin alongside micro-organisms, pollen and other particulate matters of anthropogenic origin.

The earth's atmosphere is a little thicker at the Equator and a little thinner at the poles because, the earth's spinning motion causes it to bulge slightly at the Equator. Because of the pull of gravity, the density of the atmosphere and the pressure exerted by air molecules are greatest near the earth's surface (approximately $1g/10^3m^3$ and 10^6 dynes/cm^2, respectively). Air pressure decreases rapidly with increasing altitude, reaching one-half of its sea-level value at about 5,500 m (5.5 kilometres). At standard temperature and pressure (s.t.p.), 22.4 L of air weighs 28.97g.

Table 1: Average Composition of the Dry Unpolluted Atmosphere

	Gas	Average Concentration		Approximate Residence time
		%	ppm	
1.	N_2	78.08		10^6 years
2.	O_2	20.95		5000 years
3.	Ar		9340	Not cycled
4.	CO_2		360	100 years
5.	Ne		18	Not cycled
6.	CH_4		1.8	15 years
7.	CK_r		1.1	Not cycled
8.	H_2		0.58	10 years
9.	N_2O		0.31	120 years
10.	CO		0.12	65 days
11.	Xe		0.09	Not cycled
12.	O_3		0.01- 0.1	100 days
13.	SO_2		10^{-3}- 10^{-2}	10 days
14.	NO/NO_2		10^{-6} - 10^{-2}	1 day
15.	NH_3		10^{-4}- 10^{-3}	5 days
16.	HNO_3		10^{-5}- 10^{-3}	1 day
17.	Cl_2		0.6	

Sources: J.H. Seinfeld, 1986; P. Brimblecombe, 1996; P. O'Neill, 1993.

3.2 Composition and Characteristics of the Earth's Atmospheric Layers

The Earth's atmosphere is composed of distinct layers, namely; the Troposphere, the Stratosphere, the Mesosphere, the Thermosphere and the Exosphere.

3.2.1 The Troposphere

The troposphere holds most of the air and is the place where storms occur. It extends from the Earth surface upward to a height of about 10 kilometres at the poles, 11.3 kilometres in mid-latitudes and 16.1 kilometres at the Equator. The air in the troposphere is in constant horizontal and vertical motions. Throughout the troposphere, temperature decreases with altitude at an average lapse rate of about 2°C per 305 m reaching about –57°C at the tropopause (the peak of the troposphere).

The troposphere may be considered in two smaller components: the part in contact with the earth surface is called the **boundary layer;** above it is the **free troposphere**. The boundary layer is normally bounded at its upper extreme by a temperature inversion (a horizontal band in which temperature increases with height) through which little exchange of air can occur with the free troposphere above. The depth of the boundary layer is typically around 100 metres at night and 1000 metres during the day, although these figures do vary greatly. Pollutant emissions are usually emitted into the boundary layer and are constrained within it to a large extent. Free tropospheric air contains the longer-lived atmospheric components together with contributions from pollutants, which have escaped the boundary layer, and from some downward mixing stratospheric air.

The troposphere is the layer of greatest interest with respect to pollution issues because, it is the layer in which most living things exist.

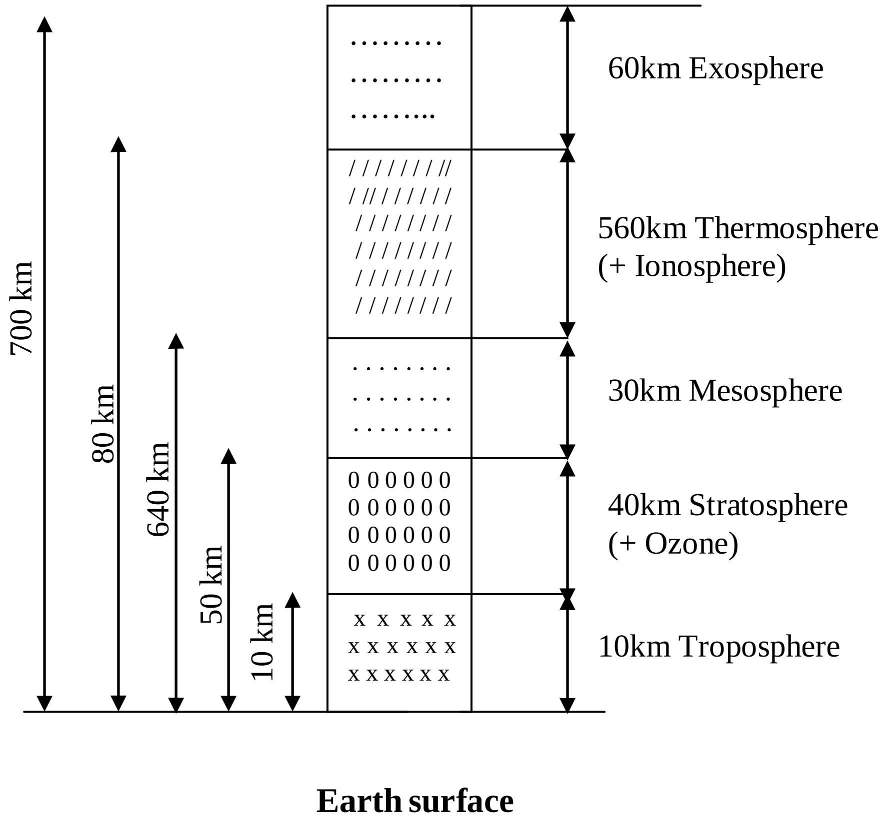


Fig. 5: The Atmospheric Layers

3.2.1.1 Some Important Tropospheric Chemical Transformations

1. Formation of Hydroxyl Radical (OH)

(a) Photolysis of ozone: When ozone undergoes photolysis in the presence of light of short wavelength (λ < 315mm) singlet atomic oxygen O (ID) is formed. This may relax to the triplet state O (^{3}P) or may react with water vapour to form OH.

$$O_3 + hv \longrightarrow O(^1D) + O_2 \quad (\lambda<315nm)$$
$$O(^1D) + M \longrightarrow O(^3P) + M$$
$$\text{or} \quad O(^2D) + H_2O \longrightarrow 2OH$$

This is the primary source of OH in the atmosphere. (M is an inert energy absorbing molecule e.g. N_2).

(b) Reactions of O(^{1}D) with CH_4 and H_2. This is one of the minor sources of OH in the atmosphere.

$$CH_4 + O(^1D) \longrightarrow CH_3 + OH$$
$$H_2 + O(^1D) \longrightarrow H + OH$$

(c) Photolysis of HONO and H_2O_2. This produces 0H directly.

$$HONO + hv \longrightarrow OH + NO \quad (\lambda<400nm)$$
$$H_2O_2 + hv \longrightarrow 2OH \quad (\lambda<360nm)$$

(d) From HO_2 radical. In polluted atmospheres, HO_2 is able to give rise to OH formation.

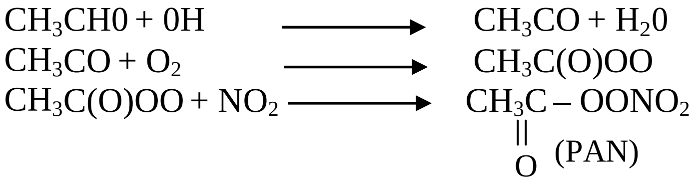
$$HO_2 + NO \longrightarrow NO_2 + OH$$

The hydroxyl radicals play a central role in the formation of ozone, peroxyacetyl nitrate (PAN), sulphuric acid and nitric acid.

2. Formation of ozone: Ozone could be formed in the atmosphere (troposphere particularly) from the oxidation of CH_4 and CO in processes involving the hydroxyl radicals.

$$CH_4 + OH \longrightarrow CH_3 + H_2O$$
$$CH_3 + O_2 + M \longrightarrow CH_3O_2 + M$$
$$CH_3O_2 + NO \longrightarrow CH_3O + NO_2$$
$$CH_3O + O_2 \longrightarrow CH_2O + HO_2$$
$$\text{Also, } CO + OH \longrightarrow CO_2 + H$$
$$H + O_2 + M \longrightarrow HO_2 + M$$
$$\text{Now, } HO_2 + NO \longrightarrow OH + NO_2$$
$$NO_2 + hv \longrightarrow NO + O(^3P) \quad (\lambda < 435nm)$$
$$O(^3P) + O_2 + M \longrightarrow O_3 + M$$

3. **Formation of peroxyacetyl nitrate (PAN):** PAN is of interest as a characteristic product of atmospheric photochemistry, as a probable reservoir of reactive nitrogen in remote atmospheres and because of its adverse health effects on plants. Its formation is acetyl radicals, CH_3CO, formed from acetaldehyde oxidation.



$$CH_3CH0 + 0H \longrightarrow CH_3CO + H_20$$
$$CH_3CO + O_2 \longrightarrow CH_3C(O)OO$$
$$CH_3C(O)OO + NO_2 \longrightarrow \underset{\substack{\|\\ O}}{CH_3C} - OONO_2 \text{ (PAN)}$$

4. **Formation of sulphuric acid:** Atmospheric oxidation of SO_2 could proceed via a range of mechanisms but formation through the hydroxyl radical reaction in the gas phase is of overwhelming importance.

$$SO_2 + OH \longrightarrow HOSO_2$$
$$HOSO_2 + O_2 \longrightarrow HO_2 + SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$

5. **Nitric acid formation:** The main daytime route of HNO_3 formation is from the reaction:

$$NO_2 + OH \longrightarrow HNO_3$$

At night, reaction of NO_3 radical becomes important which was not operative during the day due to photolytic breakdown of NO_3. The radical is formed as follows:

$$NO_2 + O_3 \longrightarrow NO_3 + O_2$$
$$NO_3 + RH \longrightarrow HNO_3 + R$$

and $$NO_3 + NO_2 \overset{M}{\rightleftharpoons} N_2O_5$$

$$N_2O_5 + H_2O \rightleftharpoons 2HNO_3$$

One of the atmospheric changes that has attracted a widespread attention over the last few decades is the phenomenon of **acid rain** or **acid deposition**. Acid rain results when gaseous emissions such as sulphur oxides (SO_x) and nitrogen oxides (NO_x) interact with water vapour and sunlight and are converted to strong acidic compounds as indicated (Nos. 4 and 5) above.

SELF ASSESSMENT EXERCISE 1

1. State two reasons why the troposphere could be considered a layer of greatest interest to an environmental chemist out of all the atmospheric layers.
2. Discuss briefly two ways by which the hydroxyl radicals can be formed in the troposphere.
3. List and explain two roles of the hydroxyl radicals in the troposphere that could result in environmental degradation.
4. Using chemical equations only, show the mechanism of either H_2SO_4 or HNO_3 formation in the atmosphere.

3.2.2 The Stratosphere

The stratosphere is the second layer of the atmosphere as one moves upward from the earth’s surface. It lies above the troposphere and below the mesosphere. The stratosphere starts at approximately 10 kilometres and extends to approximately 50 kilometres high. The altitude of the bottom of the stratosphere varies with latitude and seasons. The bottom of the stratosphere is around 16 kilometres near the equator, around 10 kilometres at mid-latitudes and around 8 kilometres near the poles. It is slightly lower in winter at mid and high-latitudes and slightly higher in the summer.

Within the stratosphere, temperature increases as altitude increases, reaching about – 3^oC at its top (the stratopause). Above the stratopause, temperature again decreases with height. In the stratosphere, air does not flow up and down, but flows parallel to the earth in a very fast moving air streams. This dynamic stability of the stratosphere is due to the warmer layers above and cooler layer below the stratosphere. The heating of the upper layer is caused by an ozone layer that absorbs solar ultra violet (UV) radiation.

The stratosphere is very dry; it contains air with little water vapour. As a result of this, few clouds are found in this layer with most clouds occurring in the lower (more humid) troposphere. However, **polar stratospheric clouds** (PSCs) nacreous clouds also called appear in the lower stratosphere near the poles in winter. They are found at altitudes of 15 to 25 kilometres and form only when temperatures at those heights dip below – 78^oC. They are suspected to play some roles in the formation of “holes in the ozone layer” by catalysing certain chemical reactions that destroy ozone. Because bacterial life survives in the stratosphere, it is considered part of the biosphere.

The Stratospheric Ozone Layer Chemistry

The ozone layer is a diffused concentration of ozone (O_3) found predominantly in the stratosphere. About 90 percent of the atmospheric ozone is located within the stratosphere. Ozone actually occurs in trace amounts throughout the atmosphere with a peak concentration of about 10 ppm by volume in the lower stratosphere between about 20 to 25 kilometres altitude. The concentration of ozone in the stratosphere shows daily, annual and seasonal variations of several per cent. Therefore, it is difficult to identify and quantify changes in concentration caused by anthropogenic effects unless these are large.

The ozone layer protects life from the harmful UV rays of the sun. Whereas acid rain and photochemical oxidant pollution are somewhat localised environmental problems, modification of stratospheric ozone is a global phenomenon. The electromagnetic UV radiation from the sun that falls on the upper layers of the atmosphere is subdivided into three regions of different energy or wavelength (λ). These regions are: highest energy ($\lambda < 290$ nm), intermediate energy ($\lambda = 290 – 320$ nm) and lowest energy ($\lambda = 320 - 400$ nm).

At altitudes above 400 kilometres, the majority of the oxygen is atomic because the bonds in the dioxygen molecule may be broken by UV ($\lambda <$ 290 nm) to form free oxygen atoms.

$$O_2 \xrightarrow{UV} 2(O).$$

At lower altitudes, as the number of dioxygen and dinitrogen molecules increases, ozone (O_3) is formed.

$$O + O_2 + M \longrightarrow O_3 + M.$$

The molecular species, M, (usually N_2 or O_2) removes the excess energy produced when ozone is formed and so prevents the ozone from decomposing immediately. Ozone is destroyed by the absorption of UV and by some other naturally occurring chemical species, X, (X = NO and HO usually) in the stratosphere by a reaction sequence that regenerates these species so that they can react again.

$$O_3 \xrightarrow{uv} O + O_2$$

or

$$O_3 + X \longrightarrow O_2 + O$$

$$XO + O \longrightarrow O_2 + X.$$

Recently, there have been significant increases in the stratospheric concentrations of Chlorine (Cl) and Bromide (Br). It has been estimated that one atom of Cl can destroy 100 000 molecules of ozone before the cycle is interrupted. The bromine cycle is not easily broken; once formed, the ozone moves towards the poles and also to lower altitudes. There is generally a higher concentration of ozone above Polar Regions because the rate of removal is slower than near the equator. The absorption of UV and infrared radiation in the stratosphere means that the temperature in the stratosphere is higher than the temperature at the top of the troposphere. This temperature inversion stabilizes air movements in the stratosphere and controls weather patterns in the stratosphere.

The stratospheric air above the Antarctic contains very little water vapour (4 – 6 ppm by volume). Consequently, nucleation and condensation to form clouds only occur at very low temperatures. When the temperature drops below – 75°C, nitric acid trihydrate ($HNO_3.3H_2O$), NAT, particles, start to condense to form type 1 polar stratospheric clouds (Type 1 PSCs). Their formation removes nitrogen oxide species from the gas phase and traps them in the clouds as solid nitric acid. Nitrogen dioxide can break the ozone, destroying the cycle initiated by chlorine by reacting with the chlorine monoxide,

$$ClO + NO_2 \longrightarrow CIONO_2$$

But this is prevented when the nitrogen species become locked up in the clouds. To worsen the condition, any chlorine nitrate, $CIONO_2$, that is present in the stratosphere can be destroyed by reactions that occur on the surface of the solid particles, but do not occur in the gas phase.

$$CIONO_2 + H_2O \longrightarrow HOCI + HNO_3$$
$$CIONO_2 + HCI \longrightarrow CI_2 + HNO_3$$

These reactions increase the quantity of the potentially reactive chlorine species Cl (from Cl_2) and HOCI and $CINO_2$.

The increased use of chlorine compounds as refrigerants, foaming agents, solvents and in aerosol-spray cans has produced a rapid rise in the concentration of chlorine in the atmosphere. Natural levels of chlorine are about 0.6 ppb by volume. In 1992, concentrations had reached 3.5 ppb and might rise further to 4 ppb before a decline is expected.

The chlorofluorocarbons (CFCs) such as CCI_3F and CCI_2F_2 were developed as inert, non-toxic compounds that could be safely used by industry and in home. Unfortunately, they are so inert that when they escape into the atmosphere they slowly pass unchanged through the troposphere and enter the stratosphere. Here, they are subjected to photochemical decomposition under the influence of UV radiation to yield free chlorine atoms that catalyse the decomposition of ozone e.g.

$$\underset{\text{Dichlorodifluoro methane}}{CCI_2F_2} \xrightarrow{uv} \underset{\text{Activated Chlorine atom}}{CI} \xrightarrow{O_3} O_2 + \underset{\text{Chlorine oxide}}{CIO} \xrightarrow{O} O_2 + CI \text{ (Can react again)}$$

The CFCs have long atmospheric lifetimes (65 years for CCI_3F and 130 years for CCI_2F_2). There are enough of these compounds in the atmosphere to support the elevated stratospheric chlorine concentrations until 2100. Since anthropogenically introduced chlorine and bromine levels will remain high for so long, it is expected that there will increase in dangerous UV radiations reaching the earth's surface. Before ozone depletion began, 70 – 80 per cent of the dangerous UV radiation was absorbed before reaching the earth surface. A 10 per cent reduction in stratospheric ozone concentration would reduce the amount of dangerous UV being absorbed to 55 – 65 per cent. This could have major effects on susceptible organisms such as plankton and land plants. Effects on humans would include increased risk of skin cancer and eye cataracts. These direct effects on human are less worrying than the interference with food production that could occur.

The increased use of fertilizers is causing an increase (0.25% per year) in the quantities of N_2O being produced by micro-organisms. Like CFCs, N_2O is very stable and passes up through the troposphere and finally enters the stratosphere. Here, (Stratosphere), is broken down under the influence of UV radiation into a mixture of about 95 per cent N_2 and 5 per cent NO. NO is one of the ozone destroying compounds. N_2O

$$2N_2O \xrightarrow{UV} \underset{(95\%)}{N_2} + 2NO$$

$$NO + O_3 \longrightarrow NO_2 + O_2$$

$$NO_2 + O \longrightarrow \underset{(5\%)}{NO} + O_2$$

The effects of increased N_2O concentrations are relatively small and may well be balanced by increases in methane (CH_4) which is capable of increasing or preserving ozone concentrations by reacting with chlorine in the stratosphere.

SELF ASSESSMENT EXERCISE 2

1. List two naturally occurring and two anthropogenic chemical species that could lead to stratospheric ozone depletion.
2. Briefly explain how a named chlorofluorocarbon can cause stratospheric ozone layer depletion.

3.2.3 The Mesosphere

The mesosphere is a layer of earth's atmosphere directly above the stratosphere and below the thermosphere. It extends from about 50kilometres to 85kilometres above the earth surface. The **stratosphere** and **mesosphere** together are sometimes referred to as the **middle atmosphere**. Throughout the mesosphere, temperatures decreases with height; the coldest temperatures (approx. - 90^0C) within the Earth's atmosphere are found near the top of the mesosphere i.e. within the mesopause.

Much about the mesosphere is still mysterious because, it is difficult to take instrumental measurements of the mesosphere directly. Weather balloons and other aircraft cannot fly high enough to reach the mesosphere and satellites orbit above it; it cannot also directly measure traits of this layer. Scientists use the instruments on sounding rockets to sample the mesosphere directly, but such flights are brief and infrequent.

Most meteors vaporise in the mesosphere. Some materials from meteors linger in the mesosphere such that this layer has a relatively high concentration of iron and other metal atoms. Very strange, high altitude clouds called “noctilucent clouds” or “polar mesospheric clouds” sometimes form in the mesosphere near the poles. These peculiar clouds form at a much higher altitude than other types of clouds. Odd electrical discharges similar to lightning called “sprites” and “ELVES” occasionally appear in the mesosphere dozens of kilometers above thunderclouds in the troposphere below. Within and below the mesopause, gases made of different types of atoms and molecules are thoroughly mixed together by turbulence in the atmosphere.

3.2.4 The Thermosphere

Above the mesosphere is the thermosphere. It extends for about 90 kilometres above the earth surface. It is the layer of the Earth's atmosphere which is first exposed to the sun's radiation. In the thermosphere, gas particles collide so infrequently and get sorted into strata based on the molecular mass and types of chemical elements they contain. Within this layer, UV radiation causes ionisation of the atmospheric particles, enabling radio waves to bounce off and be received beyond the horizon.

Thermospheric temperatures increase with altitude and can rise to 1500^0C and above due to absorption of highly energetic solar radiation by the small amount of residual oxygen still present. The air within the thermosphere is so thin that a small increase in energy can translate to a large temperature increase. Because of the thin air in the thermosphere, scientists cannot measure the temperature directly. They measure the density of the air by pressure drag it puts on satellites and then use the density to find the temperature.

The **ionosphere** is the very outer edge of the thermosphere. It is not a separate layer as such; it is a place where gas atoms drift into space from here. It is called ionosphere because in this part of the atmosphere where the sun's radiation is ionised, or pulled apart as it travels through the earth's magnetic fields to the north and south poles. This pulling apart is seen from the Earth as **auroras**. The colourful displays of **auroras** are called the "**Northern Lights**" or "**Aurora Borealis**" in the Northern Hemisphere, the "**Southern Lights**" or "**Aurora Australis**" in the Southern Hemisphere.

The dynamics of the lower thermosphere (below 120 kilometres) are dominated by atmospheric tide, which is driven in part, by the very significant diurnal heating. The atmospheric tide dissipates above this level since molecular concentrations do not support the coherent motion needed for fluid flow.

3.2.5 The Exosphere

The exosphere is the highest layer of the atmosphere. Together with the ionosphere, it could be considered as part of the thermosphere extending from 500 to about 1000 kilometers (it may extend to about 10,000 kilometres above the earth's surface). This, indeed, is the upper limit of the earth's atmosphere where the atmosphere turns or merges into space.

The highly diluted gas in this layer can reach 2500^{o}C during the day; even though the temperature is so high, one would not feel hot in the thermosphere; because it is so near vacuum that there is not enough contact with the few atoms of gas to transfer much heat. A normal thermometer would read significantly below 0^{o}C due to the energy lost by radiation overtaking the energy acquired from the atmospheric gas by direct contact.

In this region of the atmosphere, hydrogen and helium are the prime components and are only present at extremely low densities. This is the zone where many satellites orbit the Earth.

4.0 CONCLUSION

Without the over 145 kilometres plus of atmosphere above us, the closest three kilometers plus where all our weather takes place would not have been possible. Every physico-chemical activity going on in the atmosphere is not only connected, but has either positive or devastating effects, directly or indirectly, on the activities on the Earth surface.

5.0 SUMMARY

In this unit, you have learnt that:

i. the earth's atmosphere consists of five more or less distinct layers: the troposphere, the stratosphere, the mesosphere, the thermosphere and the exosphere;
ii. there are physico-chemical variations in the atmospheric layers that characterise each of the layers;
iii. the chemical reactions in the atmosphere could positively or negatively affect the atmospheric gaseous compositions; and
iv. the ozone layer of the atmosphere shields the plankton, land plants and humans from the damaging effects of excessive dangerous UV radiation from the sun or the outer space.

6.0 TUTOR-MARKED ASSIGNMENT

1. List two physico-chemical features which distinguish the stratosphere from the troposphere.
2. What particular hazards are caused by the presence of Chlorofluorocarbons (CFCs) in the stratosphere?
3. Which of NO or N_2O do you consider of concern if it is substantially present in the atmosphere? Showing necessary chemical reactions, justify your response with a brief explanation.

7.0 REFERENCES/FURTHER READING

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MODULE 2 SOURCES, TYPES AND EFFECTS OF ENVIRONMENTAL POLLUTION

UNIT 1 WATER POLLUTION

CONTENTS

1.0 INTRODUCTION

In sciences “contamination” refers to a situation when a chemical substance is present in a given sample or matrix with no evidence of harm while “pollution” is used in cases where the presence of the chemical is causing harm. Pollutants therefore are chemicals causing environmental harm.

Broadly, our environment can be classified into water, air and soil environments. Hence, we talk of water pollution, air pollution and soil pollution. In many cases, the classification has no clear-cut boundary as a pollutant found in air may soon find its way into the soil or aquatic environment and vice versa.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- differentiate between a contaminant from a pollutant
- identify chemical substances that are fundamentally responsible for the contamination or pollution of an aquatic environment
- mention the sources of the named pollutants
- classify the sources into natural or anthropogenic, and also identify the sources or diffuse sources.

3.0 MAIN CONTENT

3.1 Pollutants in Aquatic Ecosystems

3.1.2 Effects and Criteria of Pollutant Designation

Any chemical can become a pollutant in water if it is present at a high concentration. For example, serious pollution incident can result from spill of sugar and milk. When a water body becomes polluted, one or more of the following effects would be experienced:

- Aesthetic or visual nuisance including production of foul smell.
- Heightened temperature of the water body.
- Lack of oxygen or devaluation of dissolved oxygen.
- Acute or chronic toxicity causing damage to aquatic or human life.
- Disturbance of the ph regime.
- Eutrophication i.e. much availability of nutrients giving rise to excessive growth of some organisms in water.

Although any chemical can be a pollutant, certain chemicals have been identified by international agreement as being “**priority pollutants**”. These priority pollutant chemicals have been selected based on the following criteria: (i) they are toxic at low concentrations; (ii) they bioaccumulate; (iii) they are persistent; and (iv) they are carcinogens (Substances that can cause cancer).

It is true that priority pollutants can be very dangerous or hazardous even at low concentrations, but then; different chemicals can constitute priority pollutants in different contexts. For example, effluents containing biodegradable organic chemicals generally act as pollutants not because they contain chemicals at concentrations that are toxic, but because they contain chemicals that provide abundant food for microorganisms. The microorganisms thus multiply rapidly as a result of the increased food input. The microorganisms, in the process of growing and oxidising the organic chemical foodstuff, use up the dissolved oxygen rapidly leading to the death of higher organisms like fish.

3.1.3 Modes of Chemical Pollutant Release

There are two broad types of chemical release into an environment, namely: **point source discharge** or **direct discharge** and **non-point source discharge** or **diffuse discharge**. Point source or direct discharge is the release of environmental pollutants from a specific place such as industrial sites, sewage works or agricultural land. Pollution from point source discharges are easier to monitor, control, and their environmental impacts is relatively easier to determine. On the other hand, the non-point discharge of pollution refers to pollution from diffuse or even diverse places e.g. heavy metal pollution arising from harmattan loesses deposition. Such pollution sources are usually difficult to determine, and very often, statistical weapons such as factor analysis are resorted to in order to reliably predict their sources.

Currently, emphasis on priority pollutant control has shifted from control of point sources towards control of diffuse sources. This is because new technology enabling priority pollutant is now available and pollution control technology has improved tremendously. In some cases however, the availability of new technology only partially solves the existing problem, for example, hydrochlorofluorocarbons (HCFCs) are preferred to the chlorofluorocarbons (CFCs) because HCFCs are expected to break down in the atmosphere fairly rapidly. However, the trifluoroacetic acid, which some HCFCs are expected to produce, is very stable and will wash out from the atmosphere whenever rain falls. In areas like seasonal wetlands which have high evapotranspiration rates, the trifluoroacetic acid may concentrate to levels which may damage plants.

3.1.4 Pollution Control: Regulation and Control of Priority Pollutants

The growing internationalisation of priority pollutants control is mostly driven by the recognition that pollution does not recognise environmental compartmental or national boundaries. For example, a pollutant can cross from soil to aquatic environment. Likewise, pollution caused in London may soon find expression within the geographical boundary of Nigeria. It has been recognised also that protection of aquatic environments (marine water particularly) can only be accomplished by international action.

Government, regulatory agencies and industrial initiatives have recognised the following hierarchy of approaches to priority pollutant control: **Replace** – use another, more environmentally friendly chemical; **Reduce** – use as little of the priority pollutants as possible; and **Manage** – use in a way to eliminate or minimise accidental or adventitious loss and waste.

The regulation and control of priority pollutants is an international issue and is not just a case of tightening up on discharge consents as diffuse sources can be important and even dominate in some cases. It also requires a portfolio of complementary activities based on a hierarchy of **replace – reduce – manage**.

SELF ASSESSMENT EXERCISE 1

1. Differentiate between contamination and pollution.
2. List six observable effects resulting from a given water body pollution.
3. What are the criteria used to designate a chemical substance as a “priority pollutant”?

4(a) Explain what is meant by (i) point source discharge and (ii) non-point source discharge of pollutants into an environment.

(b) Give two reasons why there is greater emphasis on non-point source discharge than on point source discharge of pollutants.

5. State and briefly discuss the hierarchy of approaches to priority pollutant control.

3.2 Individual Aquatic Environment Pollutants: Their Sources and Effects

A wide range of pollutants can enter the aquatic, or more specifically, the marine environments in a number of ways. These pollutants or classes of pollutants are:

3.2.1 Crude Oil

Since crude oil is a very complex mixture of many different chemicals, the effects of an oil spill on the aquatic environment depend on the exact nature and quantity of the oil spilled. The effects are also determined by such other factors as the prevailing weather conditions and the ecological characteristics of the affected region.

Crude oil gets into water bodies through transportation (tanker operations and accidents, dry docking and non-tanker accidents), fixed installations (coastal refineries and offshore production) and other sources (municipal wastes, industrial wastes, urban run-off, atmospheric fallout and ocean dumping). Some of the damages caused to aquatic organisms by oil spills are growth inhibition of phytoplankton, large scale mortality in littoral communities through acute toxicity and smothering, fish kill, death of seabirds through drowning, hypothermia or toxic effects of ingested oil and vulnerability of coastal populations of marine mammals e.g. seal colonies.

3.2.2 Sewage

Domestic sewage, with or without the presence of industrial wastes, probably represents the commonest and most widespread contaminant of inshore and near shore waters. Sewage may reach the water bodies in different forms: untreated raw sewage discharges, partially or properly treated discharge and outright dumping of associated sewage sludge at marine sites. Sewage poses aesthetic and health risks to human populations and also acts as a vector whereby a considerable variety of other contaminants reach the aquatic environment.

3.2.3 Persistent Organic Chemicals

Persistent organic chemicals which have proved to be of concern in the aquatic environments are essentially chlorinated pesticides such as DDT, dieldrin, aldrin, endrin, lindane, hexachlorobenzene and toxaphene. Others include polychlorinated dibenzo-p-dioxins (PCDD) and polychlorinated dibenzofurans (PCDF); pesticides like 2, 4–dichlorophenoxyacetic acid (2,4-D), 2,4,5 – trichlorophenoxyacetic acid (2,4,5-T) and 2-methyl-4,6-dichlorophenoxyacetic acid (MCPA). There are other chemicals which are sufficiently common, toxic and persistent to represent potential threats e.g. polycyclic aromatic hydrocarbons (PAHs), plasticizers (e.g. phthalate esters), detergent residues, organic solvents, and so on.

These chemicals contaminate the aquatic systems through aerosol drift, surface runoff, aerial spray and direct application on water hyacinth or mulluscs. Amongst the top predators, the main deleterious effects have been eggshell thinning in birds (by DDE) and interference with the reproductive and immune system in mammals (by PCBs). A considerable number of top predator birds showed major declines in abundance during the peak period of DDT usage. Apparently responsible for the abnormalities in male sex development in wildlife and humans including members of the DDT family of compounds, chlordecone (Kepone), various sterols and possibly nonylphenol. Of these, p, p'– DDE is the most potent.

3.2.4 Heavy Metals

Metals and metalloids with an atomic density (greater than 6g/cm^3) which are associated with pollution and toxicity problems are generally referred to as **heavy metals**. Examples are As, Cd, Cr, Cu, Hg, Ni, Pb and Zn. Unlike most organic pollutants, heavy metals occur naturally in rock-forming and ore minerals. So, there is a range of normal background concentrations of these elements in soils, sediments, waters and living organisms. Thus, the presence of the metal is an insufficient evidence of pollution (we only talk of pollution when there is high concentration of the metals relative to the normal background levels).

Heavy metals find wide applications in electronics, machines and the artifacts of everyday life as well as “high-tech” applications. Hence, they tend to reach the environment from a vast array of anthropogenic sources as well as natural geochemical processes. Depending on their speciation (as well as one the condition of the organism), heavy metals like Hg, Pb and Sn in the aquatic environments are potentially harmful.

3.2.5 Eutrophication

The addition of excess nutrients to a water body is known as **eutrophication**. Important sources of these nutrients include breakdown of organic matter, phosphorus-containing detergents, agricultural runoff and leaching of artificial fertilizers and manures from intensive farming units, the burning of fossil fuels which increases the nitrogen content of rain, and so on and so forth. Nitrogen and phosphorus are the two nutrients most implicated in eutrophication. This is because growth of organism in water bodies is usually limited by phosphorus rather than nitrogen; it is the increase in phosphorus which stimulates excessive plant production in freshwaters.

One of the serious effects of eutrophication which result in huge financial loss is the stimulation of algal growth especially in water supply reservoirs; this is the main cause of water treatment problems. Large populations of algae may result in the blocking of filters in the treatment works.

Drinking water with high nitrate contents presents potential health problems. In particular, babies under six months of age who are fed with such water may develop methaemoglobinaemia (blue baby syndrome), in which the nitrate in their feeds is reduced to nitrite in their acid stomachs. The nitrite then oxidises ferrous ions in their blood haemoglobin, thereby lowering its blood carrying capacity.

3.2.6 Acidification

Generally, there are three categories of water with respect to their acidity differences; (i) those which are permanently acidic with a pH < 5.6; (ii) those which are occasionally acidic, where pH is normally above 5.6, but may drop below 5.6 periodically; and (iii) those which are never acidic, the pH never dropping below 5.6. The acids either fall directly into water bodies in form of precipitation or are washed in from vegetation and soils within the catchments. Sometimes, acids can be generated indirectly from mining activities. For example, exposed iron pyrites can undergo chemosynthetic bacterial oxidation to yield sulphuric acid, making water flowing from the area to have a pH of 3.5 or below.

When there is acidification of a water body, among the animals to first disappear are the shrimps, minnows, trout and crayfish. Normally, no species of fish reproduces at values of pH below 5.4.

3.2.7 Thermal Pollution

Water used for cooling discharge from electricity generating stations is the main source of pollution by heat. An increase in temperature alters the physical environment in terms of a reduction in both the density of the water and its oxygen concentration, while the metabolism of organisms increases.

Cold water species (of fish especially) are very sensitive to changes in temperature and tend to disappear if heated effluents are discharged to the headwaters of streams. As the temperature increases, a conflict arises; the rate of heart-beat of a fish increases to obtain oxygen for increased metabolic processes, but at the same time, the oxygen concentration of the water is decreasing.

3.2.8 Radioactivity

Sea water and marine sediments are naturally radioactive because of the natural presence of radioactive potassium 40, uranium and thorium decay series, and the creation of lighter radioisotopes through the interaction of cosmic rays and atmospheric gases, with the products subsequently transferred to the water surface. Chemically, radionuclides behave almost identically to their stable counterparts. They are, therefore, partitioned between water, sediments and biota according to their behavioural properties e.g. C_s-137 is largely water soluble, Pu-239 and Pu-240 form strong associations with fine-grained sediments.

Releases of radioactivity by anthropogenic activities into the aquatic/marine environment include: (i) radiation from Weapons Testing Programmes; (ii) routine releases from Nuclear Power Plants e.g. tritium, sulphure-35, zinc-65 and cobalt-60; (iii) releases from Nuclear Fuel Reprocessing Plants e.g. tritium, C-14, C0-60, Sr-90, Te-99, Ru-106, I-129, Cs-134 and 137, Ce-144, Pu-241 and Am-241; (iv) reactor accidents on land e.g. Chernobyl in the Ukraine (April, 1986) nuclear reactor accident; (v) dumping of low level waste e.g. radioactive material dumped at Koko village in Nigeria; and (vi) naval sources e.g. nuclear warheads and reactors from accidents to submarines.

Humans are the most sensitive of all living organisms to the effects of radiation, therefore all radiological population measures are designed to protect humans on the understanding that all other species will therefore automatically receive adequate protection. Radiation effects on humans are either **somatic** or **genetic**. Somatic effects are those that cause (noticeable) damage to the individual e.g. anemia, fatigue, loss of hair; cataracts, skin rash and cancer. Genetic effects include inheritable changes resulting from mutations in reproductive cells. It is widely held that even small dosages of radiation can have some adverse effects, genetic effects being of greatest concern.

SELF ASSESSMENT EXERCISE 2

In a tabular form similar to the one below, list five pollutants of an aquatic ecosystem, their sources and effects.

Pollutant	Source(s)	Effect(s)
(1)		
(2)		
(3)		
(4)		
(5)		

4.0 CONCLUSION

Despite the vast amount of scientific information available with respect to water pollution over the past five decades, many of our fresh waters still suffer from poor water quality, with severe consequences for the flora and fauna they support. Scientific know-how is subverted by economic and political constraints, and in many instances, by careless accidents within the catchment.

Newly synthesized materials are constantly being added to our waterways as traces or in effluents and the long-term effects of these are largely unknown. A continuing programme of surveillance is required to protect our water resources from further effects of environmental degradation that threatens our collective co-existence.

5.0 SUMMARY

In this unit, you have learnt that:

i. contamination is the presence of a chemical substance at a level causing no harm;
ii. pollution is the presence of a chemical substance at a level causing harm; a pollutant can enter on environmental compartment through a point-source or diffuse source discharge;
iii. substances (or situations) that can cause water pollution include crude oil, sewage, persistent organic chemicals, heavy metals, eutrophication, acidification and radioactivity.

6.0 TUTOR-MARKED ASSIGNMENT

Explain how (a) Sewage, (b) Eutrophication and (c) Acidification, can lead to water pollution.

7.0 REFERENCES/FURTHER READING

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UNIT 2 AIR POLLUTION

CONTENTS

1.0 INTRODUCTION

Most people tend to associate air pollution problems with the advent of the industrial revolution whereas; such problems have somehow plagued the human race for centuries. The earliest pollutants noted in the atmosphere were probably of natural origin. Smoke, fumes, ash and gases from volcanoes and forest fires; sand and dust from windstorms in arid regions; fog in humid low-lying areas; and natural terpene hazes from pine trees in mountainous regions were part of our environment long before anthropogenic (human-induced) problems came on the scene.

It is true however, that anthropogenic inputs have tremendously increased the levels of each pollutant in the atmosphere. Pollution of the atmosphere increases in almost direct proportion to the population density and is largely related to the products of combustion from heating plants, incinerators and automobiles plus gases, fumes and smokes arising from industrial processes. Air pollution of quite another type is of major concern nowadays. This results from radioactive materials that gain entrance into the atmosphere through nuclear explosions.

Except in such extreme cases as volcanic eruptions, pollution from natural processes does not usually pose problems severe enough to seriously endanger life; ultimately, human activities are to blame for pollution problems that threaten human's expectation of long and healthy life.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

name major air pollutants and their sources
state the health effects of each air pollutant
describe the mechanism of action of some of the pollutants in human body.

3.0 MAIN CONTENT

3.1 Air Pollution – Past, Present and Future

The smoke from isolated wood-burning fires of early cave dwellers went to the air almost unnoticed. But when the smoke from coal-burning furnaces in heavily populated cities started, the effects of pollution became severe enough to alarm some of the inhabitants of modern cities.

In A.D. 61, the philosopher Seneca described "the heavy air of Rome" and "the stink of the smoky chimneys thereof". In 1273, King Edward I was bothered enough by the smoke and fog mixture that brooded over London to prohibit the burning of "sea coal". By the time Queen Elizabeth I ascended the throne, the city's notorious pea-soup fogs had become smog. Because of her allergy and aversion to coal smoke, the Queen moved out of the city into the cleaner air of Nottingham. Toward the end of Elizabeth's reign, a law was passed prohibiting the burning of coal.

By late 1880s, there were some corresponding evidences of interest in overcoming air pollution, including the enactment of smoke-control laws in Chicago and Cincinnati. In 1930, an inversion trapped smog in Meuse Valley, Belgium. Sixty three persons died and several thousand others became ill. The London smog disaster of 1952 made it impossible to ignore any longer the serious consequences of air pollution. Between 4th and 9th December, 1952, 4000 deaths attributed to air pollution had been recorded, enough to move Britons to pass the Clean Air Act in 1956.

From that time till now, Clean Air Acts have been passed in places like the USA, Australia, Canada, and so on and so forth. There had been

Clean Air Act Amendments as well. Though it is likely that future changes will be made, it is probable that the move toward air pollution control has gathered enough momentum and public support to maintain a course which ensures a cleaner, healthier atmosphere for us now and generations to come.

3.2 Major Air Pollutants and their sources

Air pollutants are substances in the air that are responsible for pollution e.g. dust, fumes, gas, mist, odour, smoke, vapour, etc. Air pollution is the presence in the outdoor atmosphere of one or more air pollutants in sufficient quantities, characteristics and of such duration to reasonably interfere with the comfortable enjoyment of life or property.

3.2.1 Particulates

Particulates can either be natural e.g. pollen, spores, bacteria, viruses, protozoa, plant fibres, rusts and volcanic dust, or anthropogenic e.g. fly ash, smoke, soot particles, metallic oxides and salts, oily or tarry droplets, acid droplets, silicates and other inorganic dusts and metallic fumes.

At high concentrations, suspended particulate matter poses health hazards to humans, particularly those susceptible to respiratory illness. The nature and extent of the ill effects that may be linked to suspended particulates depend upon the concentration of particulates, the presence of other atmospheric contaminants (notably sulphur oxides) and the length of exposure.

Airborne substances such as pollens and spores causing allergies in sensitive persons are called **aeroallergens**. Ragweed pollen is one of the worst allergens. Hay fever or asthma sufferers coming into the vicinity where ragweed pollen exists may suffer allergic reactions. Other aeroallergens of biological origin include yeast, molds and animal fur, feathers or hair. Finely powdered industrial materials can also cause allergic reactions in sensitive persons.

The most serious situations of particulate air pollution develop where local conditions favour atmospheric temperature inversions and the products of combustion and of industrial processing are contained within a confined air mass. A notable example is the situation in Los Angeles, where inversions occur frequently; they also occur, though less often, in several other metropolitan areas e.g. Lagos, Nigeria.

3.2.2 Volatile Organic Compounds (VOCs)

Volatile organic compounds are a wide range of compounds with boiling points between approximately 50 and 250°C and which, at room temperature, produce vapours. In the indoor environments particularly, VOCs originate from a number of sources: furnishings, furniture and carpet adhesives, glues, building materials, cosmetics, cleaning agents, fungi, tobacco smoke and fuel combustion.

By far, the greatest peak exposure to VOCs occurs during home decorating using solvent-based paints. Some of the compounds that may occur in a typical non-industrial indoor environment are aliphatic and aromatic hydrocarbons, halogenated compounds and aldehydes. Because of the diverse range of chemical substances defined as VOCs, determination of health effects is problematic. At the levels typically found indoors however, the major effects are likely to be sensory.

3.2.3 Oxides of Sulphur

The oxides of sulphur (SO_x) are probably the most widespread and the most intensely studied of all anthropogenic air pollutants. They include six different gaseous species: sulphur monoxide (SO), sulphur dioxide (SO_2), sulphur trioxide (SO_3), sulphur tetroxide (SO_4), sulphur sesquioxide (S_2O_3) and sulphur heptoxide (S_2O_7). However, only SO_2 and SO_3 are the oxides of sulphur of most interest in the study of air pollution.

The burning of solid and fossil fuel contributes more than 80percent of anthropogenic SO_2 emissions. It is estimated that SO_2 remains airborne an average of two to four days, during which time it may be transported as far as 1000 kilometres. Thus, the problem of SO_2 can become an international one. Relatively stable in the atmosphere, SO_2 acts either as a reducing or an oxidising agent. Reacting photochemically or catalytically with other components in the atmosphere, SO_2 can produce SO_3, H_2SO_4 droplets and salts of sulphuric acid. Sulphur dioxide can react with water to form sulphurous acid, a weak acid which can react directly with organic dyes.

Sulphur dioxide, sulphuric acid and sulphate salts tend to irritate the mucous membranes of the respiratory tract and foster the development of chronic respiratory diseases such as bronchitis and pulmonary emphysema. In a dusty atmosphere, SO_2 is particularly harmful because both SO_2 and H_2SO_4 molecules paralyse the hair-like cilia which line the respiratory tract. Without the regular sweeping action of the cilia, particulates are able to penetrate to the lungs and settle there. These particulates usually carry with them concentrated amounts of SO_2, thus bringing this irritant into direct, prolonged contact with delicate lung tissues. The SO_2 – particulate combination has been cited as cause of death in several air pollution tragedies.

3.2.4 Oxides of Nitrogen

Oxides of Nitrogen (NO_x) include six known gaseous compounds: nitric oxide (NO), nitrogen dioxide (NO_2), nitrous oxide (N_2O), nitrogen sesquioxide (N_2O_3), nitrogen tetroxide (N_2O_4) and nitrogen pentoxide (N_2O_5). The two important oxides of nitrogen in air pollution are NO and NO_2, being the only two oxides of nitrogen that are emitted in significant quantities to the atmosphere. Nitrogen dioxide is readily soluble in water, forming nitric acid and either nitrous acid (HNO_2) or nitric oxide (NO).

$$2NO_2 + H_2O \longrightarrow HNO_3 + \underset{\text{nitrous acid}}{HNO_2}$$

$$3NO_2 + H_2O \longrightarrow 2HNO_3 + \underset{\text{nitric oxide}}{NO}$$

Both nitric and nitrous acid will fall out in the rain or combine with ammonia in the atmosphere to form ammonium nitrate (NH_2NO_3). A good absorber of energy in the UV range, NO_2 plays a major role in the production of secondary air contaminants such as ozone (O_3). Nitric oxide is emitted to the atmosphere in much larger quantities than NO_2. It is formed in high-temperature combustion processes when atmospheric oxygen and nitrogen combine according to the reaction.

$$N_2 + O_2 \rightleftharpoons 2NO$$

Small concentrations of the NO_x produced in the upper atmosphere by solar radiation reach the lower atmosphere through downward diffusion. Small amounts of NO_x are produced by lightning and forest fires. Bacteria decomposition of organic matter releases NO_x into the atmosphere. Find combustion in stationary sources and in transportation are the primary origins of human-induced NO_x.

Nitric oxide (NO) is a relatively inert gas and only moderately toxic.

Although NO, like CO, can combine with haemoglobin to reduce the oxygen-carrying capacity of the blood, NO concentrations are generally less than 1.22 mg/m^3 in the ambient air and are thus not considered health hazards. However, NO is readily oxidised to NO_2, which has environmental significance.

$$NO + \tfrac{1}{2} O_2 \rightleftharpoons NO_2$$

NO_2 irritates the alveoli of the lungs. Short-term animal studies showed reduced resistance to respiratory infection at exposures of 6.6 mg/m^3 for 2 hours. Experimental exposures of volunteers to 9.4 mg/m^3 NO_2, considerably above the 7.0 mg/m^3 peak recorded in Los Angeles, for 10 minutes produced a substantial but transient increase in the resistance of the lung's airways to air movement. Concentrations from 47 to 141 mg/m^3 cause reversible pneumonia. At high concentrations of 285 mg/m^3 and above, exposures to NO_2 can be fatal to humans.

3.2.5 Ozone (O_3)

Ozone, the major photochemical oxidant, makes up approximately 90percent of the atmospheric oxidant pool. Other important photochemical oxidants in air pollution monitoring include nascent oxygen (O), excited molecular oxygen (O_2), peroxyacetyl nitrate (PAN), peroxypropinol nitrate (PPN), peroxybutyl nitrate (PBN), nitrogen dioxide (NO_2), hydrogen peroxide (H_2O_2) and alkyl nitrates.

Ozone is produced in the upper atmosphere by solar radiation, and small concentrations of this gas diffuse downwards. Also, small concentrations are produced by lightning and forest fires. Ozone and other photochemical oxidants can cause coughing, shortness of breath, airway constriction, headache, chest tightness and soreness, impaired pulmonary function, altered red blood cells, pharyngitis, laryngitis, and eye, nose and throat irritation. Exposure of laboratory animals to high levels of ozone has resulted in damage to their chromosomes. Because of this, O_3 is considered to have effects similar to ionizing radiation. Chromosome breakage in human cell cultures was observed at exposures of 15673 ug/m^3 for 5 to 10 minutes.

3.2.6 Carbon Monoxide (CO)

Colourless, tasteless and odourless CO gas is chemically inert under normal conditions and has an estimated atmospheric mean life of about two and half months. At present ambient levels, it has little or no effects on property, vegetation or materials.

Carbon monoxide sources are both natural and anthropogenic. Oxidation of methane gas from decaying vegetation results in the production of up to three and half billion tonnes of CO per year. In human metabolism, the exhalation of a resting person contains approximately 1ppm CO. However, these productions are so meagre compared to the amounts coming from fossil fuel in complete combustion by stationary or mobile engines, solid-waste disposal and miscellaneous anthropogenic sources.

Carbon monoxide is especially dangerous since it has no odour, colour or taste. Its toxic action is through the displacement of oxygen in the haemoglobin to form carboxyhaemoglobin, thus depriving the tissues of the body of their oxygen supply. Early symptoms of exposure to CO include tiredness, drowsiness, headaches, dizziness, pains in the chest and stomach. Excessive exposure can lead to loss of consciousness, coma and death.

3.2.7 Airborne Carcinogens

The substances which have been shown actually or potentially to cause cancer are grouped according to International Agency for Research on Cancer (IARC) into four different categories: based on their ability to cause cancer.

Group 1 – Proven human carcinogens. Chemicals for which there is sufficient evidence for epidemiological studies to support a causal association between exposure and cancer e.g. benzene. Benzene has a proven causal association with acute non-lymphocytic leukaemia in humans. The main toxic effects occur on the bone marrow, with toxic exposures producing bone-marrow suppression and reductions in red cells, white cells and blood platelets production (pancytopenia) which may lead to bone-marrow failure (aplastic anaemia).

Group 2 – Probable human carcinogens. Chemicals for which evidence ranges from inadequate to almost sufficient.

Group 2A: Limited evidence of carcinogenicity in humans and sufficient evidence for carcinogenicity in animals e.g. benzo (a) pyrene, benzo (a) anthracene and other polycychic aromatic hydrocarbons (PAH_s).

Group 2B: Inadequate evidence for carcinogenicity in humans and sufficient evidence for carcinogenicity in animals e.g. 2-nitrofluorene, 1,6 –dinitropyrene and 1-nitropyrene.

Group 3: Unclassified chemicals. Chemicals which cannot be classified in humans, usually because of inadequate evidence.

3.2.8 Hydrocarbons

Hydrocarbons are divided into two major classes **- aliphatic** and **aromatic.** The aliphatic hydrocarbons contain alkanes, alkenes and alkynes. The alkanes are fairly inert and generally not active in atmospheric photochemical reactions; they are highly reactive in atmospheric photochemistry. The reactivity of alkenes such as ethylene makes them much more important in the study of air pollution than alkanes, because in the presence of UV radiation they react with NO_2 at high concentrations to form secondary pollutants such as peroxyacetyl nitrate (PAN) and ozone. The alkynes, though highly reactive, are relatively rare. Hence, they are not of major concern in air pollution studies.

Aromatic hydrocarbons do not display the reactivity characteristic of unsaturated aliphatic hydrocarbons. Nevertheless, the polynuclear group of aromatic hydrocarbons (i.e. polycyclic aromatic hydrocarbons, PAHs) is of concern in any study of air pollution because a number of these compounds have been shown to be carcinogenic. Increases in lung cancer in urban areas have been blamed on the effects of PAHs from automative exhaust emissions. Benzo-[a]-pyrene has been shown to be the most carcinogenic hydrocarbon for test animals. Benz-[e]-acephenanthrylene and benzo-[j]-fluroranthene follow, and benzo-[3]-pyrene, benz-[a]-anthracene and chrysene are all weakly carcinogenic.

Most natural hydrocarbons found in the air are from biological sources, though small amounts come from geothermal areas, coal fields, natural gas from petroleum fields and natural fires. The more complex, naturally produced hydrocarbons found in the atmosphere, such as volatile terpenes and isoprene, are produced by plants and trees. Industrial sources, notably refineries, have become the major anthropogenic source of hydrocarbons. Other minor sources might include incomplete combustion from car engines, evaporative emissions from petrol stations and fuel tanks, emissions from solid waste disposal, forest fires, agricultural burning and coal waste fires.

SELF ASSESSMENT EXERCISE 1

1(a) Name two examples of (i) particulate pollutants and (ii) gaseous pollutants in the atmosphere.
(b) List three effects, on the humans, of $S0_2$ gas if substantially present in the inhaled air.

2. List five air pollutants that are proven human or animal carcinogens. Name their sources.
3. Why are alkenes more important in the study of air pollution than alkanes?

3.2.9 Cigarette Smoking

Cigarette smoking is especially dangerous for those with heart disease because combustion of tobacco in this way, with limited oxygen available, introduces CO directly into the bloodstream. The products of cigarette combustion include nicotine, acetaldehyde, acetone, benzene, formaldehyde, N′-nitrosonornicotine, N-nitrosopyrrolidine, benzo-[a]-pyrene. Among the very many products of combustion, nitrosamines, benzo-[a]-pyrene and nicotine are highly poisonous. Nicotine also throws an additional strain on the heart by stimulating the basal metabolic rate. Nitrosamines are known to cause cancer in animals.

Apart from the effect on the heart, tobacco smoking exacerbates bronchial infection and causes 30 - 40percent of all deaths from cancer. The higher incidence of cancer in smokers arises from inhalation of PAHs and nitrosamines. Smoking also increases the risk to workers in industries which generate fine particles.

3.2.10 Asbestos Fibres

The group named asbestos is applied to a range of naturally occurring fibrous magnesium silicate minerals with the approximate formula $Mg_3P(Si_2O_5)(OH)_4$. Three common types are used: **crocidolite** (blue asbestos) – most hazardous; **amosite** (brown asbestos) – second most hazardous; **chrysolite** (white asbestos) – least hazardous.

Inhalation of separate dry fibres in a confined air space is the major hazard from asbestos. Such dry fibres can come from damaged thermal insulation, accumulated fibres from the manufacture, wear of asbestos, mineral materials such as brake shoe pad dust, ship breaking, waste disposal, and more insidiously, the exposure of workers’ families from particles carried on clothing.

Asbestos fibres can cause lung and bowel cancer as well as non-cancerous lung diseases. Approximately 50percent of the inhaled fibres are cleared from the lungs and swallowed, which then exposes the throat and digestive system to their hazardous effects. Water from asbestos-cement pipes also poses a further source of digestive tract exposure. Respiratory diseases include asbestosis (a pneumonia-like condition), bronchial cancer and mesothelioma, which has a latency period of 20-30 years. There appeared to be a synergistic reaction between cigarette smoke and asbestos in that the onset of disease is more pronounced in heavy smokers than in non-smokers.

3.2.11 Toxic Metals

Toxic metals are those metals that are harmful in relatively small amounts e.g. As, Hg, Cd and Pb. Very often, a given metal or its compounds are found in association with other environmental particles. As a result, there are several routes by which such metals get into the atmosphere, for example, Pb can be added into the air through exhaust emissions, re-suspension of particles, flaking of old Pb painted houses, fumes from soldering and plumbing processes, and so on.

Depending on their particle sizes and speciation, such metals can be inhaled along with the air and find their ways into vital organs in the human system. Many of the toxic metals negatively impact the nervous system. Anaemia, renal failure and neuropsychological impairment are also part of the health infarctions that can be attributed to toxic metals.

3.2.12 Radioactive Gases

The penetration of buildings by chemically inert radon gas presents a more serious risk to human health than the hazards posed by occasional failure of control of nuclear power stations. The decay of ^{238}U produces ^{222}Rn which emanates from radioactive minerals in building foundations. Because it has a half-life of only 3.8 days, the risk is only significant when the gas can rise quickly into the immediate sub-soil, conditions which obtain above fissured granite. Radon has seven times the density of air and so basements and ground floor rooms are the most exposed.

The worst cancer risk from Rn arises from the first four solid decay products of Rn:

$$^{222}Rn \longrightarrow {}^{218}P0 \longrightarrow {}^{214}Pb \longrightarrow {}^{214}Bi \longrightarrow {}^{214}P0 \longrightarrow {}^{210}Pb$$

These products are dangerous because they are associated with moisture and dust, and become deposited in the lung, so exposing the epithelium to α-particles from ^{218}Po and ^{214}Po. Other nuclides of Rn exist but they do not present the same risk as that from ^{222}Rn e.g. ^{220}Rn formed by decay of ^{232}Th has too short a half-life to allow survival above ground. Increased incidence of lung cancer in uranium miners in western USA and Czechoslovakia was attributed to their inhaling ^{222}Rn.

SELF ASSESSMENT EXERCISE 2

1. What hazards are posed by the polycyclic aromatic hydrocarbons (PAH_S)?
2. Which two of the gases that make up the oxides of nitrogen are of primary concern in air pollution considerations and why?
3. Name the major photochemical oxidant found in the atmosphere. What detrimental effects does this oxidant have on humans and animals?

4.0 CONCLUSION

Undoubtedly, the amount of each pollutant in the atmosphere is escalating and the types are also increasing. This is because of increasing anthropogenic activities some of which include the introduction of new products and by-products. While the full health effects of the already known pollutants are continuously being investigated, there is the greater challenge of not knowing yet the effects of “new” products that may have far reaching health implications on the universe as a whole. It is important to keep research activities vibrant especially in the areas of risk assessments and risk reduction with respect to environmental pollutants generally.

5.0 SUMMARY

In this unit, you have learnt that:

airborne chemical substances mostly and particulate matters, to some extent, are responsible for atmospheric pollution.
the sources of pollutants can be natural or anthropogenic;
both amount of a pollutant and length of exposure it determine the extent of health problems arising from such pollutant;
health effects arising from atmospheric pollutants can be at the levels of cells, organs, systems and may even lead to death.

6.0 TUTOR-MARKED ASSIGNMENT

1(a) Mention two situations that can lead to heightened levels of CO in the indoor air at home.
(b) Describe the mechanism of toxic action of CO as an indoor pollutant.

2. Name four principal sources of air pollution and the major types of pollutants produced by each source.
3. Discuss briefly the major health hazards associated with SO_2 in a dusty atmosphere.

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UNIT 3 SOIL POLLUTION

CONTENTS

1.0 INTRODUCTION

Soil is an essential component of terrestrial ecosystems because the growth of plants and biogeochemical cycling of nutrients depend upon it. Pollution, along with other types of degradation, such as erosion and the continuing spread of urbanisation, poses a threat to the sustainability of soil resources. Soil pollution can also be a hazard to human health when potentially toxic substances move through the food chain or reach groundwater which serves as drinking water.

In comparison with air and water, the soil is more variable and complex in composition and it functions as a sink for pollutants, a filter which retards the passage of chemicals to the groundwater and a bioreactor in which many organic pollutants can be decomposed. As a result of its occurrence at the interface between the land and the atmosphere, soil is the recipient of a diverse range of polluting chemicals transported in air. Further inputs of pollutants to the soil occur as a result of agricultural and waste disposal practices, but in general, the most severe pollution usually results from industrial and urban land use.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- name specific soil pollutants and their sources
- explain the transport mechanisms conveying pollutants to soil
- explain the mechanisms of pollutant sorption in the soil and
- state the consequences of soil pollution.

3.0 MAIN CONTENT

3.1 Soil Pollution and Contamination: A Global View

Certain contaminants/pollutants such as heavy metals are part of the earth naturally. Their natural background levels in soils are altered to various levels of pollution usually as a result of anthropogenic activities.

It is generally accepted that most of the soil in technologically advanced regions of the world is polluted or contaminated, at least, to some extent. Realistic estimate of areas affected by soil pollution is difficult owing to unreliable official figures and paucity of data for many parts of the world. Industrially contaminated land tends to contain higher concentrations and a greater possible range of pollutants than other sources of pollution. There are between 50,000and 100,000 contaminated sites in the United Kingdom (UK) which occupy up to 100 000 ha. In the United States of America (USA), 25,000 contaminated sites have been identified, 6000 sites are being cleaned-up in the Netherlands, there are known to be at least 3,115 sites in Denmark and 40,000 suspect areas have been identified on 5,000 – 6,000 sites in the former western part of Germany.

3.2 Soil Pollutants and Their Sources

3.2.1 Heavy Metals

Heavy metals have a density of$\geq$ 6gcm $^{-3}$ and occur naturally in rocks. They belong to the group of elements geochemically described as “trace elements” because they collectively comprise less than 1percent of the rocks in the earth’s crust. All trace metals are toxic to living organisms at excessive concentrations, but some are essential for normal healthy growth and reproduction by plants and/or animals at certain critical concentrations e.g. Co (for bacteria and animals), Cr (animals), Cu (plants and animals), Mn (plants and animals), Mo and Ni (plants), Se (animals) and Zn (plants and animals). Elements like Ag, As, Ba, Cd, Hg, Pb, Sb and Tl have no known essential function, but cause toxicity above a certain tolerance level. The most important heavy metals with regard to potential hazards and occurrence in contaminated soils are As, Cd, Cr, Hg, Pb and Zn.

Sources of heavy metals that contaminate or pollute a given soil site are:
Metalliferous mining e.g. As, Cd, Cu, Ni, Pb and Zn

Metal smelting e.g. As, Cd, Pb and Tl

Metallurgical industries

Other metal-using industries e.g. the electronics industry (using Cd, Ni, Pb, Hg, Se and Sb); pigments and paints (Pb, Cr, As, Sb, Se, Mo, Cd, Co, Ba and Zn); the plastics industry (polymer stabilizers e.g. Cd, Zn, Sn and Pb) and chemical industry (using catalysts and electrodes e.g. Hg, Pt, Ru, Mo, Ni, Sm, Sb, Pd and Os);

Waste disposal

Corrosion of metals in use

Agriculture – As, Cu and Zn (from pig and poultry feeds), Cd and U impurities (in some phosphatic fertilizers), As, Cu, Pb and Zn (from metal-based pesticides);

Forestry-wood preservatives containing As, Cr and Cu;

Fossil fuel combustion – Cd, Zn, As, Sb, Se, Ba, Cu, Mn and V (from coals and oils) and Se, Te, Pb, Mo, Mn and Li (added to fuels and lubricants to improve their properties);

Sports and leisure activities – game and clay pigeon shooting involving the use of pellets containing Pb, Sb, Mo and Bi.

3.2.2 Hydrocarbon Pollutants

Hydrocarbon pollutants from petroleum mainly comprise a range of saturated alkanes from CH_4 to $C_{76}H_{154}$. Aromatic hydrocarbons and organic components containing nitrogen and sulphur can also be important constituents of some petroleum deposits. The hydrocarbons derived from coal and petroleum tend to form the main group of organic macropollutants in soils. Organic solvents can be important soil pollutants at industrial sites.

Sources of hydrocarbon pollutants include fuel storage and distribution, disposal of used lubricating oils, leakage of solvents from industrial sites and coal stores.

3.2.3 Toxic Organic Micropollutants (TOMPs)

The most common toxic organic micropollutants in the soil environments include: polycyclic aromatic hydrocarbons (PAHs), polyheterocyclic hydrocarbons (PHHs), polychlorinated biphenyls (PCBs), polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and pesticide residues and their metabolites e.g. organochlorines (DDT, BHC, Endrin), organophosphates (Malathion, Parathion) and Carbamates (Aldicarb). The most serious problems associated with TOMPs are the subsequent contamination of surface and groundwaters and entry into the food chain through crops, especially.

3.2.4 Other Industrial Chemicals

It has been estimated that between 60,000 and 90,000 different chemicals are in current commercial use, worldwide. Although not all of these constitute potential toxicity hazards, many will cause pollution of soils as a result of leakage during storage, from use in the environment or from their disposal either directly, or of wastes containing them. Apart from industrial uses, a large number of chemicals are used in domestic products and so their use and disposal is less controlled than that of industrial chemicals which are subjected to strict regulations. The total world production of hazardous and special wastes was 338 x 10^6 tonnes in 1990.

3.2.5 Nutrient-Rich Wastes

The major nutrient-rich wastes are sewage sludges and livestock manures. Sewage sludge, though a valuable source of plant nutrients (N and P especially) and of organic matter which has beneficial effects on soil aggregate stability, contains potentially harmful substances such as heavy metals (Cd, Cu, Ni, Pb and Zn) and toxic organic micropollutants (polychlorinated biphenyls, PCBs; polychlorinated terphynyls, PCTs; polychlorinated naphthalenes, PCNs; polychlorinated benzenes; polychlorinated dibenzodioxins, PCDDs; halogenated aliphatics; polycyclic aromatic hydrocarbons, PAHs; aromatic amines; nitrosamines; phthalate esters and pesticides). Also, livestock manures contain large amount of N, P and K, but the manures may also contain residues of feed additives which may include As, Cu and Zn and antibiotics such as sulfonamides fed to pigs and poultry.

3.2.6 Radionuclides

Nuclear accidents like those at Windscale (UK) in 1957 and Chernobyl (Ukraine) in 1986 resulted in many different radioactive substances being dispersed into the environment. The greatest long-term pollution problem with radionuclides in soils is caused by ^{137}Cs which has a half-life of 30 years and behaves in a manner similar to K in soils and ecosystems. Atmospheric testing of nuclear weapons dispersed large amounts of ^{90}Sr which has a half-life of 29 years and behaves similarly to Ca in biological systems and poses a particularly dangerous hazard to humans because it is stored in the skeleton.

3.2.7 Pathogenic Organisms

Soils can be contaminated with pathogenic organisms such as bacteria, viruses and parasitic worm eggs from various sources: the burial of dead animals and humans, manures and sewage and germ warfare experiments. The soil’s own microbial biomass will destroy many of these pathogens but some appear to survive for relatively long times.

3.3 Transport Mechanisms Conveying Pollutants to Soils

Pollutants reach soils by four main pathways: atmospheric deposition of particulates; sorption of gases; flUV ial transport and deposition; and placement.

Atmospheric deposition: Light particulates can become airborne and get transported from one location to the other. For example, there have been cases where pollution is directly traceable in soil up to 40kilometres downwind of smelters. The critical factors determining the distance transported and the area of land affected are: the height of the emission above the ground, the wind speed, stability of the atmosphere and the size, shape and density of the particles and amounts of the pollutants emitted.

Sorption of gases: Volatile organic solvents become dispersed in the atmosphere and later get sorbed from the atmosphere onto soils or plants.

FlUV ial transport and deposition: This mechanism is only important in land subjected to flooding. This was an important pollution pathway in areas of metalliferous mining in the nineteenth century when Pb-Zn mines in the UK discharged waters from ore dressing operations directly into streams and rivers. This led to the allUV ial soils in most flood plains of rivers draining mining areas being severely contaminated with Pb, Zn and other metals. Soils on the flood plains of many major rivers in the world which drain industrial and urbanized areas have been significantly contaminated with a diverse range of substances from flood waters.

Placement: This can occur in many ways: dumping injection, surface spreading, etc; the most obvious being the spreading of wastes such as sewage sludge or metal-rich manures from pigs or poultry. Phosphatic fertilizers can contain significant concentrations of Cd and U and have been partially responsible for the significantly elevated concentrations of these elements in many parts of the world.

3.4 The Consequences of Soil Pollution

Soil pollution can restrict the uses to which land is put because of the ability of pollutants to be hazardous to human health, harmful to living resources or to damage buildings and services.

3.4.1 Types of Hazards Associated with Contaminated Soil

Direct **ingestion** of contaminated soil: As, Cd, Pb, CN^-, Cr^{6+}, Hg, coal tars (PAHs), PCBs, dioxins, phenols, pathogenic bacteria, viruses, eggs of parasites.

Inhalation of dusts and volatiles from contaminated soil: organic solvents, radon, Hg, asbestos.

Plant uptake from soil: As, Cd, ^{137}Cs, Hg, Pb, ^{90}Sr, Tl, PAHs, various pesticides. Phytotoxicity: SO_4^{2-}, Cu, Ni, Zn, CH_4, Cr, B.

Toxicity to soil microbial biomass: Cd, Cu, Ni, Zn.

Deterioration of building materials and services: SO_4^{2-}, SO_3^{2-}, Cl^-, tar, phenols, mineral oils, organic solvents.

Fires and explosions: CH_4, S, coal and coke dust, petroleum oil, tar, rubber, plastics, high calorific value wastes.

Contact with contaminants during demolition and site development: tars, phenols, asbestos, radionuclides, PCBs, TCDDs, bacteria, viruses.

Water contamination: CN^-, SO_4^{2-}, metal salts, hydrocarbons, solvents, surfactants, sewage, farm wastes, pesticides.

3.4.2 Soil-Plant Transfer of Pollutants

The transfer of pollutants from soil into plants through the roots varies considerably depending on the properties of the plants (genotypic factors) and the extent to which the pollution is absorbed in the soil in an unavailable form. The general orders of magnitude of the transfer coefficients for several heavy metals are 0.01 - 0.1 for As, Co, Cr, Hg, Pb and Sn; 0.1 - 1.0 for Cu and Ni; and 1.0 - 10 for Cd, Tl and Zn (which are the most readily accumulated by plants). Organic pollutants tend to have lower coefficients; a value of 0.033 has been suggested for dioxins and PCBs. The lower chlorinated congeners of PCBs tend to be more bioavailable and biodegradable than those with higher numbers of Cl atoms in their structure.

3.4.3 Ecotoxicological Implications of Soil Pollution

Zinc concentrations close to the maximum permissible level of 300 mg/g for European soils treated with sewage sludge, can cause a mark in the activity of the nitrogen-fixing bacteria of the species *Rhizobium leguminosum* by trifolii which occur in nodules in the roots of white clover. Although it appears that the order of toxicity of heavy metals to these bacteria is Cu > Cd > Ni > Zn, the greatest risk is posed by Zn. This is because many soils which have received several applications of sewage sludge may be approaching the maximum permissible concentration of 300 ug/g for Zn, but remains well below the maxima for these other metals.

SELF ASSESSMENT EXERCISE 1

1. List five important sources of soil heavy metal pollution and give two examples of metals from each source.
2. Give two reasons why ^{137}Cs and ^{90}Sr are considered serious pollution problems in soils.

3.5 Cases of Exposure to Pollution

3.5.1 The Seveso Chemical Plant Explosion

On 10th July, 1967, a massive release of 2, 3, 7,– tetrachlorodibenzo–p–dioxin occurred from a chemical plant in Seveso near Milan in Northern Italy. The chemical plant was being used for manufacturing 2, 4, 5–trichlorophenol (2, 4, 5 – TCP). A safety disc in a reaction vessel ruptured and a plume of chemicals containing 2, 4, 5 - TCP below 30 to 50 m above the factory. As it cooled, the material in it was deposited over a cone shaped area downwind from the factory about 2 kilometres long and 700 metres wide.

Dioxin is both extremely toxic and stable, and at sufficient dose levels, it is known to affect foetal development and to have porphyrinogenic effects (often manifesting as digestive system and skin disorders). It is not used commercially, but found as a contaminant when 2, 4, 5 - TCP is synthesized by the hydrolysis of tetrachlorobenzene at high temperatures, and it is used to make 2, 4, 5 - T and 2, 4 - D (herbicides); dioxin is often present in trace amounts in these compounds. Dioxin is also produced as a by-product of waste incineration and it continues to be of major concern as a general environmental pollutant.

A few months after the accident, 176 individuals, mostly children, were found to have the skin condition chloracne, 50 of whom came from the most contaminated area. Some neurological abnormalities including polyneuropathy were also noted. There was also evidence of liver enlargement initially, and later, reported cases of increased hepatobiliary (liver) cancer, elevated levels of leukaemias and other haematologic neoplasms in men and increased myeloma and myeloid leukaemia (cone marrow cancers) in women. Finally, many farm animals died and the site became a wasteland of dying plants and deserted homes.

3.5.2 The Bhopal Catastrophic Release of Methyl Isocyanate

The accident at Bhopal, India occurred on 3rd December, 1984 at the Union Carbide factory which had been producing the insecticide carbaryl for about eighteen years. Methyl isocyanate (MIC) was one of the main ingredients of carbaryl. MIC was produced from monomethylamine (MMA) and phosgene, phosgene being produced by reacting chlorine and carbon monoxide; chloroform served as the solvent. On the night of the accident, some water probably inadvertently got into a tank where Al tonnes of MIC were being stored, causing a runaway chemical reaction. The heat caused by the reaction led to a devastating explosion. About 100,000 people living in the vicinity were affected with at least 2,000 deaths reported.

3.5.3 Toxic Oil Syndrome in Spain

Between May and August 1981, in Madrid (Spain), there was an endemic of cooking oil poisoning that affected about 20000 persons with nearly 400 deaths. The illness began in each patient with a fever followed by severe (acute) respiratory symptoms and a variety of skin rashes similar to measles. Many of the patients developed signs of cerebral oedema (swelling of the brain) and cardiological abnormalities.

The cause of the disease was traced to adulterated cooking oil which was fraudulently sold to the public as pure olive oil. On analysis, the oil was discovered to contain up to 90percent rapeseed oil, varying amounts of soya oil, castor-oil, olive oil and animal fats. The oil also contained between one and 50 ppm aniline, 1500 and 2000 ppm of acetanilide and a number of other anilides. These compounds might have been responsible for the symptoms produced by the toxic oil.

3.5.4 River Oil Contamination by the Toxic Oil

In 1968, in Japan and Taiwan, a number of families developed chloracne, the skin condition which affected the victims of Seveso. Chloracne is more severe than the type of acne that occurs in adolescents and it has a rather different distribution on the body. Epidemiological studies revealed that those affected had been exposed to a particular batch of rice oil that was contaminated with PCBs.

At the end, the individuals examined were considered to have met the diagnostic criteria for what has come to be known as *Yusho* disease. In addition to chloracne, the patients of *Yusho* disease had a number of systemic complaints including loss of appetite, lassitude, nausea and vomiting, weakness and loss of sensation, and hyperpigmentation of the face and nails, in some cases. A number of non-specific symptoms that persisted in the patients include feeling of fatigue, headache, abdominal pain, cough with sputum, numbness and pain, changes in menstruation in females, sensory neuropathy, retarded growth in children, abnormal teeth development and anaemia in some patients. The most striking observation was a marked increase in serum triglyceride levels. To what extent the non specific symptoms are seen in the patients with *Yusho* disease were entirely due to PCBs is difficult to say since it is known that they were also exposed to polychlorinated dibenzofurans (PCDFs) and polychlorinated quarterphenyls (PCQs) – compounds formed when PCBs are heated. In animal models, PCDFs and PCQs are more toxic than PCBs.

3.5.5 Polybrominated Biphenyls (PBBs) in Cattle Feed

Polybrominated biphenyl is used mainly in plastics as a fire retardant. At Michigan in May and June of 1973, some 10 to 20 bags of PBB (labelled "Firemaster") were sent in error, instead of magnesium oxide (a livestock food additive, "Nutrimaster"), to a grain elevator. Thus PBB became incorporated into the feed and distributed throughout the state to be fed to the unsuspecting cows.

Soon, reports of sick cows began to surface. Dairy products and meat from the affected cows were contaminated. Over 1000 farmers were adversely affected. Some of the adverse effects included acne, dry skin, hyperpigmentation and discolouration of the nails, headaches, nausea, depression and a number of non-specific symptoms. Serum levels of hepatic enzymes were higher in the Michigan farmers than their neighbouring controls.

3.5.6 Mercury Poisoning in Minamata and Niigata

The Minamata Bay disease (*Kibyo* or “mystery illness”) was first noted at the end of 1953 when an unusual neurological disorder began to affect the villagers who lived on Minamata Bay, Japan. Those who were affected presented with a mixture of signs relating to the peripheral and central nervous systems. The prognosis of the condition was poor, many patients became disabled and bedridden and about 40percent died.

The disorder was associated with the consumption of fish and shellfish caught from the bay. The fish and shellfish were contaminated with methyl mercury. The source of the mercury was effluent released into the bay from a factory which was manufacturing vinyl chloride using mercury based catalyst prior to the time when there were regulations forbidding its use in Japan.

The Minamata Bay disease involved about 700 people and there was another outbreak of methyl mercury poisoning in Japan (Niigata) in 1965 affecting about 500 individuals. This resulted from pollution of the Agano River by industrial effluent containing methyl mercury and subsequent consumption of contaminated fish by the local population.

3.5.7 Methyl Mercury Poisoning in Iraq

Iraqi government imported a large consignment of seed grain treated with an alkyl mercury fungicide and distributed them to the largely illiterate rural population for sowing. The sacks were marked with warning labels “for sowing and not for eating” in English and Spanish. The seed had been treated with a red dye to distinguish it from edible grain, but the farmers found that they could remove the dye by washing and equated this with the removal of the poison.

The grain was first used to make bread in November, 1971 and the first cases of poisoning appeared in December. By the end of March 1972, there had been over 6,530 admissions to hospital and 459 of these had died. On the whole, this episode became a major outbreak in which the incidence of disease was estimated to be as high as 73 per 10,000.

3.5.8 Love Canal Chemical Odours

Love Canal was a waste disposal site containing both municipal and chemical waste disposal of over a 30 year period up to 1953. Homes were then built on the site during the 1960s and leachates began to be detected in the late 1960s.

The reporting of chemical odours in the basements of homes in the Love Canal district, USA, led to a toxicological investigation which made this area famous in the history of waste disposal and resulted in vigorous regulatory activity in the USA. Dibenzofurans and dioxins were among the chemicals detected in the organic phase of the leachates. Animal studies indicated possible risks of immunotoxic, carcinogenic and teratogenic effects. The episode resulted in significant fears of ill-health and much psychological stress. Limited follow-up of residents identified low birth weights in the offspring of Love Canal residents.

4.0 CONCLUSION

Soil pollution represents, on the average, the pollution phenomenon that could directly threaten all forms of organisms whether they are aerobic or anaerobic. Depending on the nature of the pollutants, it may take several years to overcome the effects of a given pollutant in a soil environment. When it happens, plants, animals, humans, fauna and flora may suffer varying degrees of stress and in some cases, be faced with possible extinction. Thus, it is better to control and prevent the occurrence of soil pollution than to embark on remediation steps after pollution has taken place; it is more costly.

5.0 SUMMARY

In this unit, you have learnt that:

- Compared with air and water, soil constitutes a more variable and complex sink for pollutants.
- Developed countries have been able to map out specific contaminated/polluted sites within their geographical borders, but developing countries have paucity of data with respect to soil pollution.
- Soil pollutants include heavy metals, hydrocarbons, toxic organic micropollutants, industrial chemicals, nutrient-rich wastes, radionuclides and pathogenic organisms.
- Soil pollution can result directly or indirectly in the health infarction of plants, animals and humans.
- There have been cases of massive catastrophic exposure to chemicals as a result of accidental or incidental chemical plant explosions or test-running of radiochemical substances.

6.0 TUTOR-MARKED ASSIGNMENT

Discuss briefly each of the following soil pollutants (a) lead, (b) Sr-90 and (c) organochlorines, under the sub-topics: source, mechanism of transportation to soil and health effects.

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MODULE 3 WASTE MANAGEMENT

UNIT 1 WASTEWATER TREATMENT

CONTENTS

1.0 INTRODUCTION

In modern societies, proper management of wastewater is a necessity, not an option. The practice of collecting and treating wastewater prior to disposal is relatively a recent undertaking. It began to gain the attention of the stakeholders only when it became apparent that the “available water” is inadequate to support the available people and their needs. Earlier, city dwellers (of London, Paris and Boston, for example) used to place “night soil” in buckets along the streets and workers would empty the waste into “honey wagon” tanks. The waste was transported to rural areas for disposal over agricultural land.

The invention of the flush toilet in the 19th Century drastically changed waste-disposal practices. Existing systems for transporting urban wastes for disposal on agricultural lands were not adequate to handle the large volume of liquid generated by the flush toilets. Faced with this transportation problem, cities began to use natural drainage systems and storm sewers for wastewater carriage. Since storm drain systems naturally ended at watercourses, the implication of this practice was that waterborne wastes were discharged directly to streams, lakes and estuaries without treatment such that the self-purification capacity of the receiving streams was exceeded and nuisance conditions became intolerable. Gross pollution often resulted and health problems were transferred from the sewered community to downstream users of water.

The first “modern” sewerage system for wastewater carriage was built in Hamburg, Germany in 1842 by Lindley. Lindley’s system included many of the principles that are still in use today. Advanced wastewater-treatment processes have been developed and are still being perfected to produce potable water from domestic wastewater.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

state the characteristics of wastewater
list and explain terminologies relevant to wastewater treatment processes
explain the stages involved in conventional wastewater treatment
state and explain the challenges often encountered in hot climates conventional wastewater treatment.

3.0 MAIN CONTENT

3.1 Wastewater Characteristics

Wastewatersare usually classified as **industrial** wastewater or **municipal** wastewater. Industrial wastewater with characteristics compatible with municipal wastewater is often discharged to the municipal sewers. Many industrial wastewaters require pretreatment to remove non-compatible substances prior to discharge into the municipal system.

Municipal wastewater, having been put to a wide variety of uses, contains a wide variety of contaminants: suspended solids, biodegradable organics, pathogens, nutrients, refractory organics, heavy metals and dissolved inorganic solids. Suspended solids are primarily organic in nature and are composed of some of the more objectionable materials in sewage. Body wastes, food wastes, paper, rags and biological cells form the bulk of suspended solids in wastewater. Suspended solids cause sludge deposits and anaerobic conditions in aquatic environments. Their removal is essential prior to discharge or reuse of wastewater.

Although suspended organic solids are biodegradable through hydrolysis, biodegradable materials in wastewater are usually considered to be soluble organics such as proteins (40 – 60percent), carbohydrates (25 – 50percent) and lipids (~ 10percent). All of these materials contain carbon that can be converted to carbon dioxide biologically thus, exerting an oxygen demand. Proteins also contain nitrogen; thus a nitrogenous oxygen demand is also exerted. The biological oxygen demand (BOD) is used to quantify biodegradable organics.

All forms of waterborne pathogens – bacteria, viruses, protozoa and helminths may be found in domestic wastewater. These organisms are discharged by persons who are infected with the disease and they transmit communicable diseases. Although pathogens causing some of the more exotic diseases may rarely be present, it is a safe assumption that a sufficient number of pathogens are present in all untreated wastewater to represent a substantial health hazard. Fortunately, few of the pathogens survive wastewater treatment in a viable state.

Traditional wastewater-treatment processes are designed to reduce suspended solids, biodegradable organics and pathogens to acceptable levels before disposal. Additional treatment is required to reduce levels of nutrients if the wastewater is to be discharged to a delicate ecosystem. Processes to remove refractory organics and heavy metals and to reduce the levels of dissolved inorganic solids are required where wastewater reuse is anticipated.

3.2 Terminologies in Wastewater Treatment

Unit Operations/Unit Processes: These are methods used for treating municipal wastewaters. Unit operations involve contaminant removal by physical forces while unit processes involve biological and/or chemical reactions. Although unit operations and processes are natural phenomena, they may be initiated, enhanced or controlled by altering the environment in the reactor.

Reactor: This is the vessel or containment structure, along with all of its appurtenances, in which the unit operation or process takes place.

Wastewater-treatment System: This is composed of a combination of unit operations and unit processes designed to reduce certain constituents of wastewater to an acceptable level.

Primary Treatment: The purpose is to remove solid materials (large debris, inorganic solids and organic suspended solids) from the incoming wastewater.

Secondary Treatment: Usually, this consists of biological conversion of dissolved and colloidal organics into biomass that can subsequently be removed by sedimentation.

Tertiary Treatment: This often involves further removal of suspended solids and/or the removal of nutrients from secondary treatment wastewater.

3.3 Conventional Wastewater Treatment

Conventional treatment is the term used to describe the standard method of sewage treatment. It comprises four stages of treatment: (i) preliminary treatment, (ii) primary or physical treatment (sedimentation) (iii) secondary or biological treatment (biofilteration or activated sludge), and (iv) sludge treatment (anaerobic digestion of the sludges).

3.3.1 Preliminary Wastewater Treatment

This is the first stage of sewage treatment. It deals with the removal of large suspended or floating objects (rags, maize cobs, pieces of wood) and heavy mineral particles (sand and grit). This is necessary to prevent the equipment used in the subsequent stages of treatment from being damaged. Preliminary treatment comprises screening, grit removal and comminution (a common alternative to screening).

Screening: Coarse solids are removed by a series of closely spaced mild steel bars placed across the flow commonly inclined at 60^o. There are hand-raked screens and mechanically raked screens. Screenings are particularly obnoxious both in appearance and content, and should be buried or incinerated or macerated depending on the volume of the screenings.

Grit removal: Grit (detritus) is the heavy inorganic fraction of sewage solids such as road grit, sand, eggshells, ashes, charcoal, glass and pieces of metal. It may also contain some heavy organic matter such as seeds, coffee grounds, yam and plantain peels and so on and so forth. The grit is either used for land fill or disposed of by burial.

Comminution: A comminutor is a self-cleansing shredding machine which cuts up sewage solids as they pass or are pulled through a fine screen which forms the outer periphery of the machine. Comminutors avoid the problems associated with handling and disposal of screenings, and for this reason, they are popular with plant operators.

Sedimentation: Sedimentation is the primary or physical stage of wastewater treatment involving the gravitational separation of suspension into its component solid and liquid phases. The aim is to produce high degrees of both clarification and thickening. Clarification is the removal of solids from the liquid phase and thickening the removal of liquid from the solid or sludge phase. A high degree of clarification is required to reduce the load on the secondary (biological) treatment plant and a high degree of thickening is desirable so that sludge handling and treatment (which usually accounts for 30percent of the total cost of conventional treatment) is minimised.

Biofilteration: Biofilteration (secondary or biological treatment) is a stage in which the liquid effluent (settled sewage) from primary sedimentation tanks is treated in one of two biological reactors – a biofilter or an activated sludge process. The biofilter (also known as the percolating, trickling or biological filter or bacteria bed) is a circular or rectangular bed of coarse aggregate of about 1.8m deep. Settled sewage is distributed over the bed and trickles down over the surface of the aggregate. On these surfaces, a microbial film develops and the bacteria, which constitute most of this film, oxidise the sewage as it flows past. As the sewage is oxidised, the microbial film grows.

Some of the new cells so formed are washed away from the film by the hydraulic action of the sewage. These cells exert a high BOD and must be removed before the effluent is finally discharged. This is achieved in secondary sedimentation tanks (humus tanks). Secondary tanks are basically similar to primary tanks, but without scum-skimming facilities. The clarified effluent is discharged usually to a river and the humus sludge pumped to the sludge pretreatment unit.

Activated Sludge. Activated sludge is the conventional alternative to biofilteration. Settled sewage is led to an aeration tank where oxygen is supplied either by mechanical agitation or by diffused aeration. The bacteria which grow on the settled sewage are removed in a high-rate secondary sedimentation tank. The sludge contains some inert solids, but the main components making up its loose, flocculent structure are living or active bacteria and protozoa, hence the name “activated sludge”.

Sludge Treatment: Primary and secondary sludges are most commonly treated together in a two-stage anaerobic digester. The first stage is heated, if necessary, to 30 – 33^{o}C so that digester can proceed more quickly; the methane gas released in the digestion process is commonly used to heat the digester contents. An alternative operating temperature is 50^{o}C which permits rapid digestion of the sludge by thermophilic bacteria. The second stage is a thickener for quiescent solids separation. The supernatant liquor has a BOD_5 of 5000 – 10000 mg/L and is returned to the main works inlet for complete treatment. The digested sludge, in hot climates, is most advantageously placed on drying beds. When dry, it may be sold as fertilizer because the nutrient value of the sludge is beneficial to vegetation and its granular nature may serve as a soil conditioner.

Tertiary wastewater treatment involves the removal of nutrients and additional components so as to restore wastewater to potable quality. It involves nitrogen, phosphorus and solids removal.

SELF ASSESSMENT EXERCISE

1. Name and characterize the three most significant components of municipal wastewater.
2. Differentiate between unit operations and unit processes
3. Describe the components of (a) primary treatment, (b) secondary treatment and (c) tertiary treatment.
4. What are the major types and sources of grit in municipal wastewaters? Describe the treatment methods used to remove grit.

3.4 Hot Climate Challenges

Operation and Maintenance: Conventional sewage treatment relies heavily on complex electrical machinery which requires considerable skills in installation, operation and maintenance. This skill, particularly in maintenance, is not readily available in many of the tropical developing countries including Nigeria. Thus, whenever any of the installation is not working satisfactorily or has stopped working, the usual experience is to abandon the entire plant.

Odour: In hot climates, sewage can soon become septic (malodorous) if sufficient oxygen is not made available to prevent the onset of anaerobic conditions. A higher level of odour can thus be expected in hot climates to come from primary sedimentation tanks which are, by their nature, designed for quiescent settling and not turbulent oxygenation.

Insect Nuisance: The microbial film in biofilters is used as a breeding ground by various flies and midges. In a sense, this is beneficial in that the larvae feed on the film and thus help to prevent ponding. However, although none of the species found in filters actually bites humans, their sheer numbers can be a severe nuisance in hot climates. For example, clouds of *Psychoda* flies can effectively stop all human activities in and near a sewage treatment works.

3.5 Wastewater Reuse

Reuse of completely treated wastewater (referred to as reclamation) may be dictated by several circumstances; this complete treatment of wastewater can seldom be justified except in water-scarce areas where some form of reuse is mandatory. In such places, wastewater may constitute a major portion of the available resource. Where delicate ecosystems necessitate stringent effluent requirements, reuse of the wastewater may help to offset the cost of advanced wastewater treatment, or a reuse that will accept a lower level of treatment may obviate the need for the expense of tertiary treatment prior to discharge.

Some of the purposes for which wastewater has been reused include (i) recreational facilities (e.g. swimming and skiing), (ii) industrial water supply (e.g. for cooling processes), (iii) groundwater recharge (e.g. to stabilize groundwater table), (iv) potable water systems (e.g. in pipe-to-pipe recycling or closed loop).

4.0 CONCLUSION

Wastewater treatment reduces direct or indirect contact of humans with dangerous or harmful biochemical substances. It is thus necessary to preserve the hydrological component of our ecosystem in a way that accommodates the collective well being of humans and the biota.

In the face of “water everywhere, but none to drink” experience of the world as a whole, wastewater treatment guarantees water availability for the numerous needs of man where water scarcity prevails. For example, in arid areas, wastewater treatment affords a means of getting water faster than waiting for the natural hydrological cycling processes.

5.0 SUMMARY

In this unit, you have learnt that:

- Wastewater treatment prevents gross pollution of our environment.
- Wastewater treatment ensures greater availability of water for different purposes in water-scarce areas especially.
- Conventional wastewater treatment comprises of preliminary treatment, sedimentation, biofilteration and sludge treatment.
- Tertiary (advanced) wastewater treatment ensures its use for important purposes such as portability

6.0 TUTOR-MARKED ASSIGNMENT

1. List and discuss the uses to which wastewater subjected to tertiary treatment may be put.

2(a) Describe the common methods used in removing solids from wastewater.

(b) List and discuss the major operations involved in tertiary wastewater treatment.

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UNIT 2 COMPOSITION OF SOLID WASTES

CONTENTS

1.0 INTRODUCTION

Effective handling of solid wastes in a finite world (like ours) which is constantly being exposed to threats from pollution effects can only be guaranteed by an adequate understanding of what solid wastes are, their types, sources, composition and the uses to which they may be put. Perhaps the most difficult task facing an environmental scientist is to predict the composition of solid wastes that will be collected now and in the future. The problem is complicated because of the heterogeneous nature of waste materials and the fact that unpredictable externalities can affect the long-term abundance of the individual waste components.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

identify the various types of solid wastes and their sources
state and discuss the physical and chemical composition of wastes
list and discuss types of waste management practices available.

3.0 MAIN CONTENT

3.1 Solid Wastes

Solid wastes are all the wastes arising from human and animal activities that are usually solid and discarded as useless or unwanted. The term "solid wastes" encompasses the heterogeneous mass of throw-aways from residences and commercial activities as well as the more homogeneous accumulations of a single industrial activity. Generally, solid wastes are scrap materials or other unwanted surplus substance or any such substance which to be disposed of as being broken, worn out, contaminated or otherwise spoiled.

3.2 Types and Sources of Solid Wastes

Solid wastes are often classified according to the source from which they are generated. Hence, we have municipal waste, industrial wastes, agricultural wastes and hazardous wastes.

Municipal Wastes are wastes that are related to land use and zoning. The most difficult source to deal with is open areas because, in these locations the generation of wastes is in a diffuse process. These are mainly wastes from residential and commercial sources such as food wastes, rubbish, ashes, demolition and construction wastes, special waste, and occasionally, hazardous wastes.

Industrial Wastes are those wastes arising from industrial activities and typically these include rubbish, ashes, demolition and construction wastes and special wastes.

Agricultural Wastes are wastes arising from the by-products of agricultural produce.

Hazardous Wastes are wastes that pose a substantial danger immediately or over a period of time to human, animal or plant life. A waste is classified as hazardous if it exhibits any of the following characteristics: (i) ignitability, (ii) corrosivity, (iii) reactivity and (iv) toxicity.

In the past, hazardous wastes were often grouped into the following categories: (i) radioactive substances, (ii) chemicals, (iii) biological wastes, (iv) flammable wastes and (v) explosives. The principal sources of hazardous biological wastes are hospital and biological research facilities.

3.3 Physical Composition of Solid Wastes

Individual components: Typical components of most municipal solid wastes are food wastes, paper, cardboard, plastics, textiles, rubber, leather, garden trimmings, wood, miscellaneous organics, glass, tin cans, ferrous metals, non-ferrous metals, ashes, bricks, etc. These are the readily identifiable ones consistent with component categories of solid wastes.

Particle size: The size of the component materials in solid wastes is of importance in the recovery of materials especially with mechanical means such as trommel screens and magnetic separators. The particle size distribution of solid wastes is such that those from 0.05 – 0.25m (mesh size) are often much more than those of 0.25 – 0.5m and above.

Moisture content: The moisture content of solid wastes is usually expressed as the mass of moisture per unit mass of wet or dry material. That is,

$$\text{Moisture content} = \left(\frac{a - b}{a}\right) x 100$$

where a = initial mass of sample as delivered
and b = mass of sample after drying.

To obtain the dry mass, the solid–waste material is dried in an oven at 77^0C for 24 hours. This temperature and time is used to dehydrate the material completely and to limit the vaporisation of volatile materials.

3.4 Chemical Composition of Solid Wastes

Information on the chemical composition of solid wastes is important in evaluating alternative processing and energy recovery options. If solid wastes are to be used as fuel, the four most important properties to be known are:

a. Proximate analysis

- Moisture (loss at 105^0c for 1 hour)
- Volatile matter (additional loss on ignition at 950^0c)
- Ash (residue after burring)
- Fixed carbon (remainder)

b. Fusing point of ash
c. Ultimate analysis = percent of C, H, O, N, S and ash.
d. Heating value (energy value)

3.5 Changes in Solid Waste Composition

The composition of solid wastes in Nigerian urban centres is determined by a number of factors: type of settlers (low income earners, medium income earners or high income earners), part of the city; period of the year and technological advancement. For example, the percentage of leaves used for wrapping foodstuff has been reducing progressively since mid 1980s while that of used polythene bags is increasing. Likewise, the volume of papers and cans generated as part of solid wastes in an elite settlement is likely going to be greater than that generated in a village as a whole.

The replacement of leaves and papers for "packaging" food products with polythene bags or plastics has its attendant environmental problems. While leaves and papers decay completely within two or three months of contact with soil, polythene bags take infinitely long period of time to decay. Refuse dumps where such non-biodegradable matters are numerous accumulate into long-lasting enormous heaps in most Nigerian cities. Apart from constituting eye sores, they block streets, disrupt smooth flow of rivers and cause floods, produce serious stench and constitute tremendous health hazards. The non-free flowing or sticky nature of solid wastes in a refuse dump gives rise to their accumulation on some habitable parts of the soil surface thus impairing the productive capacity of soils. Groundwater are often contaminated (through seepage), by leachate arising from solid wastes dumped on the ground.

SELF ASSESSMENT EXERCISE

1. List and explain the characteristics of hazardous wastes.
2. What are the health problems of refuse dumps in the Nigerian environment?

3.6 Solid Wastes Management

Solid waste management means the collection, transportation, storage, disposal, treatment, and recycling of waste including the care of the disposal site.

3.6.1 Collection, Transportation and Storage of Solid Wastes

In most houses and market stalls in Nigeria, metal or plastic dustbins are used to collect and temporarily store solid wastes. If the houses are easily accessible to vehicles, door-to-door collection would be done by simply emptying of the dustbins into the vehicles. But in cases where the accessibility is limited, tricycles with carriers are used for the same purpose. Alternatively, household solid wastes are deposited into solid wastes depots located within the community in a place accessible to vehicles. From the depots, sanitary inspectors transport the solid waste in their vehicles to sites where the wastes are further treated. Refuse collection and transportation take up to 75percent of the total expenses for waste disposal in countries like Nigeria.

3.6.2 Waste Disposal and Treatment

Solid waste disposal refers to the final placement or discharge or deposit of waste into a given environment in such a way that it causes little or no harm to the environment. In Nigeria, waste disposal methods have been ineffective and unsatisfactory. Wastes are often dumped indiscriminately along the streets and open spaces; passengers in transit throw wastes at will on the roads and open gutters are carelessly filled up with wastes. Where a depot is used, sanitary inspectors often delay waste collection until when the depots have been over filled.

The mostly used disposal methods are open dumping, sanitary land filling, compositing, incineration and recycling.

3.6.2.1 Open dumping

Open dumping is commonly practiced in many cities in the third world. The refuse is simply disposed of into the nearest open space on land or surface water without any environmental consideration. This method is not environmentally sound or safe because of so many hazards associated with it.

Open dumping encourages the spread of diseases by harbouring the flies and vermin acting as agents of transmission. Some of the communicable diseases associated with dump sites are fly-borne, rodent-borne and mosquito-borne. At times, open dumping is associated with burning of waste, which can cause fire accident and air pollution. Open dumping can cause contamination of surface and ground waters.

Sanitary Landfill

Landfill is one of the most environmentally sound methods of solid waste disposal adopted by many countries of the developed world. Sanitary landfill operations involve depositing solid wastes in natural or man–made depressions or trenches, compacting them into smallest practical volume and covering them with compacted earth or other material. The microbial degradation reaction which occurs in the landfill generates methane gas that can be collected and used as a source of energy.

Modern landfill sites need to be located in impermeable starter or sealed with an appropriate membrane before the wastes are deposited and should have a system for managing the leachate to prevent groundwater surface water pollution.

Composting

Composting involves shredding and separating the putrescible fraction of municipal waste, mixing it with other organic materials and allowing microbial decomposition to take place. Humus eroded from topical soils can be replaced by compost which has good moisture retaining capacity. It is not so easily washed away as chemical fertilizer. Thus, compost helps to improve soil structure and control soil erosion since it is rich in phosphorus, potassium, nitrogen, carbon and sulphure. However, compost may contain high levels of hazardous (heavy) metals which may cause soil surface or ground water pollution.

Incineration

Incineration entails passing the waste through a chamber at a temperature of approximately 1200^0C in an adequate supply of air or oxygen. In the process, all the organic materials (carbohydrates, lipids and proteins including plastics, fibres and woods) will be oxidised to volatile compounds such as CO_2, H_2O, SO_2, NO_2 etc. The residue after the incineration has a volume of about one–tenth of the original solid waste. Hence, incineration is only a system of waste reduction since the residual ash needs to be disposed of carefully afterward in a landfill.

Advantages of incineration are:

1. The heat generated can be harnessed for electricity generation and hearting of the neighbourhood.
2. Incineration reduces the need for additional landfill sites.
3. It can dispose of up to 99.999percent organic wastes. Including chlorinated organic xemobiotics of properly carried out.
4. Pathogens in the waste are effectively eliminated.
5. The ash residue may be recycled and used in the manufacture of cement, as aggregate in concrete, structural elements in road beds and in asphalt road surfacing mixes.

Disadvantages of incineration include:

1. Incineration is relatively expensive.
2. There is a danger of highly toxic pollutants such as polychlorodibenzo-dioxins (PCDDS) and

polychlorodibenzonfurans (PCDFs) being synthesized and emitted into the atmospheres.

3. Toxic heavy metals in fly ash from incinerators may constitute direct and detrimental consequences in the immediate environment as they stress up other environmental matrices such as soil, water and the biota.
4. Incineration metals and metalloids such as Se, Hg, As, Sb and Pb may be transported in the air or enriched on gaseous particulates and travel long distances before they are deposited on and or surface of crops where they may be absorbed via the roots to the foliage into the plant. For example, it has been shown that about 90percent of the total plant uptake of Pb is due to deposition from the atmosphere rather than transport from the soil. This implies that atmospheric deposition of metals could pose a significant source of heavy metal inputs to the food chain where background soil levels are even relatively low.

Recycling

Recycling encompasses the full range of waste resources recovery and reuse techniques. This does not only make the waste material harmless, but converts it to another or original useful material. The practice of recycling solid waste is an ancient one with modern improvements. Metal implements were melted down and recast in prehistoric civilisations. In 1972, in Britain, metal scrap was worth 1,250 million pounds. In that year, 60per cent of Pb, 36per cent of Cu and 32per cent of paper used in Britain came from scrap. In Nigeria too, recently more and more people are getting engaged in scavenging business of metals (steel and aluminum particularly), plastics, bottles and so on and so forth. In Cuba, a technology has been developed for collecting, selecting and preparing urban wastes to feed pigs and poultry. The prepared wastes produce between 18 and 22per cent protein. From recycling point of view, solid wastes are valuable resources in the wrong places.

Waste products, when effectively managed, can generate biogas (e.g methane), fertilizer, textile materials, paper, crude oil (by thermal depolymerization) and metals (e,g aluminum).

4.0 CONCLUSION

Recognising that the inhabitable is finite and that the continued pollution of our environment will, if uncontrolled, be difficult to rectify in the future, the subject of solid waste management is both timely and important. The overall objective of solid waste management is to minimise the adverse environmental effects caused by the indiscriminate disposal of hazardous solid wastes especially.

5.0 SUMMARY

In this unit, you have learnt that:

Solid wastes encompass the homogenous and heterogeneous mass of throw-aways from residences, commercial centres and industrial locations.

Solid wastes are divided into municipal, industrial and hazardous wastes.

Waste disposal management encompasses collection, transportation, storage and methods waste disposal such as open dumping, sanitary land filling, composting, incineration and recycling.

6.0 TUTOR-MARKED ASSIGNMENT

1. Assess and discuss two of the methods adopted in yours or a nearby community to handle the menace of solid wastes.
2. Discuss five merits and five demerits of incineration as a method of solid wastes management.

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MODULE 4 WATER CHEMISTRY AND ANALYSIS

UNIT 1 PHYSICAL PARAMETERS RELEVANT TO WATER ANALYSIS

CONTENTS

1.0 INTRODUCTION

Water appears to be the most essential of the three indispensable matters (air, water and food) to man. Although there is a common observation that without air, man can barely survive for a very few minutes (that is, between three to five minutes) and without food, he may survive for up to fifty days. However, it is also a common knowledge that without water on the wet surfaces of alveoli in humans or gills in fish for instance, intercellular oxygen exchange is impossible. Several other biochemical reactions that are vital to life are water-dependent. Water is also needed for day-to-day running of vital domestic, industrial and agricultural activities.

Water needless to say, is so important for both the sustenance and continuity of life, hence, having a good understanding of chemistry and analysis of water is vital to sustainability of man and his various activities (in the face of the fact that less than 2percent of the total water available on the surface of the earth is suitable for drinking). Apart from the seeming “localisation” of the two per cent good water, technological advancement and rapid industrialisation with their concurrent pollution tendencies have placed the limited good water under serious stress.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- list the physical parameters that are relevant to the chemistry and analysis of water
- explain how the parameters (turbidity, colour, taste and odour, solids) are measured
- interprete and apply the data obtainable from the measured parameters in solving practical problems related to water analysis.

3.0 MAIN CONTENT

3.1 Notable Physical Parameters of Water

3.1.1 Turbidity

The term “turbid” is applied to waters containing suspended matter that interferes with the passage of light through the water or in which visual depth is restricted.

Turbidity may be caused by a wide variety of suspended materials ranging in sizes from colloidal to coarse dispersions, depending upon the degree of turbulence. In lakes or other water existing under relatively quiescent conditions, most of the turbidity is due to colloidal and extremely fine dispersions; in river under flood conditions, the turbidity is as a result of to relatively coarse dispersion, while glacier–fed rivers and lakes, turbidity is due to colloidal coarse particles produced by the grinding action of the glacier. As rivers descend from mountainous areas to the plains, they receive contributions of turbidity from farming and other operations that disturb the soil. Under flood conditions, great amounts of topsoil are washed to receiving streams. Much of these materials is inorganic in nature and includes clay and silt, but considerable amounts of organic matter are included. As the rivers progress toward the ocean, they pass through urban areas where domestic and industrial treated and untreated wastewaters may be added. These wastewaters often contain large quantities of both organic and inorganic substances that produce turbidity. Street washings contribute much turbidity as well.

Organic materials reaching rivers serve as food for bacteria. The resulting bacterial growth and other microorganisms that feed upon the bacteria produce additional turbidity. Inorganic nutrients such as nitrogen and phosphorus present in wastewater discharges and agricultural runoff stimulate the growth of algae which also contribute to turbidity.

Significance of Turbidity in Public Water Supplies

Aesthetics: Any turbidity in a sample of drinking water is automatically associated with possible wastewater pollution and the health hazards occasioned by it.

Filterability: Filtration of water is rendered more difficult and costly with increasing turbidity.

Disinfection: To be effective, there must be direct contact between a given disinfectant (e.g. chlorine, ozone, chlorine dioxide or UV radiation) and the organisms it has to kill. In cases where turbidity is caused by municipal wastewater suspended solids or runoff from animal feed lots, many of the pathogenic organisms may be encased in the particles and remain protected from the action of the disinfectant.

Method of Turbidity Determination

Instrumental method that employs the principle of nephelometry is used. A light source illuminates the sample and one or more photoelectric detectors are used with a readout device to indicate the intensity of scattered light. A particular formation polymer suspension is used as a standard. Turbidity in treated drinking water must never exceed one nephelometric turbidity unit (NTU). 1 NTU = 1mg S_iO_2/L.

Applications of Turbidity Data

Water Supply: Knowledge of the turbidity variation in raw-water supplies is of prime importance to water treatment plant operations. Such measurements are used in conjunction with other information to determine whether a supply requires special treatment by chemical coagulation and filtration before it may be used for a public water supply.

Determination of Effectiveness of Coagulants**:** Water supplies obtained from rivers usually require chemical flocculation because of high turbidity. Turbidity measurements are used to determine the most effective and economical chemical to use.

Gauging the Amount of Chemicals**:** Turbidity measurements help to gauge the amount of chemicals needed from day to day in the operation of treatment works. This is particularly important on “flashy” rivers where no impoundment is provided.

Measurements of turbidity in settled water prior to filtration is useful in controlling chemical dosages so as to prevent excessive loading of rapid sand filters.

***Checking Faulty Filter Operation*:** Turbidity measurements of the filtered water are needed to check on faulty filter operation and to ensure conformity to regulatory requirements.

***Effluent Control*:** Turbidity measurements offer a quick means of determining the levels of suspended solids in an effluent so as to know the minimum amount of coagulants needed to produce high-quality effluent.

SELF ASSESSMENT EXERCISE 1

1. Discuss the nature of materials causing turbidity in (a) river water during a fresh flood, (b) polluted river water and (c) domestic wastewater.
2. Discuss briefly the causes of colour in water.
3. Differentiate between “apparent” and “true” colour
4. What is the purpose of adding cobalt chloride to colour standards?
5. Suggest one method by which colour can be removed from water.

3.1.2 Colour

Many surface waters, particularly those emanating from swampy areas, are often coloured to the extent that they are not suitable for domestic or some industrial uses without being treated to remove the colour. The colouring materials, many of which are humic substances, result from contact of water with organic debris, such as leaves, needles of conifers and woods, all in various stages of decomposition. Iron is sometimes present as ferric humate and produces a colour of high potency. Natural colour exists in water primarily as negatively charged colloidal particles and its removal can readily be accomplished by a coagulant having a trivalent metallic ion such as aluminum or iron.

Surface waters may appear highly coloured because of coloured suspended matter when in reality they are not. Rivers that drain areas of red clay soils become highly coloured during times of flood. Colour caused by suspended matter is referred to as **apparent colour** while colour caused by vegetable or organic extracts that are colloidal is called **true colour**. At times, surface waters may become coloured by the presence of dyes from textile industries and pulping operations in the paper industry which leads to production of liquors containing lignin derivatives and other materials in dissolved form.

Significance of colour in public water supplies

i. **Disinfection problem:** Waters containing colouring matter derived from natural Substances undergoing decay in swamps and forests are not considered to possess toxic properties. However, disinfection by chlorination results in the formation of chloroform, other trihalomethanes and a range of other chlorinated organics, leading to problems of much current concern.

ii. **Problem of aesthetic unacceptability:** The natural colouring materials impart a yellow-brownish appearance somewhat like that of urine to water. This makes consumers to seek other sources of drinking water if the public water supply is not aesthetically acceptable no matter how safe it may be from the hygienic viewpoint. The alternative sources sought by consumers may be springs or wells with uncertain levels of pathogenic organism. Waters intended for human use should not exceed 15 colour units.

Standard colour solutions

This is done by preparing a stock solution of potassium chloroplatinate (K_2PtCl_6) that contains 500mg/L of platinum. Cobalt chloride is added to provide the proper tint. The colour produced by 1mg/L of platinum (in the form of K_2PtCl_6) is taken as the standard unit of colour. The stock solution has a colour of 500 units, and a series of working standard is prepared from it by dilution. A matched set of colour-comparism tubes, called **Nessler tubes** are usually used to contain the standard. A series ranging from 0 to 70 colour units is employed. Samples with colour less than 70 units are tested by direct comparison with the prepared standards. For samples with a colour greater than 70 units, a dilution is made with demineralised water and colour calculation is made, using a correction factor for the dilution employed.

Suspended matter in samples must be removed to enable determination of true colour. This is usually accomplished by centrifuging; filtration is not recommended because of possible adsorption of colour on the filtering medium.

Applications of Colour Data

Consumption Specifications: The decision about whether to treat a water sample further to meet the World Health Organization (WHO) guideline of 15 colour units for drinking water can be taken from the colour data obtained.

Indicator of Possible Formation of Toxins: Colour in natural waters is an indirect indicator of the potential for trihalomethane formation during disinfection with chlorine. A water supply is generally desired with a colour low enough so that chemical treatment will not be required and trihalomethane formation will not constitute a burdensome treatment problem.

Designs of Treatment Plant: Before a chemical treatment plant is designed, research is conducted to ascertain the best chemicals to use and amounts required. Colour determinations serve as the basis of the decisions. Such data are necessary for proper selection of chemical feeding machinery and the design of storage space.

Means of Ensuring Economical Operations: Colour determinations on the raw and treated water or wastewater govern the dosages of chemicals used, to ensure economical operation and to produce low-colour water that is well within accepted limits.

3.1.3 Taste and Odour

The sensations of taste and smell are closely related and often confused. Hence, a wide variety of tastes and odours may be attributed to water by consumers. Substances that produce an odour in water will almost invariably import a taste as well. The converse is not true, as there are many mineral substances that produce taste but no odour.

Significance of Taste and Odour in Water Supply

Consumers find taste and odour aesthetically displeasing for obvious reasons. Because water is thought of as tasteless and odourless, the consumer associates taste and odour with contamination and may prefer to use a tasteless, odourless water that might actually pose more of a health threat. Odours produced by organic substances may pose more than just aesthetic problem since some of those substances are carcinogenic.

Sources of Taste and Odour

Many substances with which water comes into contact in nature or during human use may lead to perceptible taste and odour. These include minerals, metals and salts from the constituents of wastewater. Inorganic substances are more likely to produce tastes unaccompanied by odour. Alkaline materials impart a bitter taste to water, while metallic salts may give a salty or bitter taste.

Organic materials, on the other hand, are likely to produce both taste and odour. A multitude of organic chemicals may cause taste and odour problems in water, with petroleum –based products being prime offenders. Biological decomposition of organics may result in both taste and odour producing liquids and gases in water. Principal among them are the reduced products of sulphure that impart a “rotten egg” taste and odour. Also, certain species of algae secrete an oily substance that may result in both odour and taste. The combination of two or more substances, neither of which would produce taste or odour by itself, may sometimes result in taste and odour problems e.g. organics and chlorine may exhibit this synergistic effect.

Measurement of Taste and Odour

Direct measurement of materials that produce tastes and odours can be made if the causative agents are known. Several types of analysis are available for measuring taste-producing inorganic. Measurement of taste and odour-causing organics can be made using **gas or liquid chromatography.** Because chromatographic analysis is time-consuming and require expensive equipment, it is not routinely performed on water samples, but should be done it problem organics are suspected.

However, because of possible synergistic effects, quantifying the sources of organics does not necessarily quantify the nature or intensity of taste and odour. Quantitative tastes that employ the human senses of taste and smell can be used e.g. the “threshold odour number” (TON). Various amounts of odourous water are poured into containers and diluted with enough odour-free distilled water to make a 200 mL mixture. An assembled panel of five to ten “noses” is used to determine the mixture in which the odour is just barely perceptible to the sense of smell. The TON of that sample is then calculated using the formula

$$TON = \frac{A + B}{A}$$

where A = the volume (ml) of odourous water
and B = the volume of odour –free water required to produce a 200 ml mixture.

Application of TON Data

Potable water is expected to be taste and odour free. However, United States Environmental Protection Agency (USEPA) does not have a maximum standard for TON. A TON of three has been recommended by the Public Health Service and serves as a guideline rather than a legal standard.

3.1.4 Temperature

Temperature is not used to evaluate directly either potable water or wastewater. It is, however, one of the most important parameters in natural surface-water systems. The temperature of surface waters governs to a large extent the biological species present and their rates of activity. Temperature has an effect on most chemical reactions that occur in natural water system. Temperature also has a pronounced effect on the solubilities of gases in water.

Sources of Temperature

The temperature of natural water systems responds to many factors, the ambient temperature (temperature of the surrounding atmosphere) being the most universal. Generally, shallow bodies of water are more affected by ambient temperatures than the deeper bodies. The use of water for dissipation of waste heat in industry and the subsequent discharge of the heated water may result in dramatic, though perhaps localised, temperature changes in receiving streams. Removal of forest canopies and irrigation return flows can also result in increased stream temperature.

Impacts of Temperature

Cooler waters usually have a wider diversity of biological species. At lower temperatures, the rate of biological activity such as food supplies utilisations, growth, reproduction, etc, is slower. An increase of 10^0C is usually sufficient to double the biological activity, if essential nutrients are present.

At elevated temperature and increased metabolic rates, organisms that are more efficient at food utilisation and reproduction flourish, while other species decline and are perhaps eliminated altogether. Accelerated growth of algae often recurs in warm water and can become a problem when cells cluster into algae mats. Natural secretion of oils by algae into the mats and the decay products of dead algae cells can result in taste and odour problems. Higher-order species, such as fish, are affected dramatically by temperature and by dissolved oxygen levels, which are a function of temperature. Game fish generally require cooler temperatures and higher dissolved-oxygen levels.

Temperature changes affect the reaction rates and solubility levels of chemicals; most chemical reactions involving dissolution of solids are accelerated by increased temperatures, while the solubility of gases, on the other hand, decreases at elevated temperatures.

SELF ASSESSMENT EXERCISE 2

1. For a given water sample, exactly 80mL of it was needed to make its odour just detectable. Determine the TON for this water sample and state, with reason, whether the water is safe for

domestic purposes or not based on its TON value calculated given that TON < 3 is adjudged safe.

2. Discuss briefly two ways in which temperature can indirectly affect the physiochemical parameters of water.

3.1.5 Solids in Water Supplies

The total solids in a liquid sample consist of total dissolved solids and total suspended solids. Total dissolved solids are materials in the water that will pass through a filter with a 2.0 µm or smaller nominal average pore size. The material retained by the filter is the total suspended solids.

The amount and nature of dissolved and suspended matter occurring in liquid material vary greatly. In potable waters, most of the matter is in dissolved form and consists mainly of inorganic salts, small amounts of organic matter and dissolved gases. The total dissolved solids content of potable waters usually ranges from 20 to 1,000 mg/L, and as a rule, hardness increases with total dissolved solids.

Unlike the measurement of total suspended solids where sample drying is conducted at 103 to 105^{0}C, total dissolved solid analysis for water supplies is conducted at 180^{0}C. The reason for the higher temperature used in the latter is to remove all mechanically occluded water. Here, organic matter is generally very low in concentration and losses due to the higher drying temperature will be negligible.

Significance of Solids Determination

Water with a total solid content of less than 500 mg/L is most desirable for domestic use. A higher total solid content imparts taste to the water and often has a laxative and sometimes the reverse effect upon people whose bodies are not used to the higher levels.

Water with a high dissolved solid content tends to stain glassware and has adverse impacts on irrigated crops, plants and grasses.

The suspended solids analysis is used to ensure that an important wastewater discharge requirement is met.

In cases in which water softening is needed, the type of softening procedure may be dictated by the dissolved solid content, since precipitation methods decrease the solids and exchange methods increase the solids.

Corrosion control is frequently accomplished by the production of stabilised waters through pH adjustment. The pH stabilisation depends, to an extent, upon the total solids present as well as the alkalinity and temperature.

Determination of Solids in Water Supplies

Dissolved solids are the major concern in water supplies; therefore, the total solids determination and the specific conductance measurement are of greatest interest. Suspended solids tests are seldom made because of the small amounts present. They are more easily evaluated by measurement of turbidity.

Total Solids

The determination of total solids is easily made by evaporation and drying of a measured sample in a tarred container. The use of platinum dishes is highly recommended because of the ease with which they can be brought to constant weight before use. Vycor ware is a good substitute, but the use of porcelain dishes has to be avoided because of their tendency to change weight.

Specific Conductance

A rapid estimation of the dissolved solids content of a water supply can be obtained by specific conductance measurements. Such measurements indicate the capacity of a sample to carry an electric current, which in turn is related to the concentration of ionised substances in the water. Most dissolved inorganic substances in water supplies are in the ionised form and so contribute to the specific conductance. Although this measurement is affected by the nature of the various ions, their relative concentrations and the ionic strength of the water, such measurements can give a practical estimate of the variations in dissolved mineral content of a given water supply. Also, by the use of an empirical factor, specific conductance can allow a rough estimate to be made of the dissolved mineral content of water samples.

Dissolved and Suspended Matter

In cases where turbidity measurements are not adequate to provide the necessary information, the suspended solids may be determined by filtration through a glass-fibre filter. Another technique is to filter a sample of water through filter paper and determine total solids in the filtrate. The difference between total solids in unfiltered and filtered samples is a measure of the suspended solids present.

SELF ASSESSMENT EXERCISE 3

1. What significant information is furnished by the determination of solids in a water supply sample?

2. Why is 103 to 105^0C the drying temperature generally used for total solids analysis? Under what conditions and why is 180^0C sometimes used as the drying temperature?

4.0 CONCLUSION

Measurement of such parameters as turbidity, colour, pH and solids content of a water supply are germane to our practical understanding of how water treatment should be carried out. Such measurements, when thoroughly carried out, are the basis of producing potable water for a healthy population.

5.0 SUMMARY

In this study, you have learnt that:

Turbidity, colour, pH and solid content of water are important prerequisite determinants as to whether a water sample will be suitable for municipal water supply purposes.

Such parameters (turbidity, colour, pH and solid content) of a water supply affect other water characteristics of water tremendously.

6.0 TUTOR-MARKED ASSIGNMENT

1. A water supply sample contains 350mg/L of dissolved solids. Treatment facilities remove 65percent. How many litres of water supply containing 5.0percent dissolved solids will be produced per 1000 L of the water supply sample?
2. What problem might be caused by colour –causing materials in water other than the colour itself?

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UNIT 2 IMPORTANT CHEMICAL PARAMETERS IN WATER CHEMISTRY AND ANALYSIS

CONTENTS

1.0 INTRODUCTION

Like physical parameters, several chemical parameters are paramount to crucial decision-making concerning the quality of public water supplies. Among these are pH, acidity, alkalinity and hardness.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

define pH, acidity, alkalinity and water hardness
explain how to determine acidity, alkalinity, water hardness and residual chlorine of a water sample
interprete and apply the data obtained with respect to acidity, alkalinity, water hardness and residual chlorine/chlorine demand to practical decision making about water quality.

3.0 MAIN CONTENT

3.1 Some Relevant Chemical Parameters of Water

3.1.1 pH

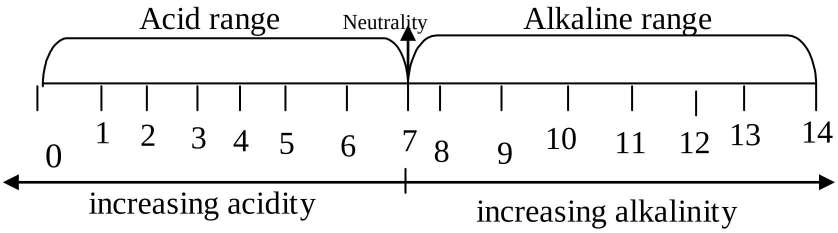
pH is a term used to express the intensity of the acid or alkaline condition of a solution. It is a way of expressing the hydrogen-ion concentration or more precisely, the hydrogen-ion activity. It is important in almost every phase of environmental science and engineering. In the field of water supplies, it is a factor that must be considered in chemical coagulation, disinfection, water softening and correction control. In wastewater treatment employing biological processes, pH must be controlled within a range favourable to the particular organisms involved. Chemical processes used to coagulate wastewaters, dewater sludges or oxidise certain substance, such as cyanide ion, require that the pH be controlled within rather narrow limits.

pH and the Ionic Product of Water (K_w)

The pH of a solution is defined as the negative logarithm to base ten of the hydrogen ion concentration of that solution. That is,

$$pH = -\log_{10} [H^+] \text{ or } pH = \log_{10} \frac{1}{[H^+]}$$

The pH scale ranges from O to 14, with pH 7 at 25^0C representing absolute neutrality.



At 250^0C, pure water dissociates as follows:

$$H_2O \longrightarrow H^+ + OH^-$$

The $[H^+]$, using the hydrogen electrode, of pure water at 25^0C has been found to be 10^{-7}? This implies that the $[OH^-]$ will also be 10^{-7}. The equilibrium equation gives:

$$K = \frac{[H^+][OH^{\square}]}{[H_2O]}$$

Since the ionisation degree is so small and the concentration is so large, it is considered that the concentration of water is constant. Hence,

$K_w = [H^+] [OH^-)$

For pure water at 25^0C, $K_w = 10^{-7} \text{ x } 10^{-7} = 10^{-14}$

By implication, pH = 7 and pOH =7

So, pH + pOH = 14

SELF ASSESSMENT EXERCISE 1

What is the pH and pOH of a solution containing (a) 1.008g of H^+ and (b) 0.1008g of H^+, per litre?

3.1.2 Acidity

Acidity is a measure of the ability of a given water sample to neutralise strong bases to an indicator end point. Most natural waters, domestic wastewaters and many industrial wastes are buffered principally by a carbon dioxide-bicarbonate system.

Sources and Nature of Acidity

Carbonic and species are formed when CO_2 enters surface waters. This happens when the concentration of CO_2 in water is less than that in equilibrium with CO_2 in the atmosphere. Through biological oxidation of organic matter particularly in polluted water, CO_2 produced can also be absorbed by water.

Ground waters and waters from the hypolimnion of stratified lakes and reservoirs often contain considerable amounts of CO_2 resulting from bacterial oxidation of organic matter with which the water has been in contact. Under these conditions, the CO_2 is not free to escape to the atmosphere. Carbon dioxide is an end product of both aerobic and anaerobic bacterial oxidation; therefore, its concentration is not limited by the amount of dissolved oxygen originally present. It is not uncommon to encounter ground waters with 30 to 50 mg/L of CO_2.

Mineral acidity is present in many industrial wastes particularly those of the metallurgical industry and some from the production of synthetic organic materials. The drainage from abandoned mines and iron ore dumps will contain significant amounts of sulphuric acid or salts of sulphuric acid if sulphure, sulphide or iron pyrite are present. Conversion of these materials to sulphuric acid and sulphate is brought about by sulphure-oxidizing bacteria under aerobic conditions.

$$2S + 3O_2 + 2H_2O \longrightarrow \text{bact. } 4H^+ + 2SO_4^{2-}$$

$$FeS_2 + 3\tfrac{1}{2}\, O_2 + H_2O \longrightarrow \text{bact } Fe^{2+} + 2H^+ + 2SO_4^{2-}$$

Salts of trivalent heavy metals particularly e.g. Fe^{3+} and Al^{3+} hydrolyse in water to release mineral acidity.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3H^+ + 3Cl^-$$

Many industrial wastes contain organic acids. Combination of fossil fuels in power plants and automobiles leads to the formation of oxides of nitrogen and sulphure, which when mixed with rain, hydrolyse to form sulphuric and nitric acids.

Significance of Acidity

Acid waters are of concern because of their corrosive characteristics and the expenses involved in removing or controlling the corrosion-producing substances. The corrosive factor in most waters is CO_2, but in many industrial wastes, it is mineral acidity. Acid rain can lower the pH in poorly buffered lakes thereby adversely affecting aquatic life, and can increase the amount of chemical, such as aluminum, leached from soil into surface.

Methods of Acidity Measurement

Both CO_2 and mineral acidity can be measured by means of standard solutions of alkaline reagents. Mineral acids are measured by titration to a pH of about 3.7, the methyl orange end point. For this reason, mineral acidity is also called **methyl orange acidity**. Titration of a sample to the phenolphthalein end point of pH 8.3 measures both mineral acidity plus acidity due to weak acids. This total acidity is also termed phenolphthalein acidity.

Determination of Acidity in Natural and Waste Waters

(a) **Methyl Orange Acidity:** While methyl orange was formerly used for this purpose, bromophenol blue is now recommended as it has a sharper colour change at pH 3.7. The titration is carried out using 0.02M NaOH. Results are reported in terms of methyl orange acidity expressed as $CaCO_3$. That is,

$$\text{Acidity (as mg/L } CaCO_3) = \frac{VxMx100000}{mLsample}$$

where V = mL sodium hydroxide titrant.
M = molarity of sodium hydroxide
The molecular weight of $CaCO_3$ = 100g (=100,000mg)

(b) **Phenolphthalein Acidity:** This measures the total acidity resulting from both mineral acids and weak acids in the sample. Either phenolphthalein or metacresol purple indicator can be used for this titration. When heavy-metal salts are present, it is usually desirable to heat the sample to boiling and then carry out the titration. The heat speeds the hydrolysis of the metal salts, allowing the titration to be completed more readily. Again, 0.02M NaOH is used as the titrating agent. Result are reported in terms of phenolphthalein acidity expressed as $CaCO_3$ as before.

Determination of Total Acidity by Mixed Indicators Method

The mixed indicator is prepared by mixing 10mL of 0.1percent thymol blue (in 50percent ethanol) with 30mL of 0.1percent phenolphthalein (in 50percent ethanol). Measure accurately 50 or 100mL of water sample into a titration flask. Add one drop of the mixed indicator. Titrate with 0.0125M barium hydroxide solution to the end point yellow (acid) to violet detected with a pH meter rather than by indicator.

$$\text{Acidity (as mg/L CaCO2)} = \frac{VxMx100000}{mLsample}$$

where V = Ml barium hydroxide
M = molarity of barium hydroxide
100000 = molar weight of $CaCO_3$ (i.e. 100g).

SELF ASSESSMENT EXERCISE 3

1. What causes acidity in natural waters?
2. What pH range is used to measure (a) Mineral Acidity and (b) Total Acidity, in water?
3. Why are we concerned with acidity in water?

3.1.3 Alkalinity

The alkalinity of a water sample is a measure of its capacity, to neutralize acids. Constituents of alkalinity in natural water systems include CO_3^{2-}, HCO_3^-, OH^-, $HSiO_3^-$, $H_2BO_3^-$, HPO_4^-, HS^- and NH_3^0. These compounds result from the dissolution of mineral substances in the soil and atmosphere. Phosphates may also originate from detergents in waste water discharges and from fertilizers and insecticides from agricultural land. Hydrogen sulphide and ammonia may be products of microbial decomposition of organic material.

By far, the most common constituents of alkalinity are bicarbonate (HCO_3^-), carbonate (CO_3^{2-}) and hydroxide (OH^-). In addition to their mineral origin, these substances can originate from CO_2, a constituent of the atmosphere and a product of microbial decomposition of organic material, according to the following reactions.

$$CO_2 + H_2O \rightleftharpoons H_2CO_3 \text{ (dissolved } CO_2 \text{ and carbonic acid)}$$

$$H_2CO_3 \rightleftharpoons H^+ + HCO_3^- \text{ (bicarbonate)}$$

$$HCO^{-}_{3} \rightleftharpoons H^{+} + HCO_{3}^{2-} \text{ (carbonate)}$$

$$CO^{2-}_{3}\ H_2O \rightleftharpoons HCO_{3}^{-} + OH^{-} \text{ (hydroxide).}$$

The last reaction is a weak reaction chemically. However, utilisation of the bicarbonate ion as a carbon source by algae can drive the reaction to the right and result in substantial accumulation of OH^-. Water with heavy algal growths often has pH values as high as 9 to 10.

Significance and Application of Alkalinity Data

The principal objection to alkaline water is the reactions that can occur between alkalinity and certain actions in the water. The resultant precipitate can foul pipes and other water-system appurtenances. Alkalinity is an important consideration in calculating the lime and soda-ash requirements in softening of water by precipitation methods. It is also a means of evaluating the buffering capacity of waste waters and sludges.

Determination of Alkalinity in Natural and Treated Waters (Titration Method)

In the natural and treated waters alkalinity determination, four quantities are commonly reported. These are phenolphthalein alkalinity, total alkalinity, carbonate alkalinity and total carbon dioxide.

Determination of Phenolphthalein Alkilinity (PA)

Put 50 mL or 100 mL of water sample into a clean conical flask. Add one drop of 0.05M sodium throsulphate solution to remove free residual chlorine if present. Add 2 drops of phenolphthalein indicator. If the solution remains coloured, then PA = 0. If the solution turns red, PA is present. Then titrate the solution with 0.02M HCl until the colour disappears.

The conversion obtained in this titration corresponds to:

$$OH^{-} + CO^{2-}_{3} + 2H^{+} \longrightarrow H_2O + HCO_{3}^{-}$$

Now,

$$\text{PA (as mg/L CaCO}_3) = \frac{V_P xMx100000}{mLsample}$$

where V_p = volume (mL) of the acid used

M = molarity of the acid

Determination of Total Alkalinity (TA)

Add two drops of mixed indicator (bromocresol green + methyl red solution) or of methyl orange indicator into 50 or 100 mL of water sample in a clean conical flask. Shake and titrate with 0.02M HCl acid until, at pH 4.6, the colour changes to pink (for mixed indicator) or from yellow to orange (for methyl orange indicator). The conversion for this titration corresponds to

$$OH^- + CO^{2-}_3 + HCO_3^- + 4H^+ \longrightarrow 3H_2O + 2CO_2$$

Now,

$$TA\ (\text{as mg/L } CaCO_3) = \frac{V_T xMx100000}{mLsample}$$

Where V_T = volume (mL) of acid used
M = molarity of acid used.

Determination of Hydroxide, Hydrogen Carbonate and Carbonate

To 50 or 100 mL of the water sample in a clean volumetric flask, add a slight excess of $BaCl_2$ solution to precipitate the carbonate. The HCO_3^- and OH^- are not affected; the HCO^-_3 is not also affected by phenolphthalein indicator. Add two drops of phenolphthalein indicator and titrate the OH^- in the water sample against 0.02M HCl until the solution is colourless. Let the volume of the acid used be V_H mL. Add two drops of the mixed indicator or methyl orange to the solution of the hydroxide/ acid titration. Shake and titrate the HCO_3^- to the end point with 0.02M HCl. Let the volume of acid used be V_{HC} mL.

To a fresh 50 or 100 mL water sample, add 2 drops of mixed indicator or methyl orange and shake. Titrate to the end point with 0.02M HCl. The volume of the acid used, V_T, is for the three species OH^-, HCO_3^- and CO_3^{2-}. Hence, the volume of acid used for CO_3^{2-} only, $V_C = [V_T - (V_H + V_{HC})]$ mL. The alkalinities can now be calculated as usual.

Determination of Total CO_2

Collect the water sample into a 500 mL flask leaving no air space. Take to the laboratory as soon as possible and siphon into a 100 mL graduated cylinder allowing overflow to occur. Add five to ten drops of phenolphthalein indicator. If the water sample turns red, the free-CO_2 is absent, but if the water remains colourless, titrate rapidly with a standard Na_2CO_3 or NaOH solution until pink colour persists for about 30 seconds.

$$\text{Alkalinity as mg/L } CO_2 = \frac{VxMx44000}{mLwatersample}$$

where V = volume (mL) of Na_2CO_3 OR NaOH used
M = molarity of the alkali (Na_2CO_3 or NaOH)
44000 = molar weight of CO_2 in mg.

3.1.4 Hardness

Hardness is defined as the concentration of multivalent metallic cations in water which determine the capacity of the water to precipitate soap. Depending on the anion with which it associates, hardness is classified as calcium and magnesium hardness, carbonate hardness and noncarbonate hardness and pseudo-hardness. Carbonate hardness is sensitive to heat and precipitates readily at high temperatures, e.g.

$$Ca(HCO_3)_2 \longrightarrow CaCO_3 + CO_2 + H_2O$$

Water hardness is due mainly to the presence of Ca^{2+} and Mg^{2+} in water. Other ions that may cause hardness include Fe^{2+}, Mn^{2+}, Sr^{2+} and Al^{3+}. The latter are found in much smaller quantities than Ca^{2+} and Mg^{2+}, and for all practical purposes, hardness may be represented by the sum of the Ca^{2+} and Mg^{2+} ions in a given water sample.

Impacts of Water Hardness

Soap consumption by hard waters represents an economic loss to the water user. Sodium soaps react with multivalent metallic cations to form a precipitate, thereby losing their surfactant properties.

$$2NaCO_2\ C_{17}H_{35} + Ca^{2+} \longrightarrow Ca^{2+}(CO_2\ C_{17}H_{35})_2 + 2Na^+$$

soap precipitate

Lathering does not occur until all of the hardness ions are precipitated. The precipitate formed adheres to surfaces of tubs, sinks, dishwashers and may stain clothing, dishes and other items. Residues of the precipitate may remain in the pores so that skin may feel rough and uncomfortable. Boiler scale, resulting from carbonate hardness, may cause considerable economic loss through fouling of water heaters and hot-water pipes. Changes in pH of the water distribution systems may also result in deposits of precipitates. Bicarbonates begin to convert to the less soluble carbonates at pH values above 9.0.

Magnesium hardness, particularly associated with the sulphate ion, has a laxative effect on persons unaccustomed to it. Magnesium concentrations of less than 50 mg/L are desirable in potable waters although many public water supplies exceed this amount.

Determination of Hardness

Hardness can be measured by using spectrophotometric techniques or chemical titration to determine the quantity of calcium and magnesium ions in a given water sample. Hardness can be measured directly by titration with ethylenediamine tetraacetic acid (EDTA) using Eriochrome Black T (EBT) as an indicator. The EBT reacts with the divalent metallic cations, forming a complex that is red in colour. The EDTA replaces the EBT in the complex, and when the replacement is complete, the solution changes from red to blue.

$$M^{n+} + EBT \longrightarrow M - EBT$$

$$\underset{\text{red}}{M - EBT} + EDTA \longrightarrow \underset{\text{blue}}{M - EDTA} + EBT$$

If 0.01M EDTA is used, 1.0 mL of the titrant measures 1.0 mg of hardness as $CaCO_3$.

Application of Hardness Data

Hardness of water is an important consideration in determining the suitability of a given water source for domestic and industrial uses. The environmental engineer uses it as a basis for recommending the need for softening processes and design types. Hardness may range from practically zero to several hundred or thousand parts per million. Although acceptability levels vary according to a consumer's acclimation to hardness, a generally accepted classification is as follows:

Soft water < 50 mg/L as $CaCO_3$
Moderately hard water 50 – 150 mg/L as $CaCO_3$
Hard water 150 – 300 mg/L as $CaCO_3$
Very hard water > 300 mg/L as $CaCO_3$

The Public Health Service Standards recommend a maximum of 500 mg/L of hardness in drinking water.

SELF ASSESSMENT EXERCISE 4

1(a) Briefly discuss the presence of alkalinity in natural waters.
(b) Of what benefits is alkalinity in natural water?

2. What effect does the (a) addition of CO_2, (b) removal of CO_2, have on the total alkalinity of water?
3. What is the difference between hardness caused by $Ca(HCO_3)_2$ and the one caused by $CaSO_4$ in water?

4.0 CONCLUSION

Water, a universal solvent, can be made good or bad under different conditions depending on its chemical parameters; its solvent capabilities are a direct function, more or less, of its chemical parameters.

5.0 SUMMARY

In this unit, you have learnt that:

pH of a given natural water sample may generally range from acidic to alkaline region.

Different organisms and chemical species respond to pH variations differently.

Acidity and alkalinity come from both natural and anthropogenic sources.

Chemical parameters of water determine, to a large extent, the purposes a given water supply may serve.

6.0 TUTOR-MARKED ASSIGNMENT

1. Discuss the principles involved in the EDTA titrimetric method of measuring hardness of water.
2. Calculate the phenolphthalein and total alkalinities of a 50 mL water sample that required 5.3 mL 0.02M HCl to reach the phenolphthalein end point and a total of 15.2 mL to reach the methyl orange end point.

7.0 REFERENCES/FURTHER READING

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UNIT 3 BIOCHEMICAL PARAMETERS IN WATER CHEMISTRY AND ANALYSIS

1.0 INTRODUCTION

Natural water courses contain many dissolved minerals and gases that interact chemically with one another in complex and varied ways. The interaction may alternately aid or obstruct natural purification processes of natural water systems. Strictly speaking, most of the chemical interactions that play a part in self-purification of water courses are biologically mediated. These chemical reactions are not spontaneous, but require an external source of energy for initiation.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- define dissolved oxygen (DO), biochemical oxygen demand (BOD) and chemical oxygen demand (COD)
- discuss the procedures of measuring DO, BOD and COD
- state the environmental significance of DO, BOD and COD data.

3.0 MAIN CONTENT

3.1 Biochemical Parameters Crucial to Water Chemistry and Analysis

3.1.1 Dissolved Oxygen (DO)

All the gases of the atmosphere are soluble in water to some degree. Both nitrogen and oxygen are classified as poorly soluble. Since they do not react with water chemically, their solubility is directly proportional to their partial pressures.

The solubility of oxygen in saline water is less than in fresh water. The solubility of atmospheric oxygen, in fresh waters ranges from 14.6 mg/L at 0^0C to about 7 mg/L at 35^0C under one atm of pressure. Dissolved oxygen is one of the most important constituents of natural water system. A stream must have a minimum of about two mg/L of dissolved oxygen to maintain higher life forms such as fish and other aquatic animal species. At least, four mg/L of dissolved oxygen is required for game fish and some species may require more.

The amount of oxygen found by determination in a sample of water at the time of collection is the dissolved oxygen.

Methods of DO Determination

The Winkler of iodometric method and its modifications are the standard volumetric procedures for determining dissolved oxygen. The test depends upon the fact that oxygen oxidises Mn^{2+} to a higher state of valence under alkaline conditions and that Mn in higher states of valence is capable of oxidising I^- to I_2 under acidic conditions. Thus, the amount of I_2 released is equivalent to the dissolved oxygen originally present. The iodine is measured with standard sodium thiosulphate solution and interpreted in terms of dissolved oxygen.

The Winkler Method (Unmodified)

The unmodified Winkler method is applicable only to relatively pure waters since the method is subject to interference from a great many substances. Certain oxidising agents such as nitrite (NO_2^-) and Fe^{3+} are capable of oxidising I^- to I_2 and produce results that are too high. Reducing agents such as Fe^{2+}, SO_3^{2-}, S^{2-} and polythionate, reduce I_2 to I^- and produce results that are too low.

The reactions involved are:
$Mn^{2+} + 20H^- \longrightarrow Mn(OH)_2(s)$ (white precipitate)
$Mn^{2+} + 20H^- + ½O_2 \longrightarrow MnO_2(s) + H_2O$
or $Mn(OH)_2 + ½O_2 \longrightarrow MnO_2(s) + H_2O$

If no oxygen is present, a white precipitate of $Mn(OH)_2$ forms when $MnSO_4$ and the alkali-iodide reagent (NaOH + KI) are added to the sample. But if oxygen is present, some of the Mn^{2+} is then oxidised to Mn^4 and precipitates as a brown hydrated oxide.

After shaking the sample for a time sufficient (at least 20 seconds) to allow all oxygen to react, the floc is allowed to settle; then H_2SO_4 is added. Under the low pH conditions, the MnO_2 OXIDISEs I^- to I_2.

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

I_2 is rather insoluble in water, but forms a complex with the excess I^- present to reversibly form the more soluble tri-iodate, thus preventing the escape of I_2 from solution

$$I_2 + I^- \rightleftarrows I_3^-$$

Stopper the sample and shake for 10 seconds or more. Titrate the samples (200 mL) with 0.0125M or 0.025N thiosulphate to the end point. The mL of thiosulphate used is interpreted directly in terms of mg/L of dissolved oxygen.

The Azide Modification of the Winkler Method

The nitrite ion is one of the most frequent interferences encountered in the DO determination of wastewaters, river waters and incubated biochemical oxygen demand (BOD) samples. It does not oxidise Mn^{2+} but does oxidise I^- to I_2 under acidic conditions. It is particularly troublesome because its reduced form, N_2O_2, is oxidised by oxygen, which enters the sample during the titration procedure and is converted to NO_2^- again, establishing a cyclic reaction that can lead to erroneously high results. The reactions involved are:

$$2NO_2^- + 2I^- + 4H^+ \longrightarrow I_3 + N_2O_2 + 2H_2O$$
$$N_2O_2 + ½O_2 + H_2O \longrightarrow 2NO_2^- + 2H^+$$

When interference from nitrite is present, it is impossible to obtain a permanent end point. As soon as the blue colour of the starch indicator is discharged, the nitrite formed will react with more I^- to produce I_2 and the blue colour of the starch indicator will return. To overcome this interference, sodium azide (NaN_3) in alkali-KI reagent is used. When H_2SO_4 acid is added, the following reactions occur and the NO_2^- is destroyed

$$NaN_3 + H^+ \longrightarrow HN_3 + Na^+$$
$$HN_3 + NO^-_2 + H^+ \longrightarrow N_2 + N_2O + H_2O$$

By this procedure, nitrite interference is eliminated and the method of determination retains the simplicity of the original Winkler procedure.

$$\text{mg/L DO} = \frac{16000xMxV}{\frac{V_2}{V_1}(V_2 - 2.0)}$$

where M = molarity of thiosulphate solution

V = Volume of thiosulphate (mL) used for titration

V_1 = Volume of the bottle with stopper in place

V_2 = Volume of aliquot taken for titration

If all the contents of the bottle are titrated, then mg/L DO = $\frac{16000xMxV}{(V_1 - 2.0)}$

3.1.2 Biochemical Oxygen Demand (BOD)

The amount of oxygen consumed during microbial utilisation of organics in a water sample is called the BOD. The greater the decomposable matter present, the greater the oxygen demand and the greater the BOD value.

Measuring the BOD

The BOD is measured by determining the oxygen consumed from a water sample placed in an air-tight container and kept in a controlled environment for a preselected period of time. In the standard test, a 300 mL BOD bottle is used and the sample is incubated for five days at 20^0C. Light must be excluded from the incubator to prevent algal growth that may produce oxygen in the bottle. Because the saturation concentration for oxygen in water at 20^0C is approximately nine mg/L, dilution of the sample with BOD-free, oxygen-saturated water is necessary to measure BOD values greater than just a few mg/L.

The BOD of a diluted sample is calculated by

$$BOD = \frac{DO_i - DO_f}{P}$$

where DO_i = the initial dissolved oxygen concentration (mg/L)

DO_f = the final dissolved oxygen concentration (mg/L).

P = the decimal fraction of the sample in the 300mL bottle.

Most natural waters and municipal wastewaters will have a population of microorganisms that will consume the organics. In sterile waters, microorganism must be added and the BOD of the material containing the organisms must be determined and subtracted from the total BOD of the mixture. The presence of toxic materials (such as residual chlorine, chloramines and copper) will invalidate the BOD results.

Determining BOD_5

The BOD of a wastewater was suspected to range from 50 to 200 mg/L. Three dilutions (5, 10 and 20 mL) of the wastewater were prepared to cover this range of 50 to 200 mg/L. First, the samples (5, 10 and 20 mL wastewater) were placed in three respective 300 mL standard BOD bottles. Each was then diluted to 300 mL with organic free, oxygen-saturated water. The initial dissolved oxygen was determined and the bottles tightly stoppered and placed in the incubator at 20^0C for five days, after which the dissolved oxygen was again determined. The values obtained are as computed in the table below.

Wastewater (mL)	DO_i mg/L	DO_5 mg/L	O_2 used mg/L	P	BOD_5 mg/L
5	9.2	6.9	2.3	$\frac{5}{300} = 0.0167$	138
10	9.1	4.4	4.7	$\frac{10}{300} = 0.033$	142
20	8.9	1.5	7.4	$\frac{20}{300} = 0.067$	110

Since the final DO is less than 2.0 mg/L, the third BOD_5 value of 110 mg/L can be disregarded. Thus, the average BOD_5 of the waste water is ½ (138+142) mg/L i.e. 140 mg/L.

Application of BOD Data

BOD is the major criterion used in stream pollution control where organic loading must be restricted to maintain desired dissolved-oxygen levels. The determination is used in studies to measure the purification capacity of streams. It helps regulatory authorities in checking the quality of effluent discharged to streams. Information concerning the BOD of wastes is an important consideration in the design of treatment facilities. After treatment plants are placed in operation, the test is used to evaluate the efficiency of various processes.

3.1.3 Chemical Oxygen Demand

COD is a measure of the total amount of oxygen required for complete oxidation to CO_2 and H_2O of organic matter present in a sample of wastewater or effluent. COD is a rapidly measured parameter used to determine the pollution strength of domestic and industrial waste.

The determination is achieved by using strong oxidising agents under acidic conditions. Excess amount of the oxidising agent is used. Oxygen is released, some is used to oxidise an equivalent amount of the waste to CO_2 and the unused is determined by titration with a reducing agent of known strength. The amount used for the oxidation of the wastes is known by difference. Potassium dichromate, $K_2Cr_2O_7$, is the most suitable oxidising agent. The reaction is:

$$Cr_2O^{2-}{}_7 + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$

or $$Cr_2O_7^{2-} + 8H^+ \longrightarrow 2Cr^{3+} + 4H_2O + 3(O).$$

Ferrous ion is an excellent reducing agent for dichromate. The reaction is:

$$Cr_2O^{2-}{}_7 + 6Fe^{2+} + 14H^+ \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O.$$

Ferroin (1, 10 – Phenanthroline monohydrate + iron (II) sulphate heptahydrate) is an excellent indicator for this purpose. It gives a very sharp brown colour change that is easily detected. Calculation of COD is made from the formula:

$$\text{COD (mg/L)} = \frac{(V_b - V_s)xMx16000}{mLsample}$$

or $$\text{COD (mg/L)} = \frac{(V_b - V_s)xNx16000}{mLsample}$$

where V_b = mL ferrous ammonium sulphate used for blank
V_s = mL ferrous ammonium sulphate used for sample
M = molarity of ferrous ammonium sulphate
N = normality of ferrous ammonium sulphate

Inorganic Interferences

Among the reduced inorganic ions that can be oxidised under the conditions of COD test, Cl^- causes the most serious problems because it is usually present in high concentrations in most wastewaters. Its presence can cause erroneously high results to be obtained.

$$6Cl^- + Cr_2O_7^{2-} + 14H^+ \longrightarrow 3Cl_2 + 2Cr^{3+} + 7H_2O.$$

However, this interference can be eliminated by the addition of mercuric sulphate to the sample prior to the addition of other reagents. The mercuric ion combines with the chloride ion to form a poorly ionised mercuric chloride complex.

$$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2$$

Nitrite ion, NO_2^-, is another source of interference capable of being oxidised to nitrate in the pressure of dichromate. This interference can be overcomes by the additioin of sulfamic acid to the dichromate solution. Nitrite ion, with other ones such as ferrous and sulphide ions that can also cause interference seldom occur to any significant amounts in waste or natural waters.

Applications of COD Data

In conjunction with the BOD test, the COD test is helpful in indicating toxic conditions and the presence of biologically resistant organic substances. The test is widely used in the operation of treatment facilities because of the speed with which results can be obtained.

SELF ASSESSMENT EXERCISE

1. How does azide eliminate the nitrite interference in the iodometric method for determining dissolved oxygen?
2. List two requirements that must be complied with in order to obtain reliable BOD data.
3. List two different applications of COD data.

4.0 CONCLUSION

Dissolved oxygen, biochemical oxygen demand and chemical oxygen demand are important parameters that help environmental scientists and engineers to make important decisions about how to handle the treatment of wastewater generally. The data generated from measuring DO, BOD and COD also aids decision making about the use of a particular water source for municipal water supply purpose. The data also facilitates the design of plants for wastewater treatment.

5.0 SUMMARY

In this unit, you have learnt that:

all the atmosphere gases can dissolve in water to some extent;

DO, BOD AND COD are informative parameters when determined to have an understanding of wastewater quality;

there can be chemical or organic species that are capable of interfering with the results obtained in DO, BOD and COD determinations.

6.0 TUTOR-MARKED ASSIGNMENT

(a) List four inorganic species that interfere with COD analysis.
(b) Which of the species is the most prevalent and how do you handle the interference caused by this particular species?

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UNIT 4 ANIONS AND OTHER CONSTITUENTS OF CONCERN IN WATER CHEMISTRY AND ANALYSIS

1.0 INTRODUCTION

Depending on their levels in a given water source and the use for which the water is intended, anions like chloride (Cl^-), fluoride (F^-), sulphate (SO_4^{2-}) and phosphate (PO_4^{3-}) and residual chlorine, nitrogen, iron and manganese, oil and grease, and volatile acids, can all constitute sources of worries. It is true that some of them occur naturally in the environmental compartments, but they can pose stressful conditions on humans and the biota whenever their natural background levels are exceeded in water bodies.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

- list some common anions usually found in water bodies and state their health and environmental implications in water supplies
- discuss the basic relevant chemistry of the anions and other water contaminants such as nitrogen and residual chlorine in water
- list relevant methods that can be used to determine the presence of Cl^-, F^-, SO_4^{2-} and PO_4^{3-} in a waste water sample.

3.0 MAIN CONTENT

3.1 Common Anions in Natural and Wastewaters

3.1.1 Chloride (Cl^-)

Chloride occurs in all natural waters in varying concentrations. The chloride content normally increases as the mineral content increases. Upland and mountain supplies are usually quite low in chloride, whereas river and ground waters usually have a considerable amount. Chloride levels in sea and ocean waters are very high.

Chloride content in a water sample can be determined by Mohr Method, Mercuric Nitrate Method and Ferricyanide Method.

In reasonable concentrations, chloride is not harmful to humans. At concentrations above 250 mg/L, it gives a salty taste to water, which is objectionable to many people. The USEPA Secondary Standard for chloride in drinking water is 250 mg/L, the same value contained in the WHO guidelines. Evapotransportation tends to increase the chloride and salinity at the root zone of irrigated plants, making it difficult for crops to take up water due to osmotic pressure differences. As such, chloride and total salinity concentrations at or below the drinking water standards are normally specified for waters used to irrigate salt-sensitive crops.

3.1.2 Fluoride (F^-)

The monitoring of the presence and level of fluoride ion in water requires greater vigilant efforts than is given to chloride ion. This is because of the health implications of fluoride ion especially in humans. Approximately one mg/L of fluoride ion is desirable in public waters for optimal dental health. At decreasing levels, dental caries becomes a serious problem, and at increasing levels, dental fluorosis (mottled enamel) becomes a problem. In the recent times, a higher level of fluoride is being implicated for liver problems as well.

The principal forms in which fluoride is added to public water supplies are sodium fluoride (NaF), calcium fluoride (CaF_2), hydrogen fluoride (HF), sodium silicofluoride (Na_2SiF_6), hydrofluosilicic acid (H_2SiF_6) and ammonium silicofluoride [$(NH_4)_2SiF_6$]. All these compounds dissociate in water to yield fluoride ion. At the concentrations of about one mg/L involved in water treatment, hydrolysis of the fluosilicate ion is essentially complete.

$SiF_6^{2-} + 3H_2O \rightleftharpoons 6F^- + 6H^+ + SiO_3^{2-}$

On this basis, the fluoride in silicofluorides can be determined by any method that is sensitive to fluoride ion e.g. the electrode method, colorimetric procedures and ion chromatography. Excess fluoride in water can be removed by passing of water through various types of defluoridation media such as tricalcium phosphate, bone char and bone meal. Activated alumina was found to accomplish fluoride removal by a combination of ion exchange and sorption. Fluoride can also be removed during lime softening through co-precipitation with magnesium hydroxide or by alum coagulation.

3.1.3 Sulphate (SO_4^{2-})

Sulphate ion is one of the major anions occurring in natural waters. It has a cathartic effect upon humans when it is presents in excessive amounts in public water supplies. The USEPA Secondary Standard for sulphate is 250 mg/L in waters intended for human consumption. Sulphate is important in both public and industrial water supplies because of the tendency of waters containing appreciable amounts to form hard scales in boilers and heat exchangers.

Sulphate is of considerable concern because it is indirectly responsible for serious problems of odour and sewer-corrosion resulting from the reduction of SO_4^{2-} to H_2S under anaerobic conditions.

$SO_4^{2-} + \text{organic matter} \xrightarrow{\text{bacteria}} S^{2-} + H_2O + CO_2$
$S^{2-} + H^+ \rightleftharpoons HS^-$
$HS^- + H^+ \rightleftharpoons H_2S$

Bacteria of the genus *Thiobacillus* are ubiquitous in nature and are capable of sulphide oxidation to sulphuric acid at a pH as low as 2 under the aerobic conditions normally prevailing in sewers.

$H_2S + 2O_2 \xrightarrow{\text{bacteria}} H_2SO_4$

Being a strong acid, H_2SO_4 attacks the concrete in the sewer. H_2SO_4 formation in this way is particularly serious in the crown, where drainage is at a minimum. Drainage running through abandoned coal mines and other exploited mineral-bearing deposits can be a source of high sulphate concentrations as well as low pH conditions in the streams within the vicinity. The sulphide minerals are oxidised through bacterial and chemical actions to produce sulphuric acid

$$2FeS_2 + 7O_2 + 2H_2O \xrightarrow{\text{bacteria}} 2Fe^{2+} + 4SO_4^{2-} + 4H^+$$

The lowered pH and high iron content procedure added harm to water quality. Combustion of fossil fuels leads to formation of gaseous oxides of sulphure which hydrolyse when dissolved in rainwater to form sulphuric acid. Analysis of SO_4^{2-} in a sample of wastewater can be carried out using gravimetric, turbidimetric and automated methylthymol blue analysis.

3.1.4 Phosphate (PO_4^{3-})

The inorganic compounds of phosphorus of significance in environmental chemistry are the phosphates or their molecularly dehydrated forms (polyphosphates) or condensed phosphates. Organically bound phosphorus is usually a minor consideration. Phosphorus compounds commonly encountered in environmental science generally are **orthophosphates** such as trisodium phosphate (Na_3PO_4), disodium phosphate (Na_2HPO_4), monosodium phosphate ((NaH_2PO_4) and diammonium phosphate (($(NH_4)_2HPO_4$), and **polyphosphates** such as sodium hexametaphosphate ($Na_3(PO_3)_6$), sodium tripolyphosphate ($Na_5P_3O_{10}$) and tetrasodium pyrophosphate ($Na_4P_2O_7$).

Polyphosphates are used in some public water supplies as a means of controlling corrosion. They are also used in some softened waters for stabilisation of calcium carbonate to eliminate the need for recarbonation. Both nitrogen and phosphorus are essential for the growth of algae and cyanobacteria. Limitation in amounts of these elements is usually the factor that controls their rate of growth. Where both nitrogen and phosphorus are plenty, algal blooms occur, which may produce a variety of nuisance conditions. The critical level for inorganic phosphorus in water has been put at approximately 0.005mg/L (5 µg/L).

Phosphorus occurring as orthophosphate (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-},PO_4^{3-}) can be measured quantitatively by gravimetric, volumetric or colorimetric methods. Polyphosphates are first converted to orthophosphates by boiling acidified sample for 90 minutes or more. Organic phosphorus is first digested before the phosphorus measurement is carried out.

SELF ASSESSMENT EXERCISE 1

Discuss briefly the effects of excess amounts of chloride fluoride, sulphate and phosphate ions in a water supply.

3.1.5 Residual Chlorine

The prime purpose of disinfecting public water supplies and wastewater effluents is to prevent the spread of water-borne diseases. The practice of disinfection with chlorine has become so widespread and generally accepted as if no problem is associated with the practice.

In more recent years, chlorination has been found to produce trichalomethanes and other organics of health concern. Thus, the use of alternative disinfectants, such as chloromines, chlorine dioxide, UV radiation and ozone, which do not cause this particular problem, is increasing. One important limitation is that chlorination alone is not sufficiently protective against some disease-causing protozoa such as *Giardia lamblia* and *Cryptosporidium paevum;* good filteration is also required. Chlorine is used to disinfect water in the form of free chlorine or as hypochlorite. In either form, it acts as a potent oxidizing agent. Chlorine combines with water to form hypchlorous and hydrochloric acids. The hydrochlorous acid formed is a weak acid and is very poorly dissociated at pH < 6.

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$
$$HOCl \rightleftharpoons H^+ + OCl^-$$

The nature of the reactions is dominated by the free Cl_2 with the resultant development of obnoxious compounds such as tri-chloramine, NCl_3. to minimise these effects, high-quality water is often used as chlorinator feed water. Hypochlorite is used in the form of solutions of sodium hypochlorites and the dry form of calcium hypochlorite. Solution of Na hypochlorite is popular where large amounts are necessary such as in wastewater disinfection, while Ca hypochlorite is popular where limited amounts are required or intermittent usage is dictated. Both compounds ionise in water to yield hypochlorite ion, OCl^-. Free chlorine tends to decrease the pH, whereas hypochlorite tends to increase the pH.

$$NaOCl \longrightarrow Na^+ + OCl^-$$
$$Ca(OCl)_2 \longrightarrow Ca^{2+} + 2OCl^-$$

Reactions of Chlorine and Hypochlorous acid with Substances in Water

Reactions with NH_3: Ammonia reacts with chlorine or hypochlorous acid to form
monochoramine, dichloramine and trichloromaine depending on the relative amounts of each, and to some extent, on the pH.

$NH_3 + HOCl \longrightarrow NH_2Cl + H_2O$

Monochloramine

$NH_2Cl + HOCl \longrightarrow NHCl_2 + H_2O$

Dichloramine

$NHCl_2 + HOCl \longrightarrow NCl_3 + H_2O$

Trichloramine

In water chemistry, chlorine, hypochlorous acid and hypochlorite ion are called free chlorine residuals while chloramines are called combined chlorine residuals.

Reactions with reducing agents: Chlorine combines with a wide variety of reducing agents such as H_2S, Fe^{2+}, Mn^{2+} and NO_2^-. Their demand for chlorine must be satisfied before chlorine becomes available to accomplish disinfection.

$$Cl_2 + H_2S \longrightarrow 2HCl + S.$$

Reactions with unsaturated organic compounds: Organic compounds that possess unsaturated linkages will add hypochlorous acid and increase the chlorine demand

$$H_2C{=}CH_2 + HOCl \longrightarrow H_2C(OH)CH_2(Cl)$$

Reactions with other halogens: Chlorine also reacts with other halogens in water e.g. hypochlorous acid reacts with bromide to form hypobromous acid.

$$HOCl + Br^- \longrightarrow HOBr + Cl^-$$

Reactions with phenols: Chlorine reacts with phenols to produce mono-, di-, or trichlorophenols, which can impart tastes and odours to waters.

Reactions with humic substances: Chlorine and hypobromous acid react with humic substances present in most halogenated products including **trihalomethanes** (THMs) such as chloroform, bromodichloromethane, dibromochloromethane and bromoform, and **haloacetic acids**. The THMs are suspected human carcinogens which are regulated in drinking water with a sum total maximum contaminant level (MCL) of 80 µg/L.

SELF ASSESSMENT EXERCISE 2

Explain the observation: “Free chlorine, used as a water supply disinfectant, tends to decrease the pH, whereas hypochlorite tends to increase the pH". Equations of the chemical reactions involved are important.

3.1.6 Nitrogen

The compounds of nitrogen are of great importance in water resources, in the atmosphere and in the life processes of all plants and animals. Nitrogen can exist in seven oxidation states, and all of them are of environmental interest: NH_3 (-3); N_2 (0); N_2O (+1); NO (+2); N_2O_3 (+3); NO_2 (+4) and N_2O_5 (+5). Three of these (NH_3, N_2O_3 and N_2O_5) combine with water to form inorganic ionised species (NH_4^+, NO_2^- and NO_3^-) that can reach high concentrations,

$$NH_2 + H_2O \longrightarrow NH_4^+ + OH^-$$
$$N_2O_3 + H_2O \longrightarrow 2H^+ + 2NO_2^-$$
$$N_2O_5 + H_2O \longrightarrow 2H^+ + 2NO_3^-$$

The respective water-soluble species formed: ammonium, nitrite and nitrate ions, are of historical environmental concern in water. Their concentrations in drinking water supplies and surface waters have been regulated for decades.

In water, most of the nitrogen is originally present in the form of organic (protein) nitrogen and ammonia. As time progresses, the organic nitrogen is gradually converted to ammonia nitrogen, and later on, if aerobic conditions are present, oxidation of ammonia to nitrite and nitrate occurs. Thus, waters that contained mostly organics and ammonia nitrogen were considered to have been recently polluted and therefore of great potential danger. Waters in which most of the nitrogen was in the form of nitrate were considered to have been polluted a long time previously and therefore offered little threat to the public health. Waters with appreciable amounts of nitrite were of highly questionable character.

Water with high nitrate content often caused methaemoglobinaemia in infants as a result of the interaction of nitrite with haemoglobin; the nitrite being formed from nitrate reduction in the digestive system. The USEPA has set a MCL requiring that the nitrate-nitrogen concentration not exceed 10 mg/L and the nitrite-nitrogen concentration not exceed 1 mg/L in public water supplies. Nitrite can also interact with amines enzymatically or chemically, especially when chlorinating for disinfection, to form nitrosamines, which are strong carcinogens.

The formation of N- nitrosodimethylamine (NDMA) by these processes has been found to result during wastewater treatment and has become an issue recently in wastewater reuse projects and contaminated groundwater supplies.

3.1.7 Iron and Manganese in Water

Both iron and manganese create serious problems in public water supplies. The problems are most extensive and critical with underground waters, but difficulties are encountered at certain seasons of the year in waters drawn from some rivers and some impounded surface supplies. Why some underground supplies are relatively free of iron and manganese and others contain so much has been a difficult explanation when viewed solely from the view point of inorganic chemistry alone. Changes in environmental conditions brought about by biological reactions, are major considerations.

It is important to consider how iron and manganese are converted to soluble forms and gain access into water since both of them are present in insoluble forms in significant amounts in nearly all soils. Iron exists in soil and minerals mainly as insoluble ferric oxides and iron sulphide (pyrite). It occurs in some areas also as ferrous carbonate (siderite) which is only very slightly soluble. Since ground waters usually contain significant amounts of CO_2, appreciable amounts of ferrous carbonate may be dissolved in a manner similar to that of calcium and magnesium carbonates dissolution.

$$FeCO_3(s) + CO_2 + H_2O \longrightarrow Fe^{2+} + 2HCO_3^-.$$

Dissolution of measurable amounts of iron from insoluble solid ferric compounds does not occur, even in the presence of appreciate amounts of CO_2, as long as dissolved oxygen is present. Under reducing (anaerobic) conditions, however, the ferric iron is reduced to ferrous iron, and solution occurs without difficulty.

Manganese exists in the soil principally as manganese dioxide, which is very insoluble in water containing carbon dioxide. Under anaerobic conditions, Mn in the dioxide form is reduced from an oxidation state of IV to II, and solution occurs, as with ferric oxides.

When oxygen-bearing water is injected into the ground for recharge of the groundwater aquifer, it is sometimes noted that the soluble iron content of the water increases. This observation seems to contradict the need for anaerobic conditions. The explanation is that the oxygen is consumed through the oxidation of insoluble pyrite (FeS_2), leading to anaerobic conditions and the formation of soluble iron sulphate. Only under anaerobic conditions are the soluble forms of iron and manganese (Fe(II) and Mn(II)) thermodynamically stable.

$$2FeS_2 + 7O_2 + 2H_2O \longrightarrow 2Fe^{2+} + 4SO^{2-}{}_4 + 4H^+.$$

As far as it is known, humans suffer no harmful effects from drinking waters containing iron and manganese. Such waters, when exposed to the air become turbid and highly unacceptable from an aesthetic viewpoint, owing to the oxidation of Fe(II) and Mn(II) to Fe(III) and Mn(IV) respectively. Both iron and manganese interfere with laundering operations, impart objectionable stains to plumbing fixtures and cause difficulties in distribution systems by supporting of iron bacteria. Iron also imparts a taste to water which is detectable at very low concentrations. For these reasons, the USEPA secondary standards for iron and manganese in public water supplies are 0.3 mg/L and 0.05 mg/L respectively.

SELF ASSESSMENT EXERCISE 3

1(a) In what forms does nitrogen normally occur in natural water?
(b) What is the importance of nitrogen analysis in water pollution control?

2. What is the environmental significance of iron and manganese in water supplies?
3. Discus briefly how iron and manganese get into underground water supplies.

3.1.8 Oil and Grease in Water

The oil and grease content of domestic and certain industrial wastes, and sludge, is an important consideration in the handling and treatment of these materials for ultimate disposal. Oil and grease have poor solubility in water and do separate from the aqueous phase. This characteristic of oil and grease complicates the transportation of wastes though pipeline, their destruction in biological treatment units and their eventual disposal into the receiving streams.

Very few processing plants have provisions for the separate disposal of waters from meat-packing industry and restaurants to scavengers or by incineration. As a result, the oil and grease which separate as scum, in primary settling tanks are normally transferred with the settled solids to disposal units. In sludge digestion tanks, oil and grease tend to separate and float on the surface to form dense scum layers. Scum problems have been particularly severe where high-grease-content wastes have been admitted to public sewer systems. The vacuum filtration of sludge is also complicated by high grease content.

Not all the oil and grease is removed from the sewage by primary settling units. Appreciable amounts remain in the clarified wastewater in a finely divided emulsified form. During subsequent biological attack in secondary treatment units or in the receiving stream, the emulsifying agents are usually destroyed, and the finely divided oil and grease particles become free to coalesce into grease particles that separate from the water. In activated-sludge plants, the grease often accumulates into “grease balls” that give an unsightly appearance to the surface of final settling tanks. Both trickling filters and the activated sludge process are adversely affected by unreasonable amounts of grease that seems to coat the biological solids sufficiently to interfere with oxygen transfer from the liquid to the interior of the living cells. This is sometimes described as a “smothering” action.

Spills of crude and refined petroleum from ships used for their transport have resulted in loss of fish, mammals and waterfowl, and the fouling of beaches. Also, oil and grease leaking from automobiles result in high concentrations in storm runoff from streets, contaminating water ways into which storm water drains.

3.1.9 Volatile Acids in Water

The volatile-acids determination is widely used in the control of anaerobic waste treatment processes. In the biochemical decomposition of organic matter that occurs, facultative and anaerobic bacteria of wide variety hydrolyse and convert the complex materials to low-molecular-weight compounds. Among the low-molecular-weight compounds formed are the short-chain fatty acids such as acetic, propionic, butyric, and to a less extent, isobutyric, valeric, isovaleric and caproic, are important components. These low-molecular-weight fatty acids are termed **volatile acids** because they can be distilled at atmospheric pressure.

An accumulation of volatile acids can have a disastrous effect upon anaerobic treatment if the buffering capacity of the system is exceeded and the pH falls to unfavourable levels.

In anaerobic digestion, units that are operating in a stabilised condition, three groups of bacteria work in harmony to accomplish the destruction of organic matter. Following hydrolysis and fermentation to complex acids, the acidogenic and dehydrogenating organisms carry the degradation to acetic acid and hydrogen. Then the methanogenic bacteria complete the conversion into methane and carbon dioxide. When a sufficient population of methanogenic bacteria is present and environmental conditions are favourable, they utilise the end products produced by acidogenic bacteria as fast as they are formed. As a result, acids do not accumulate beyond the neutralising abilities of the natural buffers present, and the pH remains in a favourable range for the methane bacteria. Under such conditions, the volatile acid content of digesting sludges, or anaerobically treated wastewaters usually runs in the range of 50 to 250 mg/L.

Untreated municipal wastewater sludges and many industrial wastewaters have a relatively low buffering capacity, and when they are allowed to ferment anaerobically, volatile acids are produced so much faster than the few methanogenetic bacteria present can consume them that the buffers are soon spent and free acids exist to depress the pH. At pH values below 6.5, methanogenetic bacteria are seriously inhibited, but many fermentative and acidogenic bacteria are not until pH levels fall to about five. Under such unbalanced conditions, the volatile-acids concentration continues to increase to levels of 2000 to 6000mg/L or more, depending upon the solids content of the sludge.

SELF ASSESSMENT EXERCISE 4

1. List four important sources that contribute oil and grease to municipal wastewaters.
2. Name five difficulties that could arise in the process of treating wastewaters with high levels of oil and grease.
3. (a) What is meant by “volatile acids”?
   (b) Indicate (i) what are the most prevalent volatile acids formed during anaerobic treatment, (ii) the general classes of organic compounds from which each of the most prevalent volatile acids result.

4.0 CONCLUSION

Water treatment must take into consideration every aspect of physicochemical characteristics including the chloride, fluoride, sulphate and phosphate content. The residual chlorine and chlorine demand, nitrogen content, levels of iron and manganese, oil and grease, and volatile acids in water all need to be assessed and be ensured to conform to the MCL of either USEPA or WHO. Until this is done, the safety of a water source is doubtful, to say the least.

5.0 SUMMARY

In this unit, you have learnt that:

i. the levels of Cl^-, F^-, $SO^{2-}{}_4$ and $PO^{2-}{}_4$ in a given water sample can be part of the indices used to assess the quality of the water.

ii. residual chlorine in water can lead to the formation such compounds known to be human carcinogens e.g. chloroform.
iii. the presence of nitrogenous compound can directly or indirectly affect a water quality and the uses to which the water can be put.
iv. metals like Fe and Mn can still find their ways into the groundwater even when the metals were not originally found in soluble forms.
v. oil and grease and volatile acids can constitute very serious problems at various stages of waste water treatment particularly.

6.0 TUTOR-MARKED ASSIGNMENT

Discuss one analytical method in each case for measuring the concentration of (i) Mn and (ii) Fe, in water supplies.

7.0 REFERENCES/FURTHER READING

Sawyer, C.; McCarty, P. & Parkin, G. (2006). *Chemistry for Environmental Engineering and Science* (5th ed.). New Delhi: Tata McGraw-Hill Put. Coy. Ltd.

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MODULE 5 CHEMICAL AND PHYSICAL INSTRUMENTATION IN ENVIRONMENTAL SCIENCES

UNIT 1 CHEMICAL INSTRUMENTATION IN ENVIRONMENTAL SCIENCES

CONTENTS

1.0 INTRODUCTION

The methods of “wet chemistry” such as titrimetric analysis and gravimetry still have an important role in modern analytical and environmental chemistry. There are many areas in which titrimetric and gravimetric procedures are quite invaluable. The advantages of titrimetric procedures include:

The precision (0.1percent) is better than most instrumental methods.

Methods are usually superior to instrumental techniques for major component analysis.

When the sample throughout is small e.g. for one-off analysis, simple titrations are often preferable.

Unlike instrumental methods, the instrument does not require constant recalibration.

Methods are relatively inexpensive with low unit costs per determination.

They are often used to calibrate and/or validate routine analysis using instruments.

The methods can be automated.

The most significant disadvantage of titrimetric procedures is that, they are normally less, sensitive and frequently less selective than instrumental methods. Also, when a large number of similar determinations are required, instrumental methods are usually much quicker and often cheaper than the more labour intensive titrimetric methods.

Like titrimetric analysis, the advantages offered by gravimetric procedure are many including the following:

It is accurate and precise when using modern analytical balances.

Possible sources of error are readily checked, since filtration can be tested for completeness of precipitation and precipitates may be examined for the presence of impurities.

It involves direct measurement without any form of calibration being required.

Determinations can be carried out with relatively inexpensive apparatus; the most expensive items are a muffle finance and sometimes platinum crucibles.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

list some applications of titrimetric and gravimetric analysis involving “wet chemistry”

explain how to carry out the analysis of such species as Cl^-, F^-, SO_4^{2-}, PO_4^{3-} e.t.c. in an environmental sample

state some precautionary measures needed to achieve both accuracy and precision in the use of titrimetric and gravimetric analyses in the determination of a given chemical species.

3.0 MAIN CONTENT

3.1 Examples of “Wet Chemistry” Analysis.

3.2 Determination of Chloride (Cl^-)

3.2.1 Mohr Method (Argentometric Procedure)

The Mohr method employs 0.I M solution of silver nitrate, $AgNO_3$, for titration. In the titration the chloride ion is precipitated as white silver chloride, AgCl.

$$Ag^+ + Cl^- \rightleftharpoons AgCl(s) \qquad (K_{sp} = 3 \times 10^{-10}).$$

The end point cannot be detected visually unless an indicator capable of demonstrating the presence of excess Ag^+ is present. The indicator normally used is **potassium chromate**, which supplies chromate ion, CrO_4^{2-}. As the concentration of Cl^- ions approaches extinction, the Ag^+ concentration increases to a level at which the solubility product of silver chromate is exceeded and it begins to form a reddish-brown precipitate.

$$2Ag^+ + CrO_4^{2-} \rightleftharpoons Ag_2CrO_4(s) \quad (K_{sp} = 5 \times 10^{-12}).$$

This is taken as evidence that all the chloride has been precipitated. Several **precautions** are to be observed in this determination if accurate results are to be obtained.

1. A uniform sample size, preferably 100 mL, must be used to that ionic concentrations needed to indicate the end point will be constant.
2. The pH must be in the range of 7 to 8 because Ag^+ is precipitated as AgOH(s) at high pH levels and the CrO_4^{2-} is converted to $Cr_2O_7^{2-}$ at low pH levels.
3. A definite amount of indicator must be used to provide a certain concentration of CrO_4^{2}; otherwise $Ag_2CrO_4(s)$ may form too soon or not soon enough.

The calculation for chloride may be simplified as

$$Cl^- \text{ (in mg/L)} = \frac{(\text{mL}AgNO_3\text{-blank}) \times 0.1 \times 35.45 \times 1000}{\text{mL sample}}$$

3.2.2 Mercuric Nitrate Method

The mercuric nitrate method is less subjected to interferences than the Mohr method because the titration is performed on a sample whose pH is adjusted to a value of about 2.5. Under these conditions, Hg^{2+} ion combines with Cl^- to form the $HgCl_2$ complex which is soluble, therefore making end-point detection easier than with the Mohr procedure. As the Cl^- concentration approaches zero, the Hg^{2+} concentration increases to a level where it becomes significant as the mercuric nitrate is added.

$$Hg^{2+} + 2Cl^- \rightleftharpoons HgCl_2(aq) \quad (\beta_2 = 1.7 \times 10^{13}).$$

Diphenylcarbazone is the indicator used to show the presence of excess Hg^{2+} ions. It combines with them to form a distinct purple colour. A blank correction is needed. Nitric acid is added to the indicator to reduce the sample pH to 2.5, a value that must be maintained uniformly in unknown samples, standards and blanks. A pH indicator, xylene cyanol FF, which is blue-green at pH 2.5 is also included and improves the end point by masking the pale colour developed by diphenylcarbazone during the titration. Using 0.1M $Hg(NO_3)_2$ solution makes the calculation similar to that of Mohr's method.

3.2.3 Ferricyanide Method

This is an automated colourimetric procedure. Mercuric ion contained in the mercuric thiocyanate titrant forms a soluble complex with chloride. This releases the thiocyanate to react with ferric ion, which is also added, to form intensely red ferric thiocyanate, the intensity of which is proportional to the chloride concentration.

SELF ASSESSMENT EXERCISE 1

1. Explain why a blank correction must be applied to the titration values in both the Mohr and mercuric nitrate methods of chloride determination.
2. Would the analytical results by the Mohr method for chloride be higher, lower or the same as the true value of an excess if indicator were accidentally added to the sample? Why?
3. What purpose is served by the nitric acid added to the indicator in the mercuric nitrate method of chloride determination?

3.3 Determination of Sulphate, SO_4^{2-}.

3.3.1 Gravimetric Method

The gravimetric method yields accurate results. The quantitative aspects of this method depend on the fact that barium ion combines with sulphate ion to form poorly soluble barium sulphate as follows:

$$Ba^{2+} + SO_4^{2-} \rightleftharpoons BaSO_4(s), Ksp = 1 \times 10^{-10}$$

The precipitate is normally accomplished by adding $BaCl_2$ solution in slight excess to samples of water acidified with HCl acid and kept near the boiling point. The samples are acidified to eliminate the possibility of precipitation of $BaCO_3$, which might occur in highly alkaline waters maintained near the boiling temperature. Excess $BaCl_2$ solution is used to produce sufficient common ion to precipitate sulphate ion as completely as possible.

Because of the great insolubility of $BaSO_4$, there is a considerable tendency for much of the precipitate to form in a colloidal condition that cannot be removed by ordinary filtration process. Digestion of the samples at temperatures near the boiling point for a few hours usually results in a transfer of the colloidal to crystalline forms. Filtration can then be accomplished. The crystals of $BaSO_4$ are quite small. Hence, a special grade of filter paper suitable for sulphate determinations should be used.

Having transferred all the sulphate crystals quantitatively to the filter paper, washing with distilled water must be sufficiently done to remove all excess $BaCl_2$ and other salts. Weigh the sulphate precipitate formed by subjecting the filter paper to a complete combustion or by drying the filter paper and the sulphate to a constant weight and then subtracting the weight of the filter paper (previously weighed) from the total to give the weight of the sulphate precipitate.

3.3.2 Turbidimetric Procedure

The turbidimetric method of measuring sulphate is based upon the fact that $BaSO_4$ formed following $BaCl_2$ solution addition to a sample tends to precipitate in a colloidal form. This tendency is enhanced in the presence of an acidic buffer solution containing magnesium chloride, potassium nitrate, sodium acetate and acetic acid.

By standardising the procedure used to produce the colloidal suspension of $BaSO_4$, it is possible to obtain quantitative and acceptable results. Sample with sulphate concentrations greater than 10 mg/L can be analysed by taking smaller portions and diluting them to the recommended 50 mL sample size. At least, one standard sample of sulphate should be included in each set of samples to verify that conditions used in the test are comparable to those used in establishing the calibration curve.

3.3.3 Automated Methylthymol Blue Method

Here, a continuous-flow analytical instrument is used in which chemicals are automatically added to and mixed with samples in a flowing stream. After a standard time passes to allow for chemical reaction to occur, the sample enters a cell where measurement of colour or turbidity is made for quantification.

In the automated procedure for sulphate, $BaCl_2$ is first automatically added to the samples of low pH to form a $BaSO_4$ precipitate; the sample pH is then adjusted to about 10. Methylthymol blue reagent is then added and combines with the excess barium added to form a blue chelate. The uncompleted methylthymol blue remaining forms a grey colour which is automatically measured.

The amount of sulphate in the original sample is based on the instrument response that is obtained. The instrument must be calibrated with standard sulphate solution, the addition of chemicals must be precise and interferences must be absent. The method of automated approach helps to accomplish all these.

3.4 Determination of Fluoride (F^-)

The concentration of fluoride in drinking or wastewater may be determined indirectly by its ability to form a complex with Zirconium. In the presence of the dye SPADNS, solutions of Zirconium form a reddish coloured compound, called a "lake", that absorbs at 570 nm. When fluoride is added, the formation of the stable ZrF_6^{2-} complex causes a portion of the lake to dissociate, decreasing the absorbance.

$$(\text{Zr-SPADNS}) + 6F^- \longrightarrow \text{SPADNS} + ZrF_6^{2-}$$

Thus, the Beer's law is satisfied in an inverse manner. A plot of absorbance versus the concentration of fluoride, therefore, has a negative slope. When photometric methods are used, care must be exercised to keep contact time and temperature the same as employed in developing the calibration curve. Good practice demands that at least one standard be included with samples each time photometric measurements are made.

3.5 Determination of Phosphate (PO_4^{3-})

3.5.1 Orthophosphate

Phosphorus occurring as orthophosphate (H_3PO_4, $H_2PO_4^-$, HPO_4^{2-}, PO_4^{3-}) can be measured quantitatively by gravimetric, volumetric or colourimetric methods. The gravimetric method is applicable where large amounts of phosphate are present, but such situation does not occur in ordinary practice. The volumetric method is applicable when phosphate concentrations exceed 50 mg/L, but such concentrations are seldom encountered except in boiler waters and anaerobic digester supernatant liquors. Colourimetric methods are the standard procedures usually adopted for water and wastewater, possibly at some sacrifice of accuracy.

In colourimetric methods, phosphate ion combines with ammonium molybdate under acid conditions to form a molybdophosphate complex.

PO_4^{3-}+12$(NH_4)_2$ MoO_4+12H^+ $(NH_4)_3PO_4 \longrightarrow 12MoO_3 + 21NH_4^+ + 12H_2O$.

When large amounts of phosphate are present, the molybdophosphate forms a yellow precipitate that can be filtered and used for volumetric determination. At concentrations under 30 mg/L (the usual range in water analysis) the yellow colour of the colloidal sol is not discernible.

Using stannous chloride, $SnCl_2$, (or ascorbic acid), the molybdenum contained in ammonium phosphomolybdate is readily reduced to produce a blue-coloured sol, molybdenum blue, that is proportional to the amount of phosphate present. Excess ammonium molybdate is not reduced and therefore does not interfere.

$$(NH_4)_3PO_4.12MoO_3 + Sn^{2+} \longrightarrow \text{Molybdenum blue} + Sn^{4+}$$

The phosphomolybdate is first extracted from the sample into a benzene-isobutarnol solution prior to addition of the stannous chloride. This extraction is necessary to enhance increased sensitivity and to obtain accurate results when excessive interferences are present in the sample.

3.5.2 Polyphosphates

The orthophosphate present is first determined, and them, the polyphosphate is converted to orthophosphate by boiling samples that have been acidified with sulphuric acid for 90 minutes or more. The excess acid added must first be neutralised before proceeding with the addition of the ammonium molybdate solution. The orthophosphate formed from the polyphosphate is measured in the presence of orthophosphate originally present in the sample by the method earlier described. The amount of polyphosphates is obtained as follows:

Total inorganic phosphate – orthophosphate = polyphosphate

3.5.3 Organic phosphorus

The organic matter (industrial wastes or sludges) is subjected to wet acid digestion using nitric acid first followed by perchloric acid. The excess

acid remaining is neutralised. The phosphorus released can be measured using the method described for orthophosphate.
Total phosphorus – inorganic phosphorus = organic phosphorus

SELF ASSESSMENT EXERCISE 2

1. In the gravimetric determination of sulphate concentration in a 400mL wastewater sample, 0.0460g $BaSO_4$ was obtained. How many mg/L of sulphate was in the sample?
2. In the photometric analysis of fluoride in a sample of water supply, Beer's law is obeyed in an inverse manner. Why?
3. Would you expect the analytical results for orthophosphate to be higher than, lower than or the same as the original value in a sample of domestic wastewater that had been acidified to prevent bacterial action and stored for several days prior to analysis? Why?

3.6 Determining Iron by Phenanthroline Method

The phenanthroline method is a reliable standard "wet chemistry" method for the measurement of Fe in water particularly when phosphate or heavy metal interference is absent. The method depends on the fact that 1, 10 - phenanthroline combines with Fe^{2+} to form a complex ion that is orange-red in colour. The colour produced conforms to Beer's law and is readily measured by visual or photometric comparison. It is necessary to make sure that all the iron is in a soluble condition. This is achieved by treating a portion of the sample with HCl acid to dissolve the ferric hydroxide:

$$Fe(OH)_3(s) + 3H^+_{(aq)} \longrightarrow Fe^{3+} + 3H_2O$$

Since 1,10 – phenanthroline will specifically measure Fe^{2+}, all iron in the Fe^{3+} form must be reduced to the ferrous (Fe^{2+}) form. This is readily accomplished by using hydroxylamine as the reducing agent.

$$4Fe^{3+} + 2NH_2OH \longrightarrow 4Fe^{2+} + N_2O + H_2O + 4H^+$$

Three molecules of 1, 10 – phenanthroline are required to sequester or form a complex ion with each Fe^{2+}. When interfering materials are present, satisfactory results can be obtained by the use of HCl to acidify the sample before the iron content is extracted into diisopropyl-ether prior to the addition of the phananthroline solution.

3.7 Persulphate Method for Manganese Determinations

This method is suited for routine determinations of manganese because pre-treatment of samples is not needed to overcome chloride interference. Ammonium persulphate is commonly used as the oxidising agent. It is subjected to deterioration during prolonged storage; hence, it is good to always include a standard sample with each set of samples to verify the potency of the persulphate used.

Chloride interference is overcome by adding Hg^{2+} to form the neutral $HgCl_2$ complex. Since the Ksp of $HgCl_2$ is about 1.7×10^{-13}, the concentration of Cl^- is decreased to such a low level that it cannot reduce the permanganate ions formed. The oxidation of Mn in lower oxidation states to permanganate by persulphate requires the presence of Ag^+ as a catalyst.

$$2Mn^{2+} + 5S_2O_8^{2-} + 8H_2O \longrightarrow Ag^{+} \quad 2MnO_4^{-} + 10SO_4^{2-} + 16H^{+}$$

The colour produced by the permanganate ion is stable for several hours, provided a good quality distilled water is used for dilution purposes and reasonable care is taken to protect the sample from contamination by dust of the atmosphere.

3.8 EDTA Titrations

Ethylenediamine tetraacetic acid (EDTA) titrations are a type of complexometric titrations widely used in the quantitative determination of several elements in environmental waters generally. The success of EDTA titration depends on its ability to account for complexes with many metals and the fact that masking/demasking processes are possible thus aiding selective titration of given metals. Also, suitable metal ion indicators are available which helps to determine a precise end point for each titration.

For example, when Ca^{2+} and Mg^{2+} occur simultaneously in a sample of hard water, the concentration of each ion can be determined successfully using EDTA titration. To determine Ca^{2+}, 2 mL of 0.1M NaOH solution is added to 50 mL of the water sample and titrated with standard EDTA using murexide indicator. To now determine Mg^{2+} in the same sample, destroy murexide colour with (1) mL of concentrated HCl, add 3 mL of NH_3-NH_4Cl buffer and titrate with EDTA using Eriochrome black T.

4.0 CONCLUSION

The methods of wet chemistry analysis are very much ideal and could conveniently be used where the luxury of high grade analytical instrumentation cannot be afforded. Provided the analysis is competently handled, the results are both informative and reliable.

5.0 SUMMARY

In this unit, you have learnt that:

wet chemistry predominates the field of chemical instrumentation in environmental sciences

mercuric nitrate method is more reliable than argentometric procedure in the analysis of Cl^- since mercuric method is less subject to interferences.

gravimetric methods are particularly suitable for species that can form stable precipitates of known molecular formula.

visual or photometric methods are suitable where colour development of a given species is possible.

certain metals e.g. Fe and Mn can be determined using visual or photometric methods.

complexometric titration (using EDTA particularly) can be used to routinely determine the levels of many metals in water for example.

6.0 TUTOR-MARKED ASSIGNMENT

(a) List four precautions that must be observed to ensure an accurate gravimetric determination of sulphate concentration in a water sample.

(b) In the determination of sulphate concentration by gravimetric procedure, a 100mL sample yielded 0.0140g of $BaSO_4$. How many mg/L of sulphate was in the sample?

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UNIT 2 PHYSICAL INSTRUMENTATION IN ENVIRONMENTAL SCIENCES

CONTENTS

1.0 INTRODUCTION

In environmental sciences, all the pollutants of interest can readily be classified as organic or inorganic. These ones are of greater concern because they occur more often than any other ones we may think of.

Inorganic pollution arises from mining and smelting of metals, fossil fuel combustion and chemical production coupled with widespread applications in engineering, electronics, industrial and agricultural practices. These activities have led to the presence of heavy metals and other trace inorganic chemicals in the atmosphere, rainfall, rivers, groundwater, soil, sediments and the biota. Organic pollution was first manifested following the growth in the use of pesticides in the years immediately after the Second World War and through the 1950s. The first organochlorine pesticides were DDT, Lindane and Dieldrin. Overuse and misuse of these compounds led to the death of wildlife, especially species at the apex of food chains including raptorial birds, foxes and badgers.

Public concern requires that pollutants in the environment are detected and controlled. Current methods popularly used in profiling heavy metal levels in an environmental matrix include Flame Atomic Absorption Spectrometry (FAAS), Graphite Furnace Atomic Absorption Spectrometry (GFAAS), Inductively Coupled Plasma-Mass

Spectrophotometry (ICP-MS) and Energy Dispersive X-Ray Fluorescence (EDXRF) to mention a few. Chromatography is the dominant analytical technique for the identification and quantification of organic pollutants.

2.0 OBJECTIVES

At the end of this unit, you should be able to:

list mostly used instrumental techniques for the analysis of heavy metals and organic compounds in an environmental sample
state the principle of operation of each instrumental technique studied
state the advantages of one technique over the other.

3.0 MAIN CONTENT

3.1 Instrumental Techniques for Heavy Metals Analysis

Various, instrumental techniques are used by chemists and other environmental scientists for the purpose of detecting and determining the levels of heavy metals in a given environmental samples. For the sake of brevity, only two of the techniques (AAS and NAA) are discussed here.

3.1.1 Atomic Absorption Spectrometry (AAS)

Atomic Absorption Spectrometry is a technique that involves the aspiration of the sample solution into a flame or an electrothermal device whose high temperature converts the analyte ions into atoms in the vapour state. When an electromagnetic radiation characteristic of the electronic transitions of atoms of a particular element is passed through an atomic vapour of that element, the radiation at certain frequencies is attenuated. The absorbed radiation excites electrons from the ground state to various higher energy levels (excited states). The degree of absorption is a quantitative measure of the concentration of ground-state atoms in the vapour.

AAS is the most widely used techniques for the quantitative determination of metals at trace levels (0.1 to 100ppm) in a wide range of materials; its relative precision is 0.5 to 2percent.

The major disadvantages include: (i) samples must be in solution or at least volatile; (ii) individual source lamps are required for each element; (iii) the technique is not capable of simultaneous multi-elemental determination; and (iv) it is not suitable for qualitative analysis.

Some of the various modifications of AAS are Flame Atomic Absorption Spectroscopy (FAAS) and Graphite Furnace Atomic Absorption spectroscopy (GFAAS).

3.1.2 Flame Atomic Absorption Spectroscopy (FAAS)

FAAS consists of a sharp-line radiation source, produced by a hollow-cathode lamp, characteristic of the element of interest, a solution nebulizer and burner, a monochromator, photomultiplier and recording system. Although FAAS is simple to operate and cheap, the burner-nebuliser system is relatively an inefficient sampling device. Only a small fraction of the sample reaches the flame and the atomised sample passes quickly through the light path thereby leading to a low detection limits, usually at the sub ∝ g/g or ∝ g/mL levels. Its dynamic range is also limited.

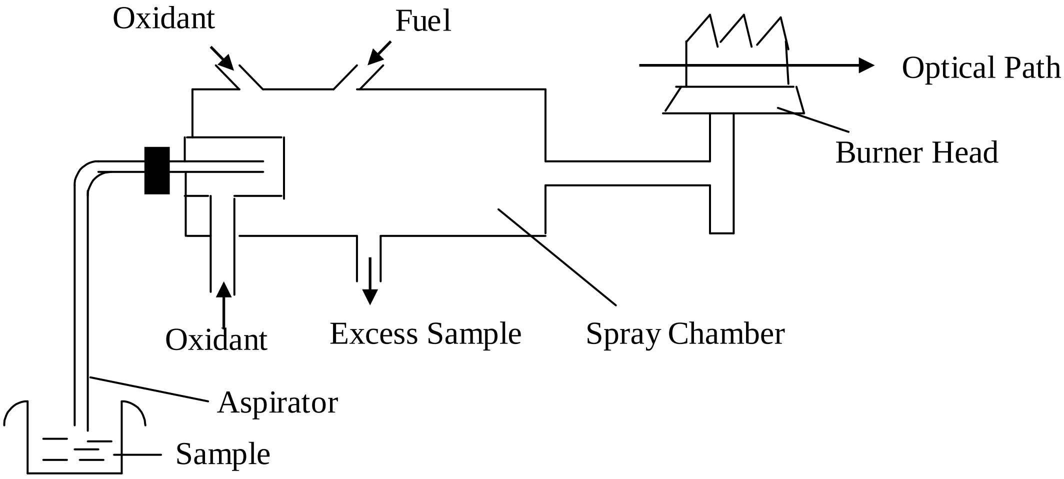

Fig. 6: **The Premix Burner of a FAAS**
Source: **D. Harvey, 2000 (Modified).**

3.1.3 Graphite Furnace Atomic Absorption spectroscopy (GFAAS)

One major instrumental difference between GFAAS and FAAS is that, graphite tube furnace (about 5 cm x 3 mm) is used in GFAAS in place of flame in the FAAS for the purpose of vapourisation and atomisation. The graphite tube furnace is flushed through with an inert gas, e.g. argon, before vapourising the sample so as to prevent the formation of refractory oxides and oxidation of the graphite tube. The axis of the furnace is aligned along the optical path of the radiation from the lamp. The sample (5 to 50 ∝ L) is deposited on the platform at the bottom inner surface of the tube near the centre to enhance maximum sensitivity. The temperature is rapidly raised to about 2500 K by the passage of a heavy current for a period of 1 to 2 minutes. The heating cycle is controlled so as to allow solvents to evaporate or organic residues to be ashed before an atomic vapour of the metal under investigation is produced.

GFAAS has relatively low detection limits capability, which makes it particularly suited to the requirements of analyses of trace elements at low concentrations in a matrix. The main drawbacks of GFAAS are: (i) it is not multi-elemental; (ii) it has limited practical sample throughout; and (iii) the presence of high electrolyte species such as Na and Cl results in numerous non-specific absorption interferences.

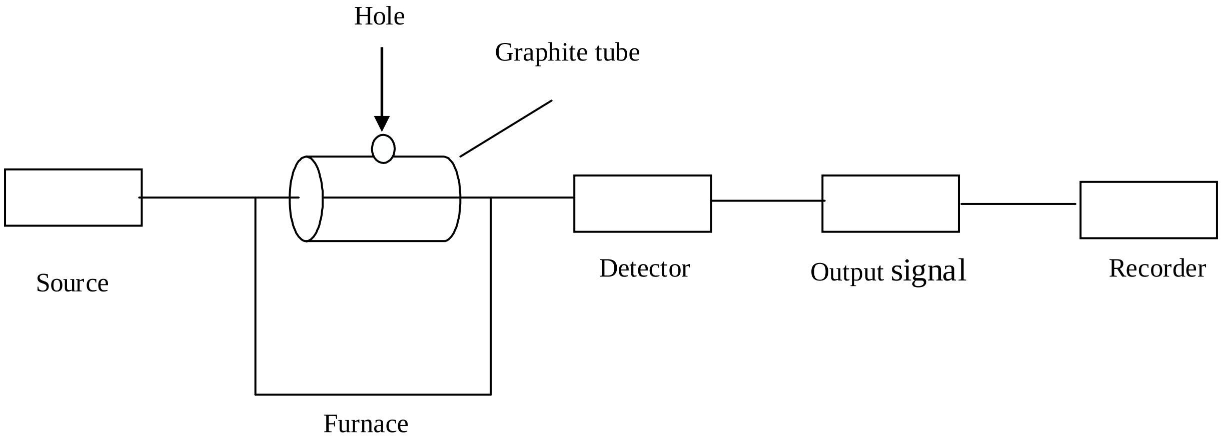

Fig. 7: A Block Diagram of GFAAS

3.2 Neutron Activation Analysis (NAA)

NAA is a non-destructive tool for routine trace element determination in many areas of innovative research. Apart from being able to determine many environmentally crucial trace elements such as Sb, Cd, Cr, Cu, Se, Ni, Zn, etc. NAA is also capable of determining major elements such as Na, Cl, and K as well as rare earth elements.

The determination of the elemental concentrations is based on the measurement of induced radioactivity through the activation of the elements by neutrons. The radioactive decay of each element emits a characteristics X-ray spectrum. Hence, an individual nuclear "fingerprint" can be measured and quantified. The neutron sources used in NAA can be produced by a neutron reactor, a particle accelerator or artificial isotopes such as phitonium, and beryllium. The most common source is from a fission reactor due to its high neutron flux.

NAA is an extremely sensitive, selective and precise technique that provides both qualitative and quantitative information at ultra trace levels. These characteristics derive from a combination of factors: (i) Extremely sensitive instrumentation with a facility for spectrometric distinction between radionuclide is available; (ii) activation cross sections can be large and interise neutron fluxes are available; (iii) the reagent blank problem which is so common in trace element analysis is largely eliminated; (iv) when sample processing prior to measurement is needed, the problem of working with $\propto$ g amounts of materials can be simplified by the addition of non-active “carrier’ which does not affect the final activity measurement; and (v) very small sample size (flakes of paint, single hair strand, etc) can be analysed and identified by NAA.

Some of the disadvantages of NAA are; (i) liquid samples cannot be activated in a standard thermal neutron nuclear reactor; (ii) practical multi-elemental analysis is restricted due to the wide spectrum of short and long-lived nuclides; (iii) for short-lived nuclides measurement, the presence of major electrolyte species (Na, Cl, P, Br) on irradiation produces high background x-ray activities; (iv) the determination of many important elements like Be, B, Pb, P and Si is difficult due to poor nuclear cross-sections not activated by neutrons or, as in the case of P, not yielding a X-ray for analysis; and (v) it is an expensive and highly specialized instrumentation.

Activity: Read about and prepare “contact period” or term papers on EDXRF and ICP-MS.

SELF ASSESSMENT EXERCISE 1

1. List some instrumental techniques suitable for the analysis of heavy/trace metals
2. What are the advantages of (a) FAAS over GFAAS; (b) GFAAS over FAAS; (c) AAS over NAA; and (d) NAA over AAS?
3. Explain the need of an inert gas to flush through the graphite furnace tube before vaporisation of an element is commenced in GFAAS analysis.

3.3 Instrumental Techniques for Organic Residues Analysis

In environmental chemistry, chromatography is the dominating technique with respect to organic matrix analysis. **Chromatography** is an instrumental analytical technique that combines separation and identification of components of a complex mixture into individual entities. The chromatographic methods have good speed, high resolution power and tendency to handle small amounts of material.

Every chromatographic system consists of moving or mobile phase in intimate contact with fixed or stationary phase. The latter is composed of the stationary or all non-moving portion of chromatographic column or bed. A sample component undergoes an equilibrium distribution between these two phases. This equilibrium in turn decides the velocity with which each component migrates on column. The band-broadening and dispersion of each component in the direction of migration also occurs. Thus differential migration and band-broadening decide the extent of separation of the sample.

The classes of chromatography are:

(i) **Adsorption chromatography**: This method is based on exploitation of the difference in adsorptivity of solute to the stationary support which is usually packed in a column e.g. various fatty acids can be separated by adsorption chromatography.

(ii) **Partition chromatography**: includes chromatographic techniques such as liquid-liquid chromatography (LLC), paper chromatography (PC) thin-layer chromatography (TLC), gas-liquid chromatography (GLC) and reversed – phase chromatography (RPC). Here, we explore the difference in the partition coefficient or distribution ratio of individual species in the mobile and stationary phase. Some partition chromatography techniques like PC and TLC use plates while others use columns.

(iii) **Ion exchange chromatography**: This method is based on differences in the exchange potential between various ion exchange resin packed in a column. Examples are CEC, AEC, IE and Liquid Exchanger (LE).

(iv) **Exclusion chromatography**: This is based fundamentally upon exploitation of the difference in size or molecular geometry of the components. In gel permeation, small constituents are retained in inter shell spaces or pores while large size components emerge first. Examples include gel permeation (GP), ion exclusion and molecular sieve chromatography.

(v) **Electro Chromatography**: Methods under this category are often classified as electrophoretic techniques. In such separations, the difference in mobility of different ions when an external potential is applied. Examples include zone electrophoresis, boundary layer electrophoresis, curtain chromatography and capillary electrophoresis of all the chromatographic techniques available, GC and HPLC are used more often for routine analysis of environmental samples.

3.3.1 The Use of Gas Chromatography (GC) in Analysis

With GC, it is possible to separate a very complex mixture containing up to 200 or more related compounds, using either partition or adsorption, with very small sample sizes. It is similar to liquid-liquid chromatography except that the mobile liquid phase is replaced by a moving gas phase. The stationary phase may be solid or liquid.

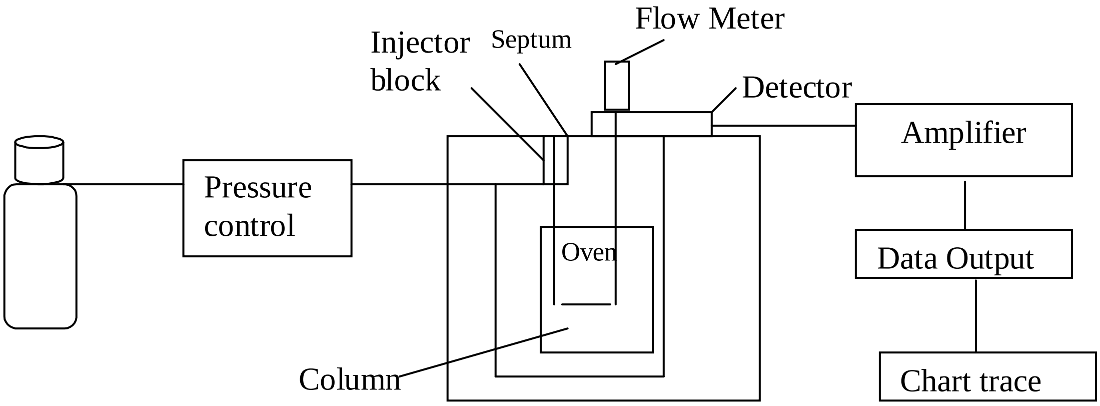

Fig. 8: Diagram of a Gas Chromatograph
Source: D. Harvey, 2000 (Modified).

The sample for GC analysis must be able to exist in the gas phase, so it may be applied to volatile materials only. Thus, non-polar substances are easier to handle than polar materials; ionic materials cannot pass through a GC. For polar substances like alcohols, amines, free fatty acids and phenols, derivatisation may be required.

$$\mathrm{Ph-OH} \quad + \quad \mathrm{Cl-SiMe_3} \longrightarrow \mathrm{Ph-O-SiMe_z} \quad + \mathrm{HCl}$$

Phenol	Trimethylsilyl chloride	Phenyltrimethylsily ether

The carrier gas, from a high-pressure cylinder is helium, nitrogen, hydrogen or argon. The choice depends on factors such as availability, purity, consumption and type of detector.

Until recently, GC analysis was handled using packed columns in which the stationary phase is a liquid that has been coated on an inert granular solid called the **column packing** (held in borosilicate glass tubing). More recently, however, the borosilicate glass tubing packed columns are being replaced by fused silica or quartz capillary columns. The column is installed in an oven with the inlet attached to a heated injector block and the outlet attached to a detector. Precise and constant temperature control of the injector block, oven and detector is maintained. Stationary phase material and concentration, column length and diameter, oven temperature, carrier gas flows and detector type are the control variables.

Sample solution is usually introduced using a microsyringe with hypodermic needle inserted through a self-sealing silicone rubber septum. The sample is smoothing injected into a heated metal block at the head of the column. Modes of placing samples onto the column can be by **split injection** or **splitless injection**. Manipulation of the syringe is an art developed with practice, and the aim is to introduce the sample in a reproducible manner. The temperature of the sample port should be such that the liquid is rapidly vaporised without either decomposing or fractionating the sample. A useful rule of the thumb is to set the sample port temperature approximately to the boiling point of the least volatile component. For greatest efficiency, the smallest possible sample size (1-10 ∝ L) consistent with detector sensitivity should be used.

In GC sample analysis, interferences may arise from contamination of samples, chromatograph improper functioning and countermeasures that may manifest inform of septum bleed, column bleed and ghost peaks manifestation.

Gas Chromatograph Detectors

The function of a GC detector is to sense and measure the small amounts of the separated components present in the carrier gas leaving the column. The choice of a detector will depend on factors such as the concentration level to be measured, the nature of the separated components and the properties of the detector e.g. high sensitivity, good linearity, stability and response.

a) **Hot-wire director (HWD)**: This is also known as the **thermal conductivity detector** (TCD) or **katherometer.** It is the oldest GC detector. Due to its inherently large volume, low sensitivity and contamination problems, it was long dismissed as unsuitable for capillary systems. It is universal in its applications.

b) **Electron capture detector (ECD)**: This usually used for the analysis of compounds that have high electron affinities such as chlorinated pesticides, drugs and their metabolites. This detector is somewhat selective in its response, being highly sensitive towards molecules containing electronegative groups: halogens, perozisdes, quinines and intro groups. It is insensitive towards such functional groups as amines, alcohols, and hydrocarbon

c) **Flame ionization detector (FID)**: This more or less universal detector is widely used because of its high sensitivity to organic carbon-containing compounds. It is perhaps the most widely used detector for GC. Its advantages include: (i) it responds to virtually all organic compounds with high level of resolution; (ii) it is resistant to common carrier gas impurities such as resistant to common carrier gas impurities such as water and carbon; (iii) it has a large linear responds range and excellent baseline stability; (iv) it is relatively insensitive to small column flow-rate fluctuations during temperature programming; (v) it is highly reliable, rugged and easy to use; and (vi) it has low detector dead-volume effects and fast response. Its two major limitations are: (i) it gives little or no response to non-combustible gases and all nobles gases; and (ii) it is a destructive detector that changes both the physical and chemical properties of samples analyzed irreversibly.

d) **Photoionization detector (PID)**: Photoionization occurs when a molecular species dissociates into a parent ion and an electron upon interaction with UV light.

$$M \xrightarrow{uv} M^+ + e^-$$

The PID detects organic and some inorganic species in the effluent of a gas chromatograph with a detection limit as low as the pictogram range. The PID has a high sensitivity, low noise and an excellent linearity. It is non-destructive and can be used in series with a second detector for more selective detection. PID can be operated as a universal or selective detector by simply manipulating the photon energy of the ionization source.

e) **Mass spectrometer (MS)**: Mass spectrometers can serve as detectors when coupled to a GC. The MS combines the ability to detect a wide variety of compounds with the capability of deducing compound structures from fragmentation patterns or mass spectra. The computer (for recording) contains and can search a library of known mass spectra to identify tentatively an unknown compounds are used for confirmation after tentative identifications are made.

f) **Fourier Transform Infrared Spectrometers (FT-IR)**: Like the MS, FT-IR is also an independent instrument which can be coupled to a GC to serve as a detector.

g) **Thermionic detector**: This particularly responds to compounds containing nitrogen or phosphorus

3.4 High-Performance Liquid Chromatography (HPLC)

Although GC is widely used, it is limited to samples that are thermally stable and easily volatilised. Non-volatile samples, such as peptides and carbohydrates, can be analysed by GC, but only after they have been made more volatile by a suitable chemical derivatisation. For this reason, the various techniques included within the general scope of liquid chromatography are among the most commonly used separation techniques.

In HPLC, a liquid sample, or a solid sample dissolved in a suitable solvent, is carried through a chromatographic column by a liquid mobile phase. Separation is determined by solute/stationary-phase interactions, including liquid-solid adsorption, liquid-liquid partitioning, ion exchange and size exclusion, and by solute/mobile-phase interactions. In each case, however, the basic instrumentation is essentially the same. An HPLC typically included two columns: the guard column and an analytical column. The guard column is an inexpensive column placed before the analytical column (a more expensive column), protecting it from contamination and damage, while the analytical column does the separation. In HPLC, the stationary phase is a liquid film coated on a packing material consisting of 3-10 ∝ m porous silica particles.

Solvent proportioning valve

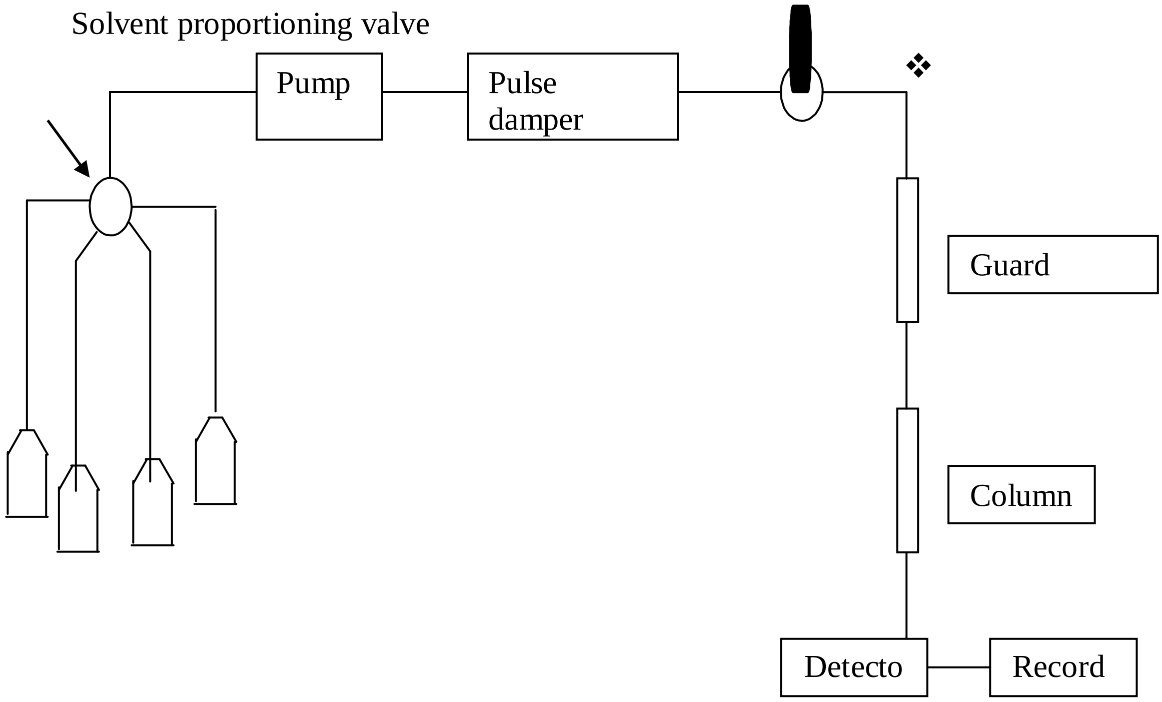

Fig. 9: Diagram of a High-performance Liquid Chromatograph
Source: D. Harvey, 2000 (modified).

The stationary phase may be partially soluble in the mobile phase, causing it to "bleed" from the column over time. To prevent this loss of stationary, it is covalently bonded to the silica particles by reacting the silica particles with an organochlorosilane ($Si(CH_3)_2$ RCl).

The elution order of solutes in HPLC is governed by polarity; the least polar solute spends less time in the polar stationary phase and is the first solute to elute from the column. Retention times in a normal-phase separation are controlled by selecting the mobile phase, with a less polar mobile phase leading to longer retention times. In a reverse-phase separation, however, the order of elution is reversed.

As with GC, numerous detectors have been developed for use in monitoring HPLC separations. To date, the most HPLC detectors are not unique to the method, but are either stand-alone instruments or modified versions of the same. The most popular ones are spectroscopic detectors (e.g. UV /visible absorption and fluorescence) and electrochemical detectors (such as amperometry, voltammetry, coulometry and conductivity based detectors). A refractive index detector is sometimes employed as a universal detector.

SELF ASSESSMENT EXERCISE 2

1. Explain the term "chemical derivatisation" as it applies to GC analyses. Advance two reasons why it is necessary.
2. List five detectors that are used in GC analysis.
3. With reasons, state the detectors you would adopt in carrying out a GC analysis of the following: Peptides, (b) Chlordane, (c) Gaseous hydrocarbons, (d) Mercaptans, (e) Carbohydrates.
4. List three advantages and two disadvantages of flame ionization detector (FID) as a GC detector.

4.0 CONCLUSION

Qualitative and quantitative identification of inorganic and organic species in a given matrix have become easier, faster and more interesting because of the availability of the state –of –art instrumental techniques of modern days. Apart from their applications by environmental chemistry, such instrumental techniques have found wide acceptance and applications in clinical analysis, consumer goods characterization and petroleum products analysis.

5.0 SUMMARY

In this unit, you have learnt that:

Levels of heavy metals in a sample can be profiled by such instrumental techniques as AAS (FAAS and GFAAS), NAA, EDXRF and ICP-MS.

Chromatographic techniques are well suited for the analysis of organic compounds in particular.

6.0 TUTOR-MARKED ASSIGNMENT

1. Briefly explain the following modes of sample injection in a GC analysis: (a) Split injection, (b) Split less injection.
2. With respect to interferences in GC analysis, explain the following: (a)Septum bleed, (b) Column bleed and (c) Ghost peaks.

7.0 REFERENCES/FURTHER READING

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Braun, R. (2000). *Introduction to Chemical Analysis.* London: McGraw-Hill Int. Editions.

Harvey, D. (2000). *Modern Analytical Chemistry*. USA: McGraw-Hill Companies Inc.