Identification of sources of wastewater, its characterization and quantification in hospitals

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CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

WWTP-Wastewater treatment plants
UWWs-Urban Wastewaters
HWWs-Hospital Wastewaters
CAS-Conventional activated sludge
MBR-Membrane bioreactor
MBBR-Membrane biofilm bioreactor
MF-Microfiltration
UF-Ultrafiltration
GAS-Granular activated carbon
PAC-Powder activated carbon
COD-Chemical oxygen demand
BOD-Biological oxygen demand
TSS-Total suspended solids
VSS-Volatiles suspended solids
TN-Total nitrogen
SN-Soluble Nitrogen
EPS-Extracellular polymeric substances
PN-Proteins
PS-Polysaccharides
HA-Humic Acid - like substances
SMBR-Submerged Membrane bioreactor
EMBR-Extern membrane bioreactor
HRT-Hydraulic retention time
AS-Activated sludge
HE-Hospital effluent
SRT-Sludge retention time
NH_4-N Ammonium nitrogen
NO_3—N Nitrate nitrogen
NO_2-N Nitrite Nitrogen
UV-Ultraviolet
PPCPs-Pharmaceutically active compounds and personal care products
DO-Dissolved oxygen
BSA-Bovine Albumin Serum
AS-Activated Sludge
IF-Indic of Fluorescence
TOC-Total organic carbon
GC-Gas Chromatography
GC/MC-Gas Chromatography/Mass spectrometry
HPLC-High Performance Liquid Chromatography
UPLC-Ultra Performance Liquid Chromatography
HILIC-Hydrodphilic Interaction Liquid Chromatography
NPLC-Normal Phase Chromatography
RPLC-Reversed- Phase Liquid Chromatography.
MS-Mass Spectrometry
LOQ-Lower limits of Quantitation
UE-Urban Effluents

CHAPTER I

INTRODUCTION

1.1 Background

Hospital wastewater generation has been increasing during the recent decades as a result of development in medical services and products (E. Emmanuel, 2005). Multiple practices that happen in hospitals (surgery, drug treatments, radiology, laundry, operation room, chemical and biological laboratories, etc.) are a principal source of pollutant discharge into the environment (Kummer, 2001). Most of these pollutants such as detergents, disinfectants and drug residues can be found in hospital effluents, municipal wastewater collection systems and finally aquatic environments (Christoph Ort, 2010). Polluted wastewater discharged from hospitals causes many environmental hazards. These problems are different in terms of the activity and nature of hospitals (Chioma C. Okore, 2014). The World Health Organization (WHO) reported that about 85% of hospital wastes are non-hazardous, 10% infective and 5% non-infective but hazardous, in the United States of America.

Hospital wastewater effluents contain pathogenic microorganisms, pharmaceutical partially metabolized, radioactive elements and other heavy metals and toxic chemical compounds such as Cu, Fe, Cd, Pb, Hg, Ni, Pt, Cyanide, Phenol and others (Amouei, Asgharnia, Fallah, Faraji, Barari, & Naghipour, 2015). Hospitals discharge plenty of undesired potential pathogens like antibiotic-resistant bacteria and viruses. These hazardous agents which remain in wastewater treatment plants can provoke the pollution of the natural environment by causing biological imbalances. In many cases, hospital wastewater is considered as an effluent with a similar quality to municipal wastewater, but due to activities that take place within the hospital it may also contain various potentially hazardous components including microbiological pathogens, hazardous chemical compounds, disinfectants, pharmaceuticals and radioactive isotopes (M. Tsakona, 2007).

Hospital wastewater (HWW) is normally discharged directly, without pre-treatment, to sewers. Despite mostly being only a small fraction of the total wastewater volume in the influent of a sewage treatment plant (STP), HWW has gained increasing scientific and public attention in the

last decade. This is, in part due to the observation and expectation that HWW is a source for undesirable constituents, such as (multi-)antibiotic-resistant bacteria (Baquero 2008; Kümmerer, 2004).In other publications, the emission from hospitals was estimated for antibiotics, anaesthetics, disinfectants, heavy metals, AOX (Adsorbable Organic Halogens), iodised X-ray contrast media and cytostatic agents (Kümmerer, 2001). The latter were also investigated in detail by Lenz (2007). Furthermore, a number of toxicity assays were performed (Boillot 2008; Ferk 2009; Hartmann1998). As a result, it has been suggested in some studies that pre-treatment of HWW prior to discharge into the sewers provides a reasonable solution (Gautam 2007; Lenz 2007; Pauwels and Verstraete, 2006). However, this view is not unanimously supported. The separate treatment of HWW to reduce the development of resistant bacteria was questioned (Kümmerer, 2009): the substantial amount of antibiotics used outside of hospitals (in Germany more than 75%) seems to be a plausible reason that resistant bacteria are also abundant in wastewater not receiving any HWW. Additionally, (Boillot 2008) found quantitatively far fewer microorganisms in the effluents of hospitals than in urban wastewaters, which is consistent with other studies. With regard to pharmaceuticals, (Lenz 2007) for some pharmaceuticals merely a small fraction of the amounts administered in the hospital were actually found in its effluent (i.e. 0.1–0.2% for doxorubicin, 0.5– 4.5% for 5-fluorouracil and 27–34% for total platinum); and a complete onsite wastewater treatment process is needed to significantly remove targeted pharmaceuticals. This includes full physical and biological treatment steps, not only advanced processes. Capturing all sources within a hospital (wards, laboratories) may be further complicated by the fact that different facilities discharge through different pipes to the common sewer. This particularly holds true for large existing hospital complexes.

1.2 Aim

The aim of this project is to study the characteristics of wastewater from the hospitals in Dehradun, by determining the ph, Dissolved Oxygen (DO), Biochemical Oxygen Demand (BOD_5), Chemical Oxygen Demand (COD), Total Suspended Solids (TSS), Total Dissolved Solids (TDS), Turbidity, Alkalinity, Heavy metal concentration (Pb, Cu, Cd) of the influent and effluent of the respective hospital wastewater treatment plant (WWTP) and composite samples of the effluent if no WWTP is available.

1.3 Objective

- Selection and classification of hospitals in Dehradun city based on their bed capacity.
- Study of hospital effluent disposal criteria and the characteristics of disposed effluent.
- Checking the characteristics of effluent from hospitals against the recommendation for effluent disposal given by Uttarakhand Environmental Protection and Pollution Control Board.

1.4 Scope

The samples for the characterization of the ingredients will be collected from the following major hospitals of Dehradun (Table 1). The bed capacity for these hospitals range from 25 to 1000 beds. The samples collection will be performed at field conditions. The collected samples will be tested as per APHA "Standard Methods for the Examination of Water and Wastewater" in the NABL certified Health Safety Environment Lab of UPES, Dehradun.

Table 1 Bed capacity and location of Selected Hospitals

S.No	Hospital Name	Capacity(Beds)	Geographical Co-ordinates
1	Shri Mahant Indiresh Hospital	1000	30°18'20.159''N 78°1'14.192'' E
2	City Heart Hospital	25	30°19'10.902''N 78°3'1.424'' E
3	Synergy Hospital	140	30°20'15.282''N 78°0'49.607'' E
4	Ashirwad Hospital	150	30°18'44.441''N 78°2'51.902'' E
5	Fortis Escorts Hospital	50	30°19'14.578''N 78°3'26.973'' E
6	Doon Hospital	150	30°19'10.668''N 78°2'31.742'' E
7	Max Hospital	230	30°22'25.4496''N 78°4'28.8624'' E

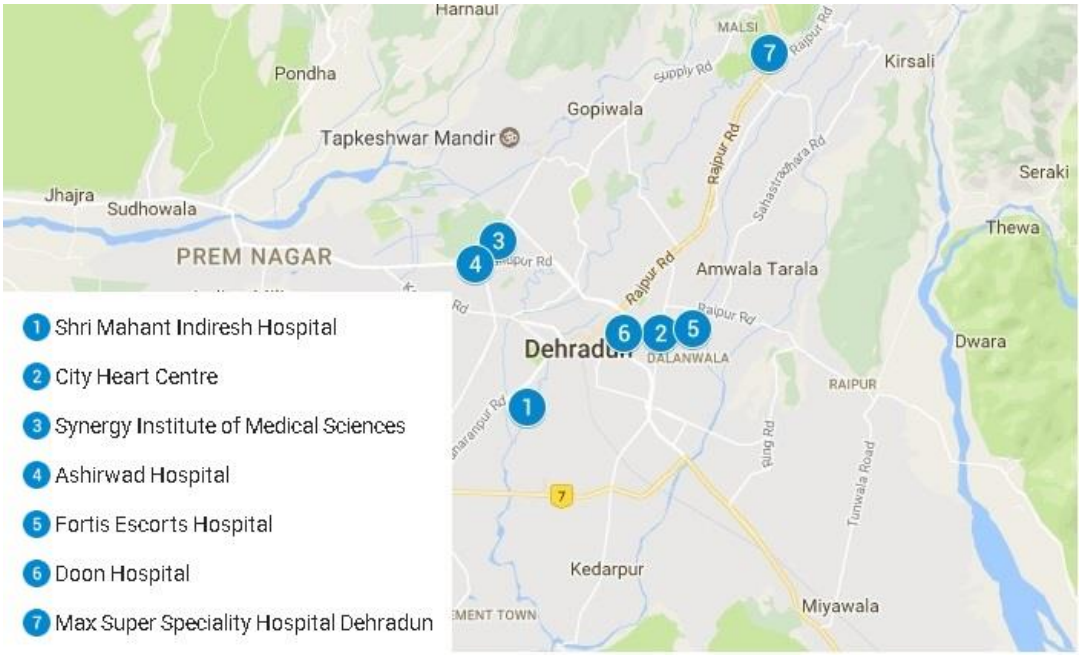

Figure 1 Location of Selected Hospitals

1.5 Methodology

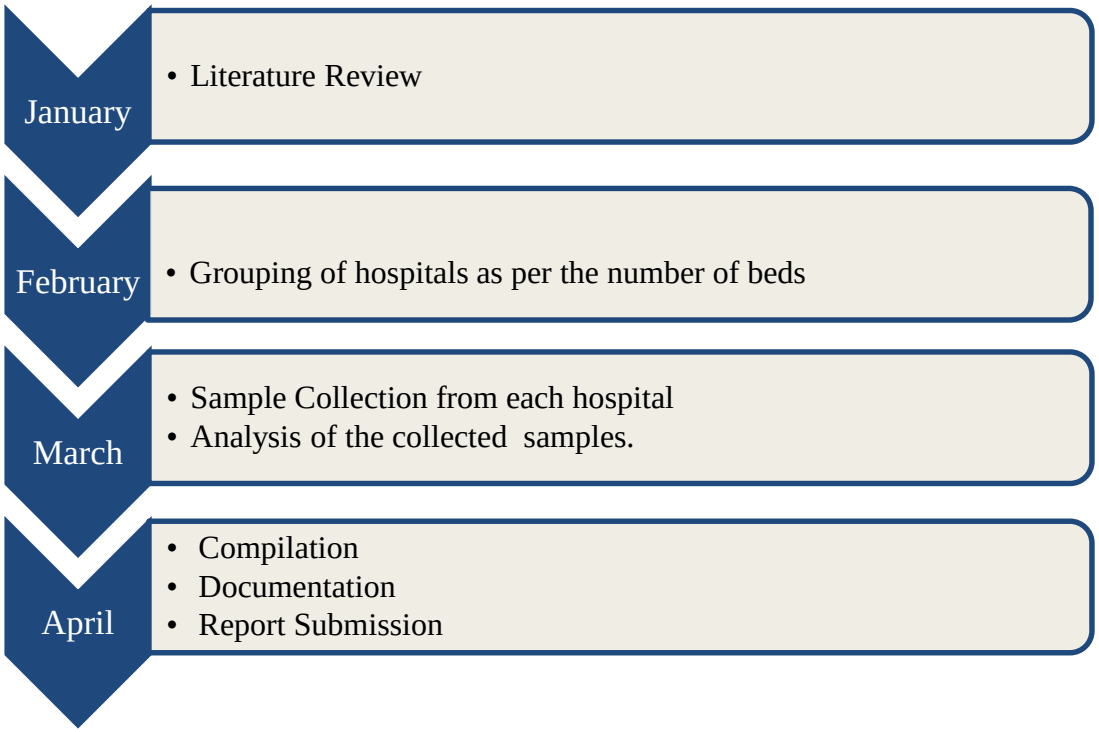

Figure 2 Project Timeline

CHAPTER II

LITERATURE REVIEW

Wastewater is defined as any water, whose quality has been adversely being abused by anthropogenic influence. This includes liquid waste discharged from domestic homes, industries, hospitals, agricultural and commercial sectors. Many of the pollutants detected in wastewaters are categorized as non-regulated "emerging pollutants" (P. Verlicchi, 2010)The contact of this kind of wastewater with the surrounding environment results in adverse effects on the biological balance of aquatic ecosystems, causing imbalance at different trophic levels possibly related to the action of toxic and genotoxic agents and indirectly by eutrophication (Evens Emmanuel, 2009).

Over the last few years, hospital effluent has been gained a significant attention in various countries in the world facing different issues. It is well established that hospitals may consume extensive amount of water in a day, ranging between 400 to 1200 L day^{-1} (Ajay Kumar Gautam, 2007) and consequently, generate equally significant volume of wastewater load. Hospital wastewaters (HWW) are generated in different sectors of a hospital including patient wards, surgery units, laboratories, clinical wards, ICU, laundries and possess a quite variable composition depending on the activities involved. In this context, HWW consist a numerous persistent chemical compounds and complex mixtures of organic matter including pharmaceuticals, radio-nuclides, detergents, antibiotics, antiseptics, surfactants, solvents, medical drugs, heavy metals, radioactive substances and microorganisms Moreover, in hospital effluents, conventional pollutant (Among them BOD5, COD, TSS) is in general higher than in urban wastewaters (UWWs) (E. Emmanuel, 2005).

Table 2 Average Values in HWW & UWW (E. Emmanuel, 2005)

Parameter	UWWs	HWWs	Ratio
BOD5	90	200	2,2
COD	170	500	3
TSS	60	160	2,7

After usage, some of these compounds and non-metabolized drugs excreted by patients are detected in HWW and then, enter the municipal sewer network without preliminary treatment. For this reason, this composition leads to extensive levels of toxicity, genotoxicity and organic load and subsequently, causes an adverse impact on the natural ecosystem and inherent hazard to human health (S.N. Mahnik, 2007).

More recently, a study by (Jean, 2012) showed that 15-20% of medicines utilized in hospitals are potentially bio-accumulative. The HWW reveals the presence of potentially toxic heavy metals such as Hg and Ag as well as chlorinated molecules in high concentrations. Additionally, significant concentrations of COD and BOD5, 1900 and 700 mg L^{-1}, have been assessed in these effluents (Ajay Kumar Gautam, 2007). Laundry wastewaters from hospitals were characterized by (Sh.Sarafraz, 2007) in Hormozgan and COD and BOD5 concentrations were as 477 and 305 mg L^{-1}, respectively, when washing stages were not subdivided. However, when washing steps were subdivided into different stages, the first rinsing was demonstrated higher COD and BOD5 concentrations, 3343 and 1906 mg L^{-1}, respectively.

Pharmaceutical drugs given to people and to domestic animals including antibiotics, hormones, strong painkillers, tranquilizers, and chemotherapy chemicals given to cancer patients are being measured in surface water, groundwater and drinking water as well. Hospitals discharge plenty of undesired potentially pathogenic propagules including antibiotic resistant bacteria, viruses and may be even prions. As a result, in some developing and industrialized countries, the outbreaks of cholera are periodically reported. Moreover, sewers of hospitals where cholera patients are treated are not always connected to efficient sewage treatment plants, and sometimes municipal sewer networks may not even exist.

One of the major environmental concerns due to hospital effluent is their discharge into urban sewerage systems without adequate treatment. HWW could be negatively affected to the ecological balance and public health. If left untreated, pathological, radiaoactive, pharmaceutical, chemical and infectious components of HWW lead to outbreaks of communicable diseases, diarrhea epidemics, cholera, skin diseases, enteric illness, water contamination and radioactive pollution. On the other hand, HWW sludge from on-site treatment plants are to be carefully managed with the precautions as municipal waste sludge. Such sludge must not be utilized as manure without proper pretreatment for food crops (Ajay Kumar Gautam, 2007).

Most often, conventional treatments have been adopted for HWW, however, they are not properly managed and slightly low removal capacities are achieved even for common parameters including BOD5, COD, TSS and total coliform (P. Verlicchi, 2010). On the other hand, only a simple primary treatment such as primary clarification and prechlorination is applied for hospital effluent, anyhow it is not efficient. Moreover, no treatment is adopted at all and direct discharge of HWW into water bodies is a common practice in the developing world. (P. Kumarathilaka, 2015).

In recent years, increasing attention has been paid to the presence of emerging pollutants in wastewaters, surface waters and ground waters. In most cases, emerging contaminants correspond to unregulated pollutants, which may be candidates for future regulation depending on research on their potential health effects and the results of monitoring of their occurrence. They include surfactants, pharmaceuticals and personal care products (PPCPs), endocrine disruptors, illicit drugs, gasoline additives and many other groups of compounds. Their main characteristic is that they do not need to persist in the environment to cause negative effects, since their high transformation/removal rates can compensated for by their continuous introduction into the environment.

2.1 Pharmaceutical and Personal Care Products (PPCPs)

Pharmaceuticals are a set of compounds, which have obtained increasing attention over the past decade. Pharmaceutical and Personal Care Products (PPCPs) are a set of chemical pollutants resulting from pharmaceutical and products for personal hygiene. They include a wide and diverse range of chemicals, including prescription drugs and medicines, perfumes, cosmetics, sunscreens, cleansers, shower gel, shampoo, deodorant and other. When these substances are freely discharged into the environment, they could cause some impact on aquatic and terrestrial organisms (Lubomira Kovalova, 2013), since they have been specifically designed to produce biological effects even at very low concentrations. This broad collection of substances includes any products consumed by individuals or domestic animals for any number of countless reasons pertinent to health, performance, cognitive and physical function, or appearance (Christoph Ort, 2010)

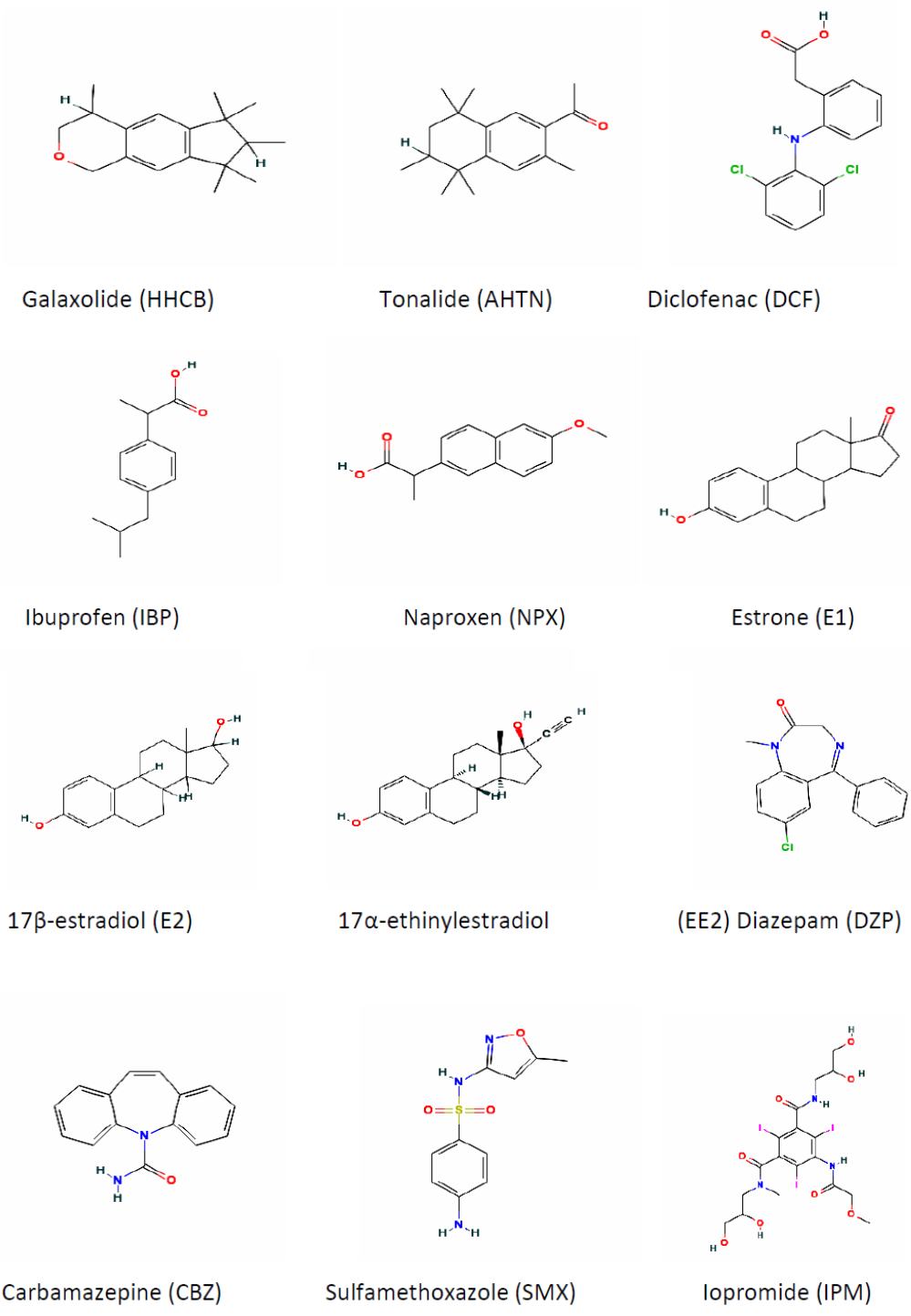

Figure 3 Chemical Structure of selected PPCPs (http://pubchem.ncbi.nlm.nih.gov).

A few compound classes will be highlighted, either because the concentrations found in water are high, because of their (increasing) high volume usage or because of the persistence of these compounds.

2.1.1 Antibiotics

Antibiotics are widely used. Hospital wastewater effluents are one source of antibiotics, although wastewater effluents from tropical fish farm plants appeared to be also an important source of antibiotics (Christoph Ort, 2010). Some of these substances sometimes show low absorbance to sewage sludge (log Kow = 1 – 6) (Brown, 2004). Antibiotics such as sulfamethoxazole, trimethoprim, penicillin and caffeine were detected in hospital wastewater at high levels (0.3 – 35 µg/l). Only sulfamethoxazole, trimethoprim and ofloxacin were present in WWTP treated effluent in concentrations ranging from 0.11 to 0.47µg/l. The substances trimethoprim and ofloxacin are part of the quinolone antibiotics (QAs) which have been widely used for the last 20 years in Europe and the United States (Beate I. Escher, 2011).

QAs consists of compounds such as pipemidic acid (PIP), ofloxacin (OFL), norfloxacin (NOR), ciprofloxacin (CIP), lomefloxacin (LOM), enrofloxacin (ENR), difloxacin (DIF), sarafloxacin (SAR), and tosufloxacin (TOS). Also antibiotics belonging to the quinolone group, including fluoroquinolones (FQs), are of particular environmental concern, because of the potential inhibition of DNA gyrase, a key enzyme in DNA replication. Ofloxacin, lomefloxacin, norfloxacin and ciprofloxacin are the QAs which are frequently found in WWTP effluents across Europe up to concentrations of 0.3 ug/L. Removal efficiencies of antibiotics in general were estimated between 20 to 70 percent in WWTPs, mainly due to the low (Kow) value of antibiotics (Log Kow ~ 1). Sulfamethoxazole, found in relatively high concentrations in hospital wastewater, displayed high persistence and is detected at concentrations up to 0.3 µg/L in WWTP effluents.

2.1.2 Antineoplastic drugs

During the past years, the growing use of antineoplastic drugs in cancer therapy is an emerging issue in environmental research and it can be expected, that consumption will increase due to a developing health care system and a higher life expectancy. Cytostatics belong to the CMR (carcinogenic, mutagenic and reprotoxic) drugs. They usually enter the hospital effluents partially transformed or even unchanged via urine and faeces of patients under medical treatment. Therefore, they are assumed to be environmentally relevant compounds. As hospital

effluents reach the municipal sewer network generally without any preliminary treatment, hospitals may represent an incontestable release source of anticancer agents.

Besides, nearly 80% of cancers therapies are administered in the outpatient treatment ward, i.e. patients leave the hospital after drug application (Mahnik et al., 2007). Subsequently, the drugs are also directly excreted into the municipal sewer network. Their quantification in hospital effluents may serve as a starting point to individualize the magnitude of potential pollution problems. Especially in Germany, investigators have been active in monitoring the fate of cytostatics in the environment after administration to patients. The concentrations of the antineoplastics cyclophosphamide and ifosfamide in the effluents of domestic WWTPs in Germany were determined to be between 6.2–8.5 ng/L and 6.5-9.3 ng/L respectively.64 In a WWTP of an oncologic hospital in Germany, much higher concentrations in the effluent were observed (0.006–1.9 µg/L and0.02-4.5 µg/L respectively). No significant reduction during sewage treatment was observed. Treatment of oncologic wastewater in a membrane bioreactor resulted in concentrations below the limit of detection. Most anticancer drugs could be eliminated to a major extent (80%) by sewage treatment plants, either by biodegradation or adsorption.

2.1.3 Endocrine disrupters (EDCs)

Endocrine disrupters (also called hormonally active agents) are any type of chemical or mixture of chemicals that affect the endocrine system, and cause negative reproductive and developmental health effects for the human or animal and/or their offspring. The endocrine system is a complex network of organs, including the thyroid, pancreas, pituitary, ovaries, testes, and adrenal glands, which secrete hormones into the bloodstream to target cell receptors in other organs or tissues, where the hormone has a specific effect (P. Verlicchi, 2010). In general, there are three major classes of endocrine disrupting compounds, which are estrogenic (compounds that mimic or block natural testosterone), androgenic (compounds that mimic or block natural testosterone), and thyroidal (compounds with direct or indirect impacts to the thyroid).

Estrogens

The most studied endocrine disruptors are those organic compounds, which mimic the hormone oestrogen. Oestrogenic steroids such as the synthetic steroid hormone 17aethynylestradiol (EE2)

prescribed as oral contraceptive for birth control or oestrogen substitution therapies and the natural hormone 17s-estradiol (E2) and its main metabolite oestrone (E1) are among the most potent EDCs causing effects in aquatic organisms (Jean, 2012). Several studies have been performed on the determination of the oestrogen activity in WWTP effluents (Sh.Sarafraz, 2007). On several locations in Europe, (Belgium, Finland, France, Germany, Norway, Sweden, Switzerland and The Netherlands), the WWTP effluents and surface water have been studied for the presence of estrogens (Verstraete, 2006). Treatment processes included primary and chemical treatment only, but also more advanced treatment processes (e.g. ozone) have been studied. In all studies, significant levels of estrogens are detected in both WWTP influent- and effluent water, ranging from 2 up to 51 ng/L and from 0.5 to 3 ng/L, respectively. The highest estrogen values were detected in the effluent of the WWTPs which only used primary treatment (35 ng/L E1, 13 ng/L E2 and 0.05-1,6 ng/L EE2). For WWTPs equipped with a secondary treatment, the concentration of E1 and E2 in the effluent was between 0.7–5.7 ng/L and 0.8-3.0 ng/L respectively. The removal efficiency of E1 and EE2 clearly depends on the redox conditions of the purification process. This is partially due to the reduction during this process of E1 into E2. A biological degradation of more than 90% of the E1, E2, and EE2 load can be expected from conventional activated sludge plants and membrane bioreactors. The removal efficiency of estrogens is improved when sludge retention times increases (Qiaoling Liu, 2010). This can be ascribed to the relatively moderate (log Kow) values of estrogens of 3-4 and a very low vapour pressure (Henry constant). The concentration of estrogens in WWTP effluents is found to be proportional to the population numbers of the city associated with the specific WWTP. For example, the stretch of the River Elbe between Dresden and Magdeburg has some big population centres and associated endocrine disrupting effects in the resident fish in some regions have now been detected. In these areas, the addition of tertiary treatments, known to reduce micro-organic pollutants in drinking water purification, such as ultra-filtration, ozonation, UV treatment, activated charcoal etc. may need to be considered for the removal of estrogens.

2.1.4 General pharmaceutical

Anti-inflammatories and analgesics, lipid regulators and s-blockers are the major groups detected in WWTP effluents across Europe and among them are acetaminophen, ketoprofen, ibuprofen, diclofenac, mevastatin, atenolol, propranolol, sulfamethoxazole, bezafibrate and trimetroprim as

the most abundant, with concentrations at levels (Lubomira Kovalova, 2013). The highest concentrations were detected for acetaminophen (paracetamol) and for trimethoprim, with average concentrations in WWTP effluent of 2.1 µg/L and 0.29 µg/L respectively, (Evens Emmanuel, 2009). Other compounds frequently detected in WWTP samples were carbamazepine and ranitidine, with average concentrations of 400 ng/L for carbamazepine and 135 ng/L for ranitidine in effluent (S.N. Mahnik, 2007). Different removal behaviour was observed for the investigated compounds. Some compounds as the antiepileptic drug carbamazepine were not removed at all in any of the sampled treatment facilities and effluent concentrations in the range of influent concentrations were measured. Other compounds as bisphenol- A, the analgesic ibuprofen or the lipid regulator bezafibrate were nearly completely removed. The drugs detected in the environment were predominantly applied in human medicine. Due to their widespread presence in the aquatic environment many of these drugs have to be classified as relevant environmental chemicals (Lubomira Kovalova, 2013).

2.1.5 Musk fragrances

Synthetic musks are a group of chemicals possessing a chemical structure that is not readily biodegradable they are capable of being bio- concentrated in aquatic organisms The most frequently used synthetic musks 18 are Musk ketone: 1-tert.-Butyl-3,5-dimethyl-2,6-dinitro-4-acetylbenzene (MK); Musk moskene: 4,6-Dinitro-1,1,3,3,5-pentamethylindane (MM); Musk ambrette: 2,6-Dinitro- 3- methoxy-4-tert.-butyltoluene (MA); Musk xylene: 1-tert.-Butyl-3,5-dimethyl-2,4,6-trinitrobenzene (MX) and Musk tibeten: 1-tert.-Butyl-2,6-dinitro-2,4,5-trimethylbenzene (MT).

The Log Kow values of these compounds and their metabolites vary from 4.3 to 6.3 and from 4.8 to 5.1 respectively. These synthetic compounds are used as more affordable substitutes for the expensive natural musks (e.g., muscone, civetone, and ambrettolide) present in many perfumes. Based on this (Log Kow) most of these musks will be more or less efficiently removed by a WWTP treatment. Many manufacturers voluntary are replacing the older and more toxic substances for newer, such as tonalide (AHTN) and galaxolide (HHCB). There are four synthetic musk fragrances accounting for 95% of the total amount used. These are the nitro-musks (musk xylene, used in detergents and soaps, and musk ketone, used in cosmetics) and two polycyclic

musks HHCB and AHTN. Synthetic musks enter city sewage systems (presumably from bathing, laundry detergents, and other washing activities), and then the aquatic ecosystem, where they may potentially bio-concentrate and bio-magnify in the tissues of aquatic organisms.Fragrances are reported in several studies and they are identified in effluents and surface water (AR Mesdaghinia, 2009).

Concentrations up to 0, 73 mg/l are found in effluents of domestic WWTP (Verstraete, 2006). Two nitro musks (musk xylene, musk ketone), a major metabolite of musk xylene and the polycyclic musk fragrance tonalide (AHTN) are suspected of having estrogenic activity (Bitsch et al., 2002). It has been established that the partial removal observed for the two fragrances AHTN and galaxolide (HHCB) during wastewater treatment is mainly due to sorption (log KOW > – 4.9) onto sludge and not to biological transformation. Due to the incomplete removal of fragrances in conventional WWTP, the ozonation has been tested as a possible tool for the enhanced removal of fragrances. By applying 10 –15 mg/l of ozone (contact time: 18 min), most of the musk fragrances were no longer detected (Lubomira Kovalova, 2013).

2.1.6 Sunscreen Agents (SSAs)

Sunscreen agents (SSAs) are more and more widely used for protection against harmful UV radiation. The concentration of these sunscreen agents in water is limited (0.004 µg/L) and considerable concentrations are found in aquatic organisms (21 µg/kg) indicating that SSAs are able to bio-concentrate (P. Verlicchi, 2010). The fact that SSAs (e.g., oxybenzone (2- hydroxy-4-methoxybenzophenone) and 2-ethylhexyl-4-methoxycinnamate) can be detected in human breast milk shows the potential for (dermal) absorption and bioconcentration in aquatic species (Christoph Ort, 2010). No data have been published on more recently used SSAs such as avobenzene.

2.1.7 Diagnostic contrast media

There are two basic types of contrast agents used; one type is based on barium sulfate, the other type on iodine. Triiodinated benzene derivatives are widely used as X-ray contrast agents. The preferential uptake of triiodinated compounds in specific organs enhances the contrast between those organs and the surrounding tissues and enables the visualization of organ details which otherwise could not be investigated. The compounds may be bound either as an organic (non-

ionic) compound or as an ionic compound. Ionic agents were developed first and are still in widespread use depending on the examination they are required for. Most commonly used X-ray contrast media are: Diatrizoate (Hypaque 50), Metrizoate (Isopaque Coronar 370), Ioxaglate (Hexabrix), Iopamidol (Isovue 370), Iohexol (Omnipaque 350), Iopromide, Iodixanol (Visipaque 320) (Beate I. Escher, 2011). These contrast media are applied by intravenous injection and are rapidly eliminated via urine or faeces. Due to the high hydrophicity of the substituted benzene derivatives (Log Kow = -2) they pass wastewater treatment plants without any cleavage and thus, are found in rivers, lakes and even raw drinking water (Lubomira Kovalova, 2013). The contrast agent diatrizoate occurs with concentrations upto 5.2 µg/L as is iopromide found in concentrations up to 5.7 µg/L in effluents of WWTPs, (Beate I. Escher, 2011). These are the most abundant and most used iodated contrast media (ICMs). In specific effluents of WWTPs near hospitals, the concentrations of ICMs can be much higher (up to 1200 µg/L).Secondary treatment and introduction of oxidation steps only enhance the removal efficiency of these iodated agents in a limited way. Even with a 15 mg/L ozone dose, the ionic diatrizoate only exhibited removal efficiencies not higher than 14%, while the non-ionic ICM (diatrizoate, iopamidol, iopromide and iomeprol) were removed to a degree of higher than 80%. Advanced oxidation processes (e.g. O_3/H_2O_2), which were nonoptimized for wastewater treatment, did not lead significantly to a higher removal efficiency for the ICM than ozone alone. It is interesting to note the high variation of the influent concentrations for iopromide: the fact that the influent load in a WWTP serving 120,000 population equivalents can vary by more than a factor of seven from one 24 h composite sample to the next suggests that most of this compound is emitted irregularly by a small number of point sources (Lubomira Kovalova, 2013). The metabolites of these contrast media have not been identified yet. The evaluation of the ecotoxicity of triiodinated contrast agents must include the transformation products. No environmental risk has to be expected from the triiodinated contrast media itself, , but the metabolites may have an ecotoxicological impact. Most likely, the transformation products carry free amino groups, which might be mutagenical, thus, identification of the transformation products is very important (Qiaoling Liu, 2010).

2.2 Sources, pathways and fate of PPCPs

Wastewater produced by hospitals and by hospital-related industries originates from many sources. The technology Identification Subgroup assigned the various medical industry wastewater streams into the following four categories (M. Tsakona, 2007):

- Wastewater from Clinical Laboratories.
- Wastewater from Research Laboratories.
- Wastewater from Medical Waste Incinerators equipped with fume scrubbers.
- Wastewater from Hospital Laundries.

To understand the characteristics of these wastestreams and the difficulties that might be encountered when attempting their pretreatment, it is important to understand the operations or sources of waste that contribute pollutants to the individual wastestreams. In this way, the chemical constituency of each wastestream can be predicted and potential interferences in a mercury removal process can be anticipated.

The following are brief overviews of typical wastewater-producing processes in each category of hospital facility. Each overview includes an interpretation of the analytical data generated from a wastewater sampling and analyses project that was performed at a representative facility. The wastewater sampling and analysis project was performed by a subgroup of the Phase II Work Group known as the Wastewater Characterization (WWC) Subgroup.

Clinical Laboratories:

Most clinical laboratories perform a wide range of services but not every clinical laboratory is the same. Some clinical laboratories are independent of hospitals. Generally, the larger the hospital, the greater the extent of services offered by the clinical laboratory.

The types of processes performed in a clinical laboratory can include: anatomic pathology (including routine histology and cytology), chemistry, drug monitoring and toxicology, hematology, immunology and serology, microbiology, transfusion medicine, and urinalysis. In addition, there can be cytogenetics, flow cytometry, histocompatibility testing, molecular pathology, mycology, and nuclear medicine (Beate I. Escher, 2011).

Wastewater from a "typical" clinical laboratory could contain ionic mercury and organomercuric compounds, other heavy metals, organic chemicals, blood products and body fluids, formaldehyde, buffers, dilute mineral acids/bases, phosphates, oxidizers, oil & grease, and particulate materials. Data from the Work Group's Wastewater Characterization Study suggests that clinical laboratory wastewater would have higher biochemical demand (BOD) and chemical oxygen demand (COD) than domestic sewage. Because there is usually some standardization of work, the wastewater from a specific clinical laboratory may be somewhat consistent in quality and characteristics over long periods.

Research Laboratories:

Perhaps the most diverse and unpredictable wastestreams are those discharged from research laboratories. Many medical institutions are conducting "cutting edge" studies in infectious disease control, blood chemistry, pathology, animal research and inorganic chemistry. Wastes may be produced in significant quantities for short periods or not at all for extended periods. Research laboratory facilities in hospitals can range from one to two laboratory sinks that produce "tens of gallons" each day to hundreds of sinks and related fixtures generating waste volumes in excess of fifty thousand gallons per day.

Wastes can originate from either automated instrumentation or from manual processes and may contain the following pollutants: oxidizers (disinfecting media such as bleach, iodine, peroxides, etc.), radionuclides, proteins (tissue and immunodiagnostics), oil & grease (from vacuum pumps and other rotating equipment), heavy metals (analytical reagents), organic solvents, blood products and other body fluids (urea is a well-known chelator of heavy metals), formaldehyde, phosphates and detergents (from glass cleaning and instrument sterilizing processes), and photographic imaging chemicals (desilvered spent fixer and developer solutions). Data from the Work Group's Wastewater Characterization Study suggests that (BOD) and (COD) are lower than for clinical laboratories but above average compared with domestic sewage (Lubomira Kovalova, 2013).

Medical Waste Incinerators:

Federal and State regulations closely govern the management of infectious medical or "Red Bag" wastes. Some facilities, trying to reduce the cost of offsite waste disposal, have chosen to install on-site medical waste incinerators to burn these wastes. Air quality regulations typically require the installation of emission controls on the incinerator stacks for particulate and oxides of nitrogen (NOx) and sulfur (SOx) (Chioma C. Okore, 2014). Most control systems involve a fume scrubber where pollutants are scrubbed from the waste gas stream into a recirculating water stream. To limit the concentration of pollutants in the recirculating water, part of the water is typically discharged into a sewer system and is replaced with fresh water. Mercury in the waste gas stream can originate from the waste being burned and also from the fuel used to burn the waste. Red Bag wastes may contain tissue, paper, saturated sorbents, plastics, mercury thermometers, and metallic objects. In some facilities, various animal or human tissues may be disposed of as Red Bag wastes. The liquid wastestream from the incinerator scrubber usually has relatively low concentrations of organic material, oxidizers, but can contain significant concentrations of particulate matter and heavy metals (including mercury). BOD and COD concentrations for incinerator wastewater are usually lower than those of domestic sewage.

Hospital Laundries:

Hospital laundries typically process linens, gowns and lab coats that will contribute a certain amount of organic material, fats, oils and grease (FOG) and an alternating range of pH (alkaline detergent followed by an acidic sanitizer) to the wastestream. This is notably different from a commercial laundry that will commonly process garments, uniforms, wipers, mops and mats often contaminated with heavy metals and petroleum products. Depending upon the processes employed, the hospital laundry wastestream can have elevated temperatures and pH extremes and can contain starch, particulate (including lint), proteins (blood products), detergents, and oxidizers (bleach or other disinfectant). BOD and COD concentrations from laundry wastewater are usually in the normal range for domestic sewage.

Some laundry chemicals (sodium hydroxide and bleach) are known to often have significant levels of mercury contamination. In addition, just one broken mercury thermometer can cause temporary high levels of mercury in the laundry wastewater. Hospital laundry wastewater flows

can vary from a few hundred gallons per day to many thousands of gallons per day (L. Liberti, 1996).

After a chemical is created, the route that it takes between initial observation and final observations is referred to as a pathway. Common pathways include manufacture to initial use, initial used to disposal and initial use to release to the environment. The result of interactions between a chemical compound and its environment over a series of events and procedures is known as its fate. Even though a number of research publications have been focused on the occurrence, fate, and effects of pharmaceuticals in the environment, we have data on the occurrence of only 10% of the registered active compounds, and very little information on their effects in the environment. There is even less information regarding the occurrence and fate of the transformation/degradation products (active or not) of pharmaceuticals. Both the qualitative and the quantitative analysis of pharmaceuticals in the environmental matrices are definitely a starting point for the establishment of new regulations for the environmental risk assessment of pharmaceutical products. Discharge of PPCPs can occur from domestic wastewater, hospital wastewaters or industrial discharges. (M. Tsakona, 2007) Hospitals are important sources of these compounds: a great variety of micro contaminants result from diagnostic, laboratory and research activities on one side and medicine excretion by patients on the other. They include active principles of drugs and their metabolites, chemicals, heavy metals, disinfectants and sterilizants, specific detergents for endoscopes and other instruments, radioactive markers and iodinated contrast media. But hospitals are not the only source: residues of pharmaceuticals can be found in all wastewater treatment plant (WWTP) effluents, due to their inefficient removal by conventional systems (Qiaoling Liu, 2010).Despite their specific nature, quite often hospital effluents are considered to be of the same pollutant load as urban wastewaters (UWWs) and are discharged into public sewer networks, collected to a WWTP and co-treated with UWWs. Before entering into the municipal sewer, chlorination is sometimes required for the whole hospital wastewater flow rate, sometimes only for the effluent from infectious disease wards (Evens Emmanuel, 2009). PPCPs eventually enter wastewater treatment plants (WWTP). During wastewater treatment, a distribution occurs between the dissolved and solid phases. Influent suspended solids are largely removed through primary clarification. The separation is relevant for the most lipophilic compounds. As a result, non-degraded PPCPs will be discharged into the

environment not only through the final effluent of the plant, but also with biosolids. (Verstraete, 2006) showed that organic wastewater contaminants could be detected in the target biosolids with high occur frequency and high concentration, which suggests that biosolids can be an important source of organic wastewater contaminants to terrestrial environment (Xianghua Wen, 2004)indicated that the PPCPs that enter wastewater treatment plants can undergo partial or complete transformation and by-products can be discharged to the environment in the final effluent or through biosolids being applied to land. One of the main sources of emerging contaminants is untreated urban wastewater and effluents from wastewater treatment plants. Most current wastewater treatment plants are not designed to treat these compounds (P. Kumarathilaka, 2015) identified diclofenac as one of the most important pharmaceuticals in the water cycle, with low mg/L concentrations in both row and treated wastewater (3.0 and 2.5 mg/L at the influent and effluent, respectively). Atenolol, metoprolol, and propranolol have been frequently identified in wastewaters, where atenolol was detected in the highest concentrations, in some cases ranging up to 1 mg/L. As a result of the incomplete removal during conventional wastewater treatment, these compounds were also found in surface waters in the ng/L to low mg/L range (Qiaoling Liu, 2010).

Antibiotics are destined to treat diseases and infection caused by bacteria. They are among the most frequently prescribed drugs for humans and animals in modern medicine. Betalactams, macrolides, sulfonamides, fluoroquinolones, and tetracyclines are the most important antibiotic groups used in both human and veterinary medicine. High global consumption of up to 200,000 tons per year high percentage of antibiotics that may be excreted without undergoing metabolism (up to 90%) result in their widespread presence in the environment. Unmetabolized pharmaceutically active forms of antibiotics concentrated in raw sludge may promote the development of bacterial resistance. Bacteria in raw sludge are more resistant than bacteria elsewhere (Jean, 2012). Many active antibiotic substances were found in raw sewage matrices, including both aqueous and solid phase. Sulfonamides, fluoroquinolone, and macrolide antibiotics show the highest persistence and are frequently detected in wastewater and surface waters (Huang et al., 2001). Sulfamethoxazole is one of the most detected sulfonamides that were reported with various concentrations and up to ca. 8mg/L (in raw influent in China).

Sulfamethoxazole is often administrated in combination with trimethoprim, and commonly analyzed together. Carbamazepine is one of the most widely prescribed and very important drug for the treatment of epilepsy, trigeminal neuralgia, and some psychiatric diseases (e.g., bipolar affective disorders. In humans, following oral administration, it is metabolized to pharmacologically active carbamazepine-10, 11-epoxide, which is further hydrolyzed to inactive carbamazepine-10, 11-trans-dihydrodiol, and conjugated products which are finally excreted in urine. Carbamazepine is almost completely transformed by metabolism with less than 5% of a dose excreted unchanged (Shorvon et al., 2004). In fact, carbamazepine and its metabolites have been detected in both wastewaters and biosolids. Carbamazepine is heavily or not degraded during wastewater treatment and many studies have found it ubiquitous in various environment matrices (groundwater, river, soil). The concentrations of carbamazepine vary from one plant to another, and they are usually around hundreds ng/L, and in some cases also few mg/L (P. Kumarathilaka, 2015). As a result, a high portion of emerging contaminants and their metabolites can pass through the treatment process and enter the aquatic environment via wastewater effluents without any elimination (Figure 4).

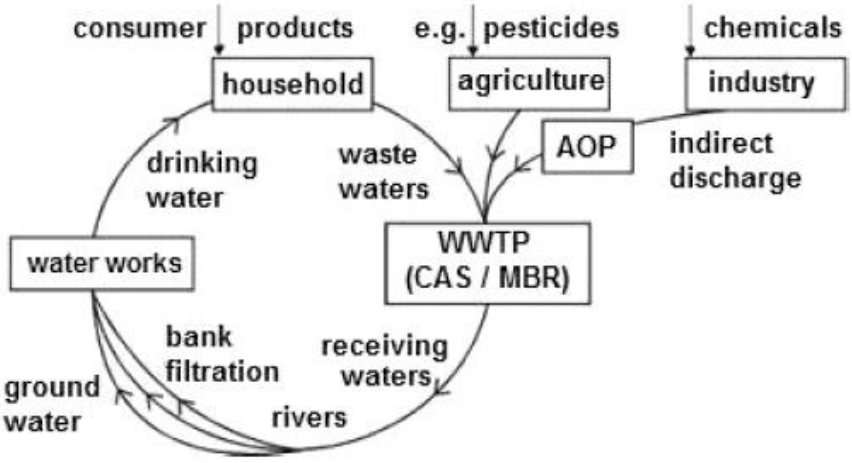

Figure 4 Pathways of emerging contaminants (Ajay Kumar Gautam, 2007)

2.3 Disposal of toxic effluent from hospitals and its environmental impact

In 2011, the World Health Organization published a report entitled "Pharmaceuticals in drinking water which reliefs the risks to human health associated with exposure to trace concentrations of pharmaceuticals in drinking-water. But, the effect and hazard of emerging contaminants to public health and environment are poorly understood. Human and veterinary applications are the main sources of PPCPs in the environment that are introduced primarily through excretion and the subsequent transport in sewage, whereas direct disposal of unwanted or expired drugs in the sewage is believed to be of minor importance (Christoph Ort, 2010).

These chemicals are designed to have a specific mode of action, and they have varying persistence in the body. These features among others suggest that it is important to evaluate the effect of pharmaceuticals on aquatic flora and fauna. PPCPs in the environment lately have been acknowledged to constitute a major health risk for humans and members of terrestrial and aquatic ecosystems (Beate I. Escher, 2011).

Ecotoxicity of emerging contaminants can be divided in to two aspects: acute and chronic. The present research indicates that LC50 or EC50 concentrations for PPCPs such as fluoxetine and diazepam are approximately 100 times greater than commonly observed environmental concentrations. There is a general lack of chronic toxicity data on pharmaceuticals, in particular in fish. Many pharmaceuticals need more investigation to determine potential long-term ecotoxicological effects, particularly with respect to potential disturbances in hormonal homeostasis (endocrine disruption), immunological status, or gene activation and silencing during long-term exposure (Sh.Sarafraz, 2007). Many PPCPs do not exhibit an acute aquatic toxicity but have a significant cumulative effect on the metabolism of non target organisms (AR Mesdaghinia, 2009) and the ecosystem as a whole. Many endocrine disruptors induce serious effects in low concentrations but also individual PhCs occurring in low concentrations may exhibit synergistic and cumulative effects. In addition, the development of antibiotic resistance may be stimulated in bacteria from exposure to low concentrations investigated that HWW is a source for undesirable constituents, such as (multi-)antibiotic-resistant bacteria. A/C to the Centers for Disease Control and Prevention, about 2 million people in hospitals get infections each year, which cause 90,000 deaths. Of these, more than 70 % of the bacteria that causes these

infections are resistant to at least one common antibiotic that is typically used to treat them (E. Emmanuel, 2005).

Confirmed that the hospital effluents have generally a very weak microbiological load resulting from the regular use of disinfectants. These bactericides can have a negative influence on the biological processes of the WWTP. Even by considering that these effluents are diluted after their discharge towards the municipal WWTP, it remains evident that it is not necessary to neglect the possibility that certain substances present in the WWTP effluents can generate by cumulative effect a biological imbalance in aquatic ecosystem. To protect the natural environment against the phenomenon of excess load in the processes of the WWTP, it seems important to consider upstream treatments of hospital wastewater before their discharge in the municipal sewage system.

As a result, it has been suggested in some studies that pre-treatment of HWW prior to discharge into the sewers provides a reasonable solution (Lubomira Kovalova, 2013). After application, some of these substances and excreted non-metabolized drugs by the patients enter into the hospital effluents which generally reach, as well as the urban wastewater (Figure 3), the municipal sewer network without preliminary treatment. Unused medications sometimes are also disposed in hospital drains. Pollutants from hospital were measured in the effluents of WWTP, and in surface water.

Due to laboratory and research activities or medicine excretion into wastewater, hospitals may represent an incontestable release source of many toxic substances in the aquatic environment. The contact of hospital pollutants with aquatic ecosystems leads to a risk directly related to the existence of hazardous substances which could have potential negative effects on biological balance of natural environments. Risk is the probability of appearance of toxic effects after organism's exposure to hazardous substances (E. Emmanuel, 2005). The ecological risk of glutaraldehyde, a dialdehyde usually recommended as the disinfectant of choice for reusable fiber-optic endoscopes, has been also treated in other study (Lubomira Kovalova, 2013). However, few studies treat the total risk resulting from the simultaneous exposure to various pollutants present in the hospital effluents.

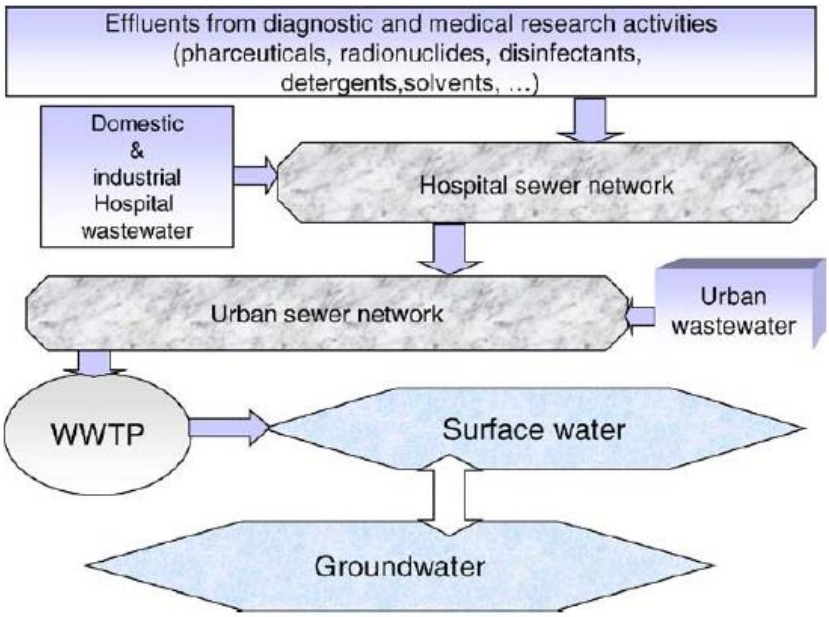

Figure 5 Problems of hospital effluents and their impacts on WWTP and natural environments (E. Emmanuel, 2005)

In the context of hospital wastewater discharge into the aquatic ecosystem, the exposure to hazardous substances, particularly disinfectants, nonmetabolized pharmaceuticals and radionuclides, requires to consider possible risks for aquatic organisms. The fate of pharmaceuticals in the aquatic environment has been reported in different reviews of the literature (Jean, 2012).

2.4 Treatment technologies for hospital wastewaters

2.4.1 Conventional Activated Sludge Process

CAS is very old technology. The basic mechanism of activated sludge process treatment is to use microorganisms to feed on organic contaminants in wastewater, producing a high quality effluent. The main principle behind all activated sludge processes is that as microorganisms grow, they form particles that clump together. These particles (floc) are allowed to settle to the bottom of the tank, leaving a relatively clear liquid free of organic materials and suspended solids (Metcalf and Eddy, 2003). Screened wastewater is mixed with varying amounts of recycled liquid containing a high proportion of organisms taken from a secondary clarifying tank, and it becomes a product called mixed liquor. This mixture is stirred and injected with large quantities of air, to provide oxygen and keep solids in suspension. After a period of time, mixed

liquor flows to a clarifier where it is allowed to settle. A portion of the bacteria is removed as it settles, and the partially cleaned water flows on for further treatment. The resulting settled solids and the activated sludge are returned to the first tank as the process continues.

The pollutants can be found in different forms, e.g. particulate, bound to colloids and dissolved. Depending on the type of pre-treatment a certain amount of pollutants in a certain form will enter the bioreactor. The treatment was originally designed for removal of COD and suspended solids. Due to problems with eutrophication of surface waters further treatment was required which included removal of nutrients like nitrogen and phosphorus. Next to the nutrients there is a long list of micro pollutants that will have to be removed from the wastewater. Special attention will have to be paid to the removal of medicine residues as well as endocrine disruptors, pesticides and heavy metals. A schematic overview of a typical conventional activated sludge process is presented in (Figure 6).

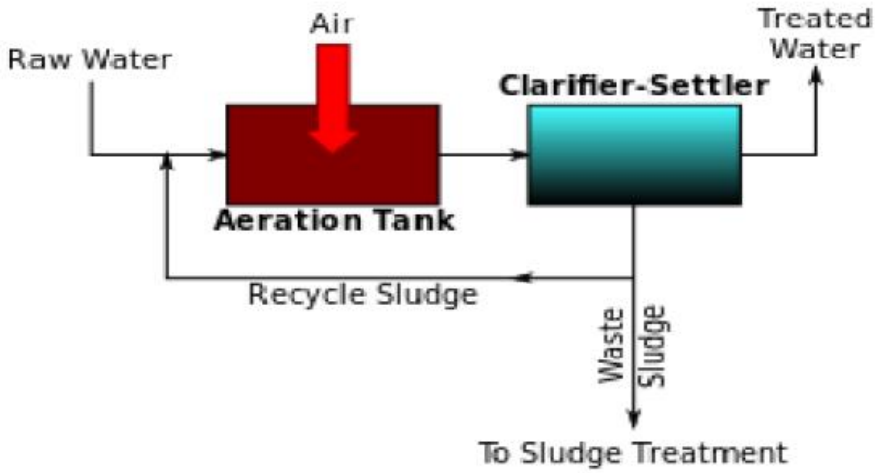

Figure 6 Schematic overview of a typical conventional activated sludge process (Verstraete, 2006)

2.4.2 Membrane Bioreactors (MBR)

The Membrane Bioreactor combines the biological activated sludge process with a membrane filtration step for sludge water separation. The membrane can be applied within the bioreactor (submerged configuration) or externally through recirculation. Since external settlers, or any other post treatment step, become super fluous by using a membrane for the suspended solid and effluent separation, the required space for an installation is small and sludge concentration in the aeration tanks can be two to three times higher than in conventional systems. Furthermore, the effluent quality is significantly better as all suspended and colloidal material such as micro contaminants, bacteria and viruses are removed (Ujang and Anderson, 2000; Trussell et al., 2005). In an MBR, biological processes are often comparable or better than in conventional activated sludge systems (Ujang et. al., 2005 a, b and c). Due to the long sludge ages, N-removal is more efficient because the slow growing autotrophic bacteria are kept efficiently in the system. Denitrification can occur by introducing anoxic tanks or intermittent aeration (Drews et. al., 2005; Gander et. al., 2000). (Figure 7) shows a typical MBR system.

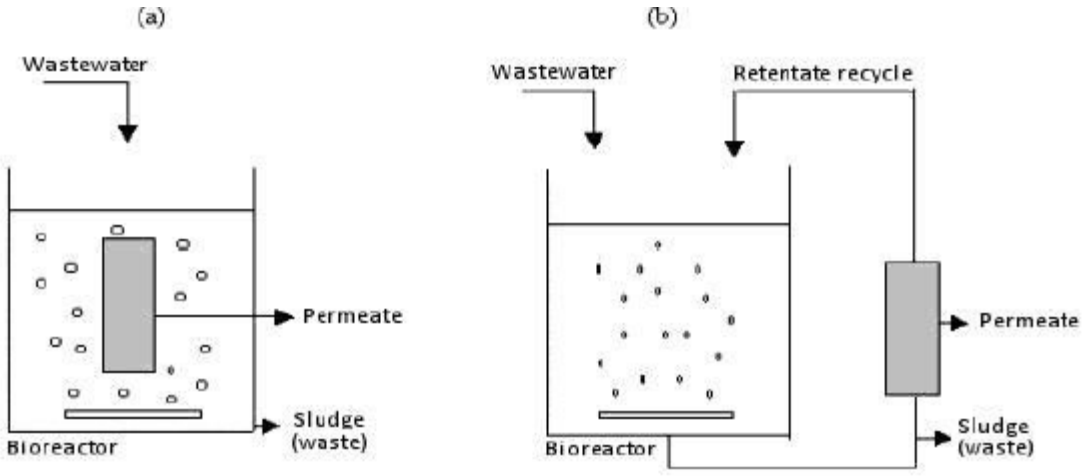

Figure 7 Typical membrane bioreactor system (Pombo *et al.*, 2011)

Membrane filtration denotes the separation process in which a membrane acts as a barrier between two phases. In water treatment the membrane consists of a finely porous medium facilitating the transport of water and solutes through the membrane. It can be also defined as a material that separates particles and molecules from liquids and gaseous. The membrane separation process is based on the presence of semi permeable membrane. The principle is quite simple: the membrane acts as a very specific filter that allows water to flow through, while it catches suspended solids and other substances. There are two factors that determine the

effectiveness of a membrane filtration process; selectivity and productivity. Selectivity is expressed as a parameter called retention or separation factor, while productivity is expressed as a parameter called flux.

2.4.2.1 Membrane Bioreactors application for treating the hospital wastewater

The use of Membrane Bioreactors (MBR) in hospital wastewater treatment has grown widely in the past decades. The MBR technology combines conventional activated sludge treatment with low-pressure membrane filtration, thus eliminating the need for a clarifier or polishing filters. The membrane separation process provided a physical barrier to contain microorganisms and assures consistent high quality reuse water. Few studies was found in the literature explained the efficiency of MBR in treating the hospital wastewater and removal the pharmaceutical s compounds. The wastewater treatment technologies analyzed included microfiltration, ultra filtration, Nano filtration, granular activated carbon, powdered activated carbon, reverse osmosis, electro dialysis reversal, membrane bioreactors, and combinations of these technologies in series.

Microfiltration was not shown to be effective at removing the majority of organic compounds tested. However, microfiltration did effectively remove steroids, especially when coupled with a membrane bioreactor.

Ultra filtration reduced concentrations but was not shown effective at removing the majority of organic compounds tested. However, ultrafiltration effectively removed steroids, especially when coupled with a membrane bioreactor. Snyder et al. (2006a) determined that ultra filtration provided an average removal rate of 59%, and ranged from 1% to 100% depending on the chemical.

Nano filtration was shown to be capable of removing almost all the pharmaceuticals tested, although a few pharmaceuticals were present in the outlet.

Based on the operational experience gained at this site and on technical and economic optimisation, the following aspects should be considered in the design of MBR treating hospital wastewaters in high density urban areas:

- Separate rainwater collection to reduce dilution effects.
- Where applicable, separation of water streams with low pharmaceutical concentrations (e.g. kitchen and laundry wastewaters) sludge age in the MBR > 100 days to allow for biomass adaptation.

- Thermal treatment of the waste activated sludge and screenings for complete destruction of the adsorbed pharmaceuticals.
- Consideration of the special requirements on emission levels (noise and aerosols) for hospital patients with a weak immune system and/or needing a quiet environment as well as those of nearby residents.

Membrane Biological Reactors (MBR) have gained significant popularity in STPs and are nowadays considered as a powerful (and expensive) technology able to produce higher quality effluents in terms of conventional pollutants, which can be appropriate for direct discharge, further postreatment or even reuse purposes. However, since membrane filtration does not enhance the elimination of most micropollutants by means of a sizeexclusion mechanism it is still not clear if these systems may effectively enhance the removal of organic micropollutants (Reif et al., 2008). The need for compact wastewater treatment plants increasingly becomes a global concern where the environmental impact by the population also sets high demands to treatment of waste produced by the community as the hospital wastewaters. The attached growth bioreactor coupled with membrane separation as attached growth membrane bioreactor (attached growth MBR) is an alternative way to achieve high effluent quality, compactness treatment plants and economical management (Degaard, 2000).

2.4.3 Attached growth biological treatment technology

The removal of organic micropollutants from wastewater has become an increasingly important consideration and has imposed new challenges in the design of wastewater treatment plants. One such technology is the submerged attached growth bioreactor (SAGB), which derives its name from the fact that the media is always submerged in the process flow. Attached growth technologies work on the principle that organic matter is removed from wastewater by microorganisms. These microorganisms are primarily aerobic, meaning they must have oxygen to live. They grow on the filter media (materials such as gravel, sand, peat, or specially woven fabric or plastic), essentially recycling the dissolved organic material into a film that develops on the media. The two primary advantages of a SAGB are the small volume requirement and the elimination of downstream clarification (Grady et al., 1999). A submerged biofilter allows for a high biomass concentration leading to a short hydraulic retention time and, thus, a significantly reduced reactor volume as compared to a different fixed film reactor or a suspended growth

reactor. In addition, the media in a SAGB may be fine enough to provide physical filtration for solids separation. Attached growth aerobic treatment reactors can be divided into two groups: with up flow and down flow of treated water. Up flow attached growth aerobic treatment reactors differ in the type of packing and the degree of bed expansion. Down flow attached growth reactors differ only in the packing material used and these can be random or tubular plastic .The neutrally plastic media within each aeration tank provides a stable base for the growth of a diverse community of microorganisms. Polyvinylchloride (PVC) media has a very high surface-to-volume ratio, allowing for a high concentration of biological growth to thrive within the protected areas of the media. There are three types of up flow attached growth processes: 1) the up flow packed bed reactor, where the pack material is fixed and the wastewater flows between the packing covered by the biofilm. The packing material can be rock or synthetic plastic. 2) The aerobic expanded bed reactor (AEBR) which uses a fine-grain sand to support the biofilm growth. 3) The fluidized-bed reactor (FBR), in which fluidization and mixing of the packing material occurs (Tchobanoglous, 2003).

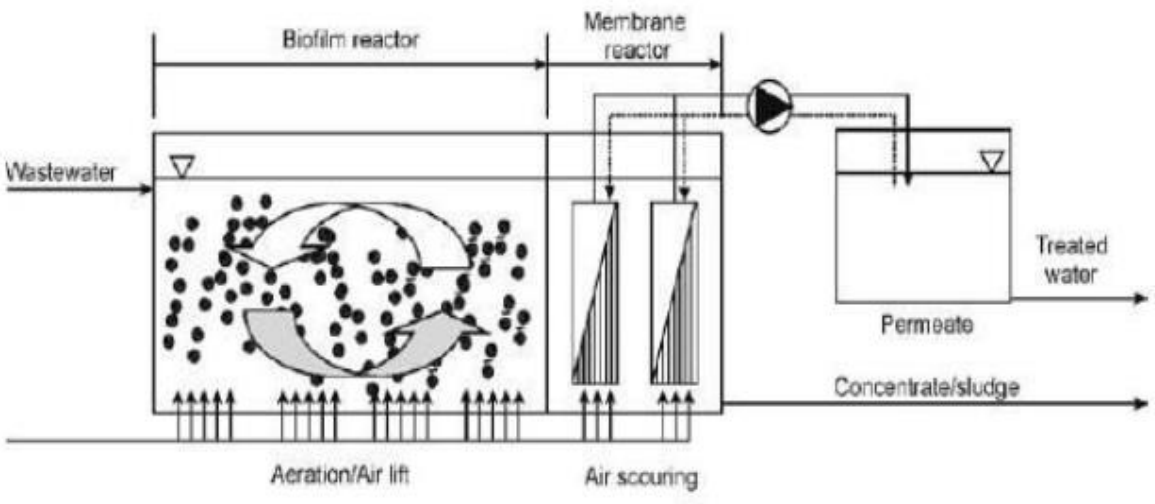

Figure 8 Typical schematics of attached membrane bioreactor (Lee et al., 2001)

The main advantages of attached growth processes over the activated sludge process are lower energy requirements, simpler operation, no bulking problems, less maintenance, and better recovery from shock loads (Metcalf and Eddy, 2003). Attached growth processes in wastewater treatment are very effective for biochemical oxygen demand (BOD) removal, nitrification, and denitrification. Disadvantages are a larger land requirement, poor operation in cold weather, and potential odour problems. In wastewater treatment processes, development of attached growth

bioreactor with high biomass concentrations has been of interests to be achieved in short hydraulic retention time (HRT) in comparison to suspended growth system with equivalent solid retention time (SRT). This results from the use of high specific surface area of carriers. Short HRT could lead to a compact system of the reactor, which can be beneficial when the plant area is limited. (Comett et al., 2004) studied a treatment of leachate wastewater from the anaerobic fermentation of solid wastes using two biofilm support media. Biofilm growing on different carrier media had different responses to the nutrient contaminated in wastewater. The sequencing batch system consisted of two reactors containing Kaldnes and Linpor carrier materials with specific areas of 490 and 270 m2/m3, respectively. The total COD removals for Linpor and Kaldnes reactors were 47% and 39%, respectively and the average ammonia removals for Linpor and Kaldnes were 72% and 42%, respectively. The surface of Linpor had higher concentrations of microorganisms than that of Kaldnes. The average dry solids in Linpor and Kaldnes were 170 g/m2 and 63 g/m2, respectively.

2.4.4 Activated carbon adsorption

Activated carbon is a solid, porous, black carbonaceous material, (see Figure 9). It is distinguished from elemental carbon by the absence of both impurities and an oxidized surface (Mattson and Mark, 1971).

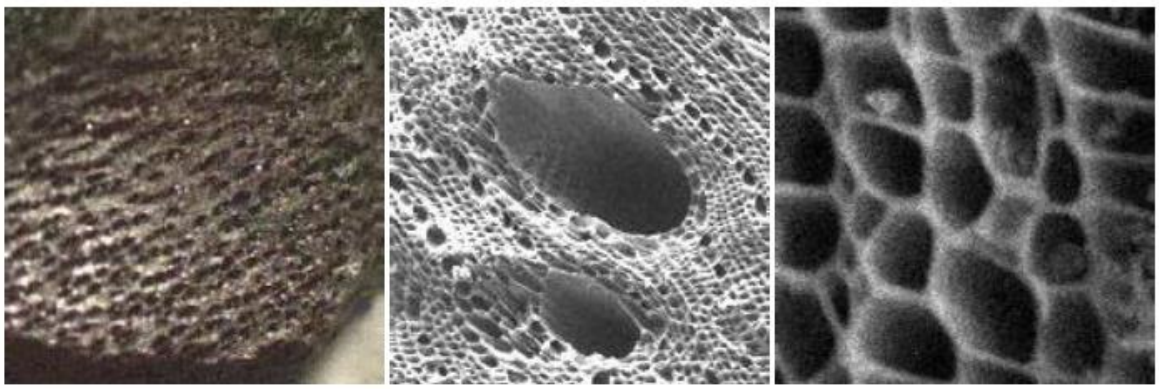

Figure 9 Activated carbon: surface and pores – scanning electron microscope image.

Activated carbon has an extraordinarily large surface area and pore volume, making it suitable for a wide range of applications. The dynamics of adsorption in a packed activated carbon bed are influenced by the shape and size of the activated carbon particles and their effect on the flow characteristics. The smaller an activated carbon particle is, the better the access to its surface area and the faster the rate of adsorption. For spherical beads, the diameter can be measured easily.

For cylindrical extrudates, an equivalent spherical diameter, d eqv, can be calculated from the radius and length of the extrudate. However, for particles of irregular shape and a wide size distribution, it is difficult to derive d eqv. In such cases particle sizes derived from sieve analyses can be useful parameters for determining adsorption rate.

The most important property of activated carbon, the property that determines its usage, is the pore structure. The total number of pores, their shape and size determine the adsorption capacity and even the dynamic adsorption rate of the activated carbon. IUPAC classifies pores as follows (Rodriguez-Reinoso and Linares-Solano, 1989):

- macropores: $d_0 > 50$ nm
- mesopores: $2 \leq d_0 \leq 50$
- micropores: $d_0 < 2$ nm
- ultramicropores: $d_0 < 0.7$ nm
- supermicropores: $0.7 < d_0 < 2$ nm

Where: d_0 is the pore width for slit type pores or the pore diameter for cylindrical pores. The macropores act as transport pathways, through which the adsorptive molecules travel to the mesopores, from where they finally enter the micropores. The micropores usually constitute the largest proportion of the internal surface of the activated carbon and contribute most to the total pore volume. Most of the adsorption of gaseous adsorptive takes place within these micro pores, where the attractive forces are enhanced and the pores are filled at low relative pressures. Thus, the total pore volume and the pore size distribution determine the adsorption capacity. The dynamics of adsorption in a packed activated carbon bed are influenced by the shape and size of the activated carbon particles and their effect on the flow characteristics. The smaller an activated carbon particle is, the better the access to its surface area and the faster the rate of adsorption. For spherical beads, the diameter can be measured easily. For cylindrical extrudates, an equivalent spherical diameter, d_{eqv}, can be calculated from the radius and length of the extrudate. However, for particles of irregular shape and a wide size distribution, it is difficult to derive d_{eqv}. In such cases particle sizes derived from sieve analyses can be useful parameters for determining adsorption rate. (Jufang Wu, 2004).

2.4.4.1 Application of Activated Carbon

In the water and wastewater treatment, activated carbon is used, single or coupled with another process, either in powdered (suspension process) or granular (fixed bed process), depending upon the specific application and process. The objectives pursued with the use of activated carbon in water treatment have changed significantly in recent decades. Years ago, activated carbon was employed primarily for the removal of excess chlorine and the elimination of substances affecting odour and taste from relatively good-quality raw water. Increasingly exacting quality requirements for drinking water, coupled with increasing pollution levels in untreated water (groundwater and surface water), have led to the optimization of activated carbon as a means of guaranteeing acceptable drinking water quality. In parallel, changes in treatment processes, such as the reduction of high-strength chorine treatment, have resulted in the elimination of traditional applications. In recent years, the use of activated carbon processes has become widely established in drinking water treatment, groundwater rehabilitation and the treatment of wastewaters. Likewise, activated carbon is being used to an increasing extent in waste water treatment, whether it be in the systematic treatment of individual effluent streams (e.g. in the chemicals industry or hospital effluents), in the removal of substances toxic to bacteria in biological waste water treatment or in tertiary waste water treatment, where effluent restrictions are particularly severe.

CHAPTER III

MATERIALS AND METHODS

Dehradun is the capital city of the state of Uttarakhand in the northern part of India. Located in the Garhwal region, it lies 236 kilometres (147 mi) north of India's capital New Delhi and is one of the "Counter Magnets" of the National Capital Region (NCR) being developed as an alternative centre of growth to help ease the migration and population explosion in the Delhi metropolitan area and creation highways to establish a smart city at Dehradun. It lies in the Doon Valley on the foothills of the Himalayas nestled between the river Ganges on the east and the river Yamuna on the west. The city is famous for its picturesque landscape and slightly milder climate and provides a gateway to the surrounding region. It is well connected and in proximity to Himalayan tourist destinations such as Mussoorie, and Auli and the Hindu holy cities of Haridwar and Rishikesh along with the Himalayan pilgrimage circuit.

The city of Dehradun mainly lies in Doon Valley and is at a varying height from 410m in Clement Town to above 600 m at Jakhan which is 4 km from the city. However, the general elevation is 450 m above sea level. Jakhan is the starting point of Lesser Himalayan Range that extends to Mussoorie and beyond. Jaunsar Bawar hills in Dehradun District rises to 3700m above sea level.

To determine the quality of wastewater effluents, 7 major educational hospitals were selected (See Table 1). Samples were collected from the influent and the effluent of the treatment plants present in the hospital and in the absence of the treatment plant composite samples from different sampling plants were collected during the advent of summer (17th of March 2017 to 13th of April), to avoid dilution effect owing to rain events. They were collected in 1 L plastic bottles properly preserved in ice box then immediately sent to the NABL certified HSE laboratory of UPES, Dehradun for analysis. Chemical and physical parameters including pH, TSS, TDS, DO, BOD5, COD, Alkanlinity, Turbidity, heavy metals concentration (Pb, Cu, Cd) were determined according to “Standard Methods for the Examination of Water and Wastewater” and heavy metals analysis was performed according to the Atomic Absorption Spectrometry method. All discussed in the further sections.

3.2 Sampling Methodology

Hospitals consume large quantity of water a day. Indeed the consumption of domestic water is on average100 litres/person/day, while the value generally admitted for hospitals varies from 400 to 1200 litres/day/bed (P. Verlicchi, 2010). In hospitals water consumed by various parts such as hospitalization, surgery rooms, laboratories, administrative units, laundry, health services, kitchen and etc, physical chemical and biological quality decreased and converted to wastewater. This high consumption of water in hospitals gives significant volumes of wastewater.

3.2.1 Collection and Preservation of Samples

The objective of sampling is to collect representative sample. Representative sample by means a sample in which relative proportions or concentration of all pertinent components will be the same as in the material being sampled. Moreover, the same sample will be handled in such a way that no significant changes in composition occur before the tests are made. The sample volume shall optimal small enough that it can be transported and large enough for analytical purposes. Because of the increasing placed on verifying the accuracy and representatives of data, greater emphasis is placed on proper sample collection, tracking, and preservation techniques. Often laboratory personnel help in planning a sampling program, in consultation with the user of the test results. Such consultation is essential to ensure selecting samples and analytical methods that provide a sound and valid basis for answering the questions that prompted the sampling and that will meet regulatory and/or project-specific requirements.

General Requirements

- Obtain a sample that meets the requirements of the sampling program and handle it so that it does not deteriorate or become contaminated before it is analyzed.
- Ensure that all sampling equipment is clean and quality-assured before use. Use sample containers that are clean and free of contaminants. Bake at 450°C all bottles to be used for organic analysis sampling.
- Fill sample containers without prerinsing with sample; prerinsing results in loss of any preadded preservative and can sometimes result in high bias when certain components adhere to the sides of the container. Depending on determinations to be performed, fill the container full (most organic compound determinations) or leave space for aeration, mixing, etc. (microbiological and inorganic analyses). If the bottle already contains

preservative, take care not to overfill the bottle, as preservative may be lost or diluted. Except when sampling for analysis of volatile organic compounds, leave an air space equivalent to approximately 1% of the container volume to allow for thermal expansion during shipment.

- Special precautions (discussed below) are necessary for samples containing organic compounds and trace metals. Since many constituents may be present at low concentrations (micro-grams or nanograms per liter), they may be totally or partially lost or easily contaminated when proper sampling and preservation procedures are not followed.
- Composite samples can be obtained by collecting over a period of time, or at many different over a period of time, depth, or at many different sampling points. The details of collection vary with local conditions, so specific recommendations are not universally applicable.
- Because of the inherent instability of certain properties and compounds, composite sampling for some analytes is not recommended where quantitative values are desired (examples inresidual, iodine, hexavalent chromium, nitrate, volatile organic compounds, radon-222, dissolved oxygen, ozone, temperature, and pH). In certain cases, such as for BOD, composite samples are routinely by regulatory agencies. Refrigerate composite samples for BOD and nitrite.
- Important factors affecting results are the presence of suspended matter or turbidity, the method chosen for removing a sample from its container, and the physical and chemical brought about by storage or aeration. Detailed procedures are essential when processing (blending, sieving, filtering) samples to be analyzed for trace constituents, especially metals and organic compounds. Some determinations can be invalidated by contamination during processing. Treat each sample individually with regard to the substances to be determined, the amount and nature of turbidity present, and other conditions that may influence the results.
- For metals it often is appropriate to collect both a filtered and an unfiltered sample to differentiate between total and dissolved metals present in the matrix. Be aware that some metals may partially sorb to filters. Beforehand, determine the acid requirements to bring the pH to <2 on a separate sample. Add the same relative amount of acid to all samples;

use ultrapure acid preservative to prevent contamination. When filtered samples are to be collected, filter them, if possible, in the field, or at the point of collection before preservation with acid. Filter samples in a laboratory-controlled environment if field conditions could cause error or contamination; in this case filter as soon as possible. Often slight turbidity can be tolerated if experience shows that it will cause no interference in gravimetric or volumetric tests and that its influence can be corrected in colorimetric tests, where it has potentially the greatest interfering effect. Sample collector must state whether or not the sample has been filtered.

General information

- Sample identification number
- Location
- Sample collector
- Date and hour
- Sample type (Grab or composite)

Specific information

- Water temperature
- Weather
- Stream blow
- Water level
- Any other information

The information may be attached tag, labeling or writing on container with water proof ink.

- Description of sampling points
  - By map using landmarks
  - Use global positioning system

3.2.2 Safety Considerations

Always prohibit eating, drinking, or smoking near samples, sampling locations, and in the laboratory. Keep sparks, flames, and excessive heat sources away from samples and sampling locations. If flammable compounds are suspected of known to be present and samples are to be refrigerated, use only specially designed *explosion-proof* refrigerators.

Label adequately any sample known or suspected to be hazardous because of flammability, corrosivity, toxicity, oxidizing chemicals, or radioactivity, so that appropriate precautions can be taken during sample handling, storage, and disposal.

3.2.3 Sampling Methods

Manual sampling: Manual sampling involves minimal equipment but may be unduly costly and time-consuming for routine or large-scale sampling programs. It requires trained field technicians and is often necessary for regulatory and research investigations for which critical appraisal of field conditions and complex sample collection techniques are essential.
Manually collect certain samples, such as waters containing oil and grease.

Automatic sampling: Automatic samplers can eliminate human errors in manual sampling, can reduce labor costs, may provide the means for more frequent sampling,[3] and are used increasingly. Be sure that the automatic sampler does not contaminate the sample. For example, plastic components may be incompatible with certain organic compounds that aresoluble in the plastic parts or that can contaminated (e.g., from phthalate esters) by contact with them. If sample constituents are generally known, contact the manufacturer of an automatic sampler regarding potential incompatibility of plastic components.

Program an automatic sampler in accordance with sampling needs. Carefully match pump speeds and tubing sizes to the type of sample to be taken.

Sorbent sampling: Use of solid sorbents, particularly membrane-type disks, is becoming more frequent. These methods offer advantages of rapid, inexpensive sampling if the analytes of interest can be adsorbed and desorbed efficiently and the water matrix is free of particulates that plug the sorbent.

3.2.4 Sample Containers

The type of sample containers used is of utmost importance. Test sample containers and document that they are free of analytes of interest, especially when sampling and analyzing for very low analyte levels. Containers typically are made of plastic or glass, but one material may be preferred over the other. For example, silica, sodium, and boron may be leached from soft glass but not plastic, and trace levels of same pesticides and metals may sorb onto the walls of glass containers.Thus, hard glass containers* are preferred. For samples containing organic compounds, do not use plastic containers except those made of fluorinated polymers such as polytetrafluoroethylene (PTFE).

Some sample analytes may dissolve (be absorbed) into the walls of plastic containers; similarly, contaminants from plastic containers may leach into samples. Avoid plastics wherever possible because of potential contamination from phthalate esters. Containers failure due to breakdown of the plastic is possible. Therefore, use glass containers for all organics analyses such as volatile organics, semivolatile organics, pesticides, PCBs, oil and grease. Some analytes (e.g.,bromine-containing compounds and some pesticides. Polynuclear aromatic compounds, etc.) are light sensitive; collect them in amber-colored glass containers to minimize photodegradation. Container caps, typically plastic, also can be a problem. Do not use caps with paper liners. Use foil or PTFE liners but be aware that metal liners can contaminate samples collected for metals analysis and they may also react with the sample if it is acidic or alkaline. Serum vials with PTFE-lined rubber or plastic septa are useful. In rare situations it may be necessary to use sample containers not specifically prepared for use, or otherwise unsuitable for the particular situation; thoroughly document these deviations. Documentations should include type and source of container, and the preparation technique, e.g., acid washed with reagent water rinse. For QA purposes the inclusion of a bottle blank may be necessary.

3.2.5 Number of Samples

Because of variability from analytical and sampling procedures (i.e., population variability), a single sample is insufficient to reach any reasonable desired level of confidence. If an overall

standard deviation (i.e. the standard deviation of combined sampling and analysis) is known, the required number of samples for a mobile matrix such as water may be estimated as follows.

$$N \geq \{(ts / U)^2$$

N = number of samples.

t = Student-t statistic for a given confidence level,

s = overall standard deviation, and

U = acceptable level of uncertainty.

To assist in calculation, use curves. As an example, if s is 0.5mg/L, U is ± 0.2 mg/L, and a 95% confidence level is desired, approximately 25 to 30 samples must be taken. The above equation assumes that total error (population variability) is known. Total variability consists of the analytes of interest within the sampling site, collection, preservation, preparation, and analysis of samples, and data handling and reporting. In simpler terms, error (variability) can be divided into sampling and analysis components. Sampling error due to population variability (including heterogeneous distribution of analytes in the environment matrix) usually is much larger than analytical error components. Unfortunately, sampling error usually is not available and the analyst is left with only the published error of the measurement system (typically obtained by using a reagent water matrix under the best analytical conditions).

More accurate equations are available.These are based on the Z distribution for determining the number of samples needed to estimate a mean concentration when variability is estimated in absolute terms using the standard deviation. The coefficient of variation (relative standard deviation) is used when variability is estimated in relative terms.

The number of random samples to be collected at a site can be influenced partly by the method that will be used. This values for standard deviation (SD) or relative standard deviation (RSD) may be obtained from each of the methods or in the literature.[6] However, calculations of estimated numbers of samples needed based only on this information will result in underestimated number of samples because only the analytical variances are considered, and the typically larger variances form the sampling operations are not included. Preferably, determine and use SDs or RSDs from overall sampling and analysis operations.

For estimates of numbers of samples needed for systematic sampling (e.g., drilling wells for sampling groundwater or for systematically sampling large water bodies such as lakes),

equations are available that relate number of samples to shape of grid, area covered, and space between nodes of grid. The grid spacing is a complex calculation that depends on the size and shape of any contaminated spot (such as a groundwater plume) to be identified, in addition to the geometric shape of the sampling grid. See individual methods for types and numbers of quality assurance (QA) and quality control (QC) samples, e.g., for normal-level (procedural) or low-level (contamination) bias or for precision, involving sampling or laboratory analysis (either overall or individually).

Estimates of numbers of QC samples needed to achieve specified confidence levels also can be calculated. Rates of false positives (Type I error) and false negatives (Type II error) are useful parameters for estimating required numbers of QC samples. A false positive is incorrect conclusion that an analyte is present when it is absent when it is present. If the frequency of false positives or false negatives desired to be detected is less than 10%, then

$$n = \text{In } \alpha / \text{In } (1\text{-}Y)$$

Where:

α = (1-desired confidence level), and

Y = frequency to detect (<10%).

If the frequency that is desirable to detect is more than 10%, iterative solution of a binomial equation is necessary. Equations are available as a computer program for computing sample number by the Z distribution, for estimating samples needed in systematic sampling, and for estimating required number of QC samples.

3.2.6 Sample Volumes

Collect a 1-L sample for most physical and chemical analyses. For certain determination, larger samples may be necessary. Table 3 lists volumes ordinarily required for analyses, but it is strongly recommended that the laboratory that will conduct the analyses also be consulted to verify the analytical needs of sampling procedures as they pertain to the goals and data quality objective of an investigation.Do not use samples from the same container for multiple testing requirements(e.g., organic, inorganic, radiological, bacteriological, and microscopic examinations) because methods of collecting and handling are different for each type of test. Always collect enough sample volume in the appropriate container in order to comply with sample handling, storage, and preservation requirements.

Table 3 Summary of Special Sampling and Handling Requirements

Parameter/Method	Preservative	Sample Holding Time	Suggested Sample Size	Type of Container	Comments
Metals (except Hg)	HNO_3 to pH <2 For dissolved metals, filter Immediately.	6 months	1 L	Plastic or glass rinsed with 1 + 1 HNO_3	
Alkalinity	Cool, 4ºC	24 hours recommend 14 days regulatory (6 hours if Biol. Activity)	200 mL	Polyethylene or Borosilicate glass	Fill container completely and cap tightly . Avoid sample agitation and prolonged exposure to air.
Ammonia	4ºC + H_2SO_4 pH<2 DECHLOR	28 days	500 mL	Plastic or glass	
Biochemical Oxygen Demand and CBOD	Analyze 2 hours or 4ºC.	6 hours recommend 48 hours regulatory	1000 mL	Plastic or glass	
Chemical Oxygen Demand	H_2SO_4 pH<2 and cooled to 4ºC	Analyze ASAP or add H2SO4 to pH <2, + Cool to 4ºC	100 mL	Plastic or glass	
Chlorine	None, analyze immediately	15 minutes	500 mL	Plastic or glass	
Color	Cool, 4ºC	48 hours	500 mL	Plastic or glass	Warm samples to room temperature before measurement
Copper	Concentrated nitric acid (2 mL/L) pH <2	6 months at room temperature	1 L	Acid-washed glass or plastic	Adjust pH to 4-6 with 8N KOH before analysis. Do not exceed pH 6.
Conductivity	Cool, 4ºC	28 days	500 mL	Plastic or glass	
Dissolved Oxygen	None, analyze immediately	15 min/ In situ	300 mL	Glass or BOD bottle	
Fecal Coliform & E. coli	4ºC (1 hour) + 10% $Na_2S_2O_3$ (0.1 mL)	6 hours and 2 hours to process	125 mL	Non reactive borosilicate glass or plastic	Bottles – cleaned & rinsed carefully, last rinse with DI, sterilize. Leave air space
Hardness	Add HNO_3 or H_2SO_4 to pH <2	6 months	100 mL	Plastic or glass	
Iron	None if analyzing immediately. Conc. nitric acid (2 mL/L) to pH <2 if not.	6 months at room temperature	1 L	Acid-washed glass or plastic	Adjust pH to 3-5 with 5.0N NaOH before analysis. Correct the test result for volume additions.
Lead	Conc. nitric acid (2 mL/L) to pH <2	6 months at room temperature	1 L	Acid-washed glass or plastic	
Nitrate (chlorinated)	Cool, 4ºC, non-acidified	28 days	100 mL	Plastic or glass	
Nitrate (non chlorinated)	Cool, 4ºC, non-acidified	48 hours	100 mL	Plastic or glass	Analyze ASAP
Nitrite	Cool, 4ºC	48 hours	100 mL	Plastic or glass	Analyze ASAP, Store only if necessary

Nitrate + Nitrite	4ºC + H_2SO_4 pH<2	28 days	200 mL	Plastic or glass	
Odor	Cool, 4ºC	6 hours	500 mL	Glass	Analyze ASAP
Oil and Grease	4ºC + H_2SO_4/HCl pH<2	28 days	1000 mL	Glass, wide mouth, calibrated	
Ph	None	15 minutes	50 mL	Plastic or glass	Analyze immediately
Orthophosphate	Filter, Cool, 4ºC	48 hours	100 mL	Glass rinsed with 1 + 1 HNO_3	Warm samples to 15-25ºC before analysis. For dissolved phosp., filter immediately

Solids (TS)	Cool, 4ºC	7 days	200 mL	Plastic or glass	
Sulfate	Cool, 4ºC	28 days	100 mL	Plastic or glass	
Temperature	None	Immersion Stab.	1 L	Plastic or glass	Analyze immediately
Total Dissolved Solids	Cool, 4ºC	5 days from receipt at laboratory	200 mL	Plastic or glass	
Total Kjeldahl Nitrogen	4ºC + H_2SO_4 pH<2 DECHLOR	7 days recommended 28 days regulatory	500 mL	Plastic or glass	
Total Phosphorus	4ºC + H_2SO_4 pH<2	28 days	100	Plastic or glass	Warm samples to 15-25ºC and neutralize with 5.0 N NaOH before analysis if acid was added. Correct for volume additions.
Total Suspended Solids	Cool, 4ºC	7 days	200 mL	Plastic or glass	
Turbidity	Cool, 4ºC	24 h. recommended 48 h. regulatory	100 mL	Plastic or glass	Analyze same day, store in dark up to 24 h, Cool
** Information taken from Standard Methods 21st Edition: p. 1-33. .					

3.3 pH

3.3.1 Principle

Measurement of pH is one of the most important and frequently used tests in water chemistry. Practically every phase of water supply and wastewater treatment, e.g., acid-base neutralization, water softening, precipitation, coagulation, disinfection, and corrosion control, is pH-dependent. pH is used in alkalinity and carbon dioxide measurements and many other acid-base equilibria. At a given temperature the intensity of the acidic or basic character of a solution is indicated by pH or hydrogen ion activity. Alkalinity and acidity are the acid- and base-neutralizing capacities of water and usually are expressed as milligrams $CaCO_3$ per liter. Buffer capacity is the amount

of strong acid or base, usually expressed in moles per liter, needed to change the pH value of a 1L sample by 1 unit. pH as defined by Sorenson1 is log $[H^+]$; it is the ‘‘intensity’’factor of acidity. Pure water is very slightly ionized and at equilibrium the ion product is

$$[H^+]\,[OH^-] = K_w \qquad (1)$$
$$= 1.01 \times 10^{-14} \text{ at } 25°C$$
$$[H^+] = [OH^-]$$
$$= 1.005 \times 10^{-7}$$

Where:

$[H^+]$ = activity of hydrogen ions, moles/L,

$[OH^-]$ = activity of hydroxyl ions, moles/L, Kw = ion product of water.

Because of ionic interactions in all but very dilute solutions, it is necessary to use the ‘‘activity’’ of an ion and not its molar concentration. Use of the term pH assumes that the activity of the hydrogen ion, H^+, is being considered. The approximate equivalence to molarity, $[H^+]$ can be presumed only in very dilute solutions (ionic strength <0.1). A logarithmic scale is convenient for expressing a wide range of ionic activities. Equation 1 in logarithmic form and corrected to reflect activity is:

$$(-\log_{10} a_{H^+}) + (-\log_{10} a_{OH^-}) = 14 \qquad (2)$$
$$\text{or}$$
$$pH + pOH = pK_w$$

Equation 2 states that as pH increases pOH decreases correspondingly and vice versa because pKw is constant for a given temperature. At 25°C, pH 7.0 is neutral, the activities of the hydrogen and hydroxyl ions are equal, and each corresponds to an approximate activity of 10^{-7} moles/L. The neutral point is temperature-dependent and is pH 7.5 at 0°C and pH 6.5 at 60°C.

3.3.2 Apparatus

- ***pH meter***

It consists of potentiometer, a glass electrode, a reference electrode, and a temperature compensating device. A circuit is completed through the potentiometer when the electrodes are immersed in the test solution. Many pH meters are capable of reading pH or millivolts and some have scale expansion that permits reading to 0. 001 pH unit, but most instruments are not that precise.

Figure 10 pH Meter

For routine work use a pH meter accurate and reproducible to 0.1 pH unit with a range of 0 to 14 and equipped with a temperature-compensation adjustment. Although manufacturers provide operating instructions, the use of different descriptive terms may be confusing. For most instruments, there are two controls: intercept (set buffer, asymmetry, standardize) and slope (temperature, offset).The intercept control shifts the response curve laterally to pass through the isopotential point with no change in slope. This permits bringing the instrument on scale (0 mV) with a pH 7 buffer that has no change in potential with temperature. The slope control rotates the emf/pH slope about the isopotential point (0 mV/pH 7).To adjust slope for temperature without disturbing the intercept, select a buffer that brackets the sample with pH 7 buffer and adjust slope control to pH of this buffer. The instrument will indicate correct millivolt change per unit pH at the test temperature.

- ***Reference electrode***

It consists of a half cell that provides a constant electrode potential. Commonly used are calomel and silver: silver-chloride electrodes. Either is available with several types of liquid junctions.
The liquid junction of the reference electrode is critical because at this point the electrode forms a salt bridge with the sample or buffer and a liquid junction potential is generated that in turn affects the potential produced by the reference electrode. Reference electrode junctions may be annular ceramic, quartz, or asbestos fiber, or the sleeve type. The quartz type is most widely used. The asbestos fiber type is not recommended for strongly basic solutions. Follow the manufacturer's recommendation on use and care of the reference electrode. Refill nonsealed electrodes with the correct electrolyte to proper level and make sure junction is properly wetted.

- ***Glass electrode:***

The sensor electrode is a bulb of special glass containing a fixed concentration of HCl or a buffered chloride solution in contact with an internal reference electrode. Upon immersion of a new electrode in a solution the outer bulb surface becomes hydrated and exchanges sodium ions for hydrogen ions to build up a surface layer of hydrogen ions. This, together with the repulsion of anions by fixed, negatively charged silicate sites, produces at the glass-solution interface a potential that is a function of hydrogen ion activity in solution.

Several types of glass electrodes are available. Combination electrodes incorporate the glass and reference electrodes into a single probe. Use a ‘‘low sodium error’’ electrode that can operate at high temperatures for measuring pH over 10 because standard glass electrodes yield erroneously low values. For measuring pH below 1 standard glass electrodes yield erroneously high values; use liquid membrane electrodes instead.

- ***Beakers***

Preferably use polyethylene or TFE*(3) beakers.

- ***Stirrer:***

Use either a magnetic, TFE-coated stirring bar or a mechanical stirrer with inert plastic-coated impeller.

- ***Flow chamber:***

Use for continuous flow measurements or for poorly buffered solutions.

3.3.3 Reagents

- ***General preparation:***

Calibrate the electrode system against standard buffer solutions of known pH. Because buffer solutions may deteriorate as a result of mold growth or contamination, prepare fresh as needed for accurate work by weighing the amounts of chemicals specified, dissolving in distilled water at 25°C, and diluting to 1000 mL. This is particularly important for borate and carbonate buffers. Boil and cool distilled water having a conductivity of less than 2μmhos/cm. To 50 mL add 1 drop of saturated KCl solution suitable for reference electrode use. If the pH of this test solution is between 6.0 and 7.0, use it to prepare all standard solutions. Dry KH_2PO_4 at 110 to 130°C for 2 h before weighing but do not heat unstable hydrated potassium tetroxalate above 60°C nor dry

the other specified buffer salts. Although ACS-grade chemicals generally are satisfactory for preparing buffer solutions, use certified materials available from the National Institute of Standards and Technology when the greatest accuracy is required. For routine analysis, use commercially available buffer tablets, powders, or solutions of tested quality. In preparing buffer solutions from solid salts, insure complete solution. As a rule, select and prepare buffer solutions classed as primary standards in reserve secondary standards for extreme situations encountered in wastewater measurements. In routine use, store buffer solutions and samples in polyethylene bottles. Replace buffer solutions every 4 weeks.

- ***Saturated potassium hydrogen tartrate solution:***

Shake vigorously an excess (5 to 10 g) of finely crystalline $KHC_4H_4O_6$ with 100 to 300 mL distilled water at 25°C in a glass-stoppered bottle. Separate clear solution from undissolved material by decantation or filtration. Preserve for 2 months or more by adding one thymol crystal (8 mm diam) per 200 mL solution.

- ***Saturated calcium hydroxide solution:***

Calcine a well-washed, low-alkali grade $CaCO_3$ in platinum dish by igniting for 1 h at 1000°C. Cool, hydrate by slowly adding distilled water with stirring, and heat to boiling. Cool, filter, and collect solid $Ca(OH)_2$ on a fritted glass filter of medium porosity. Dry at 110°C, cool, and pulverize to uniformly fine granules. Vigorously shake an excess of fine granules with distilled water in a stoppered polyethylene bottle. Let temperature come to 25°C after mixing. Filter supernatant under suction through a sintered glass filter of medium porosity and use filtrate as the buffer solution. Discard buffer solution when atmospheric CO_2 causes turbidity to appear.

3.3.4 Procedure

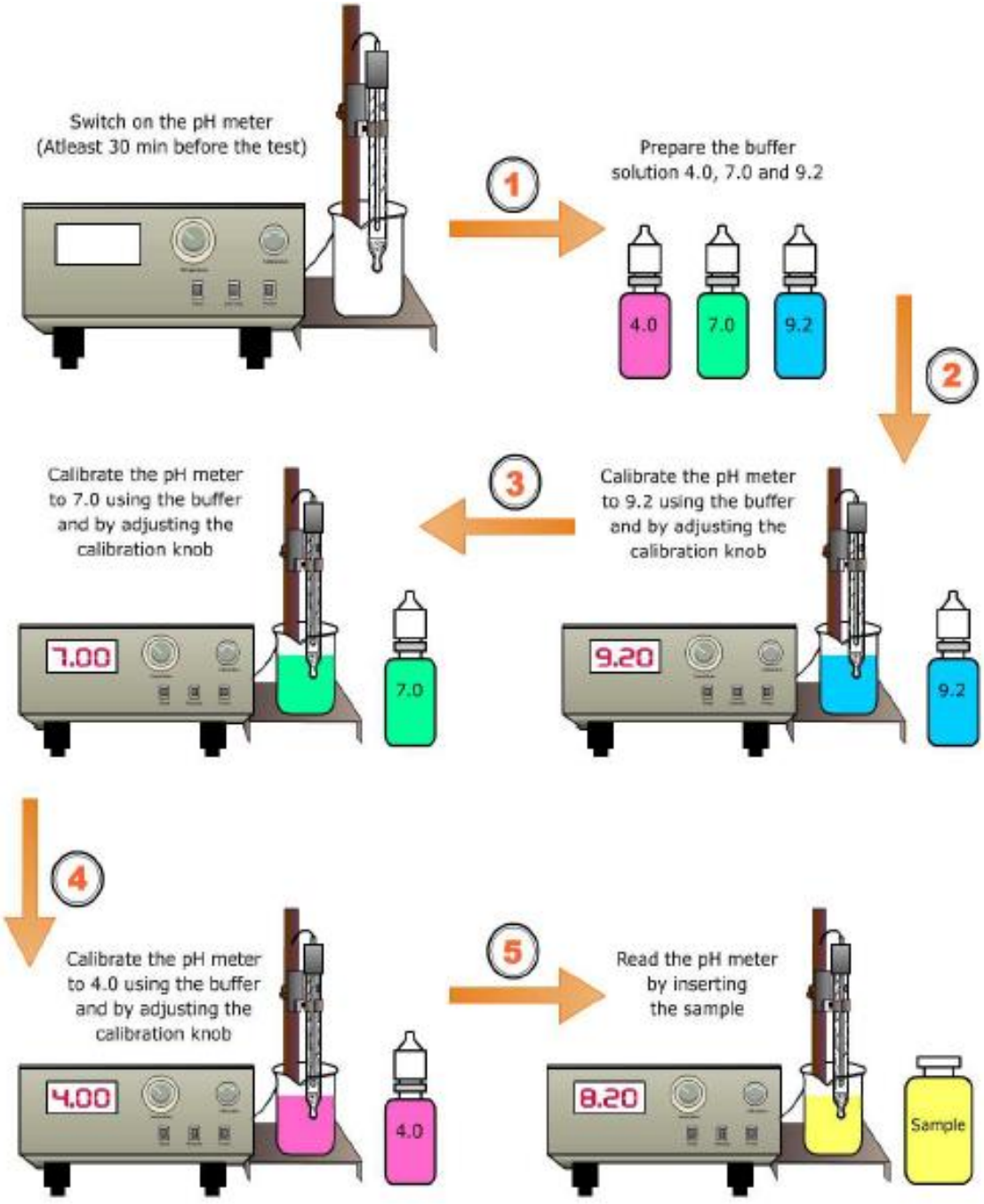

Figure 11 ph Measurement (AMERICAN WATER WORKS ASSOCIATION. 1964. Simplified Procedures for Water Examination.Manual M12, American Water Works Assoc., New York, N.Y.)

3.4 Dissolved Oxygen

3.4.1 Principle

The iodometric test is the most precise and reliable titrimetric procedure for DO analysis. It is based on the addition of divalent manganese solution, followed by strong alkali, to the sample in a glass-stoppered bottle. DO rapidly oxidizes an equivalent amount of the dispersed divalent manganous hydroxide precipitate to hydroxides of higher valency states. In the presence of iodide ions in an acidic solution, the oxidized manganese reverts to the divalent state, with the liberation of iodine equivalent to the original DO content. The iodine is then titrated with a standard solution of thiosulfate. The titration end point can be detected visually, with a starch indicator, or electrometrically, with potentiometric or dead-stop techniques. Experienced analysts can maintain a precision of ±50 μg/L with visual end-point detection and a precision of ±5 μg/L with electrometric end-point detection. The liberated iodine also can be determined directly by simple absorption spectrophotometers.This method can be used on a routine basis to provide very accurate estimates for DO in the microgram-per-liter range provided that interfering particulate matter, color, and chemical interferences are absent.

3.4.2 Selection of Method

Before selecting a method consider the effect of interferences, particularly oxidizing or reducing materials that may be present in the sample. Certain oxidizing agents liberate iodine from iodides (positive interference) and some reducing agents reduce iodine to iodide (negative interference). Most organic matter is oxidized partially when the oxidized manganese precipitate is acidified, thus causing negative errors. Several modifications of the iodometric method are given to minimize the effect of interfering materials. Among the more commonly used procedures are the azide modification, the permanganate modification, the alum flocculation modification,and the copper sulfate-sulfamic acid flocculation modification.The azide modification (C) effectively removes interference caused by nitrite, which is the most common interference in biologically treated effluents and incubated BOD samples. Use the permanganate modification (D) in the presence of ferrous iron. When the sample contains 5 or more mg ferric iron salts/L, add potassium fluoride (KF) as the first reagent in the azide modification or after the permanganate treatment for ferrous iron. Alternately, eliminate Fe(III) interference by using 85 to 87%

phosphoric acid (H_3PO_4) instead of sulfuric acid (H_2SO_4) for acidification. This procedure has not been tested for Fe (III) concentrations above 20 mg/L.

Use the alum flocculation modification (E) in the presence of suspended solids that cause interference and the copper sulfate-sulfamic acid flocculation modification (F) on activated-sludge mixed liquor.

3.4.3 Procedure for Alkali-iodide-azide Modification

To the sample collected in a 250- to 300-mL bottle, add 1 mL $MnSO_4$ solution, followed by 1 mL alkali-iodide-azide reagent. If pipets are dipped into sample, rinse them before returning them to reagent bottles. Alternatively, hold pipet tips just above liquid surface when adding reagents. Use the stopper carefully to exclude air bubbles and mix by inverting bottle a few times. When precipitate has settled sufficiently (to approximately half the bottle volume) to leave clear supernate above the manganese hydroxide floc, add 1.0 mL conc H_2SO_4. Restopper and mix by inverting several times until dissolution is complete. Titrate a volume corresponding to 200 mL original sample after correction for sample loss by displacement with reagents. Thus, for a total of 2 mL (1 mL each) of $MnSO_4$ and alkali-iodide-azide reagents in a 300-mL bottle, titrate $200 \times 300/(300 - 2) = 201$ mL.

Titrate with 0.025*M* $Na_2S_2O_3$ solution to a pale straw color. Add a few drops of starch solution and continue titration to first disappearance of blue color. If end point is overrun, back-titrate with 0.0021*M* bi-iodate solution added dropwise, or by adding a measured volume of treated sample. Correct for amount of bi-iodate solution or sample. Disregard subsequent recolorations due to the catalytic effect of nitrite or to traces of ferric salts that have not been complexed with fluoride.

3.5 Biological Oxygen Demand (BOD)

3.5.1 General Discussion

The biochemical oxygen demand (BOD) determination is an empirical test in which standardized laboratory procedures are used to determine the relative oxygen requirements of wastewaters, effluents, and polluted waters. The test has its widest application in measuring waste loadings to treatment plants and in evaluating the BOD-removal efficiency of such treatment systems. The test measures the molecular oxygen utilized during a specified incubation period for the biochemical degradation of organic material (carbonaceous demand) and the oxygen used to

oxidize inorganic material such as sulfides and ferrous iron. It also may measure the amount of oxygen used to oxidize reduced forms of nitrogen (nitrogenous demand) unless their oxidation is prevented by an inhibitor. The seeding and dilution procedures provide an estimate of the BOD at pH 6.5 to 7.5.

Measurements of oxygen consumed in a 5-d test period (5-d BOD or BOD5), oxygen consumed after 60 to 90 d of incubation (ultimate BOD or UBOD, and continuous oxygen uptake (respirometric method, Section 5210D) are described here. Many other variations of oxygen demand measurements exist, including using shorter and longer incubation periods and tests to determine rates of oxygen uptake. Alternative seeding, dilution, and incubation conditions can be chosen to mimic receiving-water conditions, thereby providing an estimate of the environmental effects of wastewaters and effluents.

The UBOD measures the oxygen required for the total degradation of organic material (ultimate carbonaceous demand) and/or the oxygen to oxidize reduced nitrogen compounds (ultimate nitrogenous demand). UBOD values and appropriate kinetic descriptions are needed in water quality modeling studies such as UBOD: BOD5 ratios for relating stream assimilative capacity to regulatory requirements; definition of river, estuary, or lake deoxygenation kinetics; and instream ultimate carbonaceous BOD (UCBOD) values for model calibration.

a. Principle:

The method consists of filling with sample, to overflowing, an airtight bottle of the specified size and incubating it at the specified temperature for 5 d. Dissolved oxygen is measured initially and after incubation, and the BOD is computed from the difference between initial and final DO. Because the initial DO is determined shortly after the dilution is made, all oxygen uptake occurring after this measurement is included in the BOD measurement.

b. Sampling and storage:

Samples for BOD analysis may degrade significantly during storage between collection and analysis, resulting in low BOD values. Minimize reduction of BOD by analyzing sample promptly or by cooling it to near-freezing temperature during storage. However, even at low temperature, keep holding time to a minimum.Warm chilled samples to 20 ± 3°C before analysis.

1) Grab samples-If analysis is begun within 2 h of collection, cold storage is unnecessary. If analysis is not started within 2 h of sample collection, keep sample at or below 4°C from the time of collection. Begin analysis within 6 h of collection; when this is not possible because the sampling site is distant from the laboratory, store at or below 4°C and report length and temperature of storage with the results. In no case start analysis more than 24 h after grab sample collection. When samples are to be used for regulatory purposes make every effort to deliver samples for analysis within 6 h of collection.

2) Composite samples—Keep samples at or below 4°C during compositing. Limit compositing period to 24 h. Use the same criteria as for storage of grab samples, starting the measurement of holding time from end of compositing period. State storage time and conditions as part of the result.

3.5.2 Apparatus

a. Incubation bottles:

Use glass bottles having 60 mL or greater capacity (300-mL bottles having a ground-glass stopper and a flared mouth are preferred). Clean bottles with a detergent, rinse thoroughly, and drain before use. As a precaution against drawing air into the dilution bottle during incubation, use a water seal.

Obtain satisfactory water seals by inverting bottles in a water bath or by adding water to the flared mouth of special BOD bottles. Place a paper or plastic cup or foil cap over flared mouth of bottle to reduce evaporation of the water seal during incubation.

b. Air incubator or water bath, thermostatically controlled at 20 ±1°C. Exclude all light to prevent possibility of photosynthetic production of DO.

3.5.3 Reagents

Prepare reagents in advance but discard if there is any sign of precipitation or biological growth in the stock bottles. Commercial equivalents of these reagents are acceptable and different stock concentrations may be used if doses are adjusted proportionally.

Phosphate buffer solution: Dissolve 8.5 g KH_2PO_4, 21.75 g K_2HPO_4, 33.4g $Na_2HPO_4 \times 7H_2O$, and 1.7 g NH4Cl in about 500 mL distilled water and dilute to 1 L. The pH should be 7.2 without

further adjustment. Alternatively, dissolve 42.5 g K_2HPO_4 or 54.3 g K_2HPO_4 in about 700 mL distilled water. Adjust pH to 7.2 with 30% NaOH and dilute to 1 L.

Magnesium sulfate solution: Dissolve 22.5 g $MgSO_4 \times 7H_2O$ in distilled water and dilute to 1L.

Calcium chloride solution: Dissolve 27.5 g $CaCl_2$ in distilled water and dilute to 1 L.

Ferric chloride solution: Dissolve 0.25 g $FeCl_3 \times 6\ H_2O$ in distilled water and dilute to1L.

Acid and alkali solutions, 1N, for neutralization of caustic or acidic waste samples.

Sodium sulfite solution: Dissolve 1.575 g Na_2SO_3 in 1000 mL distilled water. This solution is not stable; prepare daily.

Nitrification inhibitor, 2-chloro-6-(trichloromethyl) pyridine.

Glucose-glutamic acid solution: Dry reagent-grade glucose and reagent-grade glutamic acid at 103°C for 1 h. Add 150 mg glucose and 150 mg glutamic acid to distilled water and dilute to 1 L. Prepare fresh immediately before use.

Ammonium chloride solution: Dissolve 1.15 g NH_4Cl in about 500 mL distilled water, adjust pH to 7.2 with NaOH solution, and dilute to 1 L. Solution contains 0.3 mg N/mL.

Dilution water: Use demineralized, distilled, tap, or natural water for making sample dilutions.

3.5.4 Procedure

Preparation of dilution water: Place desired volume of water in a suitable bottle and add 1 mL each of phosphate buffer, $MgSO_4$, $CaCl_2$, and $FeCl_3$ solutions/L of water. Seed dilution water, if desired. Test dilution water as described in ¶ 4*h* so that water of assured quality always is on hand. Before use bring dilution water temperature to 20 ± 3°C. Saturate with DO by shaking in a partially filled bottle or by aerating with organic-free filtered air. Alternatively, store in cotton-plugged bottles long enough for water to become saturated with DO. Protect water quality by using clean glassware, tubing, and bottles.

Dilution water storage: Source water may be stored before use as long as the prepared dilution water meets quality control criteria in the dilution water blank. Such storage may improve the quality of some source waters but may allow biological growth to cause deterioration in others. Preferably do not store prepared dilution water for more than 24 h after adding nutrients, minerals, and buffer unless dilution water blanks consistently meet quality control limits. Discard stored source water if dilution water blank shows more than 0.2 mg/L DO depletion in 5d.

Glucose-glutamic acid check: Because the BOD test is a bioassay its results can be influenced greatly by the presence of toxicants or by use of a poor seeding material. Distilled waters frequently are contaminated with copper; some sewage seeds are relatively inactive. Low results always are obtained with such seeds and waters. Periodically check dilution water quality, seed effectiveness, and analytical technique by making BOD measurements on a mixture of 150 mg glucose/L and 150 mg glutamic acid/L as a ‘‘standard’’ check solution. Glucose has an exceptionally high and variable oxidation rate but when it is used with glutamic acid, the oxidation rate is stabilized and is similar to that obtained with many municipal wastes.

Alternatively, if a particular wastewater contains an identifiable major constituent that contributes to the BOD, use this compound in place of the glucose-glutamic acid.Determine the 5-d 20°C BOD of a 2% dilution of the glucose-glutamic acid standard check solution using the techniques outlined in. Adjust concentrations of commercial mixtures to give 3 mg/L glucose and 3 mg/L glutamic acid in each GGA test bottle. Evaluate data as described in, Precision and Bias.

Seeding:

1. **Seed source**-It is necessary to have present a population of microorganisms capable of oxidizing the biodegradable organic matter in the sample. Domestic wastewater, unchlorinated or otherwise-undisinfected effluents from biological waste treatment plants, and surface waters receiving wastewater discharges contain satisfactory microbial populations. Some samples do not contain a sufficient microbial population (for example, some untreated industrial wastes, disinfected wastes, high-temperature wastes, or wastes with extreme pH values). For such wastes seed the dilution water or sample by adding a population of microorganisms. The preferred seed is effluent or mixed liquor from a biological treatment system processing the waste. Where such seed is not available, use supernatant from domestic wastewater after settling at room temperature for at least 1 h but no longer than 36 h. When effluent or mixed liquor from a biological treatment process is used, inhibition of nitrification is recommended.

   Some samples may contain materials not degraded at normal rates by the microorganisms in settled domestic wastewater. Seed such samples with an adapted microbial population

obtained from the undisinfected effluent or mixed liquor of a biological process treating the waste. In the absence of such a facility, obtain seed from the receiving water below (preferably 3 to 8 km) the point of discharge. When such seed sources also are not available, develop an adapted seed in the laboratory by continuously aerating a sample of settled domestic wastewater and adding small daily increments of waste. Optionally use a soil suspension or activated sludge, or a commercial seed preparation to obtain the initial microbial population. Determine the existence of a satisfactory population by testing the performance of the seed in BOD tests on the sample. BOD values that increase with time of adaptation to a steady high value indicate successful seed adaptation.

2. **Seed control**-Determine BOD of the seeding material as for any other sample. This is the *seed control*. From the value of the seed control and a knowledge of the seeding material dilution (in the dilution water) determine seed DO uptake. Ideally, make dilutions of seed such that the largest quantity results in at least 50% DO depletion. A plot of DO depletion, in milligrams per liter, versus milliliters of seed for all bottles having a 2-mg/L depletion and a 1.0-mg/L minimum residual DO should present a straight line for which the slope indicates DO depletion per milliliter of seed. The DO-axis intercept is oxygen depletion caused by the dilution water and should be less than 0.1 mg/L . Alternatively, divide DO depletion by volume of seed in milliliters for each seed control bottle having a 2-mg/L depletion and a 1.0-mg/L residual DO.

Average the results for all bottles meeting minimum depletion and residual DO criteria. The DO uptake attributable to the seed added to each bottle should be between 0.6 and 1.0 mg/L, but the amount of seed added should be adjusted from this range to that required to provide glucose-glutamic acid check results in the range of 198 ± 30.5 mg/L. To determine DO uptake for a test bottle, subtract DO uptake attributable to the seed from total DO uptake. Techniques for adding seeding material to dilution water are described for two sample dilution methods.

Sample pretreatment:

Check pH of all samples before testing unless previous experience indicates that pH is within the acceptable range.

1) Samples containing caustic alkalinity (pH >8.5) or acidity (pH <6.0)—Neutralize samples to pH 6.5 to 7.5 with a solution of sulfuric acid (H_2SO_4) or sodium hydroxide (NaOH) of such strength that the quantity of reagent does not dilute the sample by more than 0.5%. The pH of dilution water should not be affected by the lowest sample dilution. Always seed samples that have been pH-adjusted.

2) Samples containing residual chlorine compounds—If possible, avoid samples containing residual chlorine by sampling ahead of chlorination processes. If the sample has been chlorinated but no detectable chlorine residual is present, seed the dilution water. If residual chlorine is present, dechlorinate sample and seed the dilution water. Do not test chlorinated/dechlorinated samples without seeding the dilution water. In some samples chlorine will dissipate within 1 to 2 h of standing in the light. This often occurs during sample transport and handling. For samples in which chlorine residual does not dissipate in a reasonably short time, destroy chlorine residual by adding Na_2SO_3 solution. Determine required volume of Na_2SO_3 solution on a 100- to 1000-mL portion of neutralized sample by adding 10 mL of 1 + 1 acetic acid or 1 + 50 H_2SO_4, 10 mL potassium iodide (KI) solution (10 g/100 mL) per 1000 mL portion, and titrating with Na_2SO_3 solution to the starch-iodine end point for residual. Add to neutralized sample the relative volume of Na_2SO_3 solution determined by the above test, mix, and after 10 to 20 min check sample for residual chlorine. (NOTE: Excess Na_2SO_3 exerts an oxygen demand and reacts slowly with certain organic chloramine compounds that may be present in chlorinated samples.)

3) Samples containing other toxic substances-Certain industrial wastes, for example, plating wastes, contain toxic metals. Such samples often require special study and treatment.

4) Samples supersaturated with DO-Samples containing more than 9 mg DO/L at 20°C may be encountered in cold waters or in water where photosynthesis occurs. To prevent loss of oxygen during incubation of such samples, reduce DO to saturation at 20°C by bringing sample to about 20°C in partially filled bottle while agitating by vigorous shaking or by aerating with clean, filtered compressed air.

5) Sample temperature adjustment-Bring samples to 20 ± 1°C before making dilutions.

6) Nitrification inhibition-If nitrification inhibition is desired add 3 mg 2-chloro-6-(trichloro methyl) pyridine (TCMP) to each 300-mL bottle before capping or add sufficient amounts to the dilution water to make a final concentration of 10 mg/L. (NOTE: Pure TCMP may dissolve slowly and can float on top of the sample. Some commercial formulations dissolve more readily but are not 100% TCMP; adjust dosage accordingly.) Samples that may require nitrification inhibition include, but are not limited to, biologically treated effluents, samples seeded with biologically treated effluents, and river waters. Note the use of nitrogen inhibition in reporting results.

Dilution technique:

Make several dilutions of sample that will result in a residual DO of at least 1 mg/L and a DO uptake of at least 2 mg/L after a 5-d incubation. Five dilutions are recommended unless experiences with a particular sample shows that use of a smaller number of dilutions produces at least two bottles giving acceptable minimum DO depletion and residual limits. A more rapid analysis, such as COD, may be correlated approximately with BOD and serve as a guide in selecting dilutions. In the absence of prior knowledge, use the following dilutions: 0.0 to 1.0% for strong industrial wastes, 1 to 5% for raw and settled wastewater, 5 to 25% for biologically treated effluent, and 25 to 100% for polluted river waters.

Prepare dilutions either in graduated cylinders or volumetric glassware, and then transfer to BOD bottles or prepare directly in BOD bottles. Either dilution method can be combined with any DO measurement technique. The number of bottles to be prepared for each dilution depends on the DO technique and the number of replicates desired.

When using graduated cylinders or volumetric flasks to prepare dilutions, and when seeding is necessary, add seed either directly to dilution water or to individual cylinders or flasks before dilution. Seeding of individual cylinders or flasks avoids a declining ratio of seed to sample as increasing dilutions are made. When dilutions are prepared directly in BOD bottles and when seeding is necessary, add seed directly to dilution water or directly to the BOD bottles. When a bottle contains more than 67% of the sample after dilution, nutrients may be limited in the diluted sample and subsequently reduce biological activity. In such samples, add the nutrient,

mineral, and buffer solutions directly to individual BOD bottles at a rate of 1 mL/L (0.33 mL/300-mL bottle) or use commercially prepared solutions designed to dose the appropriate bottle size.

1. Dilutions prepared in graduated cylinders or volumetric flasks— If the azide modification of the titrimetric iodometric method is used, carefully siphon dilution water, seeded if necessary, into a 1- to 2-L-capacity flask or cylinder. Fill half full without entraining air. Add desired quantity of carefully mixed sample and dilute to appropriate level with dilution water. Mix well with a plunger-type mixing rod; avoid entraining air. Siphon mixed dilution into two BOD bottles. Determine initial DO on one of these bottles. Stopper the second bottle tightly, water-seal, and incubate for 5 d at 20°C. If the membrane electrode method is used for DO measurement, siphon dilution mixture into one BOD bottle. Determine initial DO on this bottle and replace any displaced contents with sample dilution to fill the bottle. Stopper tightly, water-seal, and incubate for 5 d at 20°C.
2. Dilutions prepared directly in BOD bottles—Using a wide-tip volumetric pipet, add the desired sample volume to individual BOD bottles of known capacity. Add appropriate amounts of seed material either to the individual BOD bottles or to the dilution water. Fill bottles with enough dilution water, seeded if necessary, so that insertion of stopper will displace all air, leaving no bubbles. For dilutions greater than 1:100 make a primary dilution in a graduated cylinder before making final dilution in the bottle. When using titrimetric iodometric methods for DO measurement, prepare two bottles at each dilution. Determine initial DO on one bottle. Stopper second bottle tightly, water-seal, and incubate for 5 d at 20°C. If the membrane electrode method is used for DO measurement, prepare only one BOD bottle for each dilution. Determine initial DO on this bottle and replace any displaced contents with dilution water to fill the bottle.

Stopper tightly, water-seal, and incubate for 5 d at 20°C. Rinse DO electrode between determinations to prevent cross-contamination of samples. Use the azide modification of the iodometric method (Section 4500-O.C) or the membrane electrode method (Section 4500-O.G) to determine initial DO on all sample dilutions, dilution water blanks, and where appropriate,

seed controls. If the membrane electrode method is used, the azide modification of the iodometric method is recommended for calibrating the DO probe.

Determination of initial DO: If the sample contains materials that react rapidly with DO, determine initial DO immediately after filling BOD bottle with diluted sample. If rapid initial DO uptake is insignificant, the time period between preparing dilution and measuring initial DO is not critical but should not exceed 30 min.

Dilution water blank: Use a dilution water blank as a rough check on quality of unseeded dilution water and cleanliness of incubation bottles. Together with each batch of samples incubate a bottle of un-seeded dilution water. Determine initial and final DO . The DO uptake should not be more than 0.2 mg/L and preferably not more than 0.1 mg/L.Discard all dilution water having a DO uptake greater than 0.2 mg/L and either eliminate source of contamination or select an alternate dilution water source.

Incubation: Incubate at 20°C ± 1°C BOD bottles containing desired dilutions, seed controls, dilution water blanks, and glucose-glutamic acid checks.

Determination of final DO: After 5 d incubation determine DO in sample dilutions, blanks, and checks.

3.5.5 Calculation

For each test bottle meeting the 2.0-mg/L minimum DO depletion and the 1.0-mg/L residual DO, calculate BOD_5 as follows:

When dilution water is not seeded:

$$BOD_5,\ mg/L = \frac{D_1 - D_2}{P}$$

When dilution water is seeded:

$$BOD_5,\ mg/L = \frac{D_1 - D_2}{P}$$

Where,

D1 = DO of diluted sample immediately after preparation, mg/L,

D2 = DO of diluted sample after 5 d incubation at 20°C, mg/L,

P = decimal volumetric fraction of sample used,

B1 = DO of seed control before incubation, mg/L,

B2 = DO of seed control after incubation mg/L, and

f = ratio of seed in diluted sample to seed in seed control

$$= \frac{(\%\ \text{seed in diluted sample})}{(\%\ \text{seed in seed control}).}$$

If seed material is added directly to sample or to seed control bottles:

$$f = \frac{(volume\ of\ seed\ in\ diluted\ sample)}{(volume\ of\ seed\ in\ seed\ control)}$$

Report results as CBOD5 if nitrification is inhibited. If more than one sample dilution meets the criteria of a residual DO of at least 1 mg/L and a DO depletion of at least 2 mg/L and there is no evidence of toxicity at higher sample concentrations or the existence of an obvious anomaly, average results in the acceptable range. In these calculations, do not make corrections for DO uptake by the dilution water blank during incubation. This correction is unnecessary if dilution water meets the blank criteria stipulated above. If the dilution water does not meet these criteria, proper corrections are difficult; do not record results or, as a minimum, mark them as not meeting quality control criteria.

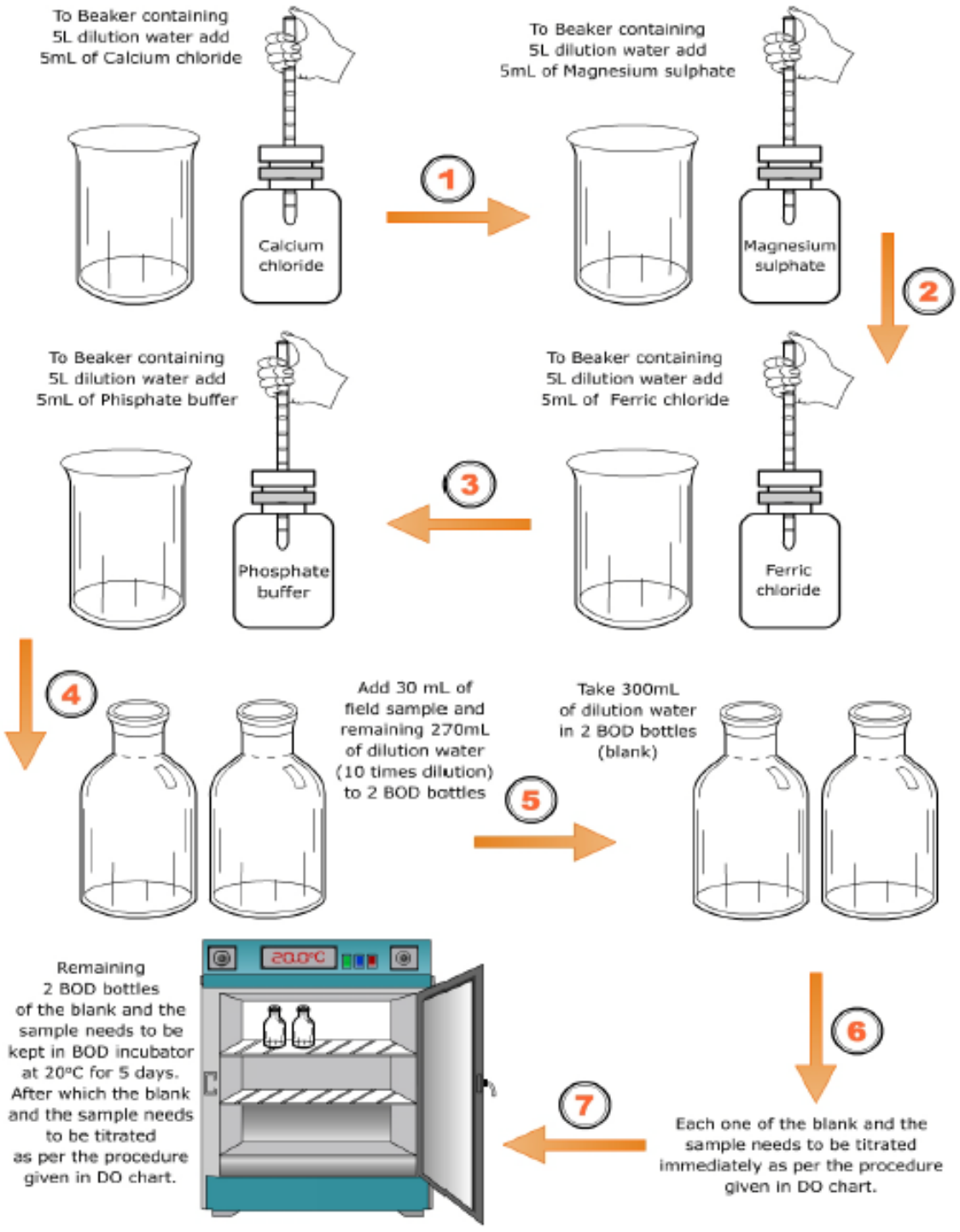

Figure 12 BOD Procedure (AMERICAN WATER WORKS ASSOCIATION.1964. Simplified Procedures for Water Examination.Manual M12, American Water Works Assoc., New York, N.Y.)

3.6 Alkalinity

3.6.1 General Discussion

Alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly with the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known.

Alkalinity is significant in many uses and treatments of natural waters and wastewaters. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constitutents. The measured values also may include contributions from borates, phosphates, silicates, or other bases if these are present. Alkalinity in excess of alkaline earth metal concentrations is significant in determining the suitability of water for irrigation. Alkalinity measurements are used in the interpretation and control of water and wastewater treatment processes. Raw domestic wastewater has an alkalinity less than, or only slightly greater than, that of the water supply. Properly operating anaerobic digesters typically have supernatant alkalinities in the range of 2000 to 4000 mg calcium carbonate ($CaCO_3$)/L.

a. Principle

Hydroxyl ions present in a sample as a result of dissociation or hydrolysis of solutes react with additions of standard acid. Alkalinity thus depends on the end-point pH used. For methods of determining inflection points from titration curves and the rationale for titrating to fixed pH end points. For samples of low alkalinity (less than 20 mg $CaCO_3$/L) use an extrapolation technique based on the near proportionality of concentration of hydrogen ions to excess of titrant beyond the equivalence point. The amount of standard acid required to reduce pH exactly 0.30 pH unit is measured carefully. Because this change in pH corresponds to an exact doubling of the hydrogen ion concentration, a simple extrapolation can be made to the equivalence point.

b. End Points

When alkalinity is due entirely to carbonate or bicarbonate content, the pH at the equivalence point of the titration is determined by the concentration of carbon dioxide (CO_2) at that stage. CO_2 concentration depends, in turn, on the total carbonate species originally present and any losses that may have occurred during titration. The pH values are suggested as the equivalence

points for the corresponding alkalinity concentrations as milligrams $CaCO_3$ per liter. ‘‘Phenolphthalein alkalinity’’ is the term traditionally used for the quantity measured by titration to pH 8.3 irrespective of the colored indicator, if any, used in the determination. Phenolphthalein or metacresol purple may be used for alkalinity titration to pH 8.3. Bromcresol green or a mixed bromcresol green-methyl red indicator may be used for pH 4.5.

c. Interference

Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

d. Selection of procedure

Determine sample alkalinity from volume of standard acid required to titrate a portion to a designated pH. Titrate at room temperature with a properly calibrated pH meter or electrically operated titrator, or use color indicators. If using color indicators, prepare and titrate an indicator blank.

3.6.2 Procedure

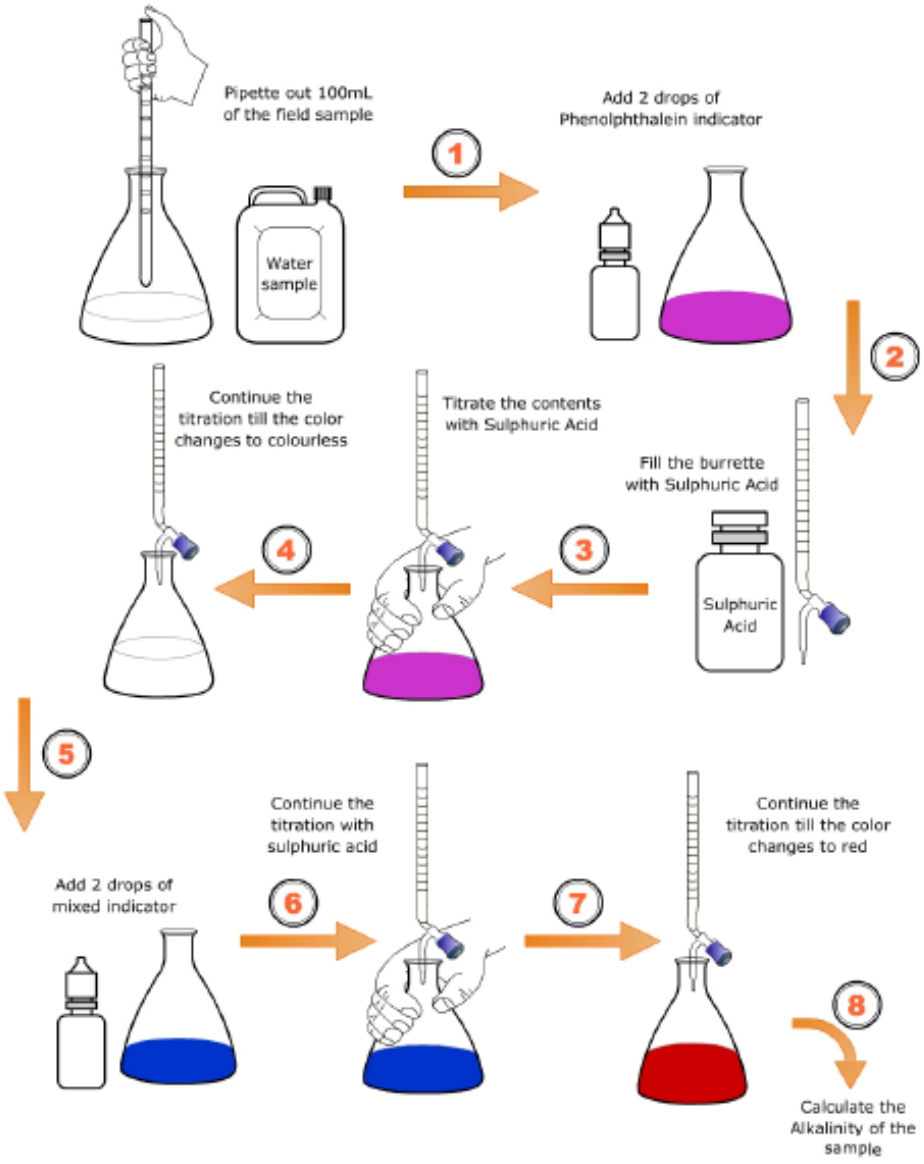

Figure 13 Alkalinity Procedure (AMERICAN WATER WORKS ASSOCIATION. 1964. Simplified Procedures for Water Examination.Manual M12, American Water Works Assoc., New York, N.Y.)

3.6.3 Calculation

Potentiometric titration to end-point pH:

$$\text{Alkalinity, mg } CaCO_3/L = \frac{A \times N \times 50\,000}{\text{mL sample}}$$

where:

A = mL standard acid used and

N = normality of standard acid

Report pH of end point used as follows: The alkalinity to pH _____ = _____ mg

CaCO3/L and indicate clearly if this pH corresponds to an inflection point of the titration curve.

3.7 Chemical Oxygen Demand

3.7.1 Introduction

Chemical oxygen demand (COD) is defined as the amount of a specified oxidant that reacts with the sample under controlled conditions. The quantity of oxidant consumed is expressed in terms of its oxygen equivalence. Because of its unique chemical properties, the dichromate ion is the specified oxidant it is reduced to the chromic ion (Cr3+) in these tests. Both organic and inorganic components of a sample are subject to oxidation, but in most cases the organic component predominates and is of the greater interest. If it is desired to measure either organic or inorganic COD alone, additional steps not described here must be taken to distinguish one from the other. COD is a defined test; the extent of sample oxidation can be affected by digestion time, reagent strength, and sample COD concentration. COD often is used as a measurement of pollutants in wastewater and natural waters. Other related analytical values are biochemical oxygen demand (BOD), total organic carbon (TOC), and total oxygen demand (TOD). In many cases it is possible to correlate two or more of these values for a given sample. BOD is a measure of oxygen consumed by microorganisms under specific conditions; TOC is a measure of organic

carbon in a sample; TOD is a measure of the amount of oxygen consumed by all elements in a sample when complete (total) oxidation is achieved.

3.7.2 Sampling & Storage

Preferably collect samples in glass bottles. Test unstable samples without delay. If delay before analysis is unavoidable, preserve sample by acidification to pH 2 using conc H2SO4.Blend (homogenize) all samples containing suspended solids before analysis. If COD is to be related to BOD, TOC, etc., ensure that all tests receive identical pretreatment. Make preliminary dilutions for wastes containing a high COD to reduce the error inherent in measuring small sample volumes.

3.7.3 Closed Reflux, Titrimetric Method

a. Principle

Most types of organic matter are oxidized by a boiling mixture of chromic and sulfuric acids. A sample is refluxed in strongly acid solution with a known excess of potassium dichromate (K2Cr2O7). After digestion, the remaining unreduced K2Cr2O7 is titrated with ferrous ammonium sulfate to determine the amount of K2Cr2O7 consumed and the oxidizable matter is calculated in terms of oxygen equivalent. Keep ratios of reagent weights, volumes, and strengths constant when sample volumes other than 50 mL are used. The standard 2-h reflux time may be reduced if it has been shown that a shorter period yields the same results. Some samples with very low COD or with highly heterogeneous solids content may need to be analyzed in replicate to yield the most reliable data. Results are further enhanced by reacting a maximum quantity of dichromate, provided that some residual dichromate remains.

b. Apparatus

Digestion vessels: Preferably use borosilicate culture tubes, 16- × 100-mm, 20- × 150-mm, or 25- × 150-mm, with TFE-lined screw caps. Alternatively, use borosilicate ampules, 10-mL capacity, 19- to 20-mm diam. Digestion vessels with premixed reagents and other accessories are available from commercial suppliers.

Block heater or similar device to operate at 150 ± 2°C, with holes to accommodate digestion vessels. Use of culture tubes probably requires the caps to be outside the vessel to protect caps from heat. CAUTION: Do not use an oven because of the possibility of leaking samples generating a corrosive and possibly explosive atmosphere. Also, culture tube caps may not withstand the 150°C temperature in an oven.
Microburet.

Ampule sealer: Use only a mechanical sealer to insure strong, consistent seals

c. Reagents

Standard potassium dichromate digestion solution, 0.01667M: Add to about 500 mL distilled water 4.903 g K2Cr2O7, primary standard grade, previously dried at 150°C for 2 h, 167 mL conc H2SO4, and 33.3 g HgSO4. Dissolve, cool to room temperature, and dilute to 1000 mL.

Sulfuric acid reagent: Add Ag2SO4, reagent or technical grade, crystals or powder, to conc H2SO4 at the rate of 5.5 g Ag2SO4/kg H2SO4. Let stand 1 to 2 d to dissolve. Mix.

Ferroin indicator solution: Dissolve 1.485 g 10-phenanthroline monohydrate and 695 mg FeSO4.7H2O in distilled water and dilute to 100 mL. This indicator solution may be purchased already prepared. Dilute this reagent by a factor of 5 (1 +4).

Standard ferrous ammonium sulfate titrant (FAS), approximately 0.10M: Dissolve 39.2 g Fe(NH4)2(SO4)2.6H2O in distilled water. Add 20 mL conc H2SO4, cool, and dilute to 1000 mL. Standardize solution daily against standard K2Cr2O7 digestion solution as follows:

Pipet 5.00 mL digestion solution into a small beaker. Add 10 mL reagent water to substitute for sample. Cool to room temperature. Add 1 to 2 drops diluted ferroin indicator and titrate with FAS titrant.

Molarity of FAS solution

$$= \frac{\text{Volume } 0.01667M \text{ } K_2Cr_2O_7 \text{ solution titrated, mL}}{\text{Volume FAS used in titration, mL}} \times 0.1000$$

d. Procedure

Wash culture tubes and caps with 20% H2SO4 before first use to prevent contamination. Make volumetric measurements as accurate as practical; use Class A volumetric ware. The most critical volumes are of the sample and digestion solution. Use a microburet for titrations. Measure H2SO4 to ±0.1 mL. The use of hand-held pipettors with non-wetting (polyethylene) pipet tips is practical and adequate. Place sample in culture tube or ampule and add digestion solution. Carefully run sulfuric acid reagent down inside of vessel so an acid layer is formed under the sample-digestion solution layer. Tightly cap tubes or seal ampules, and invert each several times to mix completely. *CAUTION: Wear face shield and protect hands from heat produced when contents of vessels are mixed*. Mix thoroughly before applying heat to prevent local heating of vessel bottom and possible explosive reaction.

Place tubes or ampules in block digester preheated to 150°C and reflux for 2 h behind a protective shield. *CAUTION: These sealed vessels may be under pressure from gases generated during digestion. Wear face and hand protection when handling. If sulfuric acid is omitted or reduced in concentration, very high and dangerous pressures will be generated at 150°C.* Cool to room temperature and place vessels in test tube rack. Some mercuric sulfate may precipitate out but this will not affect the analysis. Remove culture tube caps and add small TFE-covered magnetic stirring bar. If ampules are used, transfer contents to a larger container for titrating.

Add 0.05 to 0.10 mL (1 to 2 drops) ferroin indicator and stir rapidly on magnetic stirrer while titrating with standardized 0.10M FAS. The end point is a sharp color change from blue-green to reddish brown, although the blue-green may reappear within minutes. In the same manner reflux and titrate a blank containing the reagents and a volume of distilled water equal to that of the sample.

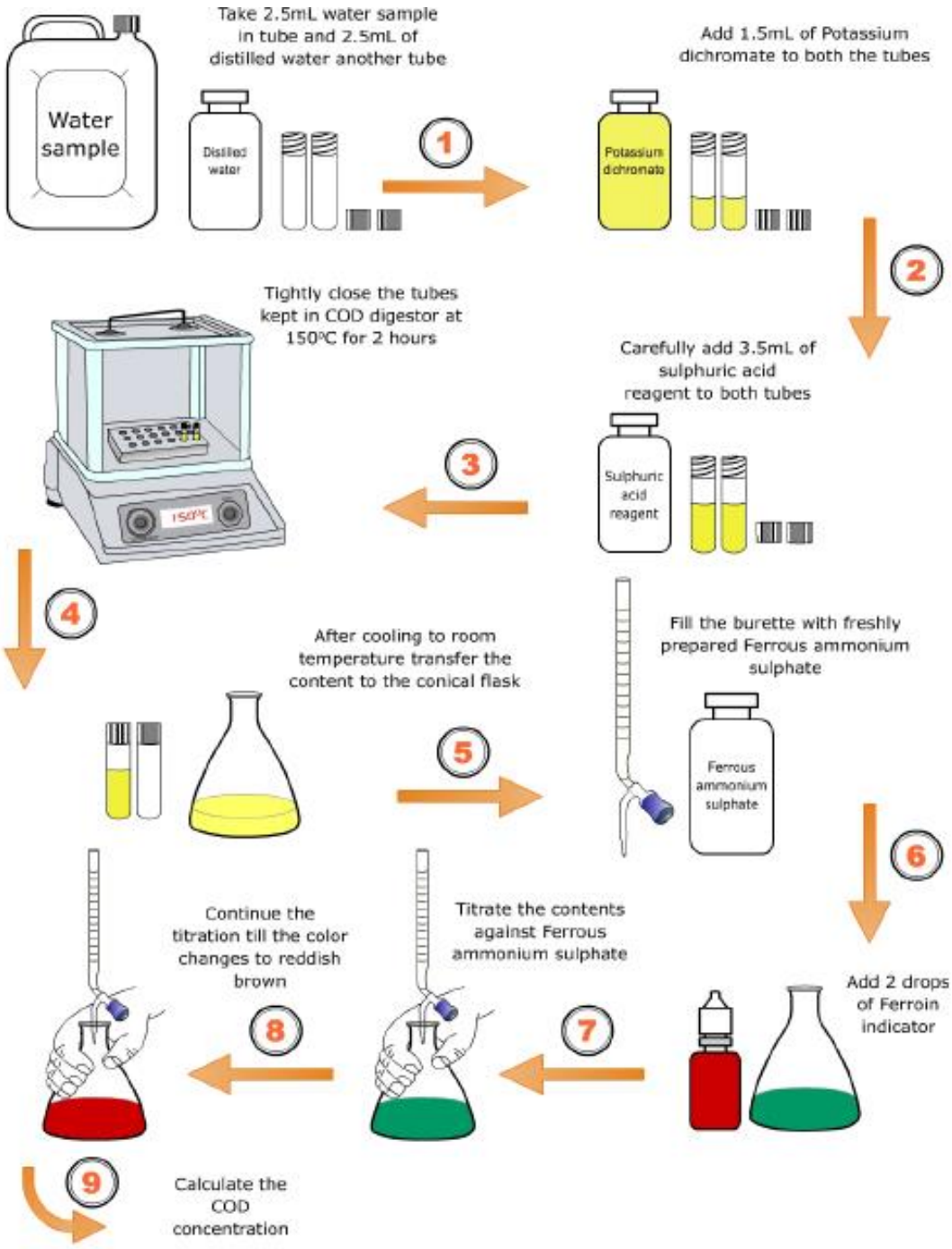

Figure 14 COD Procedure (AMERICAN WATER WORKS ASSOCIATION. 1964. Simplified Procedures for Water Examination.Manual M12, American Water Works Assoc., New York, N.Y.)

Preferably analyze samples in duplicate because of small sample size. Samples that are inhomogeneous may require multiple determinations for accurate analysis. Results should agree within ±5% of their average unless the condition of the sample dictates otherwise.

e. Calculation

$$\text{COD as mg } O_2/L = \frac{(A-B) \times M \times 8000}{\text{mL sample}}$$

Where:

A = mL FAS used for blank,

B = mL FAS used for sample,

M = molarity of FAS, and

8000 = milliequivalent weight of oxygen × 1000 mL/L.

3.8 Turbidity

3.8.1 Introduction

Clarity of water is important in producing products destined for human consumption and in many manufacturing operations. Beverage producers, food processors, and potable water treatment plants drawing from a surface water source commonly rely on fluid-particle separation processes such as sedimentation and filtration to increase clarity and insure an acceptable product. The clarity of a natural body of water is an important determinant of its condition and productivity. Turbidity in water is caused by suspended and colloidal matter such as clay, silt, finely divided organic and inorganic matter, and plankton and other microscopic organisms. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted with no change in direction or flux level through the sample. Correlation of turbidity with the weight or particle number concentration of suspended matter is difficult because the size, shape, and refractive index of the particles affect the light-scattering properties of the suspension. When present in significant concentrations, particles consisting of light-absorbing materials such as activated carbon cause a negative interference. In low concentrations these particles tend to have a positive influence because they contribute to turbidity. The presence of dissolved, color-causing substances that absorb light may cause a negative interference. Some

commercial instruments may have the capability of either correcting for slight color interference or optically blanking out the color effect.

Historically, the standard method for determination of turbidity has been based on the Jackson candle turbidimeter; however, the lowest turbidity value that can be measured directly on this device is 25 Jackson Turbidity Units (JTU). Because turbidities of water treated by conventional fluid-particle separation processes usually fall within the range of 0 to 1 unit, indirect secondary methods were developed to estimate turbidity. Electronic nephelometers are the preferred instruments for turbidity measurement.

Most commercial turbidimeters designed for measuring low turbidities give comparatively good indications of the intensity of light scattered in one particular direction, predominantly at right angles to the incident light. Turbidimeters with scattered-light detectors located at 90° to the incident beam are called nephelometers. Nephelometers are relatively unaffected by small differences in design parameters and therefore are specified as the standard instrument for measurement of low turbidities. Instruments of different make and model may vary in respons However, inter instrument variation may be effectively negligible if good measurement techniques are used and the characteristics of the particles in the measured suspensions are similar. Poor measurement technique can have a greater effect on measurement error than small differences in instrument design. Turbidimeters of nonstandard design, such as forward-scattering devices, may be more sensitive than nephelometers to the presence of larger particles. While it may not be appropriate to compare their output with that of instruments of standard design, they still may be useful for process monitoring. An additional cause of discrepancies in turbidity analysis is the use of suspensions of different types of particulate matter for instrument calibration. Like water samples, prepared suspensions have different optical properties depending on the particle size distributions, shapes, and refractive indices. A standard reference suspension having reproducible light-scattering properties is specified for nephelometer calibration. Its precision, sensitivity, and applicability over a wide turbidity range make the nephelometric method preferable to visual methods. Report nephelometric measurement results as nephelometric turbidity units (NTU).

3.8.2 Nephelometric Method

1. General Discussion

a. Principle: This method is based on a comparison of the intensity of light scattered by the sample under defined conditions with the intensity of light scattered by a standard reference suspension under the same conditions. The higher the intensity of scattered light, the higher the turbidity. Formazin polymer is used as the primary standard reference suspension. The turbidity of a specified concentration of formazin suspension is defined as 4000 NTU.

b. Interference: Turbidity can be determined for any water sample that is free of debris and rapidly settling coarse sediment. Dirty glassware and the presence of air bubbles give false results. ‘‘True color,’’ i.e., water color due to dissolved substances that absorb light, causes measured turbidities to be low. This effect usually is not significant in treated water.

2. Apparatus

a. Laboratory or process nephelometer consisting of a light source for illuminating the sample and one or more photoelectric detectors with a readout device to indicate intensity of light scattered at 90° to the path of incident light. Use an instrument designed to minimize stray light reaching the detector in the absence of turbidity and to be free from significant drift after a short warmup period. The sensitivity of the instrument should permit detecting turbidity differences of 0.02 NTU or less in the lowest range in waters having a turbidity of less than 1 NTU. Several ranges may be necessary to obtain both adequate coverage and sufficient sensitivity for low turbidities. Differences in instrument design will cause differences in measured values for turbidity even though the same suspension is used for calibration. To minimize such differences, observe the following design criteria:

1) Light source—Tungsten-filament lamp operated at a color temperature between 2200 and 3000°K.

2) Distance traversed by incident light and scattered light within the sample tube—Total not to exceed 10 cm.

3) Angle of light acceptance by detector—Centered at 90° to the incident light path and not to exceed ±30° from 90°. The detector and filter system, if used, shall have a spectral peak response between 400 and 600 nm.

b. Sample cells: Use sample cells or tubes of clear, colorless glass or plastic. Keep cells scrupulously clean, both inside and out, and discard if scratched or etched. Never handle them where the instrument's light beam will strike them. Use tubes with sufficient extra length, or with a protective case, so that they may be handled properly. Fill cells with samples and standards that have been agitated thoroughly and allow sufficient time for bubbles to escape.

Clean sample cells by thorough washing with laboratory soap inside and out followed by multiple rinses with distilled or deionized water; let cells air-dry. Handle sample cells only by the top to avoid dirt and fingerprints within the light path.

Figure 15 Turbidity Meter

Cells may be coated on the outside with a thin layer of silicone oil to mask minor imperfections and scratches that may contribute to stray light. Use silicone oil with the same refractive index as glass. Avoid excess oil because it may attract dirt and contaminate the sample compartment of the instrument. Using a soft, lint-free cloth, spread the oil uniformly and wipe off excess. The cell should appear to be nearly dry with little or no visible oil. Because small differences

between sample cells significantly impact measurement, use either matched pairs of cells or the same cell for both standardization and sample measurement.

3. Reagents

a. Dilution water: High-purity water will cause some light scattering, which is detected by nephelometers as turbidity. To obtain low-turbidity water for dilutions, nominal value 0.02 NTU, pass laboratory reagent-grade water through a filter with pore size sufficiently small to remove essentially all particles larger than 0.1 μm the usual membrane filter used for bacteriological examinations is not satisfactory. Rinse collecting flask at least twice with filtered water and discard the next 200 mL. Some commercial bottled demineralized waters have a low turbidity. These may be used when filtration is impractical or a good grade of water is not available to filter in the laboratory.

b. Stock primary standard formazin suspension:

1) Solution I—Dissolve 1.000 g hydrazine sulfate, $(NH_2)_2 \cdot H_2SO_4$, in distilled water and dilute to 100 mL in a volumetric flask. CAUTION: *Hydrazine sulfate is a carcinogen; avoid inhalation, ingestion, and skin contact. Formazin suspensions can contain residual hydrazine sulfate.*

2) Solution II—Dissolve 10.00 g hexamethylenetetramine, $(CH_2)_6N_4$, in distilled water and dilute to 100 mL in a volumetric flask.

3) In a flask, mix 5.0 mL Solution I and 5.0 mL Solution II. Let stand for 24 h at 25 ± 3°C. This results in a 4000-NTU suspension. Transfer stock suspension to an amber glass or other UV-light-blocking bottle for storage. Make dilutions from this stock suspension. The stock suspension is stable for up to 1 year when properly stored.

c. Dilute turbidity suspensions: Dilute 4000 NTU primary standard suspension with high-quality dilution water. Prepare immediately before use and discard after use.

d. Secondary standards: Secondary standards are standards that the manufacturer (or an independent testing organization) has certified will give instrument calibration results equivalent (within certain limits) to the results obtained when the instrument is calibrated with the primary

standard, i.e., user-prepared formazin. Various secondary standards are available including: commercial stock suspensions of 4000 NTU formazin, commercial suspensions of microspheres of styrene-divinylbenzene copolymer,†#(4) and items supplied by instrument manufacturers, such as sealed sample cells filled with latex suspension or with metal oxide particles in a polymer gel. The U.S. Environmental Protection Agency1 designates user-prepared formazin, commercial stock formazin suspensions, and commercial styrene-divinylbenzene suspensions as ‘‘primary standards,’’ and reserves the term ‘‘secondary standard’’ for the sealed standards mentioned above.

Secondary standards made with suspensions of microspheres of styrene-divinylbenzene copolymer typically are as stable as concentrated formazin and are much more stable than diluted formazin. These suspensions can be instrument-specific; therefore, use only suspensions formulated for the type of nephelometer being used. Secondary standards provided by the instrument manufacturer (sometimes called ‘‘permanent’’ standards) may be necessary to standardize some instruments before each reading and in other instruments only as a calibration check to determine when calibration with the primary standard is necessary. All secondary standards, even so-called ‘‘permanent’’ standards, change with time. Replace them when their age exceeds the shelf life. Deterioration can be detected by measuring the turbidity of the standard after calibrating the instrument with a fresh formazin or microsphere suspension. If there is any doubt about the integrity or turbidity value of any secondary standard, check instrument calibration first with another secondary standard and then, if necessary, with user-prepared formazin. Most secondary standards have been carefully prepared by their manufacturer and should, if properly used, give good agreement with formazin. Prepare formazin primary standard only as a last resort. Proper application of secondary standards is specific for each make and model of nephelometer. Not all secondary standards have to be discarded when comparison with a primary standard shows that their turbidity value has changed. In some cases, the secondary standard should be simply relabeled with the new turbidity value. Always follow the manufacturer’s directions.

4. Procedure

a. General measurement techniques: Proper measurement techniques are important in minimizing the effects of instrument variables as well as stray light and air bubbles. Regardless

of the instrument used, the measurement will be more accurate, precise, and repeatable if close attention is paid to proper measurement techniques. *Measure turbidity immediately to prevent temperature changes and particle flocculation and sedimentation from changing sample characteristics.* If flocculation is apparent, break up aggregates by agitation. Avoid dilution whenever possible. Particles suspended in the original sample may dissolve or otherwise change characteristics when the temperature changes or when the sample is diluted.

Remove air or other entrained gases in the sample before measurement. Preferably degas even if no bubbles are visible. Degas by applying a partial vacuum, adding a nonfoaming-type surfactant, using an ultrasonic bath, or applying heat. In some cases, two or more of these techniques may be combined for more effective bubble removal. For example, it may be necessary to combine addition of a surfactant with use of an ultrasonic bath for some severe conditions. Any of these techniques, if misapplied, can alter sample turbidity; *use with care*. If degassing cannot be applied, bubble formation will be minimized if the samples are maintained at the temperature and pressure of the water before sampling. Do not remove air bubbles by letting sample stand for a period of time because during standing, turbidity-causing particulates may settle and sample temperature may change. Both of these conditions alter sample turbidity, resulting in a nonrepresentative measurement. Condensation may occur on the outside surface of a sample cell when a cold sample is being measured in a warm, humid environment. This interferes with turbidity measurement. Remove all moisture from the outside of the sample cell before placing the cell in the instrument. If fogging recurs, let sample warm slightly by letting it stand at room temperature or by partially immersing it in a warm water bath for a short time. Make sure samples are again well mixed.

b. Nephelometer calibration: Follow the manufacturer's operating instructions. Run at least one standard in each instrument range to be used. Make certain the nephelometer gives stable readings in all sensitivity ranges used.

c. Measurement of turbidity: Gently agitate sample. Wait until air bubbles disappear and pour sample into cell. When possible, pour well-mixed sample into cell and immerse it in an ultrasonic bath for 1 to 2 s or apply vacuum degassing, causing complete bubble release. Read turbidity directly from instrument display.

d. Calibration of continuous turbidity monitors: Calibrate continuous turbidity monitors for low turbidities by determining turbidity of the water flowing out of them, using a laboratory-model nephelometer, or calibrate the instruments according to manufacturer's instructions with formazin primary standard or appropriate secondary standard.

5. Interpretation of Results

When comparing water treatment efficiencies, do not estimate turbidity more closely than specified below. Uncertainties and discrepancies in turbidity measurements make it unlikely that results can be duplicated to greater precision than specified. Report turbidity readings as mentioned in Table 4:

Table 4 Turbidity Interpretation (Standard Methods for the Examination Of Water And Wastewater; Apha, Awwa, And Wef, 21st Edition, 2005.)

Turbidity Range *NTU*	Report to the Nearest *NTU*
0–1.0	0.05
1–10	0.1
10–40	1
40–100	5
100–400	10
400–1000	50
>1000	100

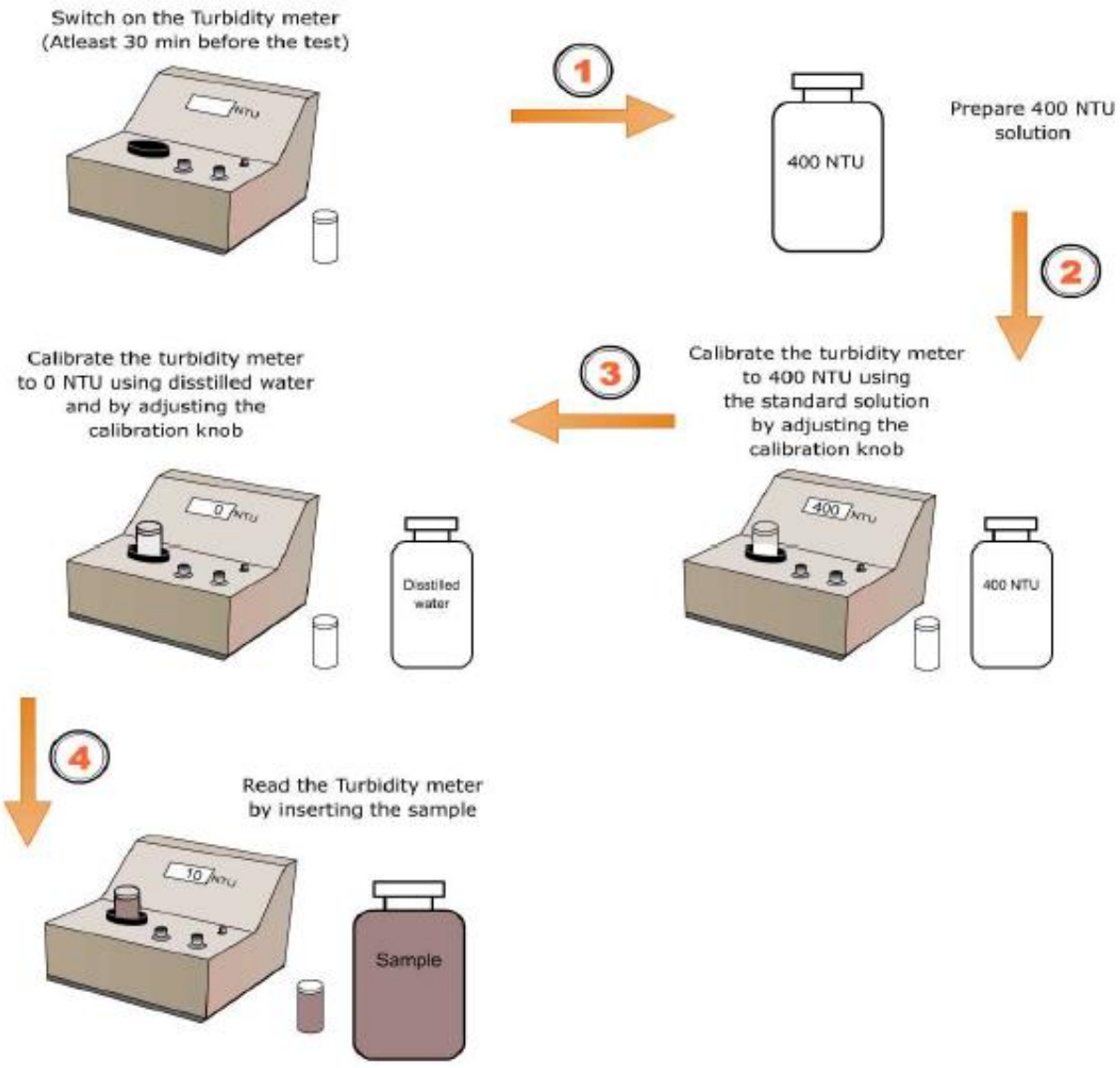

Figure 16 Turbidity Procedure (AMERICAN WATER WORKS ASSOCIATION. 1964. Simplified Procedures for Water Examination.Manual M12, American Water Works Assoc., New York, N.Y.)

3.9 Solids

3.9.1 Introduction

Solids refer to matter suspended or dissolved in water or wastewater. Solids may affect water or effluent quality adversely in a number of ways. Waters with high dissolved solids generally are of inferior palatability and may induce an unfavorable physiological reaction in the transient consumer. For these reasons, a limit of 500 mg dissolved solids/L is desirable for drinking waters. Highly mineralized waters also are unsuitable for many industrial applications. Waters high in suspended solids may be esthetically unsatisfactory for such purposes as bathing. Solids analyses are important in the control of biological and physical wastewater treatment processes and for assessing compliance with regulatory agency wastewater effluent limitations.

‘‘Total solids’’ is the term applied to the material residue left in the vessel after evaporation of a sample and its subsequent drying in an oven at a defined temperature. Total solids includes ‘‘total suspended solids,’’ the portion of total solids retained by a filter, and ‘‘total dissolved solids,’’ the portion that passes through the filter.

The type of filter holder, the pore size, porosity, area, and thickness of the filter and the physical nature, particle size, and amount of material deposited on the filter are the principal factors affecting separation of suspended from dissolved solids. ‘‘Dissolved solids’’ is the portion of solids that passes through a filter of 2.0 μm (or smaller) nominal pore size under specified conditions. ‘‘Suspended solids’’ is the portion retained on the filter.

‘‘Fixed solids’’ is the term applied to the residue of total, suspended, or dissolved solids after heating to dryness for a specified time at a specified temperature. The weight loss on ignition is called ‘‘volatile solids.’’ Determinations of fixed and volatile solids do not distinguish precisely between inorganic and organic matter because the loss on ignition is not confined to organic matter. It includes losses due to decomposition or volatilization of some mineral salts.

‘‘Settleable solids’’ is the term applied to the material settling out of suspension within a defined period. It may include floating material, depending on the technique.

3.9.2 Sources of Error &Variability

Sampling, subsampling, and pipeting two-phase or three-phase samples may introduce serious errors. Make and keep such samples homogeneous during transfer. Use special handling to insure sample integrity when subsampling. Mix small samples with a magnetic stirrer. If suspended solids are present, pipet with wide-bore pipets. If part of a sample adheres to the sample container, consider this in evaluating and reporting results. Some samples dry with the formation of a crust that prevents water evaporation; special handling is required to deal with this. Avoid using a magnetic stirrer with samples containing magnetic particles.

The temperature at which the residue is dried has an important bearing on results, because weight losses due to volatilization of organic matter, mechanically occluded water, water of crystallization, and gases from heat-induced chemical decomposition, as well as weight gains due to oxidation, depend on temperature and time of heating. Each sample requires close attention to desiccation after drying. Minimize opening desiccator because moist air enters. Some samples may be stronger desiccants than those used in the desiccator and may take on water.

Residues dried at 103 to 105°C may retain not only water of crystallization but also some mechanically occluded water. Loss of CO_2 will result in conversion of bicarbonate to carbonate. Loss of organic matter by volatilization usually will be very slight. Because removal of occluded water is marginal at this temperature, attainment of constant weight may be very slow. Residues dried at 180 ± 2°C will lose almost all mechanically occluded water. Some water of crystallization may remain, especially if sulfates are present. Organic matter may be lost by volatilization, but not completely destroyed. Loss of CO_2 results from conversion of bicarbonates to carbonates and carbonates may be decomposed partially to oxides or basic salts. Some chloride and nitrate salts may be lost.

In general, evaporating and drying water samples at 180°C yields values for dissolved solids closer to those obtained through summation of individually determined mineral species than the dissolved solids values secured through drying at the lower temperature.

To rinse filters and filtered solids and to clean labware use Type III water. Special samples may require higher quality water. Results for residues high in oil or grease may be questionable

because of the difficulty of drying to constant weight in a reasonable time. To aid in quality assurance, analyze samples in duplicate. Dry samples to constant weight if possible. This entails multiple drying-cooling-weighing cycles for each determination.

Analyses performed for some special purposes may demand deviation from the stated procedures to include an unusual constituent with the measured solids. Whenever such variations of technique are introduced, record and present them with the results.

3.9.3 Total Dissolved Solids dried at 180°C

1. General Discussion

a. Principle: A well-mixed sample is filtered through a standard glass fiber filter, and the filtrate is evaporated to dryness in a weighed dish and dried to constant weight at 180°C. The increase in dish weight represents the total dissolved solids. This procedure may be used for drying at other temperatures. The results may not agree with the theoretical value for solids calculated from chemical analysis of sample (see above). Approximate methods for correlating chemical analysis with dissolved solids are available.1 The filtrate from the total suspended solids determination may be used for determination of total dissolved solids.

b. Interferences: Highly mineralized waters with a considerable calcium, magnesium, chloride, and/or sulfate content may be hygroscopic and require prolonged drying, proper desiccation, and rapid weighing. Samples high in bicarbonate require careful and possibly prolonged drying at 180°C to insure complete conversion of bicarbonate to carbonate. Because excessive residue in the dish may form a water-trapping crust, limit sample to no more than 200 mg residue.

2. Apparatus

a. Glass-fiber filter disks without organic binder.

b. Filtration apparatus: One of the following, suitable for the filter disk selected:

1) *Membrane filter funnel.*

2) *Gooch crucible,* 25-mL to 40-mL capacity, with Gooch crucible adapter.

3) *Filtration apparatus* with reservoir and coarse (40- to 60-μm) fritted disk as filter support.

c. Suction flask, of sufficient capacity for sample size selected.

d. Drying oven, for operation at 180 ± 2°C.

3. Procedure

a. Preparation of glass-fiber filter disk: If pre-prepared glass fiber filter disks are used, eliminate this step. Insert disk with wrinkled side up into filtration apparatus. Apply vacuum and wash disk with three successive 20-mL volumes of reagent-grade water. Continue suction to remove all traces of water. Discard washings.

b. Preparation of evaporating dish: If volatile solids are to be measured, ignite cleaned evaporating dish at 550°C for 1 h in a muffle furnace. If only total dissolved solids are to be measured, heat clean dish to 180 ± 2°C for 1 h in an oven. Store in desiccator until needed. Weigh immediately before use.

c. Selection of filter and sample sizes: Choose sample volume to yield between 2.5 and 200 mg dried residue. If more than 10 min are required to complete filtration, increase filter size or decrease sample volume.

d. Sample analysis: Stir sample with a magnetic stirrer and pipet a measured volume onto a glass-fiber filter with applied vacuum. Wash with three successive 10-mL volumes of reagent-grade water, allowing complete drainage between washings, and continue suction for about 3 min after filtration is complete. Transfer total filtrate (with washings) to a weighed evaporating dish and evaporate to dryness on a steam bath or in a drying oven. If necessary, add successive portions to the same dish after evaporation. Dry evaporated sample for at least 1 h in an oven at 180 ± 2°C, cool in a desiccator to balance temperature, and weigh. Repeat drying cycle of drying, cooling, desiccating, and weighing until a constant weight is obtained or until weight change is less than 4% of previous weight or 0.5 mg, whichever is less. Analyze at least 10% of all samples in duplicate. Duplicate determinations should agree within 5% of their average weight.

4. Calculation

$$\text{mg total dissolved solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

Where:
A = weight of dried residue + dish, mg, and
B = weight of dish, mg.

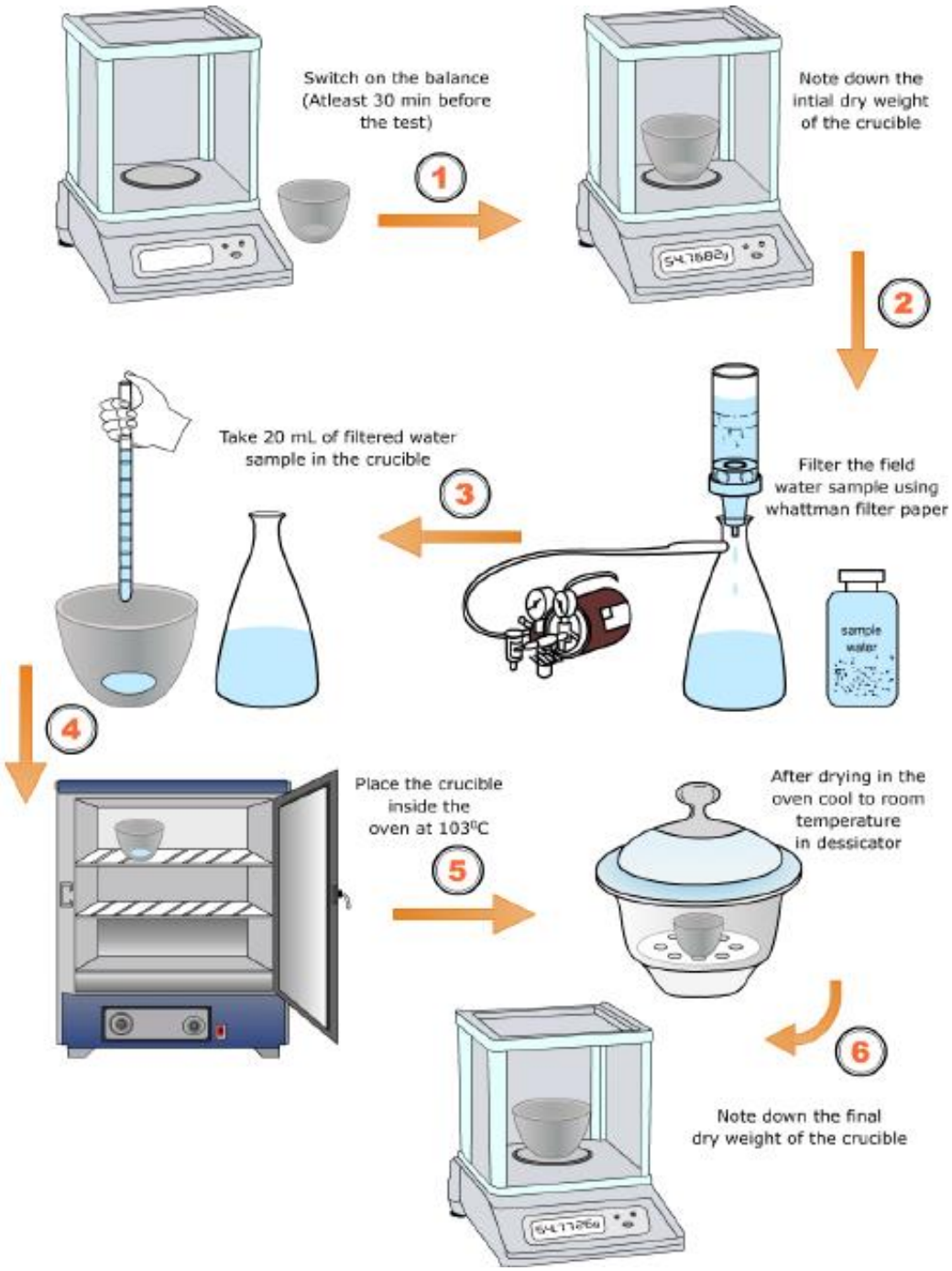

Figure 17 Total Dissolved Solids Procedure (AMERICAN WATER WORKS ASSOCIATION. 1964. Simplified Procedures for Water Examination.Manual M12, American Water Works Assoc., New York, N.Y.)

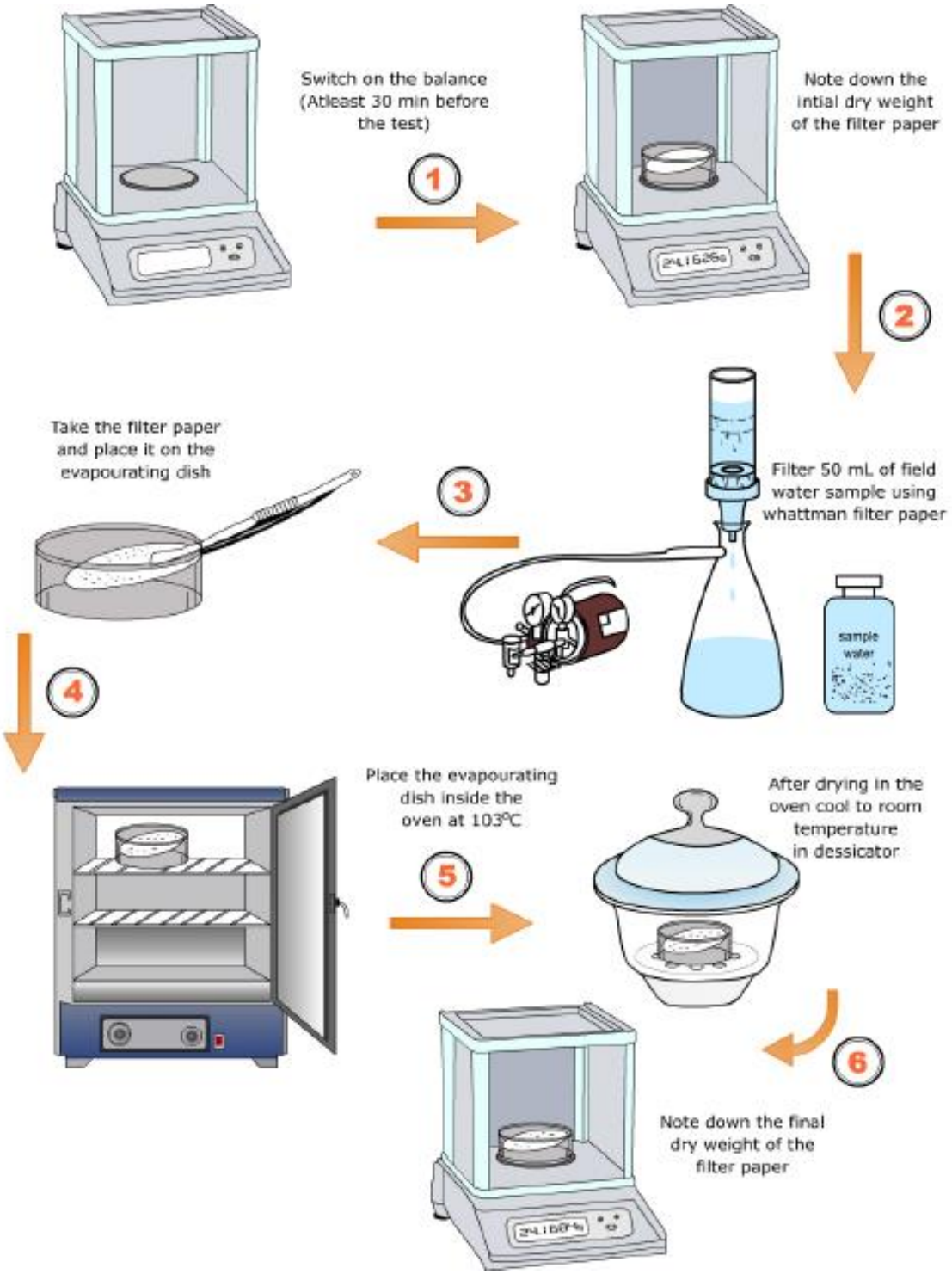

Figure 18 Total Suspended Solids Procedure (AMERICAN WATER WORKS ASSOCIATION. 1964. Simplified Procedures for Water Examination.Manual M12, American Water Works Assoc., New York, N.Y.)

3.10 Heavy Metals

3.10.1 Introduction

Water is a principle constituent of the planet earth. Natural sources of fresh water are in the form of rivers, lakes, glaciers and ample ground water system. Metals like aluminium, calcium, cadmium, chromium, copper, iron, lead, magnesium, manganese, zinc etc. may occur in drinking water due to geogenic reasons or may be due to anthropogenic activities such as uncontrolled discharge of waste waters of different types of industries. Now days, several types of detection techniques for metal ions in water samples are available like atomic absorption spectroscopy (AAS), Flame emission, Vapour generation accessory (VGA), Graphite tube atomizer (GTA), Inductively Coupled Plasma Emission, Ion Chromatography, UV-Visible spectrophotometer, High Performance Liquid Chromatography (HPLC) etc. which are capable to detect the concentration of metal ions up to ppb level. The speciation of metal ions in water samples can also be achieved by advanced instrumentation techniques including chromatographic, capillary electrophoresis, spectroscopic and other techniques. A comparison of various guide line values of metal ions in drinking water has been made in Table 5.

Table 5 Comparison of USEPA, WHO and BIS guideline values (mg/L) of metal ions for drinking water

Metal Name	USEPA (Maximum contaminant level)	WHO (Guideline value)	BIS: 10500 (Permissible limit)
Arsenic	0.01	0.01	0.05
Aluminium	0.05-0.2	NM	0.2
Boron	--	2.4	1.0
Cadmium	0.005	0.003	0.003
Chromium	0.1	0.05	0.05
Copper	1.3	2.0	1.5
Iron	0.3	NM	0.3
Lead	0.015	0.01	0.01
Mercury	0.002	0.006	0.001
Manganese	0.05	NM	0.3
Nickel	--	0.07	0.02
Selenium	0.05	0.04	0.01
Zinc	5.0	NM	15.0

3.10.2 Atomic Absorption Spectroscopy (AAS)

Atomic Absorption Spectrophotometer analytical instrument is based on the principle of atomic absorption spectroscopy and is very useful to detect the metal ion concentration present in water samples. When a sample solution is aspirated into a flame then sample element is changed into atomic vapour of that element. Flame contains atoms of element. Furthermore, some atoms are

thermally excited by flame whereas most of them remain in ground state. The ground state atoms then absorb the radiation of specific wavelength produced by source i.e. hollow cathode lamp of that specific metal. Now, the wavelength of radiation given off by the source or lamp is similar as that of absorbed by the atoms in the flame. AAS method follows the Beer's law, which states that absorbance is directly proportional to concentration. Each atomic absorption spectrophotometer possesses a light source i.e. lamp, sample cell, monochromator, detector and output device. The most common type of burner is a premix, which introduces the spray into a condensing chamber for removal of larger depletes.

a. Light Source (Lamps)

Use either a hollow-cathode lamp or electrode less discharge lamp (EDL) for a particular element being measured. Moreover, multi-element hollow-cathode lamps generally provide lower sensitivity than single element lamps whereas EDLs take a longer time to warm up and stabilize.

b. Out Put Unit (Readout)

Most of the instruments are equipped with either a digital or null meter readout mechanism. Generally, the modern instruments are with a microprocessor capable of integrating absorption signals over at high concentrations.

c. Burner

The most common type of burner is a premix, which introduces the spray into a condensing chamber for removal of large droplets. The burner may be fitted with a conventional head containing a single slot: a tree-slot boling head which may be preferred for direct aspiration with an air-acetylene flame, or a special head for use with nitrous oxide and acetylene.

d.Readout

Most instruments are equipped with either a digital or null meter readout mechanism. Most modem instruments are with microprocessor or stand-alone control computers capable of integrating absorption signals over at high concentrations.

Figure 19 Atomic Absorption Spectrophotometer

e. Pressure Controlling Valve

Generally, a separate reducing value should be used for each gas. Suitable reducing valves maintain the supplies of fuel and oxidant at pressure somewhat higher than the controlled operating pressure of the instrument.

f. Exhaust (Vent)

Fix a vent about 6-12 inches above the burner to remove the fumes and vapours from the flame. This practice protects laboratory personnel from vapours, protects the instrument from corrosive vapours, and prevents flame stability from being affected by room drafts. Besides, in laboratory sites with heavy particulate air pollution, prefer the clean laboratory facilities. AAS analysis for various metal ions needs a suitable flame-gas combination which is given in the Table 6.

Table 6 Flame-gas combination for metal ion analysis by AAS

Metal Name	Flame-Gas Combination	Metal Name	Flame-Gas Combination
Arsenic Aluminium Boron Cadmium Calcium Chromium Copper Iron	Air-Act N-Act N-Act Air-Act N-Act Air-Act Air-Act Air-Act	Mercury Manganese Magnesium Nickel Lead Selenium Zinc	Air-Act Air-Act Air-Act Air-Act Air-Act Air-Act Air-Act

3.10.3 Interferences

Chemical interference:

Many metals can be determined by direct aspiration of sample into an air-acetylene flame. The most troublesome type of interference is termed "chemical" and results from the lack of absorption by atoms bound in molecular combination in the flame. This can occur when the flame is not hot enough to dissociate the molecules or when the dissociated atom is oxidised immediately to a compound that will not dissociate further at the flame temperature.

Background correction:

Molecular absorption and light scattering caused by solid particles in the flame can cause erroneously high absorption values resulting in positive errors. When such phenomena occur, use background correction to obtain accurate values. Use any one of three types of background correction:

Continuum-source Background correction: Continuum-source background corrector utilizes either a hydrogen filled hollow cathode lamp with metal cathode or a deuterium arc lamp. When both line sources are placed in the same optical path and are time-shared, the broadband background from the elemental signal is subtracted electronically, and the resultant signal will be background-compensated.

Zeeman background correction. This correction is based on the principle that a magnetic field splits the spectral in to two linearly polarized light beams parallel and perpendicular to the

magnetic field. One is called the pi component and other sigma component. These tow line beams have exactly the same wavelength and differ only in the plane of polarisation. Zeeman background correction provides accurate background correction at much higher absorption levels than is possible with continuum sources background correction system.

Smith-Hieftje background correction: This correction is based on the principle that absorbance measured for a specific element is reduced as the hollow cathode lamp is increased while absorption of non-specific absorption substance remains identical at all current levels. When this method is applied, the absorption at a high current mode is subtracted from the absorption at a low-current mode. Under these conditions, any absorbance due to non-specific background is subtracted out and corrected for.

3.10.4 Reagents and standards

Air-Air is cleaned and dried through a suitable filter to remove oil, water, and other foreign substances. The sources may be a compressor or commercially bottled gas.

Acetylene: Standard commercial grade in which acetone is always present in acetylene cylinders. This prevents the entering and damaging the burner head by replacing a cylinder when its pressure has fallen to 689kPa (100psi) acetylene. Caution: Acetylene gas represent an explosive hazard in the laboratory. Follow instrument manufacturer's direction in plumbing and using this gas. Do no allow gas contact with copper, brass with >65% copper, silver, or liquid mercury; do not use copper or brass tubing, regulators, or fittings.

Nitrous oxide (for Aluminium): The gas is commercially available in cylinders. Fit nitrous oxide cylinder with a special non-freezable regulator or wrap a heating coil around an ordinary regulator to prevent flashback of the burner caused by regulation in nitrous oxide flow through a frozen regulator.

Caution: Use nitrous oxide with strict adherence to manufacturer's directions. Improper sequencing of gas flow at start-up and shutdown of instrument can produce explosions from flashback.

Metal-free water: Use metal-free water for preparing all reagents and calibration standards and as dilution waste. Prepare metal-free water by deionising tap water and/or by using one of the following processes, depending on the metal concentration in the sample: single distillation, reinstallation, or sub-boiling.

Standard solution: Prepare standard solutions of known metal concentrations as described. Stock standard solution can be obtained from several commercial sources that should be used as secondary standard solution for calibration of instrument and the prepared standards.

3.10.5 Procedure

Sample preparation: To reduce interference by organic matter and to convert metal associated with particulate to a form (usually the free metal) that can be determined by inductively coupled plasma spectroscopy, use one of the digestion techniques. Use the least rigorous digestion method required providing complete and consistent recovery compatible with the analytical method and the metal being analysed.

- Open digestion
- Closed system digestion (Microwave-assisted digestion).

Nitric acid will digest most samples adequately. Nitrate is an acceptable matrix for both flame and electro-thermal atomic absorption. Some samples may require addition of perchloric, hydrochloric, or sulphuric acid for complete digestion. Confirm metal recovery for each digestion and analytical procedures used. As a general rule, HNO3 alone is adequate for clean samples or easily oxidised materials; HNO3-H2SO4 or HNO3-HCl digestion is adequate for readily oxidisable organic matter; HNO3-HClO4 or HNO3-HClO4-HF digestion is necessary for difficult-to-oxidise organic matter or minerals. Dry ash formation is helpful if large amounts of organic matter are present.

Nitric Acid Digestion

a. Apparatus:

Hot plate, Conical (Erlenmeyer) flasks, 125mL or Griffin beakers 150mL, acid-washed and rinsed with double distilled water; volumetric flasks, 100mL.

b. Reagents:

Nitric acid, concentrated analytical grade or trace metal grade

c. Procedure:

Transfer a measured volume (50mL) of well-mixed, acid-preserved sample to a flask or beaker. Add 5mL conc. HNO3 and a few boiling chips or glass beads. Bring to a slow boil and evaporate on a hot plate to the lowest volume possible (about 10 to 20mL).Continue heating and adding conc. HNO3 as necessary until digestion is complete as shown by a light-coloured, clear solution. Do not let sample dry during digestion.

Wash down flask or beaker walls with water and then filter if necessary. Transfer filtrate to a 10mL volumetric flask with two 5mL portions of water, adding these rinsing to the volumetric flask. Cool, dilute to mark and mix thoroughly. Take portions of this solution for required metal determinations.

Operating conditions: Install a hollow cathode lamp for the desired metal in the instrument and roughly set the wavelength dial according to table 7 given below.

Table 7 Wavelength instrument detection level sensitivity and optimum concentration range for elements. (Guide Manual: Water and Waste Water, Central Pollution Control Board, New Delhi.)

Element	Wavelength (nm)	Flame Gases	Instrument Detection Level mg/L	Sensitivity	Optimum Concentration range mg/L
Al	328.1	N-Ac	0.1	1	5-100
Cd	228.8	A-Ac	0.002	0.025	0.05-2
Cr	357.6	A-Ac	0.2	0.1	0.2-10
Cu	324.7	A-Ac	0.1	0.1	0.2-10
Fe	248.3	A-Ac	0.02	0.12	0.3-10
Mn	279.5	A-Ac	0.01	0.05	0.1-10
Ni	232.0	A-Ac	0.02	0.15	0.3-10
Pb	283.3	A-Ac	0.05	0.5	1-20
Zn	213.9	A-Ac	0.005	0.02	0.05-2

Set slit width according to manufacturer-suggested setting for the element being measured. Turn on instrument; apply to the hollow-cathode lamp the current suggested by the manufacturer, and let instrument warm-up until energy source stablilises, generally about 10 to 20 min. Readjust current as necessary after warm-up. Optimise wavelength by adjusting wavelength dial until optimum energy gain is obtained. Align lamp in accordance with manufacturer's instruction. Install suitable burner head and adjust burner head position. Turn on air and adjust flow rate to that specified by manufacturer to give maximum sensitivity for the metal being measured. Turn on acetylene, adjust flow rate to value specified, and ignite flame. Let flame stabilise for a few minutes. Aspirate a blank consisting of deionised water containing the same concentration of

acid in standard and samples. Adjust the instrument to zero, aspirate a standard solution and adjust aspiration rate of the nebuliser to obtain maximum sensitivity. Adjust burner both vertically and horizontally to obtain maximum response. Aspirate blank again and check zero reading of the instrument, Aspirate a standard near the middle of the linear range.Record absorbance of this standard when freshly prepared and with a new hollow cathode lamp.

Refer to the data on subsequent determination of the same element to check consistency of instrument setup and aging of hollow cathode lamp and standard. The instrument now is ready to operate. When analysis is finished extinguish flame by turning off first acetylene and then air.

Standardisation: Select at least three concentrations of each standard metal solution to bracket the expected metals concentration of a sample. Aspirate blank and adjust zero of the instrument. Then aspirate each standard in turn into flame record absorbance.

Prepare a calibration curve by plotting on linear graph paper absorbance of standard versus their concentrations. For instruments equipped with direct concentration readout, this step is unnecessary. With some instrument it may be necessary to convert percent absorption by using a table generally provided by the manufacturer.

3.10.6 Calculations

Calculate concentration of each ion, in μg/L for trace elements, and in mg/L for more common metals, by referring to the appropriate calibration curve. Alternatively read concentration directly from the instrument readout if the instrument is so equipped. If the sample has high values multiply it by the appropriate dilution factor.

CHAPTER IV

RESULTS & DISCUSSION

Wastewater composition describes the actual quantity of physical and chemical constituents present in the wastewater. All the findings have been tabulated in Table 8. The wastewater was tested for pH, turbidity, DO within 3-4 hours after collecting sample. According to the results, average pH values came around 8.14 which is very well within the acceptable range of 5.5-9. Maximum pH was found at influent sample of Mahant Indiresh, but having the Sewage Treatment Plant (STP) in their premises the effluent value was found out to be around 8.5. Studying the variations of different solid contents is important from a wastewater management perspective because many recommended standards are focused substantially on solids. The average values of Total Dissolve Solids (TDS) & Total Suspended Solids (TSS) were 50 mg/L & 804 mg/L which were well above the permissible limit of 600 mg/L.

The average values of the BOD & COD were found out to be around 25 mg/L and 1567 mg/L respectively. The BOD value is well within the permissible limit of 30mg/L but COD exceeds the permissible limit of 250 mg/L. The higher values of COD can be attributed to the septic matter collected into the drainages and some of the kitchen waste added into the system. It is known that heavy metals can accumulate via food chain and reach living organisms causing serious effects. Some selected heavy metal species, Cu, Pb, Cd were inspected during study period. Pb levels were very less than the detection levels of spectrophotometer. Though Cu & Cd were detected and average value was found out to be 0.2734 ppm & 0.00275 ppm respectively which is very less than the permissible level of 3 ppm & 0.005 ppm respectively for wastewater. In the preceding sections the hospital wise results have been put up for clear understanding.

Table 8 Permissible Limit (The Environment (Protection) Rules, 1986)

Parameter	General Standards For Discharge Of Environmental Pollutants
pH (25^{o})	5.5-9
BOD(mg/L)	Not more than 30
COD(mg/L)	Not more than 250
TSS (mg/L)	Not more than 600
Pb(mg/L)	Not more than 1
Cu (mg/L)	Not more than 3
Cd (mg/L)	Not more than 1

Table 9 Wastewater Characteristics of Selected Hospitals in Dehradun

Hospital Name	Sample	Parameter										
		pH(25^0)	DO (mg/l)	BOD (mg/l)	COD (mg/l)	TSS (mg/l)	TDS (mg/l)	Alkalinity (mg/l)	Turbidity (NTU)	Pb (mg/l)	Cu (mg/l)	Cd (mg/l)
Mahant Indiresh	Influent	9.1 ± 0.1	0	45	2464	58	570	490	90	ND	.	.
	Effluent	8.5 ± 0.2	5.8	12	1760	30	550	252	46	ND	0.2437	0.0028
Doon Hospital	Composite	7.98	0.2	19.5	2112	54	1120	490	42	ND	0.2275	0.0034
City Heart Hospital	Composite	8.38	0.4	7.5	1408	36	944	232	70	ND	0.2793	0.0016
Synergy Hospital	Influent	7.93± 0.12	0	22.5	3872	64	1182	420	82	ND	.	.
	Effluent	7.61± 0.12	0.7	13.5	2816	48	1016	380	67	ND	0.3321	0.0037
Ashirwad Hospital	Composite	7.32	0	18	1056	46	942	226	31	ND	0.3015	0.0039
Fortis Hospital	Composite	8.23	0	15	2816	44	928	366	61	ND	0.2851	0.0029
Max Hospital STP	Influent	8.17	6.8	106	248	68	676	322	5	ND	.	.
	Effluent	8.37	7.1	25.2	84	26	444	244	0	ND	0.2576	0.0016
Max Hospital ETP	Influent	8.26	6.95	13.3	108	88	736	282	10	ND	.	.
	Effluent	8.41	7.2	2.35	52	36	542	296	0	ND	0.2611	0.0021

4.1 Shri Mahant Indiresh Hospital

Shri Mahant Indiresh hospital is a 1000 bedded multi-specialty and superspeciality hospital situated in the heart of the Dehradun city nearly 2 km from both the railway station & bus terminal. The hospital caters to about 2000 patients on a daily basis under the direct supervision & humane touch of the medical specialists. The staff of the hospital includes about 300 doctors and 500 paramedicals. Facilities of latest MRI, 3D CT scan, Digital X-Rays, utmost modern diagnostic equipments in central reference laboratory, full-fledged ICU with a number of ventilators, dialysis unit, plastic & burn unit, neurology and urological units, medical retina unit with laser treatment and above all 24 hrs emergency & trauma units are available. Similarly all the other specialties in the hospital impart quality patient care. Recently a complex of 17 ultra-modern operation theaters at par with international standard has become functional, along with a vast & impressive building, in order to advance the functioning and handle the increased crowd of patients in the hospital from this valley and surrounding hilly regions. The hospital started in 2002 and the medical college got the permission by Ministry of Health and Family Welfare, New Delhi to start its first MBBS Bacth from 2006. The MBBS Degree is recognised by MCI and MOHFW. The postgraduate (MD/MS) courses started in the year 2011.

Table 10 Mahant Indiresh Hospital- Obervation Table

Mahant Indiresh		
pH(25°)	Influent	9.1 ± 0.1
	Effluent	8.5 ± 0.2
DO(mg/L)	Influent	0
	Effluent	5.8
BOD(mg/L)	Influent	45
	Effluent	12
COD(mg/L)	Influent	2464
	Effluent	1760
TSS(mg/L)	Influent	58
	Effluent	30
TDS(mg/L)	Influent	570
	Effluent	550
Alkalinity(mg/L)	Influent	490
	Effluent	252
Turbidity(NTU)	Influent	90
	Effluent	46
Pb (mg/L)	Effluent	ND
Cu (mg/L)	Effluent	0.2437
Cd (mg/L)	Effluent	0.0028

Total eleven parameters were tested for this hospital. All parameters except COD, Alkalinity, Turbidity in discharge wastewater are high than permissible limits. Actions needed to be taken to reduce these levels in wastewater.

4.2 Doon Hospital

Doon Hospital in Dehradun ranked top most govt. hospital in north india. Doon hospital offers all ultra modern facilities and technologies i.e., ultra sound, brain mapping, MRI, CT-Scan, ECG, and all major surgery.

Table 11 Doon Hospital- Obervation Table

Doon Hospital		
pH(25°)	Tap Water	8.9 ± 0.2
	RO Water	7.63
	Wash water	8.2
	Composite	7.98
DO(mg/L)	Composite	0.2
BOD(mg/L)	Composite	19.5
COD(mg/L)	Composite	2112
TSS(mg/L)	Composite	54
TDS(mg/L)	Composite	1120
Alkalinity(mg/L)	Tap Water	212
	RO Water	88
	Wash water	252
	Composite	490
Turbidity (NTU)	Tap Water	26
	RO Water	0
	Wash water	42
	Composite	42
Pb (mg/L)	Composite	ND
Cu (mg/L)	Composite	0.2275
Cd (mg/L)	Composite	0.0034

*Composite-Wastewater of hospital with different time variation.

In wastewater discharge of this hospital parameters COD, TDS, Alkalinity & Turbidity are higher than permissible limits. Need of proper treatment of wastewater is required to reduce the level of mentioned parameters.

4.3 City Heart Hospital

City Heart Centre is multi-speciality hospital situated in Dehradun city of Uttarakhand state of India. City Heart Centre is serving to Dehradun since a decade and established itself as one of the best Health Care Centre in Uttarakhand and its surroundings. Although City Heart Centre provide complete body health care programs but more over that, City Heart Centre is known as the leader in Cardiac Care Services. City Heart Centre also offers a number of clinical trials and education programs, both for the public and for physicians. City Heart Centre offers a wide range of cardiovascular and pulmonary services, from prevention to surgery and rehabilitation.

Table 12 City Heart Hospital-Observation Table

City Heart		
pH(25°)	Composite	8.38
DO(mg/L)	Composite	0.4
BOD(mg/L)	Composite	7.5
COD(mg/L)	Composite	1408
TSS(mg/L)	Composite	36
TDS(mg/L)	Composite	944
Alkalinity(mg/L)	Composite	232
Turbidity(NTU)	Composite	70
Pb (mg/L)	Composite	ND
Cu (mg/L)	Composite	0.2793
Cd (mg/L)	Composite	0.0016

*Composite-Wastewater of hospital with different time variation.

In waste water of this hospital parameters COD, TDS & Alkalinity are higher than the permissible limits as per the standard and attention required to reduce the levels of these parameters before releasing waste water.

4.4 Ashirwad Hospital

Ashirwad Hospital was established in the year 1995 with the idea of creating a Cosmetic Surgical facility in an area out of town, far from its hub and pollution, yet within straight and easy reach of the people. This Centre gives very economical facilities at par with international standards.Expert in Nose jobs, Facial Plastic Surgery, Liposuctions, Breast Augmentations and Lifts, Body Contouring and Tummy Tucks, Scar removals, even Non Surgical Rejuvenation etc. Sex Reassignment, Infertility Surgery, Vitiligo & Leucoderma Surgery, Burn care, Maxillo-

Facial surgery and correction of Congenital Deformities are all done with a flair for perfection and surgical excellence.

Table 13 Ashirwad Hospital-Observation Table

Ashirwad Hospital		
pH(25°)	Composite	7.32
DO(mg/L)	Composite	0
BOD(mg/L)	Composite	18
COD(mg/L)	Composite	1056
TSS(mg/L)	Composite	46
TDS(mg/L)	Composite	942
Alkalinity(mg/L)	Composite	226
Turbidity(NTU)	Composite	31
Pb (mg/L)	Composite	ND
Cu (mg/L)	Composite	0.2793
Cd (mg/L)	Composite	0.0039

*Composite-Wastewater of hospital with different time variation.

The waste water discharge from this hospital has COD, TDS & Alkalinity levels higher than the permissible levels and proper wastewater treatment required before releasing the waste water.

4.5 Synergy Hospital

Synergy Institute of Medical Sciences, Dehradun, a unit of Padmanabh Healthcare Pvt. Ltd. is a 140 bedded multi super specialty Tertiary care hospital in Dehradun, focussing on medical and surgical super specialties of neuro sciences, cardiac sciences, gastro sciences, renal sciences, critical care, ortho-trauma, mother and child, ophthalmics, ENT and many more.

Table 14 Synergy Hospital- Observation Table

Synergy Hospital		
pH(25°)	Influent	7.93± 0.12
	Effluent	7.61± 0.12
DO(mg/L)	Influent	0
	Effluent	0.7
BOD(mg/L)	Influent	22.5
	Effluent	13.5
COD(mg/L)	Influent	3872
	Effluent	2816
TSS(mg/L)	Influent	64
	Effluent	48
TDS(mg/L)	Influent	1182
	Effluent	1016

Alkalinity(mg/L)	Influent	420
	Effluent	380
Turbidity(NTU)	Influent	245
	Effluent	204
Pb (mg/L)	Effluent	ND
Cu (mg/L)	Effluent	0.3321
Cd (mg/L)	Effluent	0.0037

The wastewater discharge from this hospital has COD, TDS, Alkalinity & Turbidity levels higher than permissible levels of waste water. Proper treatment required before discharge of waste water from the hospital.

4.6 Fortis Hospital

The Fortis Escorts Hospital Dehradun has set benchmarks in cardiac care with paediatric path breaking work over the past 3years. Today, it is recognised all over Uttarakhand as a Centre of Excellence providing the latest technology in cardiac by-pass surgery, interventional cardiology, non-invasive cardiology, paediatric cardiology and paediatric cardiac surgery.

The hospital is backed by the most advanced laboratories performing complete range of investigative tests in the field of radiology, biochemistry, pathology and microbiology. The hospital has a talented and experienced team of doctors, highly qualified, experienced and dedicated support staff.

Table 15 Fortis Hospital-Observation Table

Fortis Hospital		
pH(25°)	Composite	8.23
DO(mg/L)	Composite	0
BOD(mg/L)	Composite	15
COD(mg/L)	Composite	2816
TSS(mg/L)	Composite	44
TDS(mg/L)	Composite	928
Alkalinity(mg/L)	Composite	366
Turbidity(NTU)	Composite	70
Pb (mg/L)	Composite	ND
Cu (mg/L)	Composite	0.2851
Cd (mg/L)	Composite	0.0029

*Composite-Wastewater of hospital with different time variation.

The wastewater discharge from this hospital has parameters COD, TDS & Alkalinity levels higher than the permissible range. Attention required for treatment of wastewater before discharging it.

4.7 Max Hospital

200+ bedded facility offer services in medical disciplines of Neurosciences (MIND), Cardiac Sciences, Orthopedics, and other multi-specialties like Urology, Nephrology, Mental health and Behavioral Sciences, Aesthetics and Reconstructive surgery among several others.

The Neurosciences centre of excellence is equipped with Neuro Navigation, Stereotaxy, Microscopic Surgery (High-end microscope), advanced brain tumour centre, Endoscopic surgery, and special clinics for Epileptic, Neuromuscular and movement disorders. We offer specialized care with the best of technology like Gait Training, TENS, Muscle Stimulator, EMG Biofeedback; alongside pain management through Micro Currents and Diadynamic Currents, Laser pain relief for Migraine, Kineso Taping and Dry Needling.

Table 16 Max Hospital-Observation Table

Max Hospital STP			Max Hospital ETP		
pH(25°)	Influent	8.12	pH(25°)	Influent	8.26
	Effluent	8.37		Effluent	8.41
DO(mg/L)	Influent	6.8	DO(mg/L)	Influent	6.95
	Effluent	7.1		Effluent	7.2
BOD(mg/L)	Influent	106	BOD(mg/L)	Influent	13.3
	Effluent	25.2		Effluent	2.35
COD(mg/L)	Influent	248	COD(mg/L)	Influent	108
	Effluent	84		Effluent	52
TSS(mg/L)	Influent	68	TSS(mg/L)	Influent	88
	Effluent	26		Effluent	36
TDS(mg/L)	Influent	676	TDS(mg/L)	Influent	736
	Effluent	444		Effluent	542
Alkalinity(mg/L)	Influent	322	Alkalinity(mg/L)	Influent	282
	Effluent	244		Effluent	296
Turbidity(NTU)	Influent	5	Turbidity(NTU)	Influent	10
	Effluent	0		Effluent	0
Pb (mg/L)	Effluent	ND	Pb (mg/L)	Effluent	ND
Cu (mg/L)	Effluent	0.2576	Cu (mg/L)	Effluent	0.2611
Cd (mg/L)	Effluent	0.0016	Cd (mg/L)	Effluent	0.0021

All parameters except TDS, Alkalinity of STP & TDS and Alkalinity of ETP in discharge of wastewater are high than permissible limits. Actions needed to be taken to reduce these levels in wastewater.

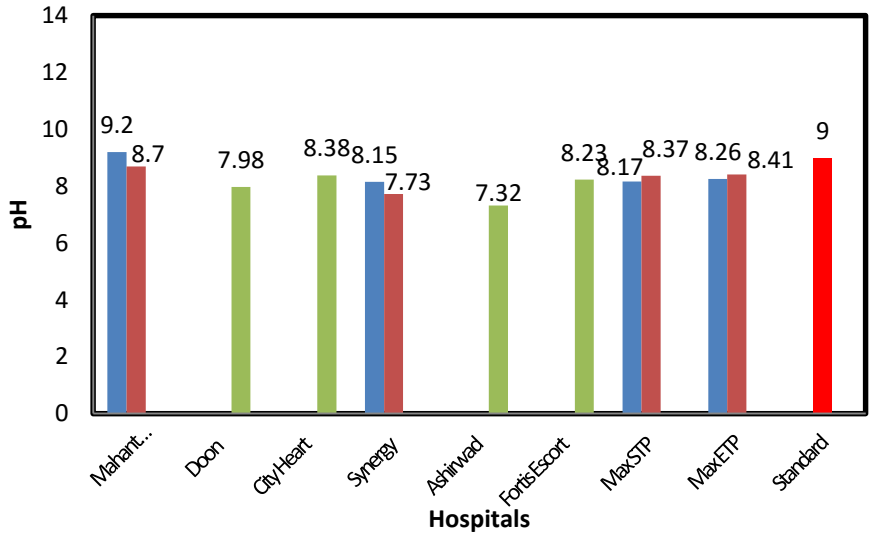

Figure 1 pH

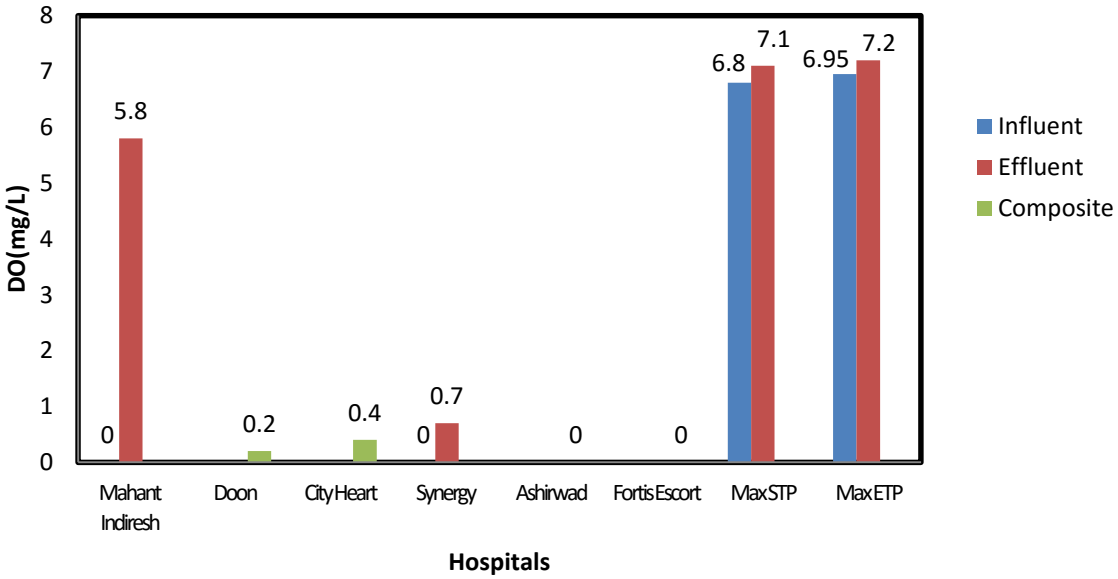

Figure 2 Dissolved Oxygen

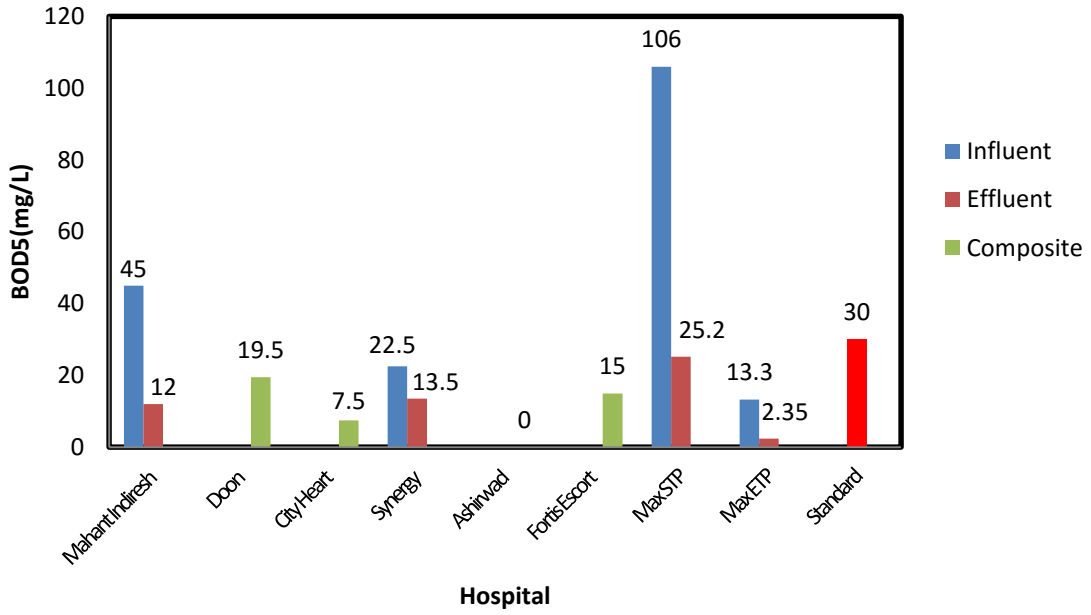

Figure 3 BOD_5

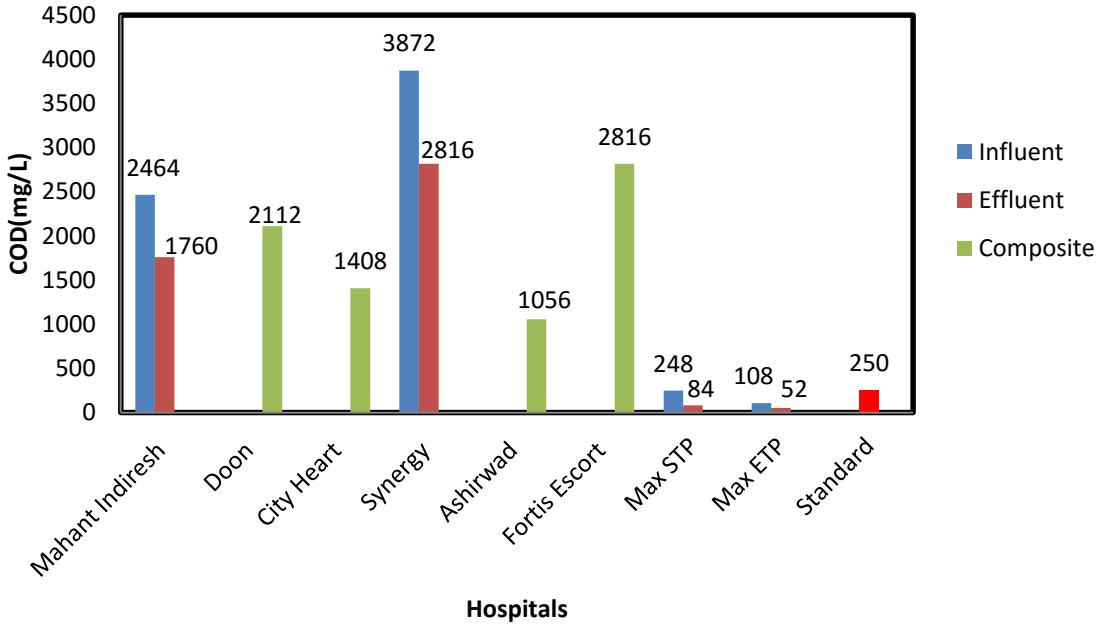

Figure 4 COD

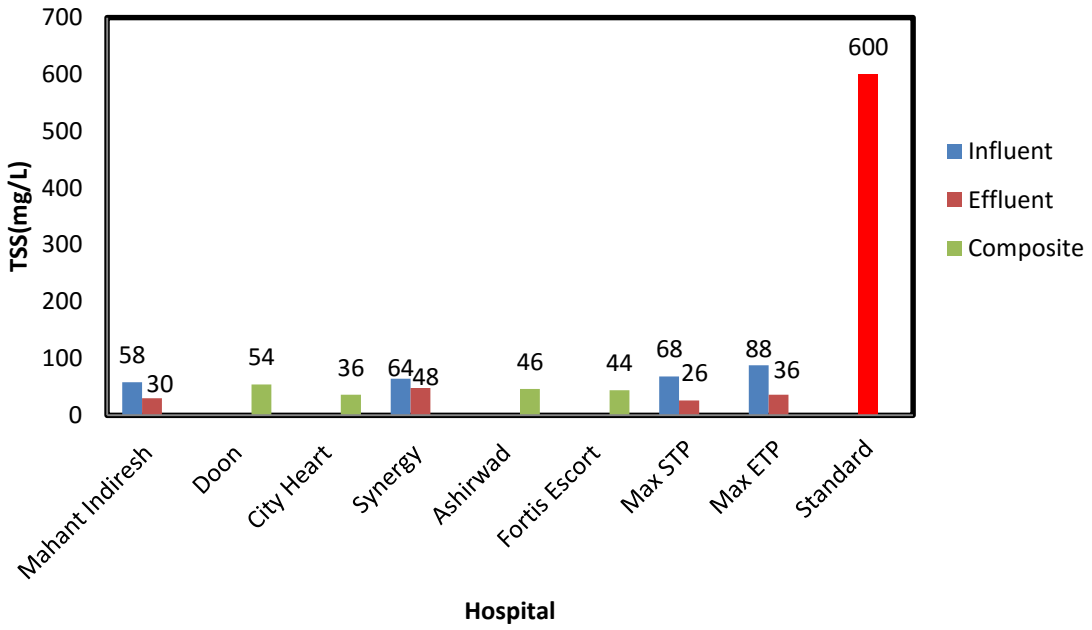

Figure 5 TSS

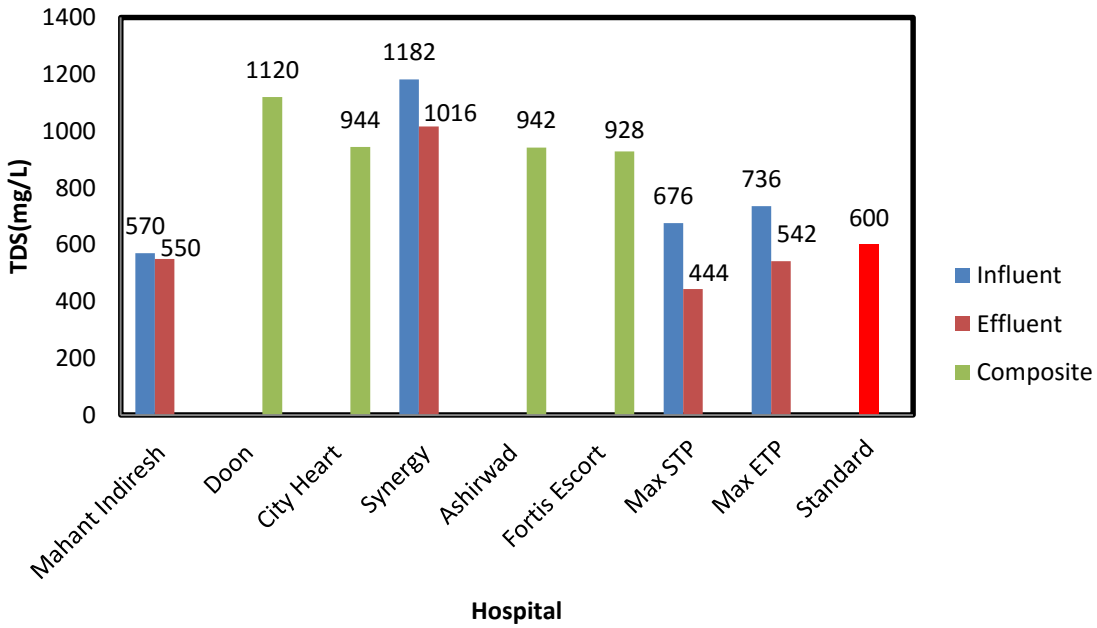

Figure 6 TDS

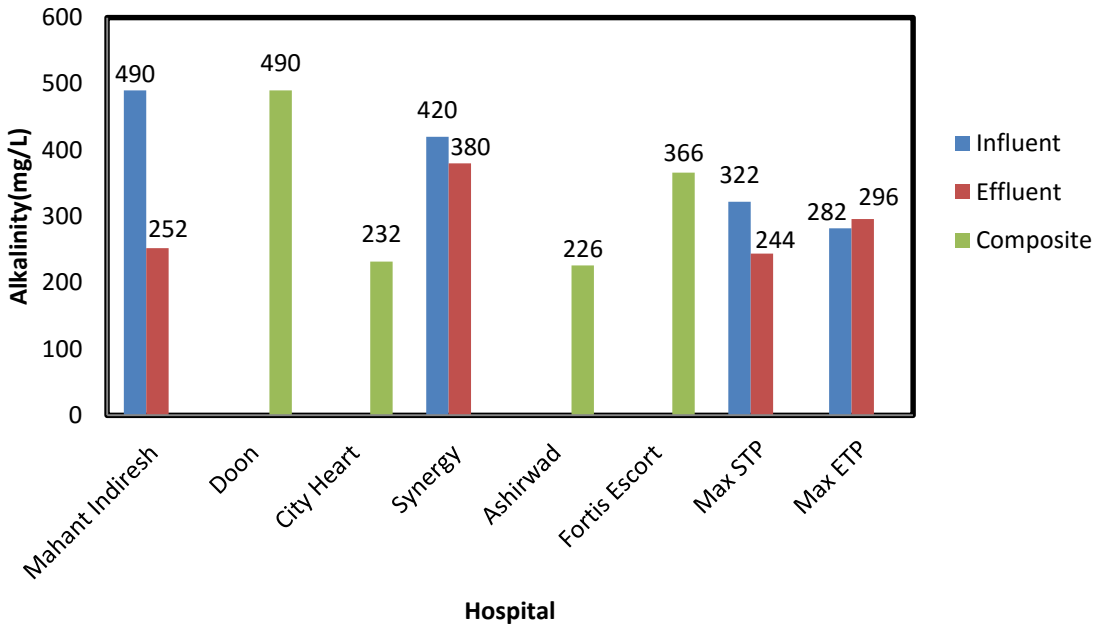

Figure 7 Alkalinity

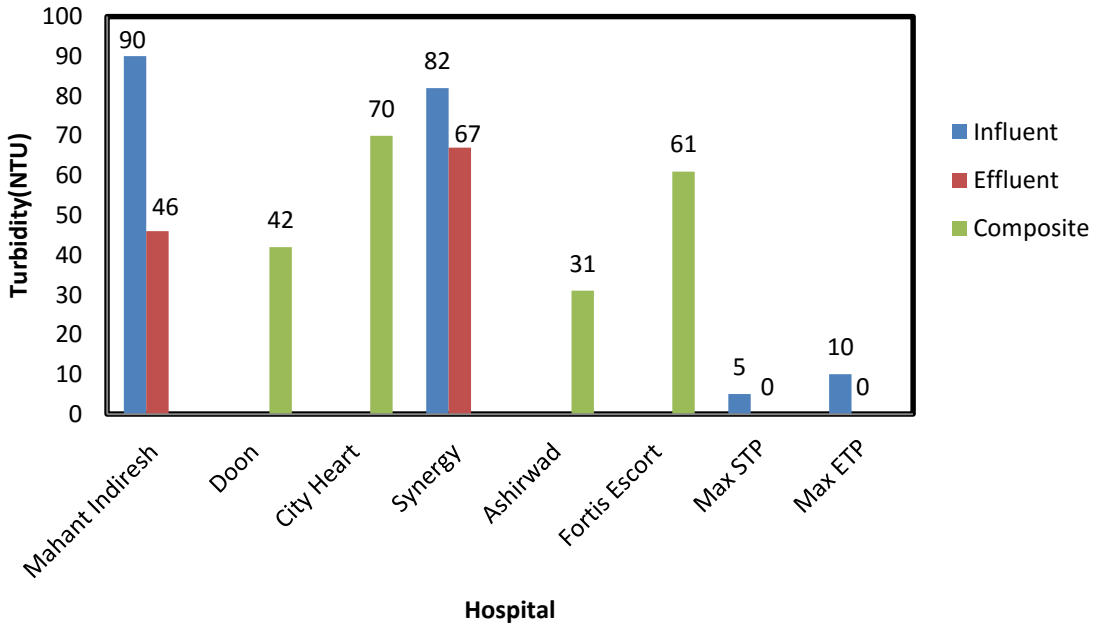

Figure 8 Turbidity

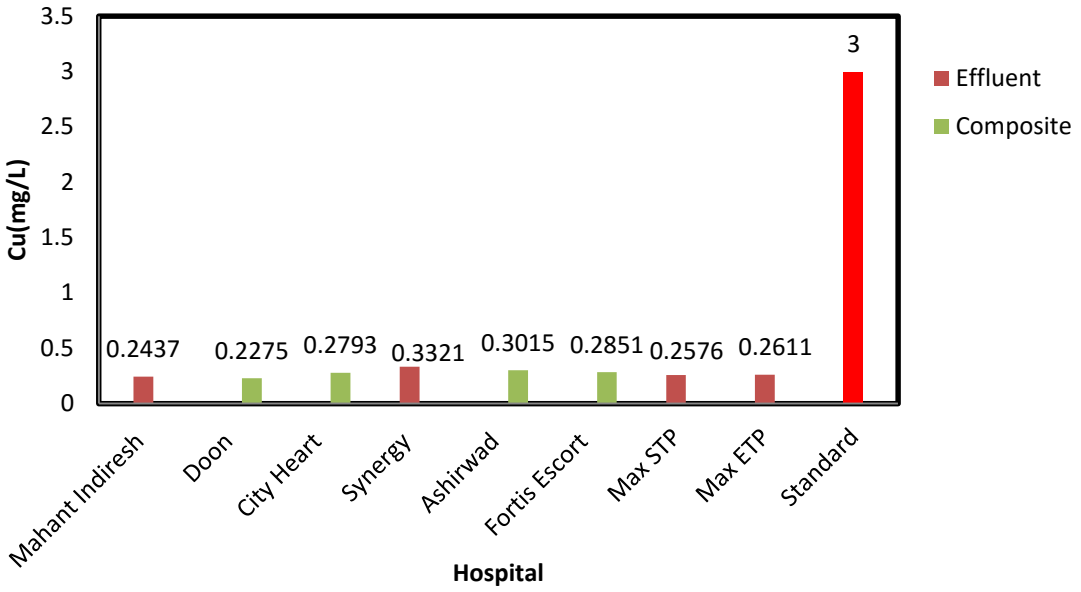

Figure 9 Heavy Metal- Cu

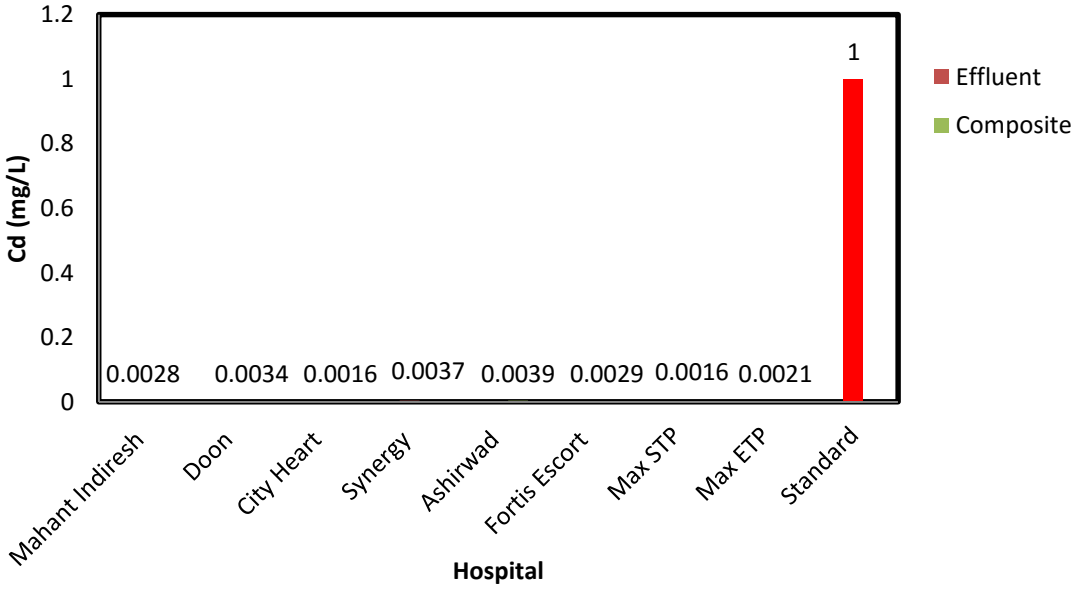

Figure 10 Heavy Metal- Cd

CHAPTER V

CONCLUSION

- Hospital and other biomedical sectors are very water intensive places and the nature of waste water generated becomes hazardous due to the presence of chemical materials such as antibiotics, anti-neo-plastics, hazardous materials their intermediaries, and derivatives which possess a great threat to the environment and consequently having harmful health effects on people nearby.
- The assessment of the risk of hospital wastewater is based upon dilution. In developed countries, most hospitals are connected to relatively large municipal wastewater collection systems and hospital wastewater represents only a small fraction of the volume of sewage. Therefore, the risk of hospital wastewater is at least because of the most dilution. Smaller systems may be more hazardous owing to smaller volumes of wastewater and hence, less dilution of contaminants. A major concern in the disposal of hospital wastewater is that hospitals have their own sewage treatment facilities. Furthermore, smaller systems are less efficient and may permit the discharge of infectious agents into groundwater and other environments which may be a hazard for both hospital personnel and the nearby community.
- As Dehradun is a valley with the presence of around 80 large, medium and small medical health facilities. Special care needs to be taken to regularly check the quality and treatment facility of waste water before discharging to any receiving body like river, public sewers.
- Presently Central Pollution Control Board has taken the initiative to check the quality of waste water generated from Hospitals on random basis in Dehradun.
- As the recommendation from the Uttarakhand Environment Protection and Pollution Control Board we have studied hospital waste water characteristics of -Mahant Indiresh Hospital, Doon Hospital, City Heart Hospital, Ashirwad Hospital, Synergy Hospital, Fortis Escort Hospital & Max Hospital.

- Wastewater samples were collected, transported, handled and analyzed as per the Standard Methods for the Examination of Water and Wastewater 22nd Edition
- For getting clear idea about the wastewater characteristics, the measured parameters were compared with the CPCB standards. The parameter analyzed were pH, Dissolved Oxygen, BOD, COD,TSS/TDS, Alkalinity, Turbidity, Heavy Metal Concentration(Pb, Cu,Cd).
- From the analysis it was found the measured average pH value of 8.14 is well within the permissible range of 5.5-9. Average value of BOD was around 25 which is under the permissible range but the value of COD exceeds way above the permissible limit. Also the presence of solids in water is above the permissible limit. The concentration of Pb, Cu & Cd is under their respective permissible limits.
- During the visit it was found that among the selected hospitals most don't treat their waste water were directly discharge into the public sewers, but there were few exceptions like Mahant Indiresh Hospital, Synergy Hospital & Max Hospital. While have their own treatment plants.
- Establishment of wastewater treatment plant or upgrading of existing wastewater treatment plant and improvement of operation and maintenance practices by employment of experienced operators is an urgent requirement for observance of effluent discharge standards in Dehradun.
- In future it is needed to investigate VOCs, chlorinated byproducts and pharmaceuticals in HWW since they are capable of adverse effect on human health.

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ANNEXURE

Questionnaire

Department of Health, Safety and Environment

University of Petroleum and Energy Studies

Name of Hospital:……..

Registration No.:……

1. Type and category of the hospital:

2. Number of beds:

3. Average Occupancy of beds:

4. No. of Employees per shift:

5. Accessibility to water/Source:

6. Water Consumption (based on water bill):

7. Types and quantity of wastewater generated from hospital:

8. Different Sectional Source contributing to Hospital waste water:

9. Segregation practice, storage & Disposal methods:

10. Occupational safety issues:

11. Status of awareness (BMW 2016) and training:

12. Strategy for regular updating of the hospital staff regarding the hazards associated with BMW handling and management, and practice of liquid waste management.

13. Cleaning in Specialized Facilities:

14. Waste Water Treatment Procedures (if available)

15. Observation: (if available)

Parameter	Effluent Discharged Standards For Sewage Treatment Plant	Value
pH	6.5-9	
BOD(mg/L)	Not more than 10	
COD(mg/L)	Not more than 50	
TSS (mg/L)	Not more than 20	
NH-4(mg/L)	Not more than 5	
N-Total (mg/L)	Not more than 10	
Fecal Coliform(MPN/100ml)	Less than 100	