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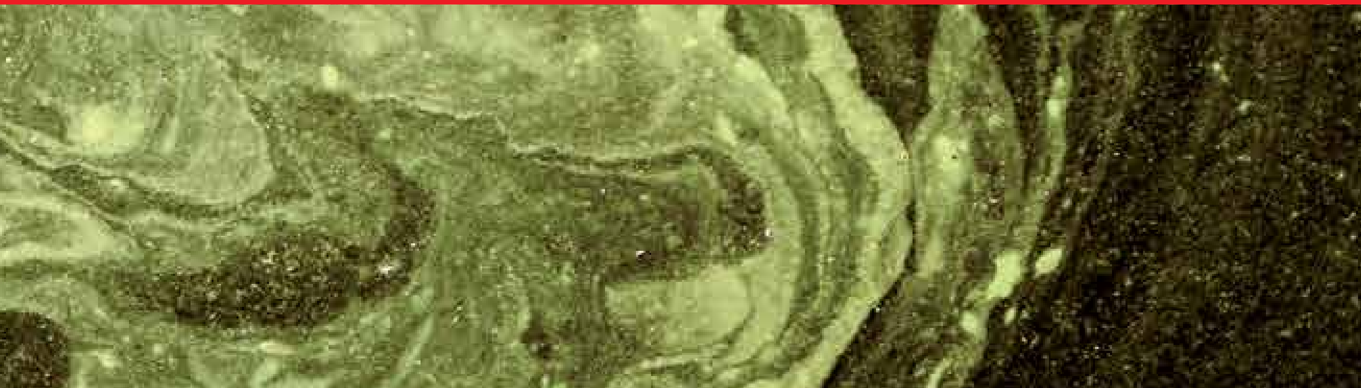
Sewage

Edited by Ivan X. Zhu



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Contributors

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Meet the editor

Dr. Ivan Zhu has highly specialized expertise in biological wastewater treatment, membrane applications to industrial and municipal water and wastewater treatment, flocs and biofilm characterization in terms of microbial community distribution and extracellular polymeric substances, and membrane fouling characterization. He has applied his extensive knowledge of separation processes to the evaluation and design of water and wastewater chemical/ biological treatment processes. Dr. Zhu worked at Xylem Water Solutions, where he gained extensive experience in drinking water treatment, wastewater tertiary treatment, denitrification, biological active filtration, ozone-enhanced biofiltration, and dissolved air flotation. Presently, he is working at Evoqua Water Technologies as an applications engineer for integrated industrial solutions for water and wastewater treatment. He holds a bachelor's degree from Shanghai Jiaotong University in Shanghai, China, and master's and doctoral degrees from the University of Toronto, Ontario, Canada.

Contents

Preface

Wastewater treatment is a process used to convert wastewater into an effluent (outflowing of water to a receiving body of water) that can be either returned to the water cycle with minimal impact on the environment or directly reused. Climate change, population growth, and water scarcity have contributed to a growing demand for sustainable management of water resources. The treatment of wastewater is part of sanitation. Sanitation also includes the management of human and solid waste, as well as storm-water (drainage) management. By-products from wastewater treatment plants, such as screenings, grit, and sewage sludge, may also be treated in a wastewater treatment plant. Municipalities and industries are now faced with the prospect of treating, conserving, or deep polishing water and wastewater before it is used for other purposes, or discharged to rivers, lakes, and other receiving water bodies. Conventional processes and technologies, such as screening, degritting, clarification and sedimentation, biological processes of suspended growth and fixed biofilm systems, media filtration, and chlorine disinfection, have been well developed and widely applied worldwide in wastewater treatment.

Rather than reviewing and discussing conventional treatment processes, this book provides a unique aspect of wastewater treatment and sludge disposal. Topics will include:

1. Natural ecological remediation and reuse of municipal wastewater in agriculture
2. Treatment of wastewater and electricity production by integrating constructed wetland coupled with microbial fuel cell (CW-MFC)
3. The application of various media materials in wastewater treatment
4. A review of trace metals in municipal sewage and sludge: a case study of Limpopo Province, South Africa
5. The fate of radiopharmaceuticals in the environment
6. Biodegradation of sludge through composting with bulking agent

While extensive research had been conducted on conventional wastewater treatment, this book is oriented to some interesting processes and selected applications, such as natural ecological remediation and the integration of treatment of wastewater and electricity production. It is anticipated that this book will shed light on the future direction of research and innovation.

Finally, during the course of editing and compiling this book, extensive support and guidance were received from Ms. Danijela Sakic, publishing process manager. The editor would like to express deep appreciation and gratefulness for her support.

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Chapter 1

Natural Ecological Remediation and Reuse of Sewage Water in Agriculture and Its Effects on Plant Health

Naeem Khan

Additional information is available at the end of the chapter

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Abstract

In rural and urban areas of most emergent countries, the application of sewerage and wastewater for irrigation is a regular practice. In these areas, polluted water is often the only supply of water for irrigation. The use of wastewater for crop growth is a centuries old practice that is getting renewed attention due to rising shortage of freshwater resources in many arid and semiarid regions of the globe. Wastewater is extensively used as an inexpensive substitute to conservative irrigation water, supporting livelihoods and generating significant value to the agriculture of urban and periurban areas in spite of the associated health and environmental risks. Water is becoming an increasingly limited resource in many dried and partially dried regions of the world due to which planners are being forced to think about other sources of water that might be used inexpensively and efficiently to encourage additional progress. It is concluded that sewage water is the richest source of micro- and macronutrients and this aims for the better growth of plants. However, sewage should be treated prior to its reuse for agriculture in order to reduce the risks of harmful effects on human and animal health.

Keywords: sewage water, developing countries, nutrients, chemical fertilizer

1. Introduction

In rural and urban areas of most emergent countries, the application of sewerage and wastewater for irrigation is a regular practice. In these areas, polluted water is often the only supply of water for irrigation. Yet small farmers often prefer wastewater where other water sources are also available because wastewater has high nutrient content which may reduce or even eliminate the need for other costly chemical fertilizers [1]. The use of wastewater for crop growth is a centuries old practice in many arid and semi-arid regions of the globe [2]. Farmers often have no alternative, so they depend on unprocessed wastewater as there is no wastewater collection and treatment and freshwater is either out of stock or too expensive [3, 4]. The uses of wastewater in agriculture create key risks to the health of the community due to chemical and microbial contaminants. Wastewater use can also produce ecological risks in terms of soil and groundwater contamination. Irrigation with wastewater can have a number of benefits and environmental applications if appropriately planned, implemented, and managed [5].

Many wastewater irrigators are generally landless people who are not land-owning farmers; they lease small plots to grow income-generating crops like vegetables that flourish when watered with nutrient-rich sewage [6]. Across Africa, Asia, and Latin America, the micro-economies of sewage water support a large number of low-income individuals. Stoppage or overregulation of these practices could take away the only income source of numerous landless people. However, in these countries, the sewage water is not processed before use for irrigation. Wastewater treatment is generally carried out in developed countries, where major investment on wastewater treatment has been made over the past 40–50 years in order to achieve high treatment levels. Most sewage water is treated in North America, usually up to secondary and, in numerous cases, up to tertiary levels [7]. The USA has made improvement as a result of a financial support program in which 56 billion USD were allocated to local governments from 1972 to 1989 to construct secondary management amenities, but they changed these grants by state revolving funds for loans to municipalities [8].

Sewage treatment (**Figure 1**) is regarded as vital in affluent countries in order to guard human health and avoid pollution of rivers and lakes, but for the majority of developing countries, this solution is too costly. Therefore, in case of developing countries, application of wastewater in agriculture is a more reasonable option and economically sound than uninhibited removal of industrial and municipal effluents addicted to lakes and streams [4]. The sewage flows to a downstream location that is hazardous due to which the population inside the streams and water sources are at risk. Such risks can be decreased or proscribed by wastewater treatment in a wastewater treatment plant consisting of physical, chemical, and biological processes [9]. Wastewater treatment may also produce sludge, which is also risky for health because it is a polluted by-product and requires secure managing and removal [10].

Use of sewage water for irrigation has many applications (**Figure 2**), including crop irrigation, aquaculture, irrigation of landscape, and fake groundwater recharge [11]. This is one of the longest and well-known traditions in most parts of the world. According to estimation, the total area under wastewater irrigation is about 20 million hectares throughout the world [12]. It has been found that the maximum number of crop plants viz. lettuce, mangoes, tomatoes, and coconut are irrigated with sewage water, and a large quantity of this water is unprocessed [12]. Sewage and industrial wastewater is commonly used to water farming fields in developing countries including Pakistan [13, 14]. Sewage irrigation has proven beneficial effects on plant health and soil quality in countries having low water resources

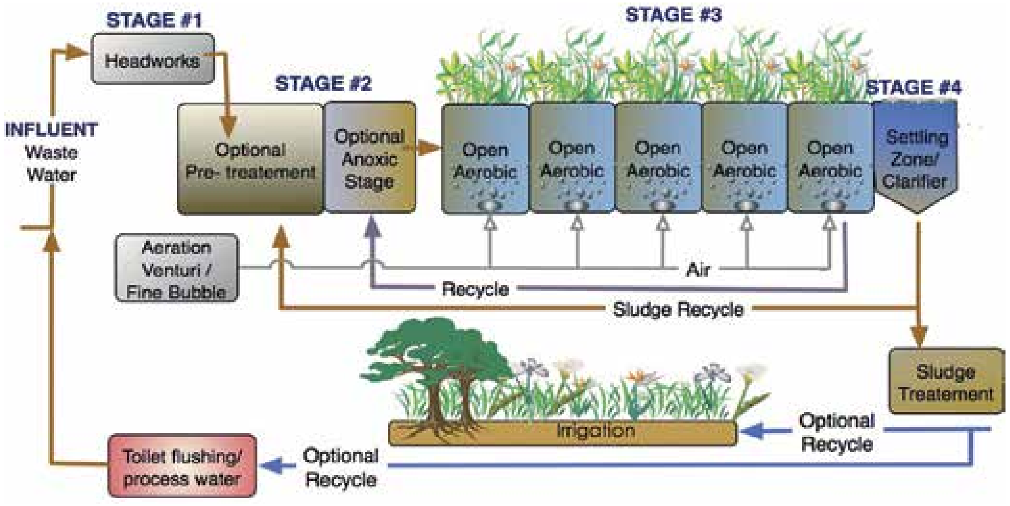

Figure1. Ecologicalsewagetreatment(http://ingienous.com/sectors/the-environment/eliminating-waste-and-inefficiency/sewage-treatment-via-bionutrient-recycling/).

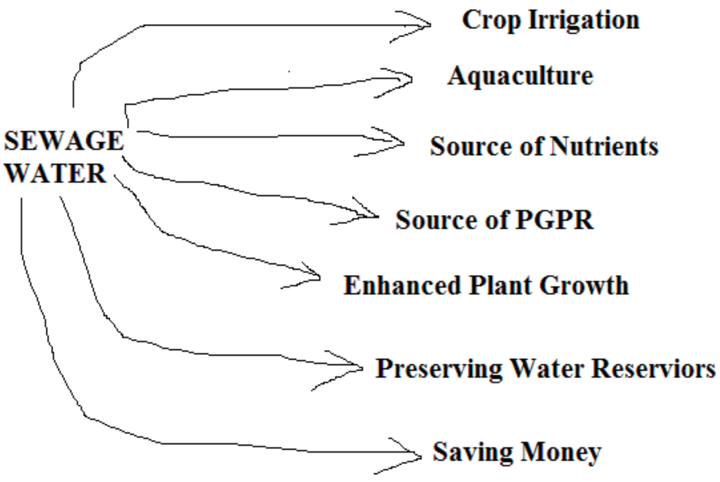

Figure 2. Impacts of sewage water irrigation on plants and freshwater reservoirs.

such as Mediterranean Basin and the Middle East, for instance, Bahrain, Cyprus, Kuwait, Malta, Israel, Qatar, Oman, Saudi Arabia, and the United Arab Emirates [15]. Numerous investigations have reported positive impacts of sewage irrigation on plants and soil properties. Wastewater can be used as an important plant nutrient source for soils with low fertility. Municipal wastewater could possibly be used for crop irrigation with negligible environmental concerns if it does not contain excessive heavy metals. Use of wastewater for irrigation purposes can decrease the necessity for fertilizers [16]. For these reasons, both treated and untreated wastewaters have been used for irrigation worldwide. Earlier studies, carried out in areas irrigated with wastewater over a long period of time, have confirmed improved soil biological activity and nutrient cycling as a result of the resulting input of easily degradable organic material and nutrients [4].

The application of wastewater to cropland and forests is a smart option for disposal because it can improve the physical properties and nutrient content in soils. Wastewater can often contain substantial concentrations of organic and inorganic nutrients, for example, nitrogen and phosphate, which are crucial for crop growth. One possible advantage is that the soil microorganisms have been observed to have increased metabolic activity when a sewage effluent is reused in irrigation [17]. Castro et al. [18] reported that dry and fresh weight, average height, and diameter were significantly higher in treated wastewater-irrigated plants. The highest values were observed in the second crop season. El-Nahhal et al. [18] investigated the effects of sewage water on the growth of Chinese cabbage and found that the sewage water was effective in supplying the necessary nutrients required for the normal growth of plants and noted higher biomass in plants irrigated with wastewater as compared to fresh water. Castro et al. [19] reported significant increase in fresh and dry weights, average height, and diameter of *Lactuca sativa* irrigated with sewage water when compared to control. Alghobar et al. [20] reported improved chemical properties and fertility status of soils irrigated with sewage water. They also found enhanced growth in grass crop after irrigation with sewage water.

Safary and Hajrasoliha [21] carried out experiments on plants irrigated with sewage water and noted that after 7 years of irrigation with sewage significantly enhanced carbon, nitrogen, and phosphorus contents and decreased soil salinity and sodicity. Rattan et al. [22] reported the beneficial effects of sewage effluents when applied to cereals, vegetables, and fodder crops. Singh et al. [23] used sewage water for irrigation of several crop plants including wheat, gram, palak, methi, and berseem. They recorded improvement in physiochemical properties of soil, nutrient stats of soil, and yield of crops as compared to plants irrigated with normal groundwater. Wang et al. [24] also noted that long-term irrigation with sewage water significantly enhanced soil micro- and macronutrient content that in turn enhanced plant growth. Recently, Khan and Bano [25] reported the beneficial effects of sewage irrigation on the total chlorophyll and carotenoids content of maize plant. They also recorded increased nutrient content in plants and soil.

To fully understand the vital issue of wastewater reuse with regard to benefits and mitigate the risks, this chapter was aimed at determining the effects of sewage on the growth parameters of plants and to review the natural ecological and engineered approaches for the treatment of sewage water before its application to irrigation. Regulations of wastewater reuse in different countries are also reviewed and discussed.

2. Natural ecological and engineered sewage treatment

Sewage treatment (**Figures 3** and **4**) is the process of eradicating microorganism, heavy metal, and other types of contaminants from wastewater. The practice of wastewater treatment varies

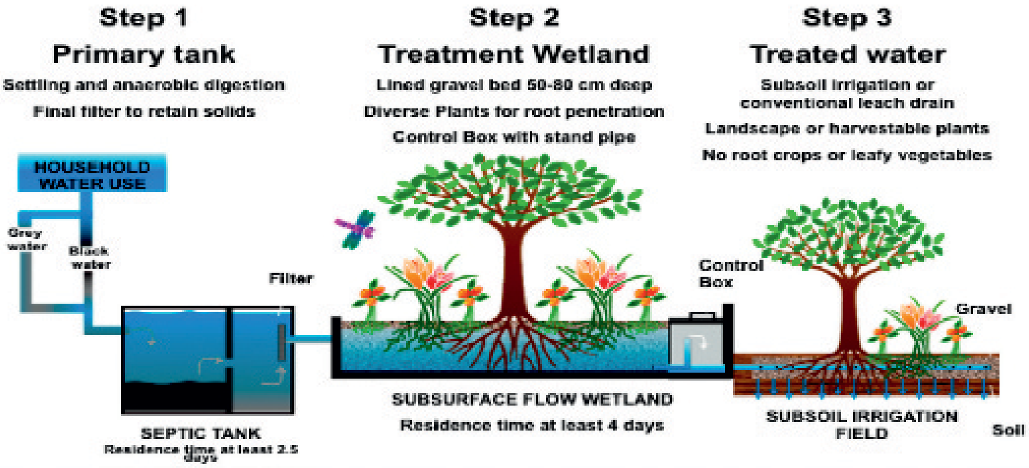

Figure 3. Biological treatment of wastewater for reuse in agriculture. (http://saleemindia.blogspot.com/2017/01/constructed-wetlands-for-sewage.html).

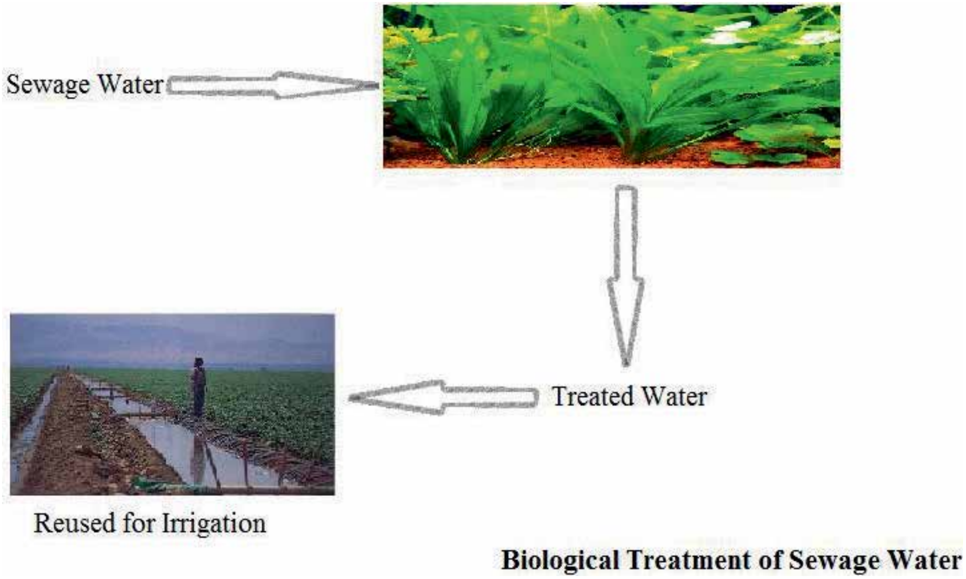

Figure 4. Reuse of sewage water for irrigation after treatment.

from one region to another across the world. In developed countries, a centralized aerobic wastewater treatment, consisting of plants, has been carried out for both industrial and domestic wastewater. Sewage treatment using natural ecological approach has been carried out throughout the world because certain terrestrial and aquatic plants have the ability to accrue large quantities of certain metals in their shoots [26]. The use of wetland and aquatic plants, such as water velvet and duckweed for the removal of contaminants from the sewage water, is considered the most effective method for the removal of heavy metals.

Zayed et al. [27] tested the potential of duckweed for the removal of Cd, Cr, Cu, Ni, Pb, and Se and found that duckweed was a good accumulator of Cd, Se, and Cu. Zhu et al. [28] reported the dominant role of water hyacinth in the sewage treatment as this plant possesses a very good fibrous root system and a large biomass. They found that the water hyacinth was excellent in accumulation of organic and inorganic nutrients and trace elements including Cd, Pb, and Ag. Dos Santos and Lenzi [29] carried out experiments with aquatic *Eiochhornia crassipes* and found it useful for the removal of Pb from contaminated water. Wang et al. [30] investigated the role of five different wetland species including duckweed, sharp dock, water hyacinth, calamus, and water dropwort for their possible use in treating the polluted waters. They reported that water hyacinth and duckweed were good accumulators of Cd, water dropwort accumulated Hg, calamus was the best for the accumulation of Pb, while sharp dock was a good accumulator of N and P. Li et al. [31] conducted hydroponic experiment in order to investigate the role of three hydrophytes, that is, *Gladiolus*, *Isoetes taiwanensis and Echinodorus amazonicus* for the accumulation of Cd from contaminated water. They found that the *Gladiolus* was the best Cd accumulator as compared to other two plants. Lone et al. [32] examined the efficacy of Cu elimination from the contaminated water by *Elsholtzia argyi* and *Elsholtzia splendens* in hydroponics. The results show that *Elsholtzia argyi* showed better Cu phytofiltration than *Elsholtzia splendens*, which was associated with better ability to absorb higher Cu concentrations and translocation to shoots. Tangahu et al. [33] investigated the role of different wetland plant species for the treatment of sewage water. They found that most of the wetland species were capable for accumulation of N, P, Cd, Pb, and Hg.

Among the ferns, *Pteris vitta* has been identified as hyperaccumulator of As-contaminated soils and waters. It can accumulate up to 7500 mg of As/kg on a contaminated site without showing toxicity symptoms [34]. Trees have been recommended as a low-cost and ecologically sound solution for the remediation of heavy metals from sewage water. This ability of the trees is due to their large biomass, which can absorb large quantities of contaminants present in wastewater [35]. Plants remove contaminants from sewage water by one of the following methods:

Phytoextraction: Plants remove heavy metals and other pollutants from the water and soil as well as groundwater and concentrate them into their harvestable parts [36]. These plants accumulate contaminants from the water in above-ground shoot.

Phytodegradation: In phytodegradation process, the pollutants present in contaminated water are degraded by plants and associated microbes [37]. Plant roots in conjunction with their rhizospheric microorganisms are utilized to remediate soils irrigated with sewage water.

Phytostabilization: In this case, the availability and mobility of pollutants present in sewage are reduced by plants, thus reducing the risk of leaching of pollutants into groundwater [38].

Phytovolatilization: Plants volatilize pollutants present in sewage water. Plants extract volatile pollutants added in the soil due to irrigation with sewage water and volatilize them from the foliage [39].

Rhizofiltration: It is the removal of pollutants from the contaminated waters by accumulation into plant biomass. Several aquatic species including sharp dock, duckweed, and so on, have been identified and tested for the phytoremediation of heavy metals from the polluted water [40].

Besides these natural ecological treatments, other engineered approaches are also widely carried out worldwide for wastewater treatment to remove pathogen and other harmful substances. These include".

Oxidation Ponds: Oxidation ponds are used for reducing the biochemical oxygen demand (BOD) of wastewater. This is a very effective and simple technology, which consists of a ring-shaped channel equipped with mechanical aeration devices. The wastewater is screened and aerated through these devices which circulates at 0.25–0.35 ms^{-1} [41].

Anaerobic Ponds: It is a biological treatment of wastewater in which naturally occurring bacteria are utilized for breaking the biodegradable compounds present in wastewater. These bacteria under anaerobic condition may remove high concentrations of BOD and chemical oxygen demand (COD). The presence of anaerobic bacteria in these ponds break the organic matter present in the effluents and thus release methane and CO_2 whereby sludge is deposited at the bottom, while crust is formed on the surface [42].

Aerobic Ponds: In aerobic treatment of wastewater, bacteria and algae are used that maintain aerobic condition throughout its depth. The aerobic ponds may be shallow or aerated [43].

Trickling Filter: This technique is used to remove or reduce pathogen and level of nitrogen in the wastewater as pathogens present in wastewater may cause serious threats to humans mostly in developing countries of the world. This trickling filter is composed of some porous material like rocks, sledge, or plastic medium having large surface area and permeability. The microorganism in the wastewater gets attached with the filter media [44].

Activated Sludge System: This is a biological wastewater treatment, which is mainly used for the removal of biodegradable compounds and pathogens present in wastewater. Its efficiency depends on retention time, temperature, pH, and the presence of other biological flora present in wastewater [43, 45].

3. Regulations in the use of sewage water

The World Health Organization (WHO), the US Environmental Protection Agency (USEPA), and the World Bank have reviewed the public health aspects concerning the use of sewage water for crop irrigation and prepared recommendations for the microbiological quality of treated wastewater used for this purpose. The limit of microorganism in sewage water used for irrigation of crop plants should not be more than 1000 fecal/100 ml of bacteria [46]. Similarly, the amount of other harmful substances in sewage water should be under minimal range. Rules and regulations in the use of sewage water vary from state to state and from country to country. In Pakistan, there is no national policy for the reuse of sewage water for crop irrigation. Furthermore, the industries do not follow the government guidelines, and there are also no government economic incentives for these industries. In Pakistan, the sewage water is used straightaway for agricultural purpose without any purification treatment. Only Islamabad and Karachi treat a minor portion (10%) of sewage water before disposal. All the effluents are discharged in Kabul River from various industries in Khyber Pakhtunkhwa (KPK) province [47]. In Lahore, a major city of Punjab province, only three industries have wastewater treatment plants. In some regions of the country, laws and regulations have been developed for the treatment of wastewater prior to use in irrigation, but their enforcement in reality is an issue due to the absence of resources and experience.

Problems in the disposition of wastewater tend to stem from distortions due to economy-wide policies, miscarriage of directed environmental policies, and failure of institution. Inefficient water pricing worsens the problem in urban areas, where water is provided free of charge, a policy that encourages the use of wastewater for irrigation. Similarly, environmental committees have been established, but their ability to deal with specified cases is very limited due to deficiency of staff [48].

In the USA, standards are set for the reuse of wastewater in agriculture. These standards vary from state to state. In California, strictest standards have been developed for **the reuse of wastewater** [49]. California, with the lengthiest history about the regulating of reclaimed wastewater in agriculture, which only permits high-quality effluents to be used on crops. Similarly, Arizona, Florida, Hawaii, and Texas have also active water reuse programs. These states developed comprehensive, numerical water quality criteria for different water uses, including crop irrigation. Florida usually has the limits of the reuse of reclaimed water for irrigation of crop plants that are skinned and cooked before consumption [50]. **Billions of dollars are being spent on recycling of wastewater and reused in large quantities in different countries of the world (Figures 5** and **6).**

There have been no reports of contagious disease linked with agricultural reuse projects, and current criteria are considered to be acceptable in most states of the USA. Most states differentiate between produce from crops that are commercially treated or cooked before consumption, and need more strict water quality levels for produce crops. Yet, states differ in the manner in which wastewater irrigation can be implemented.

Microbiological standards for the harmless reuse of wastewater for irrigation in Latin America are varied as, for example, Brazil has no legislation. Argentina has a general reuse water law, which aimed to prevent surface water contamination which did not mention wastewater specifically [51]. Chile, introduced guidelines for the discharge of domestic and industrial effluents into rivers, lakes, and the sea; however, use of wastewater for irrigation has not been included in the legislation. Peru established roles for the reuse of wastewater after primary and secondary treatments; however, it has not established any bacterial nor nematode treatment. The Saudi Standards for effluents are strict and inadvertently enforce needless limitations on disposal and reuse of wastewater, which prevent its application for irrigation [52]. Some countries of the world have developed standards for wastewater reuse that only permit the controlled reuse of wastewater for irrigation of crop plants. Many of these are based on the WHO guidelines, including Mexico, France, Spain and Andalusia Province. Microbiological standards for wastewater reuse in agriculture have been established in Mexico over the last

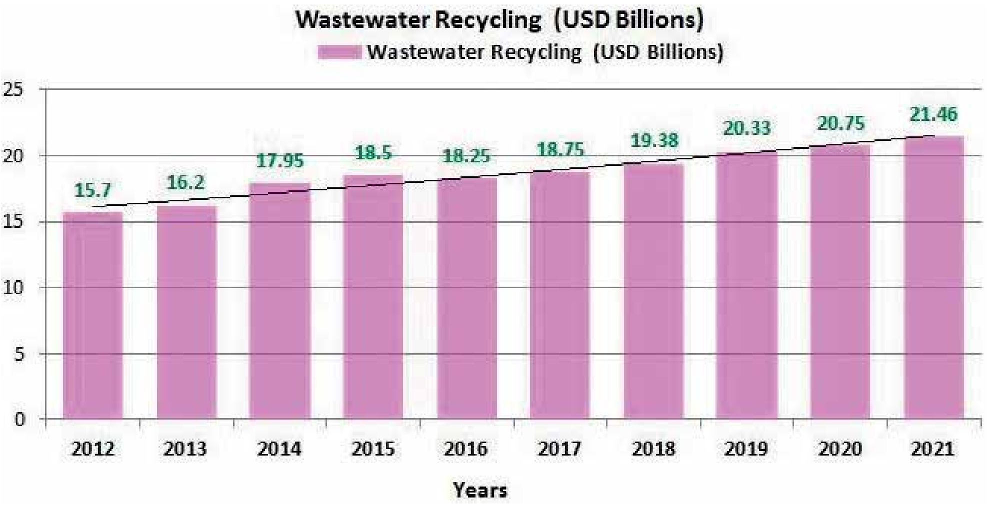

Figure 5. Expenditures on recycling and reuse technologies used for wastewater treatments (https://recycling.conferenceseries.com/).

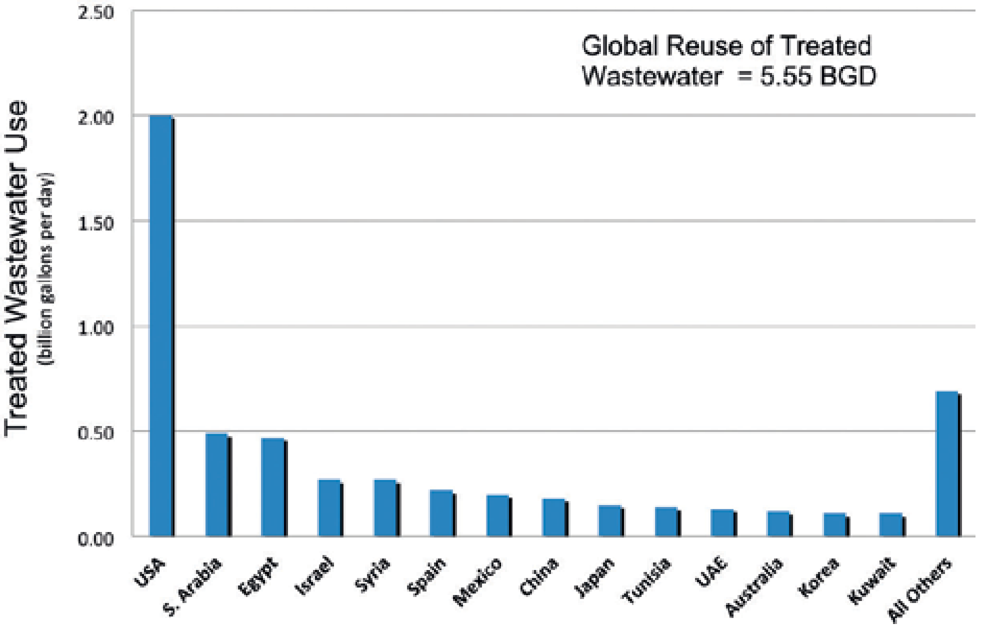

Figure 6. Reuse of wastewater per day in different countries of the world (http://nas-sites.org/waterreuse).

20 years. In France, the Ministry of Health delivered a provisional regulation on the reuse of wastewater for irrigation. The WHO guidelines for the reuse of wastewater for agriculture and aquacultural purposes had been published in 1989, which suggest different guidelines for different water qualities dependent on the endpoint of discharge [53].

3.1. Challenging issues

The most challenging issue with the use of sewage water for irrigation is the infection of farmers and consumers exposed to wastewater. Besides this, the presence of organic and inorganic elements may also have human health risks. Farmers and their relatives using sewage water are exposed to health risks from parasitic worms, protozoa, viruses, and bacteria. Some farmers cannot treat some of the health problems caused by pathogenic microorganisms due to weak economic conditions. Generally, farmers irrigating with wastewater have higher rates of helminth infections and, in addition, skin and nail problems may happen to farmers using wastewater [54]. Women are most vulnerable to these infections and mostly important target group. In several countries of the world, women offer much of the labor essential to produce vegetables and perform most of the weeding and transplanting that can expose them to long periods of contact with wastewater. Women usually cook meals, making chance for transferring pathogens to the family members if good hygiene is not sustained. In West Africa, where vegetables are produced in most of the countries, women dominate the marketing process, particularly retail, of most vegetables; thus, the main target group for risk reduction measures in markets [55]. Post-harvest infection in markets can be a vital issue disturbing public health, but the implication differs, which makes it an often ignored issue in the wastewater discussion [56].

Wastewater risks may be short or long term, depending on the resistance of humans and animals, while, in some cases, the impacts lies for a long period of time, especially in persons that continuously use wastewater. Beside human risks, continuous use of wastewater for irrigation results in soil salinity and sodicity. On the other hand, the presence of trace elements such as heavy metals, which are harmful for human health, can be found in sewage water effluents. The presence of microbial pollution becomes more severe with vegetables as many of them are consumed raw [57].

4. Water quality improvements

Preliminary improvements in water quality can be attained in several developing countries by at least primary treatment of sewage water, mainly where sewage water is used for irrigation. Secondary treatment can be applied at reasonable cost in some areas, using methods such as infiltration-percolation, constructed wetlands, waste-stabilization ponds and up-flow anaerobic sludge blanket reactors [58]. It is vital to aim at standards, which can be attained in the local context. WHO guidelines provide complementary alternatives for wastewater treatment and control of human exposure. Storage of reclaimed water in reservoirs develops microbiological quality and provides peak-equalization capacity, which surges the consistency of supply and increases the rate of reuse [59, 60].

5. Conclusion

Use of sewage water for irrigation not only improves the growth rate of plants but also reduces the cost of chemical fertilizers. The application of wastewater to cropland and forests is a smart option for disposal because it can improve the physical properties and nutrient content in soils. However, the practice of sewage water pre-treatment is uncommon in most developing countries of the world due to which several health issues may occur. Sewage water should be treated prior to its reuse for agriculture in order to reduce the risks of harmful effects on human and animal health. One of the viable solutions for developing countries seems to be the use of natural ecological approaches.

Conflict of interest

The author declares no conflict of interest.

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Chapter 2

Treatment of Sewage (Domestic Wastewater or Municipal Wastewater) and Electricity Production by Integrating Constructed Wetland with Microbial Fuel Cell

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Additional information is available at the end of the chapter

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Abstract

Proper treatment of wastewater is important to human health and societal development, and the commonly applied wastewater treatment technologies based on aerobic treatment have a significant demand for energy. Thus, new treatment technologies with low energy consumption and possible recovery of valuable resources (e.g., energy and water) from wastewater become of strong interest. Among the newly developed concepts, microbial fuel cells (MFCs) integrated with constructed wetland appear to be very attractive because of direct electricity generation from organic compounds and treatment of wastewater. Constructed wetland coupled with microbial fuel cell (CW-MFC) is an emerging technology in recent years and has attracted a lot of attention from researchers in the fields of wastewater treatment and bioenergy production. CW-MFC is a promising technology in the fields of wastewater treatment and bioenergy. However, at current power levels, the advantage of combining the two is mainly because of the enhancement of wastewater treatment in anaerobic zones within the wetland. New operational strategies need to be explored to increase and utilize electricity output.

Keywords: microbial fuel cell, constructed wetland, electricity production, wastewater treatment, bioenergy

1. Introduction

1.1. Water

Water is derived from the Anglo-Saxon and Low German word, *wæter* which is an odorless, flavorless, and colorless substance that is necessary to all living beings that we all are aware of. It is the main constituent of earth's streams, lakes, oceans, and the fluids of most living organisms [1]. Its chemical formula is H_2O, which means that each of its molecules contains one atom oxygen and two atoms hydrogen that are connected by a bond known as "covalent bond". Water is found in three different forms on earth, that is, solid, liquid, and gas [2]. These forms of water depend on the temperature. Water on our planet is present as a **solid form** in the ice-caped areas at the North and South Poles, **liquid** in rivers, streams, and oceans and is **gas** or vapor form in the atmosphere [3].

But the present scenario says that all the water resources that are present in the globe are under a major stress. Today, however, expansion of industries, agriculture, damming, urbanization, population, and pollution threaten these unique resources in many parts of the earth [4].

But the main concern now is providing safe drinking water to the more than 1 billion people who currently lack it; this is one of the utmost public health challenges facing governments today. In many developing countries, safe water, free of pathogens and other contaminants, is unavailable to much of the population, and water contamination remains a concern even for developed countries too with good water supplies and advanced treatment systems [5].

1.2. Distribution of water

The first living organisms undoubtedly arose in an aqueous environment and during the course of evolution it has been shaped by the properties of the aqueous medium in which life began [6]. Therefore, life on the earth that is originated from sea and water plays a pioneer role for evolutionary development of species, life forms, and relatively complex molecules [7]. It is an abundant essential resource on earth and covers 71% of the earth's surface. This earth's water consists of 3% freshwater of total water supply and is found as either surface water or groundwater, however, 97% as saltwater [8]. Therefore [9] has concluded that the human interference, inadequate supply, and inappropriate management are the major causes [10] leading to scarcity of resources that impedes sustainable development [11].

1.3. Wastewater

Wastewater or sewage is the byproduct of water. There are the household uses such as bathing, dishwashing, laundry, and, of course, flushing the toilet. Additionally, industries use water for many purposes including processing and cleaning or rinsing of parts. With rapid growth of cities, urbanization, and industrialization the quantity of gray/wastewater is increasing in the same proportion. As per Central Public Health and Environmental Engineering Organization (CPHEEO) estimates about 70–80% of total water supplied for domestic use gets generated as wastewater. Typically, 200–500 L of wastewater are generated for every person. In India, there are 234 Sewage Water Treatment plants (STPs). Most of these were developed under various river action plans (from 1978 to 1979 onward) and are located in (just 5% of) cities/towns along the banks of major rivers [12].

1.4. Energy cost of wastewater treatment

Energy use can account for as much as 10% of a local government's annual operating budget [13]. A considerable amount of this municipal energy use occurs at water and wastewater treatment services. With pumps, motors, and other equipment operating 24 h a day, 7 days a week, water and wastewater services can be among the largest consumers of energy in a community and thus among the largest contributors to the community's total GHG emissions. Nationally, the energy used by water and wastewater utilities accounts for 35% of typical U.S. municipal energy budgets [14]. Electricity use accounts for 25–40% of the operating budgets for wastewater utilities and approximately 80% of drinking water processing and distribution costs [14]. Drinking water and wastewater systems account for approximately 3–4% of energy use in the United States, resulting in the emissions of more than 45 million tons of GHGs annually [15].

2. Introduction of bioelectrochemical systems

2.1. Biochemical system

There is a growing demand for new energy sources due to the limited accessibility and pollution caused by the use of fossil fuels. At present, the annual energy demand is approximately 13 terawatts (TW) worldwide and it is estimated to reach around 23 TW by the year 2050 [16]. Bioelectrochemical systems (BESs) have considerably boomed over the past decade for their contribution as an emerging sustainable technology for concurrent electricity production and wastewater treatment [17]. Microbial fuel cells (MFCs) and microbial electrolysis cells (MECs) are two examples of a speedily developing biotechnology, generally known as bioelectrochemical systems (BES), that combine biological and electrochemical processes to generate electricity, hydrogen, or other useful chemicals. Moreover, BESs are also identified as efficient bioreactors for the treatment of recalcitrant pollutants and toxic wastewaters; the process is termed as bioelectrochemical treatment (BET) or microbial electroremediation [18].

2.2. Microbial fuel cell

Microbial fuel cell (MFC) technology is the symbol of the newest approach for generating electricity from biomass using microorganisms. While the first observation of electrical current generated by bacteria is generally credited to Potter in 1911 [19], very few practical advances were achieved in this field even 55 years later [20]. In the early 1990s, fuel cells became of more interest and work on MFCs began to increase [21]. A microbial fuel cell is a tool that converts chemical energy to electrical energy with the help of the catalytic reaction of bacteria [21–26].

A microbial fuel cell consists of anode and cathode sections, which are separated by a specific membrane. Microbes are present in the anode section and they oxidize fuel (electron donor) which finally generates electrons and protons. Electrons are transferred to the cathode area through the circuit and the protons through the specific membrane. Electrons and protons are consumed in the cathode compartment reducing oxygen to water.

2.3. Design of MFCs

A suitable design is foremost an important characteristic feature in MFCs and researchers have come up with several designs of MFCs over the past few years with better performance [27].

2.3.1. Single chamber microbial fuel cells

Single compartment MFC offers simpler design and cost savings. It typically consists of an anode chamber with a microfiltration membrane air-cathode. The cathode was exposed to air on one side and water on the other side (inside). There is no proton exchange membrane. The microfiltration membrane is applied directly onto the water-facing side of the cathode.

2.3.2. Dual chamber microbial fuel cells

Dual chamber MFC consists of an anaerobic anode chamber and an aerobic cathode chamber which are usually separated by a proton exchange membrane (PEM). Substrate is oxidized by bacteria generating electrons and protons at the anode chamber. The protons traveling through the PEM and the electrons traveling through the external circuit are combined with electron acceptors at the cathode chamber. The anode is inoculated with a mixed solution of anaerobic sludge and substrate like glucose. On the other hand, cathode is inoculated with aerobic sludge.

2.3.3. Air-chamber microbial fuel cells

Dual-chamber MFCs are mainly used in laboratory range and cannot be adapted for continuous treatment of organic matter due to the demand of oxygenated water. In a substitute design without aqueous cathode, cathodic electrode is bonded straight to proton exchange membrane so that air can be openly reduced [28–32]. The earliest air-cathode MFC architecture was designed and reported that an oxygen gas diffusion electrode could be used as a cathode in bioelectrochemical fuel cell [33]. But this air-cathode design has not drawn much attention in MFC research until Liu reported the air-cathode MFC could produce much greater power than typical aqueous-cathode ones.

The architecture of air-cathode MFCs is aimed to optimize some characteristics of two-chamber MFCs, such as low relative power output, high cost of cathode catalysts and membranes, and energy requirement for intensive air/oxygen sparging. Another advantage of the air-cathode over the two-chamber is the reduction of the high internal resistance of MFCs, which is a key factor to enhance electricity production.

2.4. Substrates used in microbial fuel cells

In generating electricity in MFCs, substrate is regarded as one of the most important biological factors [34]. A huge variety of substrates can be used in MFCs for power generation. The substrates not only influence the MFC performance including the power density (PD) and Coulombic efficiency (CE) but also the integral composition of the microorganism's community in the anode [35]. During the development of this technology, low molecular weight substrates were employed, that is, carbohydrates such as glucose, fructose, xylose, sucrose, maltose, and trehalose [36–38], organic acids such as acetate, propionate, butyrate, lactate, succinate, and malate [39–42], alcohols such as ethanol and methanol [43], and inorganic compounds such as sulfate [44].

3. Constructed wetland

Constructed wetlands (CW) systems are entirely man-made wetlands for wastewater treatment, which relate various technological designs, using natural wetland processes, associated with wetland hydrology, soils, microorganisms, and plants. Thus, CWs are engineered systems that have been designed and constructed to utilize the natural processes involving wetland vegetation, soils, and their associated microbial assemblages to assist in treating wastewater. Synonymous terms to "constructed" include "man-made," "engineered," or "artificial" [45].

Constructed wetlands (CWs) have been used to treat wastewater ranging from domestic to industrial and from urban to agricultural along with treating stormwater runoff, leachates and mine drainage, and for sludge dewatering through a combination of physical, chemical, and biological processes. Constructed wetlands (CW) are a feasible alternative option for removing nutrients and other contaminants from wastewater and have been used to treat many different types of wastewater for decades. CW mimics the properties of a natural wetland, and filtration occurs as a result of physical, chemical, and biological processes that are similar to those that take place in a natural wetland. There are numerous types of CW, and they can be differentiated based on dominant vegetation type, hydrology (surface vs. subsurface water flow), and direction of flow.

3.1. Surface flow (free water surface)

A surface flow CW is comprised of a sealed packed basin or series of basins filled with 20–30 cm of gravel and with a water depth of 20–40 cm. Planted macrophytes emerge over the surface of the water but roots are in the soil. Effluent water is treated as it flows over the soil/substrate. These systems effectively remove organic material through microbial degradation and settling and inorganic materials through settling alone [46]. They are efficient at removing nitrogen (N) through denitrification and ammonia volatilization but are unable to effectively remove phosphorus (P) as water does not tend to come in contact with soil particles which adsorb or precipitate phosphorus (P) [47] (**Figure 1**).

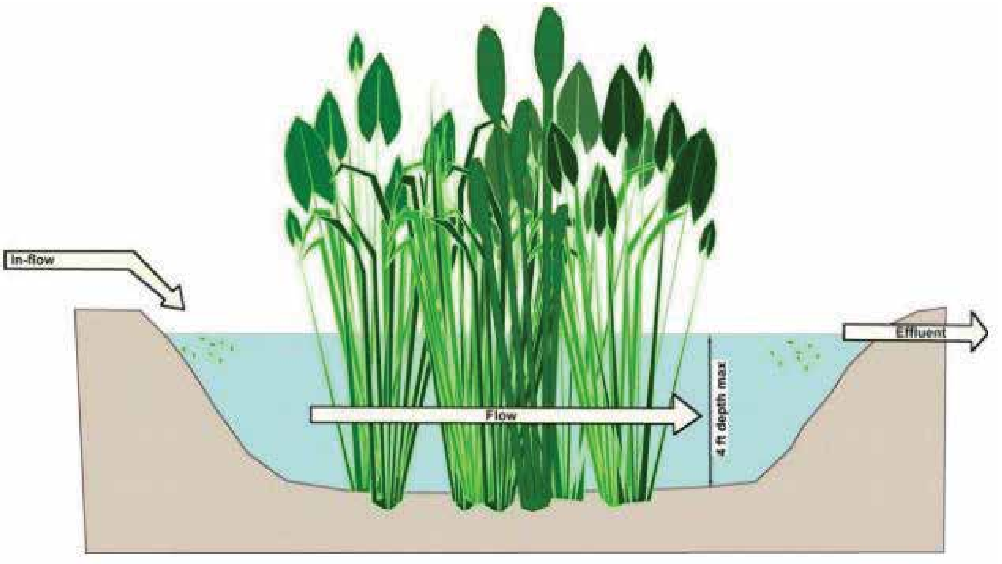

Figure 1. Diagram of a surface flow constructed wetland. Image by Dr. Sarah white [48].

3.2. Subsurface flow

Subsurface flow wetlands are made up of an impervious basin filled with a layer of gravel of size 10–20 mm [46]. Wetland plants are grown in the gravel layer and water flows through the gravel layer, around the plant roots. Subsurface flow systems are differentiated based on whether the main direction of flow is horizontal or vertical [48]. In a horizontal flow (HF) system, water enters through an inlet, flows slowly through the substrate, and exits through an outlet on the other side of the system. HF systems effectively remove organic material and suspended solids through anaerobic microbial and sedimentation, respectively. Nitrogen is removed mainly via denitrification, as ammonia volatilization may not take place due to lack of oxygen. Generally, because of the lack of ammonia volatilization occurring, total N removal by these systems is low [45] (**Figure 2**).

3.3. Hybrid constructed wetlands

Various types of CWs can be combined to achieve higher removal efficiency. The design consists of two stages, several parallel vertical flow (VF) beds followed by several horizontal flow (HF) beds in series (VSSF-HSSF system). The VSSF wetland is intended to remove organics and suspended solids and to promote nitrification, while in HSSF wetland denitrification and further removal of organics and suspended solids occur. Another configuration is a HSSF-VSSF system. A large HSSF bed is placed first to remove organics and suspended solids and to promote denitrification. An intermittently loaded small VF bed is used for additional removal of organics and suspended solids and for nitrification of ammonia into nitrate. To maximize removal of total N, however, the nitrified effluent from the VF bed must be recycled to a sedimentation tank [49] (**Figure 3**).

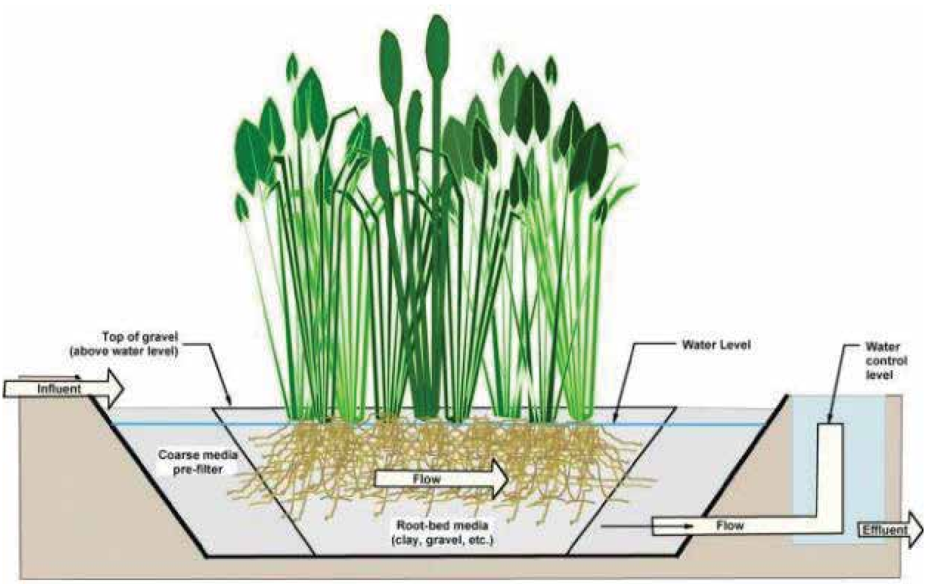

Figure 2. Diagram of a subsurface flow constructed wetland. Image by Dr. Sarah white [48].

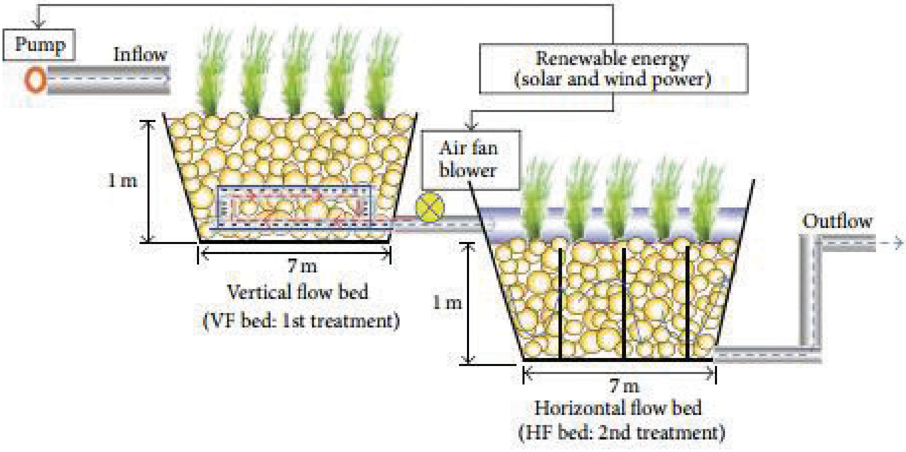

Figure 3. Diagram of a hybrid constructed wetland [50].

4. Microbial fuel cell implemented in constructed wetland: Recently emerged technology

A microbial fuel cell coupled constructed wetland (CW-MFC) system is a latest mechanism that embeds the MFC into the constructed wetland (CW) to treat the wastewater and produce electricity. Research suggested that wetland plants promote the cathode performance of MFCs [51]. Technology combining CW systems with microbial fuel cells (CW-MFC) has promise for both wastewater treatment and bio-electric production [52–54]. In this system approach, electricity is produced with biodegradable substances as bacteria oxidize organic or inorganic matter in wetland soils [54].

4.1. Architecture and operation of constructed wetland coupled with microbial fuel cells

In order to maximize the redox gradient (as it is an essential factor in producing an electrical current in MFCs), most CW-MFCs have been operated under upflow conditions with a buried anode and a cathode at the surface and/or in the plant rhizosphere. This arrangement minimizes the dissolved oxygen (DO) at the anode while ensuring maximum availability in the cathode region. Initially a glass wool separator was used by [55, 56] to provide a 'sharp' redox profile. However, the use of a separator where an upflow regime is being used with a buried anode and a cathode at the surface may not be necessary as this arrangement provides a sufficient redox profile for MFC integration [57–59]. Unfortunately, utilizing the natural redox gradient afforded by an upflow regime results in large electrode separation and contributes greatly to the ohmic resistance of the system [60–64]. Carbon and graphite are commonly used as electrode materials in MFC studies since they offer long-term sustainability owing to their high electrical conductivity, non-oxidative nature, and the fact that they offer a good medium for the attachment and growth of microbial communities.

4.2. Performance of constructed wetland coupled with microbial fuel cells

4.2.1. Functioning as constructed wetland regarding wastewater treatment

MFC integrated into CW is a possible and economical way to achieve the objectives of both wastewater treatment and electricity generation. The ability of CWs to treat wastewater is well established [65, 66] and, as such, integrating MFCs into CWs should not come at the price of reducing their effectiveness at removing contaminants from wastewater. Preliminary investigations indicated that CW-MFCs perform similarly to previous CW studies by removing 75% [55] and 76.5% [56] of COD. The inclusion of the MFC component has shown the ability to improve the COD removal efficiency in CWs. The inclusion of plant roots at the cathode of CW-MFCs slightly improves COD removal efficiencies in the wetland compared with non-planted and rhizosphere-anode CW-MFCs [58, 57]. The presence of the anode improved COD removal efficiencies by 12.65%. Thirty-three percent of COD was removed at the anode occupying 13.6% of the liquid volume in a CW-MFC operated by [53].

4.2.2. Functioning as MFC regarding electricity production

MFC converts the biodegradable compounds to generate electricity by utilizing bacteria. COD loading greatly affects the performance of CW-MFCs. A balance is necessary between providing sufficient organics for oxidation at the anode and limiting the amount of COD arriving at the cathode. In a vertical upflow CW-MFC designed by [67], an increasing trend in power densities was observed as influent COD was increased from 50 to 250 mg/L. However, further increases in concentration to 500 and 1000 mg/L resulted in average power densities of 33.7

and 21.33 mW/m^2, respectively, compared with 44.63 mW/m^2 for influent COD concentrations of 250 mg/L. Current densities were increased when the SSM was embedded in carbon cloth (49.68 ± 2.83 mA/m^2) and granular activated charcoal (GAC) (63.69 ± 1.78 mA/m^2). Both the carbon cloth and GAC increased the surface area of the electrode thereby facilitating bacterial growth and providing more reaction sites for the reduction of O_2. Other compounds in the wastewater will affect the ability of electrogenic bacteria to produce power. **Table 1** has shown the performance of CW-MFC by using different electrode materials and also of organic loads. Operating under batch mode, [55] noted that as dye concentration increased from 1000 to 1500 mg/L the average power density more than halved due to the toxic effect of the dye.

Type	Liquid volume (L)	Electrode material	Initial COD (mg/L) and (% removal)	Max. power	References
Vertical flow	5.4	Anode-graphite plate Cathode-graphite plate	1500 (74.9)	15.7 mW/m^2	[55]
Vertical upflow	3.7	Anode-graphite plates Cathode-graphite plates	1058 (76.5)	9.4 mW/m^2	[56]
Vertical flow	12.4	Anode-granular activated carbon Cathode-granular activated carbon	180 (86)	0.302 W/m^3	[57]
Horizontal subsurface flow	96	Anode-graphite plates Cathode-graphite plates	250 (80–100)	0.15 mW/m^2	[51]
Vertical flow	12.4	Anode-granular activated carbon Cathode-granular activated carbon	193–205 (94.8)	12.42 mW/m^2	[58]
Vertical flow	—	Anode-granular activated carbon Cathode-granular activated carbon	300 (72.5)	0.852 W/m^3	[68]
Vertical upflow	8.1	Anode-granular graphite Cathode-granular graphite	411–854 (64)	0.268 W/m^3	[53]
Vertical upflow	—	Anode-carbon felt Cathode-carbon felt	314.8 (100)	6.12 mW/m^2	[54]

Table 1. Reported performance of CW-MFCs.

Similarly, [68] reported that as the proportion of ABRX3 dye (measured as COD) increased incrementally from 10 to 90% the maximum power density, obtained from the power density curves, fell from 0.455 to 0.138 W/m^3. The reduction in electrical performance was primarily attributed to anodic polarization.

The CW-MFCs tested in this study were suitable for long-term stable operation and showed strong adaptability to different water qualities. HRT significantly influenced the decolorization process in the anode layer. The power density, the Coulombic efficiency, the open circuit voltage, the decolorization rate, and the COD removal rate increased initially and then decreased with the elongation of the HRT.

5. Comparison of CW-MFC with traditional biological treatment processes

Biological treatment is an important and integral part of any wastewater treatment plant that treats wastewater from either municipality or industry having soluble organic impurities or a mix of the two types of wastewater sources. The obvious economic advantage, both in terms of capital investment and operating costs, of biological treatment over other treatment processes like chemical oxidation, thermal oxidation, and so on, has cemented its place in any integrated wastewater treatment plant. Conventional activated sludge process (ASP) system is the most common and oldest bio-treatment process used to treat municipal and industrial wastewater, but the main problem with this is that it requires aeration, which uses a large amount of electrical energy. But on the other hand, MFC-centered hybrid technologies have attracted attention during the last few years due to their compatibility and dual advantages of energy recovery and wastewater treatment. In this system, oxygen is needed for the aerobic chamber but oxygen enters into that chamber through rhizosphere zone and no energy is required for this purpose but in fact electricity is harnessed during the system operation. **Table 2** lists the comparison of CW-MFC and conventional activated sludge process and highlights the benefits of CW-MFC which not only treating the wastewater but also we are harnessing electricity out of it.

Biological treatment system uses two processes, that is, aerobic and anaerobic. Aerobic, as the name suggests, means that the reactions takes place in the presence of air (oxygen) while anaerobic means in the absence of air (oxygen). These two terms are directly related to the type of bacteria or microorganisms that are involved in the degradation of impurities in a given wastewater and the operating conditions of the bioreactor. Therefore, aerobic treatment utilizes those microorganisms that use molecular/free oxygen to assimilate organic impurities, that is, convert them into carbon dioxide, water, and biomass. The anaerobic treatment processes, on the other hand, take place in the absence of air (and thus molecular/free oxygen) by those microorganisms (also called anaerobes) which do not require air (molecular/free oxygen) to assimilate organic impurities. As this process takes place in the absence of air, it is relatively slow compared to aerobic, because to create an anaerobic environment is a very difficult task.

Parameters	CW-MFC	Biological treatment
Process principle	Microbial reactions take place, no chemicals required	Microbial reactions take place, along with it chemicals are also required
Applications	Wastewater with medium to high organic impurities	Wastewater with low to medium organic impurities
Reaction kinetic	Moderate	Relatively low
Net sludge yield	No sludge formation	Relatively high (e.g., aerobic treatment)
Post-treatment	No post-treatment	Required (for anaerobic treatment, invariably followed by aerobic treatment)
Capital investment	Relatively low	Relatively high
Energy	No energy required	Energy required for aeration
Production of electricity	Yes	No
Land	Large piece of land not required	Large piece of land is required

Table 2. Differences between CW-MFC and biological treatment system.

If we talk about land requirement for the biological treatment system, lots of land are needed for different purposes like *Trickling filter, Rotating biological filter, Facultative (waste stabilization) ponds, Aerated lagoons, Activated sludge process, Anaerobic ponds, Septic tanks, Imhoff tanks,* and so on.

6. Conclusions and future perspectives

Wastewater treatment using conventional system like activated sludge technology is still energy and cost consuming, and chemicals have to be used in the treatment process. Constructed wetlands in combination with bioelectrochemical technology can provide an alternative. Wastewater treatment through CW-MFC is possible using a small-scale, constructed wetland-microbial fuel cell system. Good results were obtained with regard to organics removal, filtration of suspended solids, nutrient removal, and passive disinfection.

The CW-MFC is a promising technology in the fields of wastewater treatment and bioenergy. However, at current power levels, the biggest advantage of combining the two may come from the enhancement of wastewater treatment in anaerobic zones within the wetland. For the electrical output to be increased new operational strategies need to be explored to reduce the electrode spacing while maintaining the required redox conditions in the system. If the existing limitations of the combined system can be addressed, this prototype CW-MFC system can provide a real alternative for wastewater treatment, when built on a larger scale. Since the operational costs of a constructed wetland are very low, and given the MFC can produce electricity at a relatively low cost, this system could be competitive to existing water treatment plants.

MFCs implemented in CWs may increase not only CW treatment capacity but also would be of use as a biosensor tool to monitor treatment performance and operational conditions (such as influent organic matter concentration). Organic matter concentration is currently determined by means of analysis of the biochemical oxygen demand (BOD) after 5 days (BOD_5) or the chemical oxygen demand (COD). Despite the fact that these methods are universally used, BOD_5 has a limitation in terms of being time consuming, and is not suitable for online process monitoring.

COD is a faster procedure for assessing organic matter concentration in wastewater, yet it is quite costly and produces toxic reagents that might pose a threat to the environment. Overall, the synergy between CWs and MFCs has been so far mostly based on optimization for energy production. Besides the interest that an energy surplus can have in the context of CW technology, further research shall be focused on the optimization of both technologies to fully address other benefits of MFC implementation in CWs such as treatment efficiency improvement, process monitoring, and the reduction of clogging, or methane emissions.

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The Importance of Media in Wastewater Treatment

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Additional information is available at the end of the chapter

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Abstract

The chapter reviews the importance of media in wastewater treatment. The chapter discusses the application of natural fillings (i.e. quartz sand, zeolite and clay) and plastic materials fillings (i.e. PET flakes) for domestic sewage treatment. The effectiveness of removing biogenic compounds (NH_4^+ and PO_4^{3-} ions) and indicator bacteria (*Escherichia coli* and coliform bacteria) by using secondary and tertiary filters have been presented. The effectiveness of one-layer filters and multi-layer filters during the filtration of wastewater pre-treated in a septic tank has been discussed. The possibility of statistical tools (e.g. ANOVA and principal component analysis) to evaluate the filters performance has been described. The phenomena affected the removal of ammonium and phosphates ions from domestic sewage in a vertical flow filter filled with a calcined limestone-silicate rock were also presented.

Keywords: vertical flow filter, ammonium and phosphate ions, indicator bacteria

1. Introduction

Safe water and proper sanitation are crucial for human health and quality of our environment. According to a WHO/UNICEF monitoring program, in 2015 still around 660 million people did not have access to proper quality sources of drinking water. Estimated number of people lacking access to an appropriate sanitary system is 2.4 billion [1, 2].

Leaky septic tanks, introducing pre-treated sewage directly into the ground by drainage or discharging untreated sewage directly into watercourses contaminate groundwater and surface water. Eutrophication of water bodies is a serious problem but their contamination with pathogens is even more dangerous.

There are a number of pathogenic microorganisms transferred through water. They include rotaviruses and polioviruses, pathogenic bacteria or parasitic Protozoa (*Cryptosporidium sp.* oocysts and *Giardia sp.* cysts) [3, 4], as well as *an opportunistic pathogen Pseudomonas aeruginosa* [5–7]. The presence of pathogenic coliform bacteria (*Citrobacter sp., Enterobacter sp., Escherichia coli, Klebsiella sp.* and *Proteus sp.*) in aquatic environment indicates fresh contamination with urine and feces.

Escherichia coli is commonly used in the assessment of sanitary condition of water and technological processes. This species is a mesophilous, non-spore forming facultative anaerobe capable of withstanding temperatures between 7 and 45°C and pH 4.7–9.5 [8]. *Escherichia coli* that belongs to the normal flora of the lower intestine in humans and warm-blooded animals may sometimes cause gastroenteritis. Detection of *E. coli* may indicate the presence of other, much more dangerous pathogenic bacteria, such as *Salmonella* sp. (causing typhoid or paratyphoid fever), *Shigella* sp.(causing dysentery) or *Vibrio cholerae* (causing cholera) [9].

It is therefore highly important to use such an on-site wastewater treatment system (OWTS) that is not only effective in removing organic and biogenic compounds but also protects the receiving water against bacterial contamination. Langenbach et al. [10, 11] suggested using a sand filter as a third stage of sewage treatment allowing for removing feces bacteria. A system comprising a settling tank and a sand filter with vertical flow seems to be more cost-effective solution that allows for highly efficient reduction of physical and chemical [12, 13], as well as bacteriological contamination. Using sand as the filter filling may result in elimination level of 1×10^2–2×10^4 CFU/100 cm^3 for *Escherichia coli* and 5×10^3–3×10^5 CFU/100 cm^3 for coliform bacteria [14–16]. Other media materials such as clay, zeolite and plastic fillings have also been widely used in wastewater treatment such as moving bed biofilm reactors, trickling filters, rotating biological contactors, etc., which address specific treatment requirements and enhance treatment efficiency.

This chapter discusses the application of natural fillings and plastic materials fillings for domestic sewage treatment. The chapter presents the possibility of using secondary and tertiary filters effective for ammonium and phosphorus ions removal and the pathogen bacteria removal. The effectiveness of one-layer filters and multi-layer filters during the secondary filtration of wastewater pre-treated in a septic tank is also presented.

2. The application of natural materials

2.1. The sand

Effectiveness of the system comprising a septic tank and a sand filter with vertical flow is based on physical and chemical properties of the filter filling. Filtration is a technology commonly used to remove particulate matter and microbial contaminants in the processes of water treatment and sewage purification. It is based on retaining contaminants too big to get through water filled pores of a filter.

Effective operation of a sand filter involves also a formation of a biofilm called schmutzdecke on the top layer of the filter filling material [10, 11, 17–21]. This layer is formed at water and sand boundary and is made of biologically active microorganisms and other associated organic and inorganic substances. The biofilm may grow and reach from a few to a few dozen centimeters inside the bed [10, 11]. Quality of the treated sewage discharged from biosand filters (BSF) depends on sand grain size, filtration rate and intensity of biochemical processes occurring in the filter.

Heterotrophic bacteria that develop in an aerated sand bed are responsible for removing biodegradable organic substances as determined by BOD. As per literature reports, sand bed filtration of pre-treated wastewater allows for a removal of 92% of organic carbon [22] and a reduction of BOD by over 98% [14, 23–25]. An experiment by Wąsik et al. [25] showed that in a system septic tank/vertical filter with no additional aeration, filled with washed sand with equivalent grain diameter d_{10} = 0.62 mm, the removal of organic substances from domestic sewage was the most intense when the filter layers were 15 and 30 cm thick. Apart from heterotrophic bacteria, the sand filters in the presence of ammonium nitrogen are also colonized by nitrifying bacteria responsible for oxidation of ammonium nitrogen to nitrate nitrogen. White [22] reported 91% nitrification of sewage treated with sand filtering of secondary clarifier effluent. Chmielowski [14] demonstrated nitrification effectiveness for treatment of septic tank effluent to reach 92%. Chmielowski and Ślizowski claimed [12, 13] that equivalent diameter of sand bed grain exceeding 1.65 mm lowered sewage treatment effectiveness. Additionally, denitrification may occur in non-aerated zones of the filter. According to literature, the effectiveness of nitrate nitrogen removal in sand filters may be as high as 98% [23].

Properly designed vertical flow sand filters in the system with septic tank also provide a significant reduction of pathogenic bacteria count. In a field study on a technical scale, Chmielowski [14] received treated sewage containing 1×10^2–1×10^4 CFU of *Escherichia coli* and on average 10 CFU of *Salmonella sp*. and *Shigella sp.* **Table 1** lists the effectiveness of pathogenic bacteria removal from wastewater on sand filters in various studies [26–30].

Langenbach et al. [10, 11] confirmed usability of a vertical flow sand filter in the removal of feces bacteria from secondary clarifier effluents over 59–148 days of the filter operation. They managed to reduced *Escherichia coli* count by ca. 2 log10 units, while medium count of the bacteria in the filtrate was not higher than 1×10^2 CFU/100 cm^3. Such a good performance of

Type of material, grain size	Scale of work, medium	Removal efficiency, log10	References
Desert sand, river sand, beach sand	Effluent from an anoxic denitryfying reactor treating domestic wastewater	2.4 log units fecal coliforms	Yettefti et al. 2013 [26]
Sand, 1.05 mm	WWTP effluent	95.32–98.02%	Aloo et al. 2014 [27]
Sand, 0–8 mm	Raw municipal post-screen wastewater	2.2–3.5 log units *Escherichia coli*	Kauppinen et al. 2014 [28]
Sand, d_{10} = 0.25 mm; d_{10} = 0.40 mm; d_{10} = 0.63 mm	Lab model SSF, secondary effluent of WWTP	1.6–2.2 log units *Escherichia coli*	Pfannes et al. 2015 [29]
Sand, d_{10} = 0.21 mm	Lab model SSF, secondary effluent of WWTP	1.1–4.7 log units *Escherichia coli*	Seeger et al. 2016 [30]

Table 1. Summary of pathogenic bacteria removal on sand filters used in various studies.

the filter depends on sand surface, determined by grain size distribution and filter height and on the schmutzdecke layer. In the sand filter, bacteria are slowly removed by their adhesion to the biofilm surface that coats the grains of the filler [31]. In an 8 week study with silica sand Accusand, Elliot et al. [17] found that the growth of schmutzdecke layer was the most important factor enhancing *Escherichia coli* removal by up to 5 log10 units from the drinking water mixed with wastewater. Jenkins et al. [32] reported an average removal of 1.8 log10 units, that is, 98.5% of fecal *coli* bacteria from a river water augmented with wastewater over 10 weeks in a filter filled with fine sand. They identified grain size as a major factor affecting the performance of sand filters. Similar conclusions were drawn by Wąsik and Chmielowski [15] who conducted semi-technical studies in biofilter models the operation of which in variable hydraulic conditions continued for 10–11 months. Observing variable hydraulic load of the filter surface that ranged from 16 to 64 mm·d^{-1}, the authors concluded that the degree of indicator bacteria removal was determined mostly by the range of filling grain size and not its percentage share or type. The filter filled with quartz sand with equivalent diameter $d_{10} = 0.32$ mm was found the most suitable for a reduction of bacterial contamination. The treated domestic sewage in a secondary level for OWTS had a very low count of *Escherichia coli* (10^2–10^3 CFU). Filling the vertical filters with fine sand allowed for exceptional effective removal of the indicator bacteria by 41–4.8 log10 units, that is, 99.993–99.997% [16]. Similar values were given by Seeger et al. [30] who used a sand with equivalent diameter $d_{10} = 0.21$ mm.

The quality of biochemically treated sewage depends on microbial metabolism that slows down together with falling temperature. This is related, for example, to the climatic conditions occurring during the sewage treatment process. Kauppinen et al. [28] conducted a pilot study to evaluate annual efficacy of three different sand filters (SF) for the clarified raw municipal post-screen wastewater treatment operating in cold moderate climate. The SF with grain size of 0.8 mm removed on average 95.6% of BOD_7. An additional biotite layer with grain size 0.2 mm increased this value up to 98.4%. Both filters provided a removal of ca. 30% nitrogen and ca. 78% phosphorus. Kauppinen et al. [28] confirmed that climatic conditions considerably affected the effectiveness of indicator bacteria and viruses removal. Sand filled filters retained on average 99.994% of *Escherichia coli*, and an additional biotite layer boosted this result to 99.999%. In winter, the values were reduced to 99.987 and 99.985%, respectively. Moreover, virus removal was also less effective in this season.

Aronino et al. [33] investigated the removal of viruses and noticed that a filtration of secondary effluents through a sand filter was associated with higher colloidal and organic loads. This caused a formation of a cake layer on the filter surface but did not change the kinetics of virus filtration process. Upper 40 cm of the filter served as a buffer layer, and actual filtration of the sewage occurred in the lower 60 cm layer of the filter. Microscopic studies confirmed that the size of the viruses was the only factor that determined their removal.

2.2. The clay

To improve biofilter performance, the sand filling may be partially or entirely replaced with porous materials. IUPAC (*International Union of Pure and Applied Chemistry*) defines porous materials as solid bodies with pores, cavities, channels or interstices that are deeper than they are wide [34]. Their adsorption capacity is determined by the internal structure of micropore systems, transition pores and macropores. Inexpensive solids with sorption properties strong enough to be used for sewage and water treatment include chalcedonite [35, 36] or expanded clay. Expanded clay is produced by heating clay loam. The expanded granules are oval and have a characteristic ceramic coating (bisque) on their surface. Inside the granules, there are evenly distributed small closed pores. Porosity of the material, however, depends on the number of open pores created in the external ceramic coating or on the boundary of the bisque and granule body [37].

Adsorption is a main mechanism of retaining bacteria by porous solids with pore diameter exceeding that of the bacterial cells. Adsorption of the bacterial cells to porous solids depends on three types of parameters: physical (carrier porosity, concentration of organic compounds, temperature and medium flow rate), chemical (ionic strength and pH) and microbiological (hydrophobicity and static charge on the surface of the bacterial cells) [38]. As the microorganisms are retained not only on the surface but also inside the pores, the resulting biofilm may further increase the sorption of contaminants.

Masłoń and Tomaszek [39], who investigated non-granulated expanded clay as a biofilm carrier in *Moving Bed Sequencing Batch Biofilm Reactor*, observed unevenly developed biofilm in both open and closed pores of the filling. Expanded clay with a grain size of 4–8 mm facilitated a stable course of nitrification and a removal of up to 99% of ammonium nitrogen. Lekang and Kleppe [40] investigated a trickling filter filled with lightweight expanded clay aggregate (LECA) of three granule diameters: 2–4, 2–7 and 4–10 mm. After 7–8 weeks of LECA bed operation, 100% of ammonium nitrogen was removed irrespective of either granule size or filtration time.

Wąsik and Chmielowski [15] compared filters working with no additional aeration at variable hydraulic conditions filled with sand or non-granulated expanded clay and achieved ammonium nitrogen removal at the level of 52.4 and 68.4%, respectively. Domestic wastewater inflow changed over a few months from 250 to 2000 $m^3 \cdot d^{-1}$ and hydraulic retention time (HRT) varied throughout the study from 1.8 to 56 days.

Jucherski and Nastawny [41] demonstrated that the use of expanded clay as a biofilm substrate for nitrification required optimization of the treatment process by reducing the organic matter load. High BOD_5 intensifies growth of heterotrophic bacteria that compete with nitrifying bacteria and affect the removal of ammonium nitrogen.

Wąsik [71] achieved ca. 40% removal of PO_4^{3-} ions on expanded clay and did not show high affinity of phosphorus compounds to Ca, Fe or Al ions that were LECA components.

Treatment of domestic sewage in the expanded clay filled filter [16] allowed for 98.33% reduction of *Escherichia coli* (to the mean level of 2×10^4–1×10^6 CFU/100 cm^3), and 99.71% reduction of coliforms (to the mean level of 1×10^3–1×10^6 CFU/100 cm^3). Fine expanded clay with granule size 1.0–2.5 mm facilitated reduction of indicator bacteria by ca. 4 log10 units to an average level of 3.08×10^3 CFU/100 cm^3 for *Escherichia coli* and 5.05×10^4 CFU/100 cm^3 for coliform bacteria [16].

2.3. The zeolite

Natural zeolites are aluminosilicates with a skeletal structure comprising free spaces filled with ions and water molecules with high freedom of movement. They have net negative structural charge due to an isomorphic substitution of cations in crystal lattice [42, 43]. This negative charge is balanced by such cations as Na^+, which results in their high cation-exchange capacity, for example, toward ammonium ions NH_4^+. Apart from their ion-exchange properties, zeolites have also excellent sorption capacity. Efficiency of contamination removal with zeolites is determined by zeolite chemical composition, granule size, hydraulic load, concentration of the removed ions and pH of the reaction environment [44, 45].

The most common natural zeolite is clinoptilolite with molecular formula $(Na,K,Ca)_{2-3}Al_3(Al,Si)_2Si_{13}O_{36}\cdot 12H_2O$ [46]. Due to their considerable ion-exchange and adsorption capacity, clinoptilolites are mainly used to remove NH_4^+ from water [47–51] and sewage [52–58]. Clinoptilolites may replace quartz sand and their selective properties may be successfully used to filter water or sewage. Clinoptilolite filled filters help in cleaning water not only from ammonium nitrogen but also from suspended solids, colloidal particles or bacteria. **Table 2** presents ammonium exchange capacities of clinoptilolites used for wastewater treatment in various studies [58–65].

Effectiveness of ammonium ion removal depends on the type and dose of the zeolite, time of its exposure to sewage, temperature, pH and the presence of other anions and cations in the solution [66]. Kalló [67] showed a removal of ammonium nitrogen from biologically treated wastewater via ion exchange in a column filled with Hungarian clinoptilolite with granule size 0.5–2.0 mm. The author reported that in the column filled with 0.5–1.6 mm granules, the ion exchange was controlled by diffusion as the ion-exchange rate increased for smaller granule sizes.

Wiśniowska et al. [63] evaluated zeolite suitability as a supportive measure of nitrogen removal in the systems based on activated sludge. They concluded that zeolite was an effective sorbent in emergency situations as it prevented disturbances in the removal of biogenic

Type of zeolite	Medium	Sorption capacity	References
P1 zeolite	Wastewater	0.1–0.18 meq NH_4^+/g	Juan et al. 2009 [61]
K-F zeolite		0.09–0.15 meq NH_4^+/g	
K-Chabazite/K-Phillipsite zeolite (mixture)		0.1–0.16 meq NH_4^+/g	
Hungarian clinoptilolite	Wastewater	3.79 mg NH_4^+/g	Zabochnicka-Swiatek and Malinska 2010 [59]
Zeolite type A-carbon	Greywater	115.213 mg NH_4^+/g	Widiastuti et al. 2011 [58]
Nanozeolite - palygorskite nanocomposite	Synthetic wastewater	237.6 mg NH_4^+/g	Wang et al. 2014 [61]
Clinoptilolite ECOLIN	Wastewater	0.3 mg NH_4^+/g	Ferronato et al. 2015 [62]
Clinoptilolite	Wastewater	7.80 mg N-NH_4^+/g	Wisniowska et al. 2015 [63]
Synthetic zeolite	Synthetic wastewater	12.5–44.3 mg NH_4/dm^3	Turan 2016 [64]
Commercial zeolite 13X	Synthetic wastewater	131.04–184.8 mg NH_4/dm^3	Das et al. 2017 [75]
Fly ash zeolite		115.36–155.68 mg NH_4/dm^3	

Table 2. Summary of ammonium ions sorption capacities of zeolites used in various studies.

compounds. A comparison of ammonium nitrogen removal with zeolite and bentonite identified zeolite, with absorption level of 7.80 mg N-$NH_4^+ \cdot g^{-1}$, as 11% more effective than bentonite. This effectiveness of N-NH_4^+ removal was within the range for natural zeolite reported by other authors, that is, 0.4–25.5 mg·g^{-1} of the sorbent [40, 66, 68]. A study by Wąsik et al. [69] showed higher efficiency of zeolite than sand filters in removing biogenic compounds from domestic sewage. The use of zeolite allowed for effective average elimination of ammonium nitrogen (73.31%) and orthophosphates (62.93%).

Ferronato et al. [62] investigated the capability of granulated clinoptilolite manufactured by ECOLIN in removing pathogenic microorganisms and NH_4^+ from wastewater. In a short-term (24 h) experiment, they evaluated the adsorption rate of clinoptilolite in a laminar flow bed. The initial count of *Escherichia coli* and total coliform was 1.2×10^5 and 1.77×10^5 CFU/100 cm^3, respectively, while the concentration of ammonium ions was 13.9 mg·dm^{-3}. The experiment demonstrated a decrease in the adsorption of NH_4^+ from 0.3 to 0.06 mg/g/l due to the availability of clinoptilolite binding sites for these ions. High degree of ammonium ion adsorption in clinoptilolite bed was in line with the data reported by other authors [70]. A reduced count of pathogenic microorganisms was also observed, by 90.4–95.2% for *Escherichia coli* and 89.9–94.8% for total coliforms.

According to the literature, the processes of filtration and adsorption control immobilization of pathogenic bacteria contained in the sewage flowing through a porous substrate [11, 38]. The first mechanism is highly controlled by the size of the filter filling. Stevik [38] reported that the effectiveness of bacteria retention due to filtration was inversely proportional to the grain size of a filtration material. Adsorption is the main mechanism of bacteria retention in porous media with pore diameter larger than the bacteria. As the microorganisms are retained not only on the surface but also inside the pores, the resulting biofilm may serve as an additional sorbent and increase adhesion of the bacterial contaminants. Natural zeolites are capable of entrapping microorganisms thanks to micropores [71], Van der Waals forces, hydrogen bonding or ion bridging [71–73]. Additionally, selective, positively charged materials may attract Gram-negative bacteria such as *Escherichia coli* [74, 75]. However, it should be taken into account that soluble organic compounds contained in the sewage may block the substrate surface and consequently the charges that attract *Escherichia coli* [76].

Wąsik and Chmielowski [16] reported an increased count of pathogenic bacteria in treated wastewater together with increasing size of zeolite granules. Enlarging the zeolite equivalent diameter d_{10} from 1.0 to 3.6 mm resulted in rising the count of *Escherichia coli* and coliform bacteria, respectively, from 5.75×10^2 to 8.67×10^3 CFU/100 cm^3 and from 1.85×10^4 to 3.47×10^4 CFU/100 cm^3. The highest removal rate of pathogenic bacteria at the level of 99.995% was observed for zeolite with granule size 1.0–2.5 mm.

2.4. Multi-layer filters

New solutions based on biological beds filled with porous or modified materials often increase the efficiency of wastewater treatment but they may be inadequate in terms of their microbiological quality. Therefore, supplementation of the porous materials with a layer of quartz sand seems a simple solution to this problem. Quartz sand is inexpensive and provides an effective barrier for the pathogenic bacteria. A study by Kanawade [77] focused on using a multi-layer filter to remove ammonium and suspended solids from effluents of a domestic wastewater plant. The filter was filled with sand of grain size 0.5–1.0 mm that filtered out suspended solids and the top layer was made of clinoptilolite that removed ammonium nitrogen. Turkish clinoptilolite with adsorption capability of 10.4 $mg \cdot g^{-1}$ was used. As a result, 100% of ammonium nitrogen and 75% of suspended solids were removed by the multi-layer filter over 38 hours of its operation.

Kalenik [78] investigated treatment of model wastewater in a sandy soil bed with a layer of clinoptilolite. He showed that phosphorus removal efficiency was 53.1% in a 0.10 m thick layer and as high as 89.2% when the bed was 0.20 m thick. The use of medium sand alone (without additional layer of clinoptilolite) allowed for a removal of 23% of total phosphorus.

Syafalni et al. [79] filtrated dyed wastewater on granular activated carbon (GAC) and zeolite with particle size range of 1.18–2.00 mm. A filter comprising GAC as a top layer and zeolite as a bottom layer removed 59.46% COD, 60.82% of ammonia and 58.4% of the dye.

Wąsik and Chmielowski [80, 81] investigated a multi-layer filter filled with sand and granulated activated carbon exposed to variable hydraulic load (from 43 to 88 $mm \cdot d^{-1}$). They noticed huge variations in the efficiency of reduction of BOD_5 (6–99%), COD_{Cr} (31–90%) and total suspended solids (55–95%) due to variable conditions prevailing in individual layers of the filter. They concluded that a monolayer filter filled with granulated activated carbon was the most suitable for treatment of domestic sewage over a 3-month study cycle. Average efficiency of BOD_5, COD_{Cr} and suspended solids elimination was very high irrespective of rising hydraulic load and reached, respectively, 98, 97 and 87%. This was consistent with the reports of other authors on biologically active carbon filters [82, 83]. Mean efficiency of bacterial elimination in a two-layer filter comprising 75% of fine sand (d_{10} = 0.32 mm) in its bottom layer and 25% of fine zeolite (d_{10} = 1.8 mm) in the top layer was 97% for BOD_5, 92% for COD_{Cr}, 99.993% for *Escherichia coli* and 99.953% for other coliform bacteria.

3. Plastic materials

Natural materials commonly used as a filling for biological systems may be replaced with a plastic filling. Compared with conventional media (quartz sand, gravel, clay and rock) plastic fillings have high specific surface area and lower tendency to clogging. Modern biological filters have a large specific area of up to 150–200 m^2/m^3 (filter media in trickling filters), which provides more space for growth of heterotrophic and nitrifying bacteria [84]. Reportedly, the plastic media in a Moving Bed Biofilm Reactor present up to 1200 m^2/m^3 specific area [85].

Plastic filter media are light and can be constructed to greater depths, thus increasing the hydraulic load capacity and improving mass transfer. Plastic fillings are characterized by the highest abrasion resistance and better gas transfer due to the greater draft [86, 87]. Filters with natural filling, such as rock or sand are often poorly aerated as they contain less empty/hollow fractions [66]. Currently used plastic fillings of biological systems are produced as random or modular packing media.

Galbraith et al. [88] discussed high costs of obtaining molten mineral material, that is, sand of grain size suitable for a construction of filters meeting legal requirements (VDH 2011). The authors claimed materials such as organic fiber, synthetic foam or textile to be more economically advantageous. Systems based on non-mineral materials may be smaller than filters filled with mineral materials. Several systems based on the use of artificial materials sold by commercial vendors have been approved for use in Virginia. Non-mineral media systems can be prefabricated, transported and assembled locally from modules, while mineral-filled filters are typically built on-site.

Harwanto et al. [89] evaluated the use of a polystyrene microbead filter (PF) and Kaldnes filter (KF) in trickle filters. They determined mean efficiency of ammonium ion removal to be 35.0–310.5 $g{\cdot}m^{-3}d^{-1}$ for PF and 32.1–288.1 $g{\cdot}m^{-3}d^{-1}$ for KF. Nijhof [90], who investigated the efficiency of a leaching system filled with Filterpack CR50 Mass Transfer filling with specific area of 200 $m^2{\cdot}m^{-3}$, established the nitrification index as ranging from 0.1 to 0.8 $g{\cdot}m^{-2}d^{-1}$. Moulick et al. [91] used nylon pot scrubber media as a filling in trickling filters. They reported 28–68% efficiency of ammonia removal and nitrification indices within the range 0.11–1.29 $g{\cdot}m^{-2}d^{-1}$.

Kishimoto et al. [92] researched nitrification efficiency in restaurant wastewater treated in trickling filters filled with plastic media of the same material, the same shape but different roughness. One media type had a smooth surface (KT-15, Dainippon Plastics, Japan) and the other a rough surface (LT-15, Dainippon Plastics, Japan). They found that the removal of organic compounds (defined as COD) and nitrification were more effective in rough surface media filling (LT-15) than in smooth surface media filling (KT-15). Better performance of LT-15 filling was concluded to be due to twice larger biomass of microorganisms attached to this media.

Stephenson et al. [93] examined eight different plastic media (acrylonitrile butadiene styrene, nylon, polycarbonate, polyethylene, polypropylene, polytetraflouroethylene (PTFE), polyvinyl chloride and tufnol) in a reactor receiving settled domestic wastewater. They found that nitrification rates did not correlate with biomass concentration or surface roughness of the media. The use of PTFE, that is, a material with the lowest surface adhesion force, allowed for development of a biofilm with the highest nitrification rate of 1.5 $g{\cdot}m^{-1}d^{-1}$.

Wąsik and Chmielowski [15] determined the effects of ammonia and indicator bacteria removal during the treatment of domestic sewage on a vertical flow filter filled with plastic material (PET flakes). The experiments were performed in previously developed models that continuously operated for a few months at variable hydraulical conditions (250–2000 $cm^3{\cdot}d^{-1}$) and hydraulic retention time (HRT) from 1.8 to 56 days. PET flakes provided favorable conditions for nitrifying bacteria, as mean ammonium nitrogen removal rate for this material was 66.74%. The filters with plastic filling reduced the count of *Escherichia coli* by 98.08% and of coliform bacteria by 98.41%.

4. The calcined limestone-silicate rock

The calcined limestone-silicate rock is formed in a thermal processing as a result of calcium carbonate decomposition to calcium oxide and carbon dioxide. The process is associated with an increase in sorption capacity of limestone-silicate rock (so called gaize) from 19.6to 119.6 $g\ P{\cdot}kg^{-1}$ for the material burnt at 1000°C [94]. The presence of calcium ions and high pH make the calcined rock suitable for the removal of phosphorus compounds. Alkaline environment (pH ca. 8) facilitates binding of orthophosphate ions by calcium ions and formation of hydroxyapatite crystals. Renman [95] confirmed the presence of amorphous tricalcium phosphate in an exhausted filter filling commercially known as Polonite®. She also demonstrated that 82% of the exhausted filling was calcium and phosphorus compounds in the form of hydroxyapatite.

Most studies investigating the use of calcined rock focused on the removal of phosphates [96, 97]. **Table 3** presents the use of limestone-silicate rock or its calcined form in the removal of phosphate ions as reported by various researchers [98–101]. In their study on the use of calcined rock (Polonite®) in the removal of phosphates from wastewater, Renman et al. [98, 102] noticed also about 18% removal of inorganic forms of nitrogen, which they considered to be losses associated with their evaporation.

An experiment of Wąsik et al. [103] investigating the use of calcined rock as a filling of a vertical flow filter operating under variable hydraulic retention time (HRT) identified chemical processes, and not biofiltration, as the basic cause of PO_4^{3-} and NH_4^+ removal. A few months long filtration of pre-treated domestic sewage through calcined limestone-silicate rock revealed a very high (95%) positive correlation between the removal of phosphates and ammonium

Type of material, grain size	Wastewater treatment system; phosphates concentration in a influent	Sorption capacity, removal efficiency	References
Polonite (2–5.6 mm) mixed with 8% peat	Septic tank + biofilter; 1.9–4.9 mg P-PO_4^{3-}/l	89% PO_4^{3-}	Renmann 2008 [95]
Calcined opoka (Polonite), 2–6 mm	Septic tank (domestic wastewater)	>90% PO_4^{3-}	Cucarella et al. 2009 [98]
Polonite®, 2–5.6 mm	Septic tank (domestic wastewater) + column with Polonite; 1) 4.68 ± 1.88 mg PO_4^{3-}/l and 2)5.19 ± 1.86 mg PO_4^{3-}/l	(1) 91 ± 11% PO_4^{3-} (2) 87 ± 19% PO_4^{3-}	Renmam A, Renmam G. 2010 [96]
Calcined Opoka, 10–50 mm	Wetland + opoka; 4–9.1 mgP/l	0.727–1.258 g/kg, 18.2–35.7% P	Jóźwiakowski 2012 [99]
Polonite® (Bioptech, Hallstavik), 2–5.6 mm	Septic tank (domestic wastewater) + column with Polonite (1) mean BZT$_7$ 120 mg/l), total phosphorus 8.0 ± 1.7 mg/l; (2) + SBR; mean BZT$_7$ 20 mg/l, total phosphorus 5.3 ± 2.6 mg/l	Mean: (1) 47–97% TP (2) 76–97% TP	Nilsson et al. 2013 [97]
Calcined carbonate–silica rock (opoka) (1) 1–2 mm; (2) 2–5 mm; (3) 5–10 mm	Vertical flow filter; domestic wastewater	(1) 0.38 g TP/kg; (2) 0.30 g TP/kg (3) 0.28 g TP/kg	Jóźwiakowski et al. 2017 [100]
Polonite® (Ecofiltration NORDIC), 2–6 mm LECA, 4–10 mm	Mechanically treated wastewater, after septic tank in on-site wastewater treatment system	40.9 mg P-PO_4^{3-}/g 5.1 mg P-PO_4^{3-}/g	Karczmarczyk et al. 2017 [101]

Table 3. Summary of phosphorus ions sorption capacities for carbonate-silica rocks used in various studies.

nitrogen. The study revealed also a considerable (73–74%) dependency between the reduction of coliform count and biogenic compounds. Authors claimed that alkalization of the environment and chemical reactions involving NH_4^+ and PO_4^{3-} in the presence of magnesium and calcium ions as well as carbonates and coliform bacteria created suitable conditions to the formation of struvite ($MgNH_4PO_4·6H_2O$) and apatite $Ca_5(PO_{34})_3·OH$ and $Ca_5(PO_4)_3·CO_3$ crystals. The formation of struvite crystals by microorganisms in the presence of ammonia ions and magnesium phosphate was first described by Robinson [104]. Struvite is spontaneously precipitated during domestic sewage treatment [105] in the presence of high concentration of soluble phosphorus, ammonium and magnesium, and low concentration of total suspension solids and alkaline pH. If the formation and accumulation of struvite was controlled, it could have a market potential as a slow release fertilizer [106, 107].

Wąsik et al. [103] showed that microscopic examination of sediment samples taken from the surface and interior of the filter confirmed the formation of magnesium ammonium phosphate (struvite) and apatite crystals. The crystallization process was carried out both on the surface and inside of the bacterial cells and total elimination of the coliform bacteria confirmed their role as nuclei of crystallization. Microscopic research confirmed tricalcium phosphates were more abundant than struvite.

5. The importance of statistical tools

Statistical tools helps us analyze the data generated in lab scale systems and full scale installations, and are able to identify the critical factors that govern the process treatment efficiencies, and provide engineering design guidance with confidence.

Variance analysis ANOVA performed by Wąsik [69] identified selectivity, porosity and grain size of the filling as the factors responsible for effective removal of ammonium nitrogen, orthophosphates and *Escherichia coli* and coliform bacteria from domestic sewage treated in a septic tank and a vertical flow filter. Natural selective and porous materials were found to be the most effective in the removal of biogenic compounds. The filling of grain size from 1.0 to 2.5 mm provided highly efficient removal of ammonium (75.34%) and orthophosphate (>79%) ions. The filter filled with natural porous material of fine grain size was the most suitable for removing pathogenic bacteria, and allowed for elimination of 99.98% of *Escherichia coli* and 99.94% of coliform bacteria.

Wąsik and Chmielowski [15, 16] used the principal component analysis (PCA) to determine the mechanisms of pathogenic bacteria removal. PCA showed that in the case of natural materials the effectiveness of *Escherichia coli* elimination depends mainly on the filling grain size and not the filling type.

6. Summary

Treatment of domestic sewage in the areas with scattered development remains a serious issue. Discharging ineffectively treated sewage into the environment may cause an increase in the count of pathogenic organisms. In developing countries, where water and sanitation infrastructure is still inadequate, billions of people are exposed to diseases resulting from using unsafe water. The World Health Organization (WHO) estimates that around 1.7 million deaths globally are related to inadequate Water, Sanitation and Hygiene (WaSH) [2, 7]. It is therefore crucial to prevent the spread of gastric and infectious diseases via water. Humans are exposed not only as a result of consumption of contaminated water but also via skin contact during various forms of recreation (e.g. swimming and diving).

While one of popular approaches to on-site wastewater treatment system (OWTS) are activated sludge processes such as sequential batch reactors (SBR) due to their cost effectiveness, an inexpensive and simple solution for the treatment of domestic sewage especially in rural areas is septic tank followed by vertical flow filters with different natural media fillings, that is, quartz sand, zeolite and clay. This process route seems to be an economically attractive alternative to sewage treatment for residents without access to a public sewerage system.

Natural materials like zeolite offer the highest mean rate of ammonium nitrogen removal compared with sand or clay media. Sand filters are the most effective in reduction of the indicator bacteria but they have the highest tendency for clogging. It is recommended to undertake research in the field of developing an idea that would protect the sand filter against clogging. Natural materials commonly used as a filling of vertical flow filters may be partly replaced with a plastic filling like PET flakes. Compared with conventional media plastic fillings have high specific surface area and lower tendency to clogging. It is proposed to conduct further research using different materials used alternatively in the multi-layer vertical filters (i.e. sand and plastic media) [108].

Filter media cost is one of the most important factor that affects the cost of vertical flow filters. In areas where the sand are commonly found, its cost is nominal. Alternative filling of filters like clay are moderately cheap. Zeolite is the most expensive filling. Cost of clay, zeolite, calcium-silicate rock is all subject to availability and cost of transport. PET flakes are obtained in the recycling process of commercially available bottles. Detailed cost and long-term costs of plastic media is not available because the PET flakes media is still under study.

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A Review: Assessment of Trace Metals in Municipal Sewage and Sludge: A Case Study of Limpopo Province, South Africa

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Abstract

Trace metals including nanosilver in our aquatic environment are on the increase in part due to discharge from municipal sewage and indirectly from leaching from abandoned mine tailings and from sludge spread on farmland. The presence of the trace metals will likely impact negatively on the aquatic environment in excess of background levels. This review reports on the concentration of trace metals in municipal sewage in Limpopo province and the impact on fish and human health. Human health risks associated with the consumption of contaminated fish are discussed. The presence of silver is also highlighted and the remedial actions that are available in reducing the health risks including positive outcomes are discussed. The source of silver may be from the use of silver nanoproducts. There is a need for a paradigm shift of zero effluent discharge and start with harvesting of metals from the sewage effluent and sludge in order to protect the environment.

Keywords: trace metals, bioaccumulation, biomagnification, fish consumption, human health

1. Introduction

Trace metals in our aquatic environment are on the increase due to discharge from municipal sewage, active and abandoned mine tailings, and non-point pollution sources. Here, the trace metals may originate from metal fabrication industry [1], road runoff stormwater drains that are connected to municipal sewage plants [2–4], tannery industry [5], and from domestic households where zinc/copper scrubbers are used [6]. Trace metals have been known to originate from active and abandoned mine tailings, and these trace metals enter the aquatic environment during rainy events [7–9] or windy events [10]. Some of the non-point pollutions are as follows: trace metals also leaching from sewage sludge spread on farmland [11] and discharge of bath water to the terrestrial environment where there is leaching to the aquatic environment. In rural areas of developing countries, there is no municipal sewer system, and the communities practicing disposal of wastewater to the terrestrial environment is common. Silver and silver nanoparticles have been found in the terrestrial environment and in municipal sewage as a result of the human use of silver deodorant products and silver nanoproducts [12, 13]. The sewage sludge disposal and the fate of silver nanoparticles and trace metals and their possible effects to the environment are reviewed. The presence of the trace metals will likely impact negatively on the aquatic environment in excess of background levels (**Figure 1**).

However, the municipal sewage sludge and sewage wastewater are also a source of trace metals that are essential for plant and human growth. The municipal sewage sludge is applied on farmland in order to improve land fertility, and irrigation of crops/vegetables with sewage wastewater is also beneficial. We choose Limpopo province for the following reasons. The Limpopo province is the fifth gross domestic product (GDP), based on 2010 figures, of South Africa based on commercial agriculture, mining, manufacturing, goods and services, and tourism with world renowned Kruger National Park [14, 15]. Secondly, the Limpopo province has experienced a surge in crocodiles and fish mortalities in freshwater

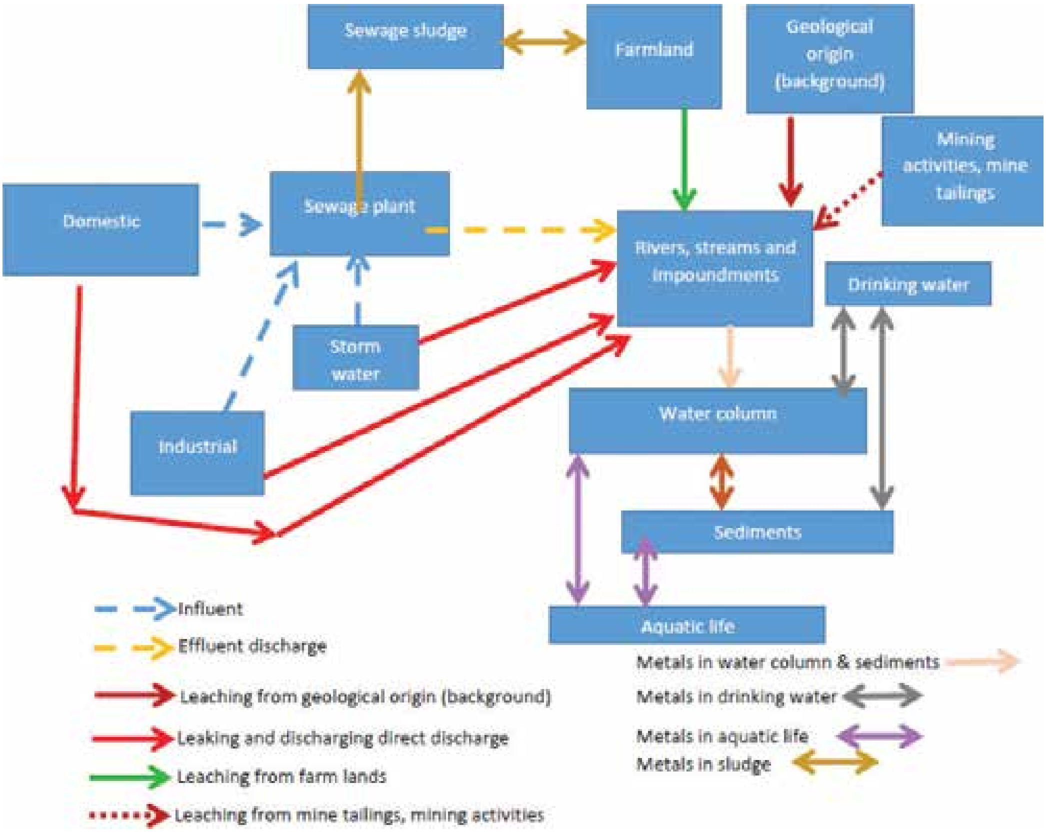

Figure 1. Schematic diagram illustrating the movement of trace metals toward freshwater environment.

impoundments and rivers inside the Kruger National Park and other nature conservation areas directly and indirectly linked to metal pollution [15]. In the 2013 Green Drop assessment by the Department of Water Affairs (DWA), Limpopo province was forth from last on assessment performance [16]. Lastly, the drinking water sources for major urban areas such as Polokwane rely on groundwater for additional water supply sources which are recharge with wastewater effluent [18], and rural areas rely on surface water and groundwater sources for human consumption. The review investigates the studies that have occurred looking at the discharge of sewage effluent in terms of metal content and the environmental impact of these metals on aquatic fauna and flora. The study also investigates the metal content of trace metals of the municipal sewage sludge in the selected sewage plants in the study period.

2. Methodology

The review is based on articles between 2012 and 2018. The keywords were sewage, wastewater, Limpopo, crocodile, metals, effluent, fish, risk assessment, and human health.

3. Characteristics of the study area

The major river systems in the Limpopo province are the Nyl River, the Sand River, the Nzhelele River, and the Luvuvhu River; Oliphant River and these are some of the tributaries of the Limpopo River in South Africa. The municipal sewage plants are located near these major rivers or their tributaries. The Nyl River system is fed by the Klein and Groot Nyl Rivers and has a floodplain and a Ramsar wetland. The likely source of metal pollution is sewage plants from Modimolle and Mookgophong that discharge their effluent into the Nyl River [17]. The Sand River originates from Drakensberg Mountains and flows past Polokwane city and flows northward, past farming areas, formal and informal residential areas, mines, nature reserves, and joins the Limpopo River [18]. The Seshego township sewage plant discharges its effluent into the Blood River. The Polokwane sewage plant serving the Polokwane city discharges its effluent into the Sand River. Thus, the source of metal pollution of the Sand River is effluent discharged from sewage plants. The Luvuvhu River originates in Soutpansberg Mountains, flows into Albasini and Nandoni dams, and joins the Limpopo River. There are formal and informal residential and towns, subsistence and commercial farming that are taking place along the Luvuvhu River. Thohoyandou town is the major urban settlement, and the Thohoyandou sewage plant discharges its effluent into Mvudi River [19]. Other sewage plants are located in Waterval Township and urban area of Elim and these discharge their effluent into the Mudzwiriti and Doringspruit Rivers which flow into the Luvuvhu River and Albasini dam, respectively [20].

The Nzhelele River originates from Soutpansberg Mountains, meanders past rural communities, and flows past Nzhelele dam northwards into the Limpopo River. The sources of metal pollution are Siloam and Makhado oxidation ponds which discharge their effluent into the Nzhelele River [21, 22]. The area is characterized by urban settlements of Biaba and residential houses, some with pit latrines, subsistence and commercial farming and nature reserves. On the Oliphant River catchment, there are a number of municipal sewage plants that discharge effluent either directly into the Oliphant River [15] or via some of tributaries such as the Elands River [23] and Ga-Selati River [24]. The Oliphant River is the most polluted river in South Africa and this is mainly due to mining activities, especially acid mine drainage, commercial and subsistence farming, and formal and informal residential discharges from municipal sewage plants [15, 25].

4. Results and discussion

4.1. Evidence of trace metal in freshwater environment

South Africa is a dry country, and rivers and streams flow during the rainy seasons. However, the location of sewage plants near streams and rivers means that the effluent is discharged into the streams and rivers and this contributes to base flow even during periods of no rainfall [20, 25]. The inflow from sewage effluents contributes to the build-up of trace metals in the freshwater environment. There are a number of studies that have shown the presence of trace metals on the freshwater environment (rivers and impoundments) in the Limpopo province of South Africa [15, 18–21, 24, 26–28]. In some cases, the trace metals are in excess of background levels, and the trace metals may become toxic to aquatic life and contaminate drinking water sources (**Table 1**). The pH values in the study sites were generally near the neutral, and therefore there was no contribution of metals due to the dissolution of bedrock or mining activities.

4.1.1. Aluminum (Al)

The study by Greenfield et al. [17] on the Nyl River system showed that the Al levels are higher than the target water-quality range (TWQR) of 10 μg/l during the study period. The presence of Al was attributed in part due to discharge of sewage effluent into the Groot Nyl River, a subtributary of the Nyl River, and rainfall-induced erosion of local bedrock. The study by Edokpayi et al. [19, 21, 24] showed variation in the Al level in the Ga-Selati, Nzhelele, Mvudi, and Dzindi Rivers in excess of the target water-quality range. The high level of Al may be attributed to the Thohoyandou sewage plant which discharges treated effluent into the Mvudi River and Vuwani oxidation ponds which discharge into Dzindi River [19, 20, 29]. Nibamureke [27] found that high levels of Al in Albasini dam in excess of TQWR aquatic life guidelines were probably linked to a combination of leaching of bedrock (geology of area) by high rainfall and discharge of sewage effluent from Elim oxidation ponds [20]. The Al target water-quality range was established to safeguard the aquatic environment against the effect of toxic metals [30]. The high Al levels are a hazard to aquatic organism affecting their respiratory function and osmotic balance [17].

4.1.2. Chromium (Cr)

Water samples showed high levels of total Cr of 3679 μg/l at Nysvley in August 2001, and this sample point is downstream of Modimolle sewage plant [17]. The study by Edokpayi et al. [19, 21, 24, 28] showed high levels of Cr (total) in the Nzhelele, Ga-Selati, Mvudi, and Dzindi rivers in excess of the target water-quality range with the Mvudi River having

Reference	[27]	[23]	[17]	[28]	[19]	[26]	[21]	[24]	[24]	[33]	[30]
Dam or river	**[a]Albasin i dam**	**[b]Flag Boshielo dam**	**[c]Nyl River**	**[d]Sand River**	**[e]Mvudi River**	**[f]Dzindi River**	**[g]Mandzoro River**	**[h]Nzhelele River**	**[i]Ga-Selati River**	**[j]Mawoni River**	**TQWR µg/l**
Name of River	**Doringspruit**	**Elands & Oliphant**	**Nyl**	**Sand**	**Mvudi**	**Tshishushuru**	**Mandzoro**	**Nzhelele**	**Ga-Selati**	**Mawoni**	
Name of sewage plant	**Elim**	**Marble Hall**	**Modimolle**	**Polokwane**	**Thohoyandou**	**Vuwani**	**Malamulele**	**Siloam**	**Phalaborwa & Namakgale**	**Makhado**	
pH	7.5 ± 0.1	8.28 – 9.42	5.52 – 9.95	7.49 – 8.48	7.72 – 7.7	7.47 – 7.53	6.7 ± 0.3	7.21 – 7.76	7.72 – 9.81	7.35 – 9.07	6.5 – 9
A1	280 ± 0.075	10.5 – 11.9	0 – 2089	–	393 – 13810	200 – 400	–	1172 – 29094	350	1.99 – 265.9	10
Cr (total)	2 ± 0	–	0 – 3679	–	12 – 593	30 – 110	–	45 – 396	60	0.58 – 46.04	Cr^{6+}7 and Cr^{3+1}12
Mn	6 ± 8	0.5 – 10.0	0 – 5047	50 – 680	29 – 675	80 – 200	–	52 – 545	210	1.02 – 2271.48	180
Fe	382 ± 62	2.4 – 27.5	0 – 19901	10 – 140	425 – 5070	790 – 1720	546 ± 50	1028 – 4991	730	25.34 – 6000.83	*
As	–	–	0 – 79	–	–	–	–	–	–	0.43 – 3.10	10
Cd	2 ± 1	–	0 – 24	10	0.2 – 4.3	–	<0.1	0.4 – 2	10	0.01 – 0.27	0.25**
Cu	–	–	0 – 729	10	11 – 567	30 – 50	420 ± 240	25.7 – 66	–	2.38 – 83.51	0.8**
Zn	3 ± 2	–	0 – 1350	10 – 20	1 – 548	50 – 210	88 ± 38	42 – 131	–	0.97 – 113.4	2
Pb	2 ± 1	–	0 – 175	90	bdl – 46	10 – 50	22 ± 0.09	1 – 13	60	0.01 – 3.40	0.5**
Se	–	–	0 – 11	–	–	–	–	–	–	2	2

Notes: – not available; bdl below detection limit; *not more than 10% of background value; **medium water hardness of $CaCO_3$ with range 60 – 119 mg/l, [a]average of three samples on the Albasini dam basin; [b]considered the sample point FBI; [c]considered the sample points along the Nyl River; [d]range in values; [e,f]range is values from Jan to Jun 2014; [g]downstream sample point; [h]downstream sample point; [i]considered the sum of wet and dry seasons; [j]considered the downstream sample point

Table 1. Concentrations for trace metals (range OR mean) in selected freshwater impoundments and rivers in Limpopo receiving sewage effluent.

higher Cr levels. The high levels of Cr in the rivers were attributed to sewage effluent discharge into the rivers as a result of inefficient metal removal during the wastewater treatment process [29]. The Cr level is in excess of the TWQR of Cr^{6+} (70 μg/l) and Cr^{3+} (120 μg/l) and is a threat to aquatic fauna [30, 31]. In the study by Shibambu et al. [32], the wastewater effluent flowed past a natural wetland which removed some of Cr and thus reducing Cr in the river water.

4.1.3. Manganese (Mn)

At Mosdene sample point, the manganese levels were 5047 μg/l in March 2002 (a period of high rainfall), indicating that part of Mn origins is geological other than sewage effluent discharge [17]. This sample point Mosdene is also downstream of the Modimolle sewage plant, and part of the increased levels is probably from the sewage inflows. The studies of [18, 33] for the Sand and Mawoni Rivers also found that high levels of Mn were probably due to rainfall erosion of bedrock. The study by Edokpayi et al. [19, 21, 24, 28] showed high levels of Mn in the Nzhelele, Ga-Selati, Mvudi, and Dzindi Rivers in excess of the target water-quality range as a result of sewage discharge. The Mn level is in excess of the TWQR of 189 μg/l and is a threat to aquatic fauna especially fish [30, 33] and is an essential component in physiological processes of living organisms such as algae at trace levels [34].

4.1.4. Iron (Fe)

The Fe levels of 19,000 μg/l were recorded at Mosdene, in March 2002 (a period of high rainfall), indicating that part of Fe origins is geological other than sewage effluent discharge [17]. The sample point is also downstream of the Modimolle sewage plant. The study by Edokpayi et al. [19, 21, 24, 28] showed high levels of Fe in the Nzhelele, Ga-Selati, Mvudi, and Dzindi Rivers during the rainfall months of January to March 2014 and the Mvudi River having higher Fe levels and sewage effluent discharges. The studies of [18, 26, 32] for the Mandzoro, Sand, and Mawoni Rivers also found that high levels of Fe were probably due to rainfall erosion of bedrock. Nibamureke [27] found that high levels of Fe in water in excess of TQWR aquatic life guidelines were probably linked to a combination of leaching of bedrock (geology of area) by high rainfall and discharge of sewage effluent from Elim oxidation ponds [20]. The Fe level is within the guideline value range of 500 and 50,000 μg/l for freshwater [17]. Fe at trace level is an essential component of living organism including hemoglobin and myoglobin [35].

4.1.5. Arsenic (As)

The As levels of 79 μg/l were recorded at Mosdene on Nyl River, in August 2002 (a period of no rainfall), indicating that part of As origins is geological other than sewage effluent discharge [17]. The sample point is also downstream of the Modimolle sewage plant. The study by Shibambu [32] found low As levels in the Mawoni River downstream of a natural wetland showing the As removal as this was within the TWQR guideline values. The As level is in excess of the TWQR of 10 μg/l and is a threat to aquatic fauna especially fish [17, 30] and aquatic freshwater invertebrates such as *Daphnia magna* and *Ceriodaphnia dubia* [36].

4.1.6. Cadmium (Cd)

The Cd levels of 21 and 22 μg/l were recorded at Klein and Groot Nyl rivers, respectively, in August 2002 (a period of no rainfall), indicating that part of As origins is geological other than sewage effluent discharge [17]. The sample point is also upstream of the Modimolle sewage plant. The studies by Seanego [18] and Edokpayi et al. [21, 24, 28] found high Cd levels in the Sand, Ga-Selati, Nzhelele, and Mvudi Rivers and attributed the high Cd values to discharge of sewage effluent to these rivers. The Cd level is in excess of the TWQR of 0.25 μg/l and is a threat to aquatic fauna especially fish [30, 37] and aquatic flora such as altering small heat shock protein (HSP) genes in aquatic midge *Chironomus riparius* [38].

4.1.7. Copper (Cu)

The Cu levels in the range of 0–729 μg/l were recorded at Klein and Groot Nyl Rivers, respectively, in November 2001 (a period of rainfall), indicating that part of Cu origins is geological other than sewage effluent discharge [17]. High levels of Cu at 150 μg/l were recorded at Nysvley in November 2001, and this sample point is downstream of Modimolle sewage plant [17]. The studies of [18, 19, 21, 26, 28, 33] also found high Cu levels in the Mandzoro, Sand, Mawoni, Dzindi, Nzhelele, and Mvudi Rivers and attributed the high Cu values to discharge of sewage effluent to these rivers. The Cu level is in excess of the TWQR of 0.30 μg/l and is a threat to aquatic fauna especially fish [17, 30]. Copper is an essential component of aquatic organisms' enzymes and co-enzymes [39].

4.1.8. Zinc (Zn)

At Mosdene, the Zn levels of 1350 μg/l were recorded in August 2002 (a period of no rainfall), indicating that part of Zn origins is geological other than sewage effluent discharge [17]. The sample point is also downstream of the Modimolle sewage plant. The studies of [18, 19, 21, 26, 28, 33] also found high Zn levels in the Mandzoro, Sand, Mawoni, Dzindi, Nzhelele, and Mvudi Rivers and attributed the high Zn values to discharge of sewage effluent to these rivers. Nibamureke [27] found Zn levels just in water in excess of TQWR aquatic life guidelines and were unlikely to be a threat to aquatic life. The Zn level is in excess of the TWQR of 2 μg/l and is a threat to aquatic fauna especially the functioning of gills in fish [17, 30]. Zn at trace level is an essential component for biochemical and physiological processes in aquatic organisms [39].

4.1.9. Lead (Pb)

The Pb levels in the range of 2–175 μg/l were recorded at sewage plant and other Nyl River sites, respectively, in November 2002 (a period of rainfall), indicating that part of Pb origins is geological other than sewage effluent discharge (Greenfield et al. [17]). The studies of [18, 19, 21, 26, 28, 33] also found high Pb levels in the Mandzoro, Sand, Mawoni, Dzindi, Nzhelele, and Mvudi Rivers and attributed the high Pb values to discharge of sewage effluent to these rivers. Nibamureke [27] showed that low levels of Pb in water were within the TQWR aquatic life guidelines and were no threat to aquatic life. The Pb level is in excess of the TWQR of 0.5 μg/l and is a threat to aquatic fauna especially the functioning of gills in fish [17, 30] and is considered a non-essential component in biological systems [39].

4.1.10. Selenium (Se)

The study by Greenfield et al. [17] found low Se levels in the Nyl River and attributed Se content to factors such as diffuse pollution and chemical weathering of bedrock. The leaching of Se from farmlands into the aquatic environment is a result of rainfall or irrigation that is practiced in the study area. Se is found in synthetic pesticides used in the study area. Shibambu [33] showed low levels of Se in the Mawoni River and were within the TQWR aquatic life guidelines and also showing the removal of Se by the natural wetland. However, high Se levels are toxic and may induce skeletal deformities in animals [17].

4.2. Trace metals in sludge of selected municipal sewage plants in Limpopo

A number of studies have been conducted in Limpopo to determine the metal removal efficiency of municipal sewage plants [18, 19, 26]. The metal efficiencies were generally low for these metals as high levels were found in the dried sludge (**Table 2**). The trace metals, Zn, Pb, and Cu, exceed the maximum permissible Department of Water Affairs & Forestry (DWAF) guidelines, and the metals have a significant environmental impact.

The studies by Baloyi et al. [26] and Shamuyarira [41] showed that Cu and Zn contents were very high. The application of sludge rich in Cu and Zn as this case to agricultural land may result in leaching to the aquatic environment in the event of rainfall event or during irrigation. At minute quantities, Cu and Zn are essential elements and are necessary for plant growth [11]. Thus, a careful application of sludge to agricultural land is required in order to safeguard the aquatic environment, taking into account the presence of Cu or Zn content of the land. The Co content was variable among the sewage plants and showed no discernible trend. At high levels, Co is harmful to plants but is an essential element at trace levels in enzymatic biochemical reactions [42].

The Pb content in sludge was generally low with the exception of Louis Trichardt which had Pb content greatly exceeding the maximum DWAF guidelines [40]. Pb has no known nutritional function in plant growth and thus is a potential hazard to the plants and crops that may be grown on the agricultural land. The presence of Cu, Zn, and Fe in wastewater streams and eventually in the sludge may be due to household use of brass (copper and zinc), copper, and iron scrubbers in washing of cooking pots [26].

The presence of high Pb in wastewater and then in the sludge for Polokwane and Louis Trichardt may be due to a dense vehicular traffic. In a 15-year study by Iglesias et al. [43] in Spain, they showed that the sludge application to agricultural land resulted in an increase in Pb, Hg, Zn, and Ag in treated soils and Cu, Pb, and Zn contents in maize and barley crops which was similar to the control site. In a similar study in South Africa, Ogbazghi et al. [44] also found a similar trend of increase in metals, Zn, Cd, Ni, and Pb soils, amended with sludge in a 10-year study.

Another trace metal of interest is silver and aluminum in municipal dried sludge, since in these urban towns, there are no heavy metal-intensive industries (**Table 2**). The presence of Ag in the sludge may be attributed to the use of silver nanoproducts. The study by Shamuyarira and

Reference	[41]	[41]	[41]	[41]	[41]	[26]	[40]	
Trace metals (mg/kg dry mass)	**Thohoyandou sewage plant**	**Polokwane sewage plant**	**Tzaneen sewage plant**	**Louis Trichardt sewage plant**	**Musina sewage plant**	**Malamulele sewage plant**	**DWAF***	
							Total maximum threshold	**Maximum permissible level**
Al	13388 ± 293	12238 ± 357	11953 ± 470	12583 ± 173	6958 ± 272	NA	–	–
Fe	29228 ± 491	10080 ± 57	18085 ± 509	19273 ± 223	8000 ± 750	11337 ± 1057	–	–
Mn	629 ± 10	263 ± 0	288 ± 7	1348 ± 29	201 ± 17	NA	–	–
As	2.6 ± 0.1	5.1 ± 0.1	4.2 ± 0.1	3.3 ± 0.2	4.8 ± 0.0	NA	2	20
Ni	33.9 ± 0.1	47.3 ± 1.3	31.3 ± 1.7	514 ± 0.6	35.2 ± 1.0	NA	150	200
Cr (total)	64.4 ± 0.7	134.5 ± 5.2	53.5 ± 2.4	97.1 ± 2.2	35.1 ± 1.6	NA	350	450
Cd	0.82 ± 0.03	3.11 ± 0.16	1.39 ± 0.06	1.66 ± 0.09	1.06 ± 0.04	2.7 ± 0.4	3	5
Pb	35.6 ± 0.1	103.8 ± 3.8	52.3 ± 2.4	172.9 ± 0.9**	21.3 ± 0.8	18.4 ± 3.6	100	150
Cu	378.0 ± 3.5**	324.8 ± 2.8	263.7 ± 9.1	499.3 ± 1.7**	626.0 ± 5.0**	178 ± 23	120	375
Zn	1193 ± 28**	1552 ± 35**	951 ± 36**	1732 ± 5**	1032 ± 21**	821 ± 124**	200	700
Ag	6.1 ± 0.1	6.9 ± 0.1	13.4 ± 0.5	21.9 ± 0.4	7.1 ± 0.0	NA	–	–
Hg	1.1 ± 0.0	1.2 ± 0.1	1.4 ± 0.1	1.7 ± 0.1	1.1 ± 0.0	NA	1	9
V	70.6 ± 0.6	39.3 ± 0.1	28.0 ± 1.1	57.4 ± 0.7	70.2 ± 2.0	NA	–	–
Se	4.1 ± 0.1	4.0 ± 0.4	4.1 ± 1.2	4.9 ± 0.4	5.4 ± 0.1	NA	–	–
Mo	3.0 ± 0.0	9.8 ± 0.2	5.0 ± 0.2	5.9 ± 0.0	20.1 ± 0.0	NA	–	–
Co	12.0 ± 0.0	53 ± 0.2	5.6 ± 0.2	12.6 ± 0.0	4.7 ± 03	NA	–	–

Notes: *DWAF guidelines for metal limit receiving high sludge loads; **Exceeds DWAF guidelines; – not available.

Table 2. Average concentrations for trace metals from selected sewage sludge in Limpopo.

Gumbo [6] of five selected municipal plants in the Limpopo province of South Africa found that silver was in the range of 6.13 ± 0.12 mg/kg dry mass to 21.93 ± 0.38 mg/kg dry mass. A recent study by Mackevica et al. [45] in Denmark showed that the maximum silver nanoparticles per toothbrush were released into the wastewater during a normal toothbrush exercise and were 10.2 ng silver content. The commercial toothbrushes are embeded with silver nanoparticles, and the adult and children toothbrush had a total silver content of 16.07 ± 0.11 and 13.53 ± 0.04 g for the whole tooth brush, respectively. Based on these studies, it can be assumed that most of the nanosilver and silver, which is used domestically, finds its way to the municipal sewage plants [6, 46] or to the environment if there is no municipal sewage plant connection as in most rural areas of developing countries [12]. The silver content of sewage wastewater is lower in comparison with sewage sludge since the silver is adsorbed onto sewage biomass to form insoluble silver sulfide (Ag_2S) [47]. Thus, the hazard may arise when the sludge is applied on farmland as fertilizer. A recent study by Wu et al. [13] in China, showed under pH conditions, metal promoters Cu and Zn, aerobic conditions, and the presence of sulfur-dominated amino acids, that the insoluble Ag_2S might become mobile and available for uptake by crops such as wheat mostly than in brown rice.

In South Africa, the Department of Water & Sanitation has not developed guideline values for silver in the sewage sludge or the disposal of sewage containing silver [48]. Elsewhere in the United States of America, the Environment Protection Agency has regulated silver ion generators as pesticides under the Federal Insecticide, Fungicide and Rodenticide Act (FIFRA) but not silver in sewage sludge [36, 49]. In the European Union, the biosolids directive (sewage sludge directive 86/278/EEC) states that all biocides that contain silver should be screened and approved by May 14, 2014 [50].

Aluminium is another trace metal that is also found in high concentrations in the dried municipal sludge in excess of 6900 mg/kg (**Table 2**). The origin of Al in the domestic wastewater is probable probably the use of deodorants that contain Al as shown by the study of Modika [51] or the use of Al cookware where upon washing releases Al in the wastewater [52]. In a separate case studied by Modika [51], in South Africa, the Ag and Al contents in wastewater were in the range of 0.03–0.52 ppb and 0.03–0.21 ppm, respectively, over the 5-day period. The Ag and Al contents in soap B were found to be <0.032 ppb and 0.07 ppm, respectively. The Nivea deodorant spray had the silver and aluminum of 7.03 ppb and 124.88 ppm, respectively. The wastewater was disposed to the natural environment since in the village there is no municipal sewerage connection.

4.3. Trace metals in sediments of impoundments and rivers receiving sewage effluent

The sewage effluent rich in metals is discharged into rivers and streams, and the metals either stay in solution or are trapped in complex sediments and pollution sinks [53]. The metals in the sediments can be released back into the water column should the environmental conditions change, such as pH becoming acidic, with devastating consequences on aquatic life and human health [15, 54] or during flood conditions [55]. The pH values in the study sites were generally near the neutral to alkaline, and therefore there was no contribution of metals due to the dissolution of bedrock or mining activities (**Table 3**). The trace metals that are likely to have an impact on aquatic life are Cd, Cr, V, Pb, Ni, and Zn.

Trace metals (mg/kg dry weight)	^{a}[27] mg/kg dry weight Average concentration	^{b}[18] mg/kg dry weight range concentration	^{c}[28] mg/kg dry weight range concentration	^{d}[21] mg/kg dry weight range concentration	^{e}[15] mg/kg dry weight Average concentration	^{e}[15] mg/kg dry weight Average concentration	^{e}[15] mg/kg dry weight Average concentration	^{e}[15] mg/kg dry weight Average concentration	Australian and New Zealand (ANZECC) [56] mg/kg dry weight	
Name of River or dam	**Doringspruit flows into Albasini dam**	**Sand**	**Mvudi**	**Nzhelele**	**Ga-Selati**	**Oliphant River @ Phalaborwa a barrage**	**Letaba River, enters KNP**	**Luvuvhu River, enters KNP**	**Low risk**	**High risk**
Name of sewage plant	**Elim**	**Polokwane**	**Thohoyandou**	**Siloam**	**Namakgale, Phalaborwa**	**Upstream sewage plants**	**Malamulele**	**Thohoyandou**	**Freshwater & reservoirs**	
pH*	7.34 – 7.63	7.49 – 8.30	7.3 – 7.7	7.21 – 7.76	8.7	8.6	8.1	8.1	6.5	8.0
Al	136.660 ± NA	–	4080 – 9090	2331 – 4707	145392.94	93046.9	23865.48	36066.5	–	–
Cr (total)	0.337 ± 0.045	–	31.96 – 175	7.804 – 51.288	969.29	623.41	270.48	312.58	80	370
Mn	4.801 ± 0.185	39.3 – 225	160 – 2160	120 – 516	3295.57	1209.61	1352.38	2019.72	–	–
Fe	196.128 ± NA	25.6 – 256.4	2900 – 7460	1175 – 5252	164778.67	148875.04	62050.25	110603.95	–	
As	–	–	–	–	18.42	16.75	14.96	15.15	20	70
Cd	0.058 ± 0.041	0.0192 – 0.0284	bdl – 2.189	0.006 – 4.056	0.16	0.09	0.19	0.12	1.5	10
Cu	0.260 ± 0.056	0.89 – 2.28	7.68 – 5690	2.182 – 566	174.47	195.4	68.41	158.69	65	270
Zn	0.412 ± 0.009	6.67 – 15	9.78 – 1524	2.605 – 202	155.09	139.57	71.6	88.96	200	410
Pb	0.426 ± 0.024	0.71 – 3.38	1.17 – 8.37	0.248 – 2.71	30.05	25.12	15.75	17.07	50	220
Ni	0.161 ± 0.033	–	–	–	562.19	334.97	116.15	175.52	21	52
Co	0.279 ± 0.006	–	–	–	135.7	84.67	5.75	81.75	–	–
V	0.583 ± 0.079	–	–	–	310.17	558.28	175.01	360.67	–	–

Notes: bdl: below detection limit; – not available; KNP: Kruger National Park; *pH is for water column above the sediments; ^{a}range is for the 2 samples sites; ^{b}range is for the 8 sample sites; ^{c,d}range is values from Jan to Jun 2014; ^{e}normalised to 10% taking into account background values.

Table 3. Concentrations for trace metals in sediments of selected freshwater impoundments and rivers in Limpopo receiving sewage effluent.

Nibamureke [27] found high levels of Fe and Al in sediments in excess of TQWR aquatic life guidelines which were probably linked to rainfall that may have occurred during the sampling trip (**Table 4**). However, the near neutral pH of the water samples would imply that the Al and Fe would not be available for uptake by the fish and cause harm especially to the gills. Nibamureke [27] showed that the high Cr (0.337 mg/l) levels would likely affect fish health as shown by changes in blood variables (hematocrit and plasma proteins) and were consistent with Cr exposure. The Cr ions are toxic since the alkaline pH contributes to the availability of Cr in sediments and becomes available in the water column.

Nibamureke [27] concluded that Cu levels were not harmful to fish health since the high Cu levels were transitional as a result of rainfall events that occurred during the sampling period. Also, other variables such as dissolved oxygen, total hardness metals (Ca and Mg), and Zn compete with Cu in fish physiology, thus reducing Cu toxicity [30]. Nibamureke [27] concluded that Mn levels in the sediments were likely to be harmful to fish health as a result of Mn becoming soluble due to alkaline pH. Though Mn is an essential metal in fish health, higher levels become toxic and cause reduced red and white blood cells, causing damage to kidney and spleen [27].

Nibamureke [27] showed that a high Pb level in the sediment is a cause of concern since Pb has been implicated in endocrine disruption chemical. However, other variables such as low DO levels and hardness (Ca and Mg) metals tend to inhibit Pb toxicity in fish, thus preventing its bioavailability [27]. Thus, the presence of Pb in the sediments may be linked to sewage inflows originating from Elim oxidation ponds and leaching from surrounding farms [20]. The levels of Cd in sediments are harmful to aquatic life. The Cd metal accumulates in the sediment and may become toxic to aquatic life such as *C. riparius* since these midge larvae live at the bottom sediments [38]. Their study showed that at laboratory exposure of 18.33 mg/l, Cd treatment altered the gene profile of small heat shock proteins (sHSPs). These sHSPs protect the organism against adverse conditions that may be encountered such as high Cd levels found in the sediments.

4.4. Impact of metal on aquatic environment

There are a number of studies that have shown the impact of trace metals on aquatic flora (plants) and aquatic fauna [15, 18, 27]. The study by Nibamureke [27] on fish species, *Clarias griepinus, Coptodon rendalli,* and *Oreochromis mossambicus* on their health from Albasini dam showed the presence of trace metals and so on. The source of trace metals is probably the effluent discharge from Elim sewage plant into Doringspruit River which then flows into Albasini dam [20].

The studies by Seanego [18] and Nibamureke [27] showed that the metals, Al, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Pb, V, and Zn, were present in fish body in various organs (**Table 4**). These metals contribute to the well-being of the fish at trace levels. However, there are two metals, Al and Fe that were in toxic levels and were likely to cause histopathological damage to the fish as shown from the study by Nibamureke [27]. The study by Seanego [18] on the Sand River, the Limpopo province of South Africa, also found high Fe levels in the body mass of *O. mossambicus* fish.

In another study in Loskop dam, South Africa, Oberholster et al. [58] showed that the Al and Fe bioaccumulate in algae which in turn is consumed by *O. mossambicus* as part of their diet and the Al and Fe are now present in the fish. In a separate study by Magonono [59] and

Trace metals (mg/kg)	**Albasini dam** [27] **Average concentration**		**Sand River** [18] **range concentration**	**Flag Boshielo dam** – [57] **Average concentration**	**Phalaborwa barrage** [57] **Average concentration**
Name of River	**Doringspruit River**		**Sand River**	**Elands & Oliphant**	**Oliphant**
Name of sewage plant	**Elim**		**Polokwane**	**Marble Hall & upstream of Oliphant Rivers**	**Sewage plants upstream of Oliphant River**
Fish muscle	***C. gariepinus***	***O. mossambicus***	***O. mossambicus***	***O. mossambicus***	***O. mossambicus***
Al	0.813 ± 0.199	0.911 ± 0.291	–	59.8	59.4
Cr (total)	–	–	–	36.9	13.5
Mn	0.012 ± 0.002	0.021 ± 0.009	113.6 – 290.9	5.3	15.3
Fe	0.241 ± 0.064	0.247 ± 0.079	1286 – 3429	647	125
As	–	–		0.7	0.0
Cd	–	–	0.0898	0.0	0.2
Cu	0.009 ± 0.001	0.012 ± 0.004	8 – 14	10.5	4.9
Zn	0.202 ± 0.025	0.243 ± 0.042	78 – 159	25.8	214
Pb	0.003 ± 0.000	0.003 ± 0.000	–	4	4.8
Ni	–	–	–	2	4.9
Co	–	–	–	2	0.4
Se	–	–	–	1.7	2

Notes: – not available.

Table 4. Average and range concentrations for trace metals in fish in freshwater impoundments and rivers in Limpopo receiving sewage effluent.

Gumbo et al. [20], they showed the presence of algae in the Sand River and the Albasini dam as a result of the availability of nutrients. The source of Fe in the body mass of *O. mossambicus* was in part attributed to bedrock of the Sand River which is dominated by the granite which on weathering produces Fe and Mn [18] and effluent discharge from Polokwane sewage plant rich in Fe and Mn since there are high levels of Fe and Mn in the sewage sludge [41].

Another hypothesis advanced by Oberholster et al. [58] was that the consumption of algae with Al led to a drop in pH to 2.9 in the stomach of *O. mossambicus,* thus contributing to the Al bioavailability. The same process of biomagnification in the food chain may be occurring with fish in Albasini dam and may account for the high Al and Fe levels in fish body muscles. Again in the same study by Oberholster et al., they found evidence of yellow fat which was associated with a high Al level in the *O. mossambicus* fish, and the yellow fat is associated with pansteatitis. The pansteatitis has been linked with the death of crocodiles and fish in the Kruger National Park [15]. The studies by Seanego [18] and Nibamureke [27] did not show if this condition of pansteatitis was occurring within the *O. mossambicus* fish in the Albasini dam or in the Sand River.

4.5. Human health-risk assessment

The consumption of fish by rural communities in South Africa is on the increase since fish is an affordable protein source in comparison with other animal or plant protein sources [60]. The fish are provided by illegal fisherman or from small-holder fish farms that are located in the Limpopo province [61, 62]. However, for wild stock fisheries, a number of studies in South Africa have shown that the popular *O. mossambicus* fish is contaminated with metals such as Al, Fe, and Pb at toxic levels [18, 27, 57, 58]. Thus, studies have been conducted to evaluate human health-risk assessment of the consumption of fish contaminated with toxic metal (**Table 5**).

The average daily dose (ADD) is expressed in mg/kg human body mass per day from this expression (1) as per the procedure by Addo-Bediako et al. [57].

$$ADD = \frac{(average\ metal\ in\ fish\ muscle\ (fw))x\ (massof\ fish\ consumed)}{(adult\ body\ mass)x\ (number\ of\ days\ in\ between\ fish\ meals)} \tag{1}$$

where the average metal concentration (mg/kg) in fish muscle, mass of fish consumed (kg) was 0.150 kg portion once per 7 days, adult body mass (kg) was 70 kg, and days is the number of day in between fish meals.

The hazard quotient (HQ) for fish from the Albasini dam and the Sand River was calculated from the data that were provided on the trace metals in the fish muscles based on the procedure by Addo-Bediako et al. [57]. The assumptions were that an individual would eat 150 g of fish per week and the adult body mass was 70 kg as per the study by Addo-Bediako et al. [57]. The studies clearly showed the high levels of trace metals in the fish muscle, and these metals, Cr, Pb, and Sb [57] and Fe and Pb [18], were likely to affect human health (**Table 5**). The human-risk assessment (HQ) was near 1 or was above 1 and thus posed hazard to fish consumers near the Phalaborwa Barrage, Flag Boshielo dam, and the Sand River.

The presence of Cr poses human health issues especially the Cr^{6+} ion which is toxic and carcinogenic to humans [39]. The presence of Pb is a serious concern in South Africa since the phased out of Pb in petroleum fuels is due to impairments of cognitive development in children [20, 39]. The presence of Fe is that the fish at these high levels poses a challenge since Fe is an essential element of human physiology hemoglobin, for instance, but may cause hemosiderosis (lung complications) [39]. The presence of Sb is a serious concern in South Africa since the Sb is a waste by-product of the manufacture of electronic circuitry and light-emitting diodes (LEDs) [63] and Sb origins maybe industrial waste or geological [64]. The Sb is not known to be essential to human health and has been associated with dermatitis, a skin disease [65], and cancer [66]. The presence of Ag is a serious concern in South Africa since the Ag may originate from the discharge of Ag-based nanoproducts in sewage effluent or in sludge [6]. Thus, there is a cause of concern since the sewage effluent continues to be discharged into these freshwater impoundments and rivers and the metal contamination of fish is likely to increase due to the detriment of rural fish consumers.

		Addo-Bediako et al. [57]						[a]**Nibamureke** [27]						[b]**Seanego** [18]		
Fish species	**Reference dose (RfD) (μg/kg)**	*O. mossambicus*			*O. mossambicus*			*C. gariepinus*			*O. mossambicus*			*O. mossambicus*		
Name of sewage plant		**upstream of Oliphant River**			**Marble Hall & upstream of Oliphant Rivers**			**Elim**			**Elim**			**Polokwane & Seshego**		
Name of river or dam		**Phalaborwa barrage**			**Flag Boshielo dam**			**Albasini dam**			**Albasini dam**			**Sand River**		
Trace metals		**[Metal] (mg/kg fw)**	**Average daily (ADD) μg/kg**	**HQ**	**[Metal] (mg/kg fw)**	**Average daily dose (ADD) μg/kg**	**HQ**	**[Metal] (mg/kg dw)**	**Average daily dose (ADD) μg/kg**	**HQ**	**[Metal] (mg/kg dw)**	**Average daily dose (ADD) μg/kg**	**HQ**	**[Metal] (mg/kg dw)**	**Average daily dose (ADD) μg/kg**	**HQ**
A1	1000	14.9	4.55	0.00	15.0	4.58	0.0	0.813	0.24	0.00	0.911	0.27	0.00	0	0	0
Fe	700	31.4	9.61	0.01	161.7	49.49	0.07	0.241	0.07	0.00	0.247	0.07	0.00	2550	744.45	1.06
Mn	140	3.8	1.17	0.01	1.3	0.4	0.0	0.012	0.00	0.00	0.021	0.01	0.00	206.2	60.21	0.43
Cu	40	1.2	0.37	0.01	2.6	0.81	0.02	0.003	0.00	0.00	0.012	0.00	0.00	0	0	0
Cr	3	3.4	1.04	0.35	9.2	2.82	0.94	0	0	0	0	0.00	0	0	0	0
Ni	20	1.2	0.38	0.02	0.5	0.15	0.01	0	0	0	0	0	0	0	0	0
Zn	300	53.6	16.4	0.05	6.4	1.97	0.01	0.202	0.06	0.00	0.243	0.07	0.00	131.8	38.5	0.128
Pb	0.057	1.2	0.37	6.14	1.0	0.31	5.12	0.003	0.00	0.015	0.003	0.003	0.015	3	0.88	14.365
Sb	0.4	0.3	0.09	0.23	5.0	1.52	3.79	0	0	0	0	0	0	0	0	0
V	5	53.6	0.15	0.05	7.7	2.37	0.47	0.004	0.00	0.00	0.005	0.005	0.00	0	0	0
As	0.3	0.01	0.00	0.01	0.2	0.06	0.19	0	0	0	0	0	0	0	0	0
Cd	3	0.0	0.01	0.00	0.0	0.0	0.0	0	0	0	0	0	0	0	0	0
Co	0.4	0.1	0.03	0.07	0.5	0.15	0.38	0	0	0	0	0	0	0		0
Ag	5	1.3	0.40	0.08	0.0	0.0	0.0	0	0	0	0	0	0	0		0

Notes: Fw fresh wet: dw dry weight; [a]average dry weight of the fish; [b]average of dry weight of four sample points.

Table 5. The hazard quotients (HQ) for the fish species in freshwater impoundments and rivers receiving sewage effluent.

4.6. Future management strategy dealing wastewater and sludge

The continued discharge of sewage effluent and sludge rich in trace metals is likely to continue in future as population increases in urban areas driven in part by rural to urban migration and naturally. Also, there is a need for more studies on other river catchments where there is lack of information in the Limpopo province. Other studies by Sibanda et al. [25], Shibambu [32], Gumbo et al. [68], and Olowoyo and Lion [69] have shown that the wastewater is rich in nutrients and essential traces such that the wastewater is usable for irrigation of crops, fruit trees, and vegetables. Limpopo province is a dry and arid region and the use of wastewater for irrigation is a welcome idea but there should be safeguards in place to protect the food consumers and irrigators from the negative impacts of wastewater reuse [68, 69]. The sludge may be used for innovative ways such as top soil cover (mined areas), biofertilizer, building materials, veld fire retardant and control, erosion control, forestry fertilization, and recovery of phosphorus [1]. Also, there is a need for a paradigm shift of sewage plants of just treating sewage to mining or to recover valuable and economic metals according to Mulchandani and Westerhoff [67]. The disposal of trace metals with engineered nanosized scale such as Ag, Ti, and Zn to sewage sludge is also on the increase worldwide as scientists develop and introduce new nanotechnological products. In order to safeguard the environment, there is a need to mine these trace metals from sewage sludge.

5. Conclusion

The municipal sewage plants continue to discharge effluent rich in trace metals to the aquatic environment. Some of these trace metals are harmful to the humans as they biomagnify through the food web such as the consumption of fish. The introduction of nanosized metals to the sewage effluent exacerbates the situation of metal pollution of the aquatic environment. There is a need for a paradigm shift where sewage plants discharge zero effluent and start harvesting the valuable trace metals in order to protect the environment.

Conflict of interest

The authors declare no conflict of interest.

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Chapter 5

Fate of Radiopharmaceuticals in the Environment

Markus R. Zehringer

Additional information is available at the end of the chapter

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Abstract

After World War II, the use of artificially produced radionuclides in medicine began and led to great success in the fight against cancer and other diseases. However, the highly radioactive compounds had to be handled with great care to protect patients and hospital personnel from radiation. The survey of these radionuclides in the environment followed some years later. In Switzerland, double-tracked monitoring programs were started. On the emission side, hospitals and industries handling radiopharmaceuticals had to report their consummation of radionuclides yearly. A monitoring program of their waste waters and solid wastes was also started. On the immission side, the remaining radioactive wastes, which were released to the environment, had to be surveyed. Overall, only a few violations of the limits for radiopharmaceuticals were observed over the last 30 years in Switzerland. Nevertheless, the monitoring of radioactivity in the environment remains an important task as long as radionuclides are used in medicine.

Keywords: radiopharmaceuticals, y-90, Lu-177, I-131, sewage sludge, sewer sludge, suspended matter

1. Introduction

Radiopharmaceuticals were first synthesised back in 1933. In Paris, Irène and Frédéric Joliot-Curie produced the first synthetic radionuclide by irradiating aluminium foil with alpha particles. They obtained a radioactive phosphor nuclide (^{30}P). The irradiation of boron resulted in a radioactive nitrogen nuclide [1]. Soon after their discovery of synthetic radionuclides, first applications were published (e.g., studies of metabolism with radioactive tracers and the use of radionuclides in diagnosis and therapy started). After World War II, the nuclear pharmacy industry started in USA. In the 1960s, a group of scientists founded the "radiological chemistry" at the University of Basel. Their focus was on the synthesis and applications of protein-bound radionuclides. They were the first to develop DOTATOC[1]-bound ^{111}In and ^{90}Y and apply them with success against tumours.

1.1. Application of radiopharmaceuticals

- **i.** Today, a broad range of radiopharmaceuticals are used for diagnostics and the fight against cancer and other diseases. Radionuclides are either used in their pure form (e.g., $^{223}RaCl_2$) or bound on a carrier. For diagnosis, they are used in scintigraphy, positron emission tomography (PET), single photon emission computed tomography (SPECT) and others. Specific radionuclides that are in use include the following:^{99m}Tc (technetium-99m), which is used for the scintigraphy of the skeleton, heart, lung, brain, liver, kidney, marrow etc. It is also used in techniques, such as myocardia- and parotid scintigraphy.
- **ii.** For the detection of neuroendocrine tumours, ^{111}In (indium-111) and ^{68}Ga (gallium-68) can be used.
- **iii.** For the diagnosis of prostate tumours, brain tumours and metastases in bones, ^{18}F (fluorine-18) is commonly used as the radionuclide in scintigraphy.

Specific radionuclides used in therapeutical applications include the following:

^{131}I (iodine-131), a thyreostatica which is administered in the form of swallowable ^{131}I–capsules, is used to treat diseases of the thyrea (hyperthyroidism and Basedow's disease). In Switzerland, 200 MBq may be applied for ambulatory treated patients. For higher activities, patients have to stay at specially isolated rooms, until the required dose becomes less than 5 μSv/h at a distance of 1 m. ^{131}I is also applied bound with MIBG (metaiodobenzyl-guanidine).

- **i.** ^{90}Y (yttrium-90) and ^{177}Lu (lutetium-177) are applied successfully against neuroendocrine tumours. These radionuclides are bound to DOTATOC, an octapeptide, which has a similar structure as the hormone somatostatin. ^{90}Y is applied in selective, internal radiotherapy (SIRT) bound on spherical polymer particles.
- **ii.** ^{90}Y–Zevalin is used against lymphoma.
- **iii.** Other radionuclides, such as ^{90}Y, ^{188}Re (rhenium-188), ^{169}Er (erbium-169), are applied for radiation synovectomy[2].
- **iv.** A recently available radionuclide is ^{223}Ra (radium-223). In the form of radium dichloride, Xofigo, it can be used against prostate tumours that have spread to the skeleton. In Basel, it has been administered since 2013.

1.2. Use of radiopharmaceuticals in Basel and Switzerland

The Federal Office for Public Health, Radioprotection Section, publishes annually the consumption of radionuclides and radiopharmaceuticals by industry and hospitals together with data from the radioactivity monitoring of the effluents of waste water treatment plants (WWTP) and other emission sources in Switzerland [2].

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[1] DOTATOC: 1,4,7,10-tetraazacyclododecane-1,4,7,10-tetraacetate coupled with an octapeptide.

[2] An application of radiopharmaceuticals to fight arthritis and arthrosis.

Today, 33 Swiss hospitals use radionuclides. Twenty-three of these hospitals discharge their contaminated waste waters to WWTPs, which are connected to the Rhine/Aar River system. **Table 1** lists the most used radionuclides in Switzerland and the percentage of their use in Basel compared to the whole Switzerland [3].

As can be observed, the Basel University Hospital is highly specialised in applications of ^{90}Y and ^{177}Lu. Only a few GBq of ^{177}Lu are applied in hospital centres at Bern, St. Gallen, Lausanne and Zurich. ^{90}Y is used in many hospitals, but in remarkably lower activities than in Basel. **Figure 1** shows consumption of radionuclides of radionuclides over the last 18 years. The consumption of ^{131}I is almost stable between 300 and 500 GBq/year. ^{90}Y shows a maximum in 2009 (2500 GBq/year); its use has been reduced since 2009 to almost 1000 GBq/year. Applications of

	Switzerland	Hospitals in Basel City	Percentage of Basel City
^{131}I ambulant appl.	25.2	0	0
^{131}I hospitalised appl.	2.593	221	9
^{186}Re	2.3	0.4	16
^{169}Er	1.0	0	0
^{90}Y	1.099	568	52
^{153}Sm	4.0	0	0
^{177}Lu	3.040	2.608	86
^{223}Ra	4.1	0.2	3

Data from [2]. appl: applications for ambulatory or hospitalised patients; LE: exemption limit.

Table 1. Applied radionuclides in Switzerland 2016, in GBq.

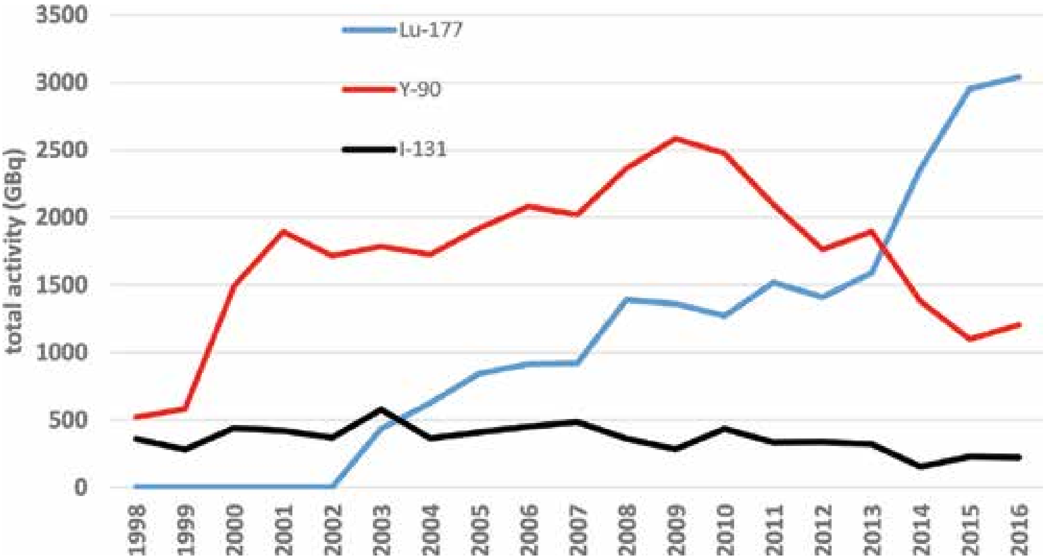

Figure 1. Yearly consumed activities of radiopharmaceuticals at Basel hospitals since 1998.

^{177}Lu started in 2002 and started to rise over the years to 3000 GBq/year in 2016. In that year, the hospitals of Basel used overall 4.5 TBq activity. In Basel, more than 8000 persons per year were treated with radiopharmaceuticals for diagnosis and therapies against cancer and for other applications [4].

Waste water and other wastes of patients are collected in special stainless steel tanks, while the patients are hospitalised. Due to their short half-lives, the activity of the radionuclides declines very fast. Cooling time in the storage tanks is several weeks. Once a week, tanks are discharged into the waste net when the activity of the radionuclides falls below a specified activity level. This level is fixed in such a way that the limit values for rivers cannot be reached.

2. Legislation in Switzerland

Since 1991, in Switzerland, radionuclides are regulated by the Radioprotection Act (from 22 March 1991) [5] and the Radioprotection Ordinance (RPO) (from 22 June 1994) [6]. In Annex

Radionuclide	Half-life	decay	LE Bq/kg	Activity limit (Bq/kg)[1]	Activity load per month[2] (kBq)	Limit value for surface water[3] (Bq/kg)
^{18}F	109.8 m	β^+	200.000	2.000	20.000	4.000
^{44}Sc	3.93 h	β^+, γ	30.000	300	3.000	600
^{67}Ga	78.3 h	γ	50.000	500	5.000	1.000
^{68}Ga	68 m	β^+, γ	100.000	1.000	10.000	2.000
^{85}Sr	65 d	γ	20.000	200	2.000	400
^{90}Y	64 h	β^-	4.000	40	400	80
^{99m}Tc	60.2 h	γ	500.000	5′000	50.000	10.000
^{110m}Ag	249.9 d	β^-, γ	4.000	40	400	80
^{111}In	2.83 d	γ	30.000	300	3.000	600
^{131}I	8.04 d	β^-, γ	500	5	50	10
^{133}I	20.8 h	β^-, γ	2.000	20	200	40
^{153}Sm	46.7 h	β^-, γ	10.000	100	1.000	200
^{169}Er	9.3 d	β^-, γ	30.000	300	3.000	600
^{177}Lu	6.71 d	β^-, γ	20.000	200	2.000	400
^{177m}Lu	160.9 d	β^-, γ	6.000	60	600	120
^{186}Re	90.6 h	β^-, γ	7.000	70	700	140
^{188}Re	17.0 h	β^-, γ	7.000	70	700	140
^{223}Ra	11.4	α, γ	100	1	10	2

Source: Swiss Radioprotection Ordinance [6].

[1] About 1% of the exemption limit (LE).

[2] About 100 fold of LE for waste water.

[3] About 1/50 of LE for rivers and lakes.

Table 2. Limits for radionuclides used in medicine.

2 of the RPO, solid and liquid wastes may not reach activities higher than a permitted limit (EL[3]). For higher activities, the material has to be treated as "radioactive" according to the Ordinance. For waste water, the activity limit is set to 1% of the EL of each radionuclide. Mixtures of radionuclides are considered as follows (summation rule):

$$a_1/EL_1 + a_2/EL_2 + \ldots + A_n/EL_n < 0.01 \tag{1}$$

with axe: activity of radionuclide x, EL_x: exemption limit of radionuclide x.

The sum in Eq. (1) has to be below 0.01; then, the activity of the waste water is under the limit value. Further, a specific discharge limit per month for treated and untreated waste water has to be fulfilled. A violation is present when both limits are overridden. The aim of these restrictions is to guarantee a limit value of 1/50 of EL for each radionuclide in rivers and lakes (according to Art.102. Par. 2 of the RPO). The Federal Office of Public Health uses the same limits for treated waste waters that are discharged to rivers and lakes (**Table 2**).

3. The waste treatment in Basel City

3.1. The waste water treatment: The municipal WWTP of Basel

The whole waste water of the city of Basel is treated at the *WWTP Pro Rheno*. In this plant, the waste water (A) is treated in three main steps (see **Figure 2**): First solids are taken out by a coarse screen (3). Yearly, 370 tonnes of solid wastes are extracted in that way and burnt at the incineration station *KVA Basel* (a) [7]. Then, the waste water runs through degritters (4). The filtered off solid materials are disposed at a nearby landfill site (b). The pre-cleaned waste water undergoes a preliminary cleaning with a primary clarification step (5). Then follows a biological treatment of

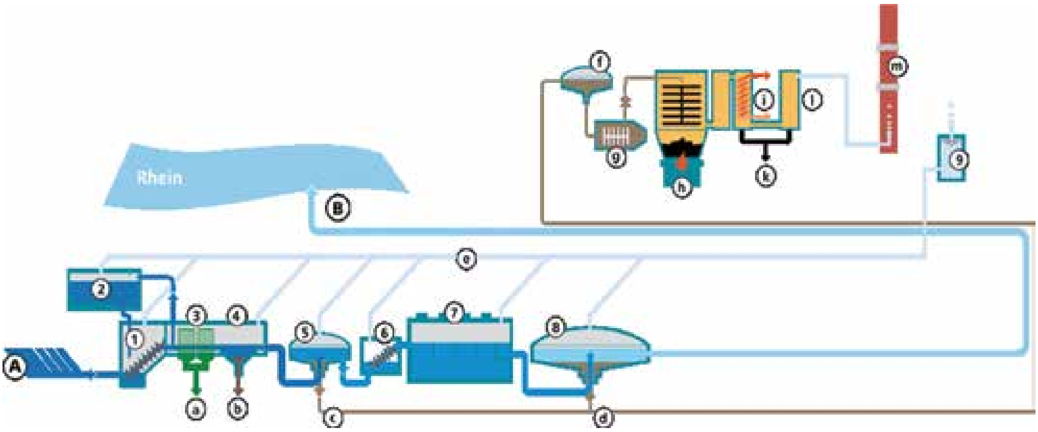

Figure 2. Scheme of the municipal WWTP of the city of Basel, *ProRheno* (source: *ProRheno* AG (with the kind permission of *ProRheno AG* [7]). Details explained in the text.

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[3] EL: exemption limit. The ingestion of 1 kg of a radionuclide with a specific activity of 1 EL yields a committed effective dose of 10 μSv [6].

the waste water with activated sludge and oxygen, where most organic substances are degraded (7). The produced sewage sludge is isolated by sedimentation. At last, the waste water undergoes a secondary clarifying step (8). Over 90% of the organic carbon is degradable. Phosphates, which are the most important nutrient for algae, are eliminated by chemical precipitation. Nitrogen is not eliminated (e.g., by a nitrification/denitrification process). The so treated waste water is then released to the Rhine River below the city of Basel, near the border to Germany and France (B). The isolated sewage sludge is centrifuged (c, d). This thickened sludge is then burnt in fluidized bed furnaces (9). The ashes are disposed at a nearby landfill site (**Figure 2**).

A total of 270,000 inhabitants of Basel City and surrounding villages (several villages of France and Germany included) release their waste waters to the waste net of the city, which has a length of about 360 km. It ends at the WWTP in the north of the city. The WWTP treats 82,000 m^3 of waste water a day; 30 million m^3 waste water a year, respectively. About 40% of the waste water originates from households (170 L of water are used per person per day). Special waste waters are discharged by the hospitals and industries. Waste waters from chemical industries in Basel are treated in a separate, independent WWTP, especially built for the treatment of chemical waste waters. For more details about the WWTP, visit the website of *ProRheno* [8].

3.2. The solid waste treatment at Basel: The municipal waste incineration plant of Basel

The waste incineration plant *KVA Basel* has a capacity of 230,000 tonnes/year for burning wastes from households and permitted wastes from industries (that means 103 tonnes a day) [9]. Only 29% of the wastes are from the city of Basel. About 54% of the wastes are delivered from the state of Basel-Campaign and other Swiss states. The German Landkreis Lörrach delivers another 17%. The wastes originate from about 700,000 persons. They are burnt in two oven lines, which produce 537 GWh/year of heating energy (the value for energy consumption is 76%). The fire gases are cleaned in several steps: dust is eliminated by electrofilters. Nitrogen oxides are neutralised with ammonia. To destroy toxic dioxins and furans, special catalysts are used. The pre-cleaned air then undergoes a wet scrubbing with water. This waste water is treated on site with the incinerator's own treatment plant. The chemical quality of the cleaned water (about 190 m^3/d) satisfies the quality criteria for treated waste water and can therefore be discharged directly to the Rhine River. The ashes are cooled down with water and stored in bunkers. About 43,800 tonnes of ashes are disposed of at a nearby landfill site. For more information, see [10].

4. Materials and methods

4.1. Swiss monitoring programme

Since 1956, environmental radioactivity has been continuously monitored in Switzerland. The motivation for the programme was the occurrence of the global fallout from bomb tests. Since 1986, the Federal Office of Public Health (BAG) is authorized to survey the ionising radiation and radioactivity in the environment. It has to organise a yearly monitoring programme. Part of this programme is the survey of the consumption of radiopharmaceuticals from hospitals and their discharge to the environment. The basic data are delivered by the hospitals (yearly consumption of radiopharmaceuticals and the discharge of total activity in ^{131}I–equivalents to the rivers). Several Swiss WWTPs and waste incineration plants, which are in the catchment area of hospitals, chemical radionuclide producing industries and watch industries are monitored continuously. Yearly, the BAG publishes the data [2].

4.2. Sampling

4.2.1. Water samples

For balancing radionuclides in waste water, a permanent sampling is necessary. This is only possible by using automatic water samplers. At the WWTP *ProRheno*, several samplers continuously collect water samples at several locations. Most important is the sampling of the untreated, raw waste water, before it enters the WWTP, and the treated waste water, before it is discharged to the Rhine River. The sampling rate of the samplers is fixed by the continuously recorded water flow rate. At higher rates, more water is sampled. Other samplers are necessary to control and optimise the waste water treatment processes inside the WWTP. At the waste incineration of Basel *KVA Basel*, the treated waste water from wet scrubbing of the flue gases is sampled permanently over 24 hours a day. This sampling is not operated by the water flow rate. The monitoring programmes of WWTP *ProRheno* and the waste incineration plant *KVA Basel* are based on water samples, which are representative for the whole time period (24 hours or a week). The water samples are delivered once a week to the State Laboratory of Basel City. The cleaned waste water from WWTP *ProRheno* consists of a 1 L sample, which was sampled over a whole week. The cleaned waste water contains a small amount of insoluble material (20–40 mg/L). The water samples from *KVA Basel* are daily samples, which are mixed in the laboratory to get a week sample. These samples are free from insoluble materials. The water samples are filled into 1 L Marinelli beakers for gamma ray spectrometry.

4.2.2. Solid samples

For the balancing experiments at WWTP *ProRheno*, sewage sludge and ash samples have to be analysed. These samples are filled into cylindrical beakers of 500 mL volume or, where possible, into 1 L Marinelli beakers. Sewer samples (sewer sludge or sewer slime) are collected in the waste net of the city of Basel. The sewer is filled into petri dishes (6.5 cm Ø). Considering the short half-lives of the radionuclides of interest (e.g., ^{99m}Tc), the gamma ray counting has to be started immediately after having received the samples. All solid samples were counted without drying to take into account the short half-life of some radionuclides and the volatility of certain radionuclides (e.g., ^{131}I). Afterwards, all solid samples were dried at 110°C. All activities were calculated back to a dry-weight basis.

In 1980–2012, suspended matter of the Rhine River was collected in 50 L barrels in three months periods upstream of the city of Basel. The suspended matter was then co-precipitated with potassium zinc hexacyanoferrate-(II), clarified using Carrez solutions, dried and analysed with gamma ray spectrometry. After 2002, the suspended matter from Rhine River was sampled once a month at the *International Monitoring Station (Rüs) at Weil am Rhein*, Germany, near Basel. To filter off the suspended matter from the water, a centrifuge was continuously loaded with Rhine water. This water was a mixture of the Rhine water over the whole profile of the river. Depending on the water flow, the sampling time took one to several days.

The suspended matter was freeze-dried in the laboratory of the Office for Environmental Protection and Energy Basel City. The dried material was ground and filled into petri dishes (6.5 cm Ø and 4 cm height, volume: 77 mL) for gamma ray counting [11]. The counting time for suspended matter was 2–3 days.

4.3. Gamma ray spectrometry

The water samples are filled without filtration into 1 L Marinelli beakers and counted for 24 hours with high resolution gamma ray spectrometers (Ge detectors). Different Ge detectors from Ortec and Canberra are used at the State Laboratory of Basel City (25–50% relative efficiencies, all detectors are of coaxial type). For recording and analysis of the pulse high spectra, Maestro Dspec jr. from Ortec combined with Interwinner-software from ITEC is used. Regularly, all detectors are recalibrated with calibration sources from Czech Metrology Institute at Prague (mixtures of ^{241}Am and ^{152}Eu). All spectra are background subtracted. For water samples, no density correction is necessary because of the same density of the calibration sources ($d = 1.0$). Solid samples are corrected according to their density and composition. No summation corrections are done. Experimental details are described in [12]. For the identification and quantification of the most important radionuclides, the following emission lines (with emission probability in %) are used: ^{131}I: 284.3 keV (6.2), 364.5 keV (81.6) and 637.0 keV (7.1), ^{177}Lu: 112.95 keV (6.4) and 208.4 keV (11.0), ^{177m}Lu: 208.4 keV (62.2), 228.4 keV (37.8) and 378.5 keV (28.3), ^{111}In: 171.3 keV (90.2) and 245.4 keV (94.0), ^{186}Re: 63.0 keV (1.9) and 137.2 keV (9.4), ^{99m}Tc: 140.5 keV (89.0), ^{153}Sm: 69.7 keV (5.3) and 103.2 keV (28.3), ^{67}Ga: 93.3 keV (39.0), 184.6 keV (21.3), 300.2 keV (16.8) and 393.5 keV (4.6), ^{110m}Ag: 657.8 keV (94.4), 763.9 keV (22.5), 884.7 keV (72.2) and 937.5 keV (34.3) and ^{223}Ra: 81.1 keV (14.9), 83.8 keV (24.5) and 94.9 keV (8.5).

4.4. Beta ray spectrometry

Radionuclides, such as ^{90}Y, are pure beta-emitters. Therefore, pre-treatment is necessary before a sample can be analysed with beta-spectrometry. Hospitals usually convert these activities into ^{131}I–equivalent values. For a specific analysis of ^{90}Y, samples of 50–100 mL are prepared as follows. First, the ^{90}Y is co-precipitated with oxalic acid in the presence of a non-active Y-carrier (Y_3Cl). The precipitates are isolated and ashed at 850°C. They are then dissolved in HCl and precipitated again at a pH of 5. ^{40}K and most of the alkaline earth metals are isolated in this step. The ^{90}Y is then precipitated in a strong alkaline medium as Y_2Ox_3. The decay of ^{90}Y in these pure beta-sources is measured in 10 consecutive runs of 400 minutes each by means of a gas proportional counter (LB 4000 from Canberra). Beta-background and relative efficiencies of the beta-detectors (30–40%) have to be considered. The beta-efficiencies of the detectors are regularly tested using own ^{90}Sr/^{90}Y oxalate sources [13].

5. Results

5.1. The waste water monitoring at WWTP *ProRheno*

In 1997, a monitoring programme for cleaned waste water was started in Basel. This treated waste water is analysed on a weekly basis for ^{3}H and gamma-active radiopharmaceuticals. In

1998, higher activities for ^{131}I near the limit value were noted. The activity limit of 5 Bq/L was not crossed, but the discharge activity of 12 GBq exceeded by far the limit of 50 kBq for ^{131}I. In that year, four violations were noted. Three of the four violations were due to discharges of waste water from the University Hospital. The reasons for the violations were diverse: overfilling of waste water storage tanks, emptying of a wrong tank and technical problems with tank filling indication devices at the University Hospital. The State Laboratory Basel City started disciplinary proceedings against the responsible personnel [14]. The fourth violation was caused by the waste incineration plant of *KVA Basel*. At that time, the WWT at *KVA Basel* was stopped for revision works and the uncleaned waste water of the wet scrubbing was redirected for treatment to the WWTP *ProRheno*. This fourth violation demonstrated that radioactive contaminated wastes are also disposed of at *KVA Basel*.

Since 1999, no more violations of the limit values (e.g., 5 Bq/L for ^{131}I, see **Table 2**) have been noted. In 2005, first activities of ^{111}In were detected in the treated waste water of the city. In 2003, the University Hospital of Basel started applications of ^{177}Lu, which were growing over the years. This can clearly be seen in **Figure 3**. Besides ^{177}Lu, ^{131}I and ^{111}In, other radionuclides are detected sporadically, such as ^{188}Re, ^{67}Ga, ^{153}Sm and ^{99m}Tc (**Table 3**). Radionuclides with very short half-lives, such as ^{99m}Tc or ^{18}F, normally are not detected in the waste water [15].

At the hospitals, only a part of the applied radioactivity is released to the waste net. A non negligible amount of radioactive wastes is released at homes. Here, all treated patients remain emission sources for the following weeks. In Section 5.3, we present measurements in the waste net that clearly show this fact. Most of the patients treated at the local hospitals live in the vicinity of Basel. Their wastes are also treated at *ProRheno* and at *KVA Basel*.

5.2. Waste water monitoring at the incineration plant *KVA Basel*

Originally, the monitoring programme of cleaned waste water from wet scrubbing of flue gases was focused on the survey of the beta-nuclide ^{3}H (tritium). From time to time, violations of the limits occurred, but no polluter could be identified. In 2001, the monitoring was extended for the survey of radiopharmaceuticals. To date, ^{131}I is the only radionuclide that caused several violations of the limit values. In April 2008, a violation of both limits for ^{131}I was noted. The activity of the effluent was 30 Bq/L and the discharge was calculated to be 15 MBq/month; both values were clearly over the limit [16]. In May 2014, a further violation of ^{131}I was noted. The mean activity then was 24 Bq/L (limit value: 5 Bq/L) and the discharge was 6.4 MBq per month (limit: 50 kBq/month) [17]. In both cases, no specific polluter could be found. We suppose that the ^{131}I–containing wastes were delivered by the local hospitals. Other radiopharmaceuticals were only detected sporadically (**Figure 4**, **Table 4**). Without specific indications, it is almost impossible to find a polluter. *KVA Basel* has to deal with over 500 waste deliveries per day. In 2018, according to the revised Radioprotection Ordinance, waste incineration plants are obliged to install a gamma-detecting portal where all wastes are monitored for gamma rays when delivered at the plant. Overall, the detected activities in the effluent of the waste incineration plant *KVA Basel* were of minor concern due to the low discharge volume of about 500 m^3/day of waste water to Rhine River.

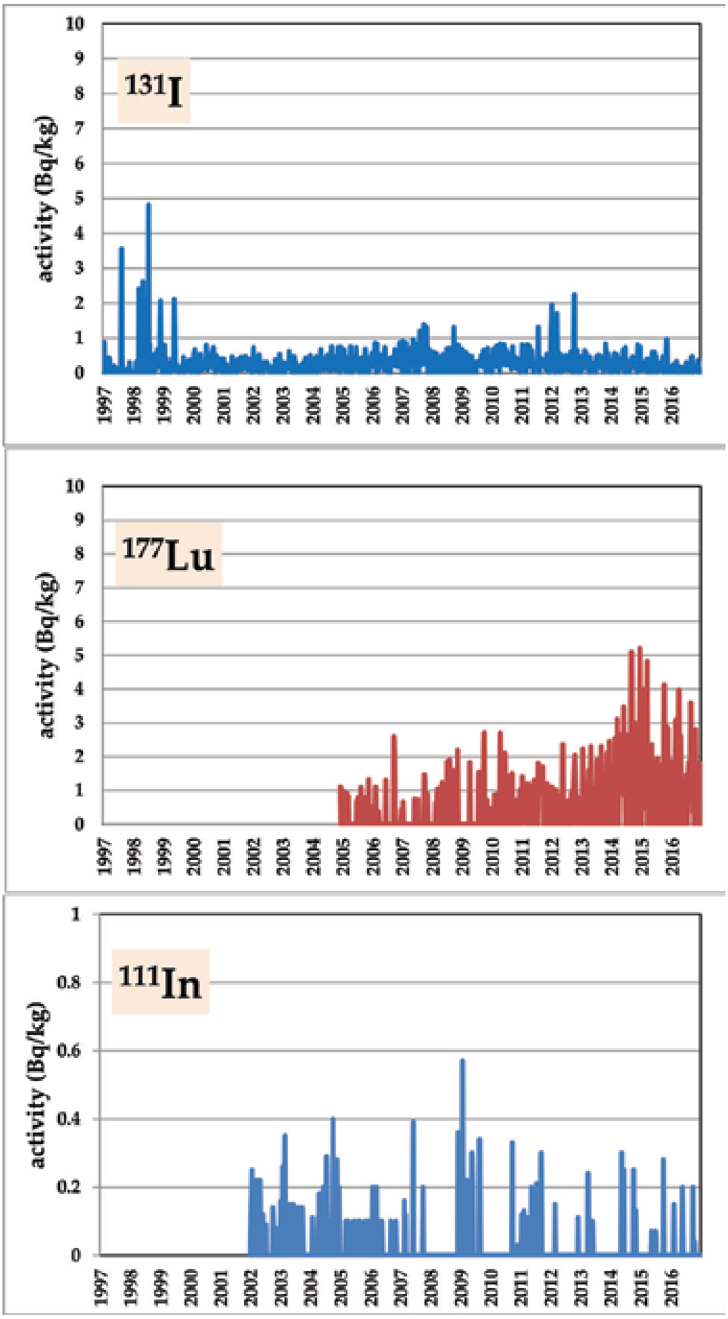

Figure 3. Monitoring of the treated waste water of the WWTP *ProRheno* since 1997.

5.3. Detection of radioactive contamination in the waste net

The investigation of waste water by taking random samples in a waste net does not lead to representative results. This can only be achieved by using automatic water samplers. The installation and use of such samplers in the waste net is a difficult task. Therefore, it is only

Radionuclide	Activity range	Number of positive samples	Mean ± s.d.
^{131}I	<0.1–4.8	1015	0.3 ± 0.3
^{177}Lu	<0.5–5.2	605	0.6 ± 0.9
^{111}In	<0.1–0.6	97	0.2 ± 0.1
^{67}Ga	<0.3–8.4	48	0.5 ± 1.5
^{186}Re	<0.5–23	7	4.4 ± 7.8
^{153}Sm	<0.3–0.72	3	0.5 ± 0.2

All values in Bq/kg. s.d.: standard deviation.

Table 3. Overview of the waste water monitoring at WWTP *ProRheno* from 1999 to 2016.

realised for the monitoring of specific emissions sources, which are under suspicion to violate the law. Another approach is the monitoring of sewer sludge or sewer slime. Sewer sludge is called a biofilm that grows on the interface of the waste water and the concrete of the waste net. Algae, bacteria and fungi build this biofilm, which acts as an excellent sorbent surface for many contaminants, such as heavy metals, polycyclic aromatic hydrocarbons, organochlorine compounds etc. [18, 19]. Radionuclides too, are adsorbed on this biofilms. The substances stay adsorbed until they are washed away from the concrete walls together with the sewer sludge or, in the case of the radionuclides, they have disintegrated. Therefore, sewer sludge can serve as a memory of the load of the run through waste water (**Figure 5**) [20].

Table 5 shows impressively the discrepancy between random sampling of waste water and the sampling of sewer sludge, which memorizes contamination of the waste system for a certain time. Only at two positions, site B and E, were traces of ^{131}I and ^{177}Lu detectable in the waste water on the sampling day, whereas ^{131}I and ^{177}Lu were detectable in the sewer sludge of several sites above and below the emission source. These activities are the result from past discharges of radioactive waste water. The fact that even above the emission source, radionuclides were detected shows that patients at home are also emission sources for a certain time [21]. The sampling of sewer sludge illustrates the contamination of the waste net over a certain time period (some days, depending on the half-life of the analysed radionuclide); but it is not representative enough for the calculation of loads or the release of radionuclides in the waste net. Sewer slime analyses can be very useful to look for specific emission sources in a waste net [20].

5.4. Balance of radiopharmaceuticals at WWTPs

In 2014, Rumpel analysed influents and effluents of the WWTP *ProRheno* for two time periods of a month [20]. During this time, 24 hour samples from the untreated waste water and the cleaned waste water were collected and analysed with gamma ray spectrometry. Samples were collected with automatic samplers at the entrance of the WWTP (untreated waste water) and before the cleaned waste water was discharged to the Rhine River (cleaned waste water). The accumulated sewage sludge was collected and analysed daily before it was burnt. The ashes were collected in containers for transportation to the landfill site. Samples were taken from each container (four samples a month). The activities of the discharges were calculated

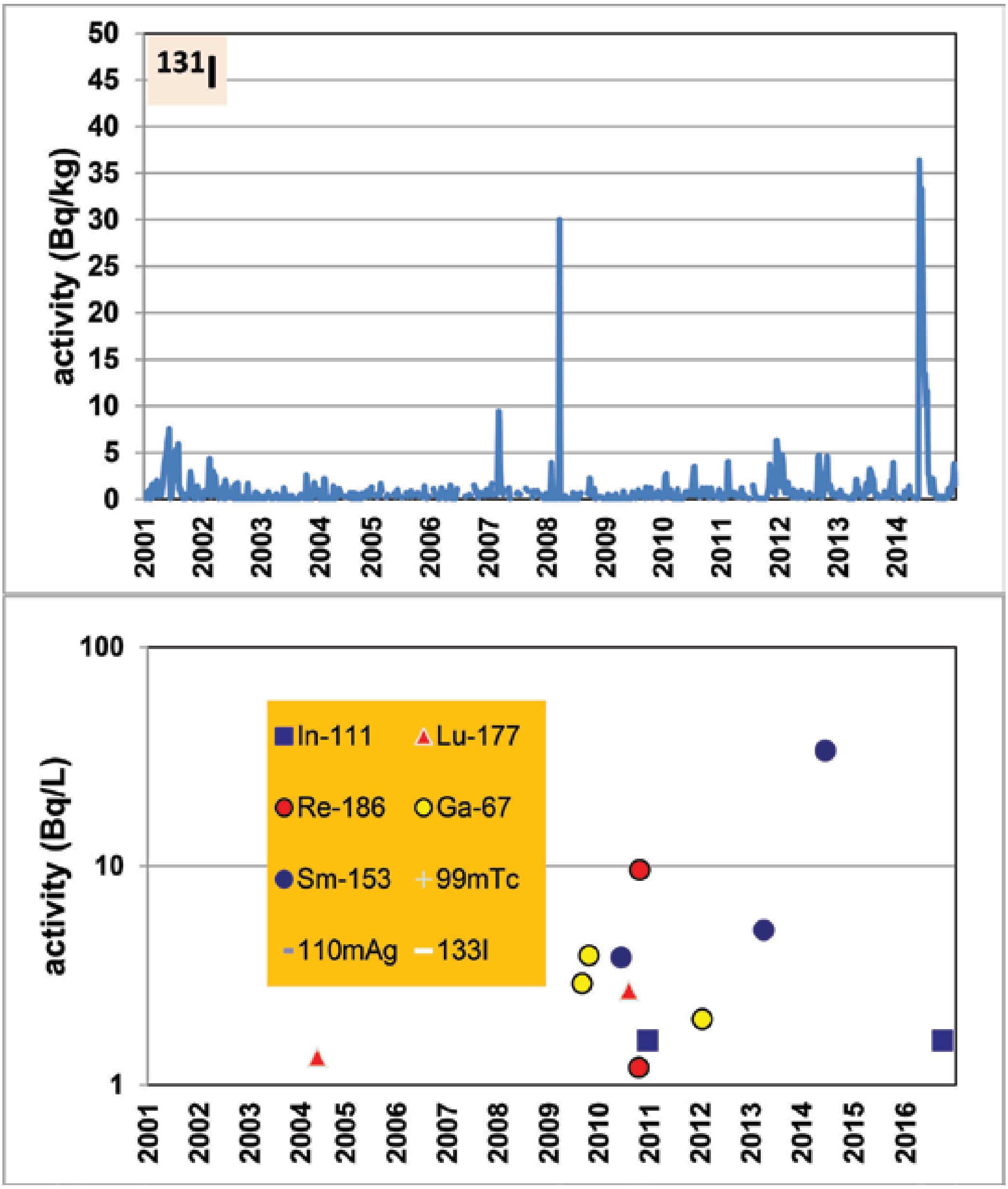

Figure 4. Monitoring of the cleaned effluent from wet scrubbing at the waste incineration plant *KVA Basel* since 2001.

by multiplying the activities with the daily waste water and sewage sludge discharges. **Table 6** shows clearly the bad elimination of ^{131}I. Only 14% are eliminated by the WWT process. Almost 90% of the ^{131}I is dissolved in the water, passes the WWT and is discharged to Rhine River. The 14%, which are taken out of the waste water are lost by the burning of the sewage sludge (the ashes are free of ^{131}I). On the other hand, 42% of ^{177}Lu was eliminated in the WWT. This is not surprising. It corresponds to the elimination rate of heavy metals. The eliminated part

Radionuclide	Activity range	Number of positive samples	Mean ± s.d.
^{131}I	<0.1–36	708	1.0 ± 2.8
^{111}In	<0.1–1.6	7	0.7 ± 0.6
^{177}Lu	<0.5–2.7	6	1.0 ± 0.8
^{153}Sm	<0.3–34	4	11 ± 13
^{110m}Ag	<0.1–0.14	3	0.1 ± 0.03
^{186}Re	<0.5–9.6	2	5.4 ± 4.2

All values in Bq/kg. s.d.: standard deviation.

Table 4. Overview of the waste water monitoring at the waste incineration *KVA Basel* from 2001 to 2016.

Figure 5. Sewer sludge (left) and the sampling of it in the waste net (right).

Sample date: 21.10.2014	Waste water (Bq/L)		Sewer sludge (Bq/kg d.w.)	
Radionuclide analysed	^{131}I	^{177}Lu	^{131}I	^{177}Lu
Above University Hospital	<0.1	<0.3	<1	32
Site A	1.2	<0.3	564	<20
Site B				
Below University Hospital	<0.1	<0.4	<1	282
Site C	<0.1	<0.4	<1	<4
Site D	<0.1	4	115	9.570
Site E				

Table 5. Comparison of waste water and sewer sludge at the same places in the waste net above and below the emission source (university hospital Basel).

Radionuclide MBq/m^3	Untreated waste water	Treated waste water	Sewage sludge	Ash from sewage sludge	Elimination rate %
^{131}I	812	701	52	0.2	~14
^{177}Lu	5.500	3.207	1.628	856	~42

Table 6. Balance of radionuclides in the WWTP *ProRheno*.

remains in the ashes from the burning of the sewage sludge, where it disintegrates according to its half-life of 6.7 days [14].

For ^{131}I, similar observations were reported by Rose. The investigations of six WWTP's in USA showed that most of the ^{131}I passed the WWTP's with the treated waste water [22]. In Finland, most of the ^{131}I (up to 94 Bq/L) was found in the water phase, whereas, in the sewage sludge, ^{51}Cr, ^{111}In, $^{201/202}$Tl and other radionuclides were found. Also, sporadically other radionuclides from nuclear power stations were detectable, such as ^{58}Co, ^{60}Co, ^{110m}Ag, or ^{124}Sb [23]. In Kurume City, Japan, four hospitals discharge their waste waters to the local WWTP. The main activities of radiopharmaceuticals were found in the waste water. About 1–4% of the applied activities of ^{99m}Tc, ^{123}I, ^{67}Ga and ^{201}Tl were detected in the WWTP. ^{131}I was only found in the sewage sludge [24]. This is confirmed by others. Investigations in Canada, Italy, France and Sweden showed that the main activities were in the sewage sludge [25–28]. About 1–250 Bq/kg of ^{201}Tl, ^{99m}Tc, ^{131}I were measured in the sewage sludge of French WWTPs [29]. In the WWTP of Valladolid, Spain, 75–1238 Bq/kg d.w. of ^{131}I was found in sewage sludge [30]. Hormann and Fischer investigated the WWTP of Bremen-Seehausen in Germany. They found an overall elimination rate of 50–75% for ^{131}I. Most of the ^{131}I was bound to the sewage sludge. They concluded that ^{131}I was bound to the return sludge and therefore a longer residence time of the waste water resulted. About 30% of the input was organically bound. After the cleaning processes, over 90% was organically bound and therefore could be eliminated from the waste water cycle [31].

Such discrepancies of the fate of radiopharmaceuticals in WWTPs can be explained as follows. The waste water treatment processes, which can vary from WWTP to WWTP, also have influence on the behaviour of the radiopharmaceuticals during the waste water cleaning process. How radiopharmaceuticals are administered (inorganic unbound, or organically bound) is crucial for the elimination behaviour of radiopharmaceuticals in a WWTP.

5.5. Monitoring of suspended matter of Rhine River at Basel

Since 1982, the suspended matter of Rhine River is collected periodically and analysed for radio contamination. This is part of the monitoring programmes of the BAG for the survey of Swiss Nuclear Power Plants (NPP) and WWTPs. From 1982 to 2002, suspended matter was collected in three month periods upstream of the city of Basel. Since 2002, suspended matter was collected monthly by means of a centrifuge at the river monitoring station Weil am Rhein downstream of the city.

In 1982 and 1986, high activities of ^{131}I were found in suspended matter of Rhine River. In 1982, the NPP of Mühleberg discharged radioactive water to Aar River, which is connected to Rhine River [32]. As a consequence, in 1982, the suspended matter contained 14.8 Bq/kg of ^{131}I and 88 Bq/kg of ^{137}Cs. Additionally, some activation products typically found in emissions from NPPs, such as ^{60}Co (85 Bq/kg) and ^{54}Mn (14.8 Bq/kg), could be detected [33].

In 1986, 2,580 ± 1,680 Bq/kg of ^{131}I were found in the suspended matter of Rhine River, together with 1,720 ± 930 Bq/kg of ^{134}Cs and 3,500 ± 1,740 Bq/kg of ^{137}Cs. These high contaminations originated from the fallout of the reactor fire at Chernobyl in that year [34]. Only after 2006, a regular monitoring for short-lived radionuclides from pharmaceutical use was realised. When short-lived radionuclides have to be monitored, it is important to analyse the collected suspended matter as soon as possible. Before 2006, samples were collected over a year and analysed at the end of the year. Therefore, the short-lived radionuclides were already disintegrated. In suspended matter, the radionuclides ^{131}I and ^{177}Lu are prominent. Since 2009, they are detectable in almost every sample and reflect mainly the local emissions from the WWTP *ProRheno* (**Figure 6, Table 7**). In 2015 and 2016, the radionuclide ^{177m}Lu was found. We suppose

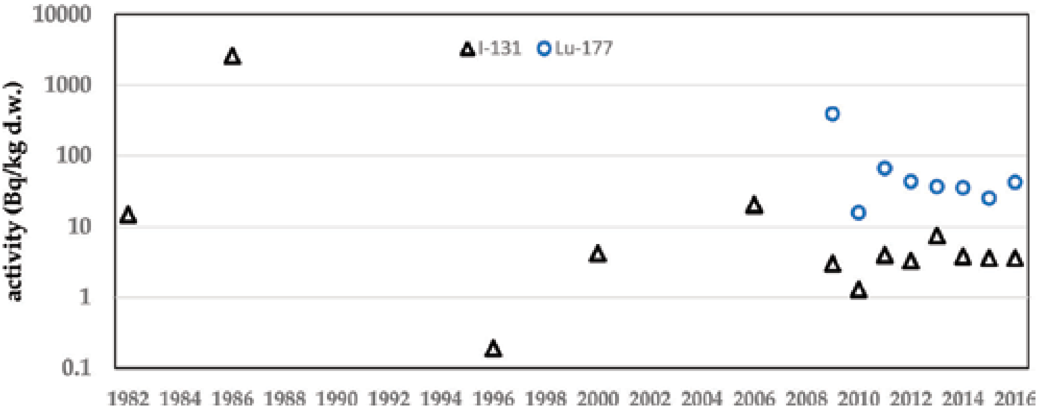

Figure 6. Results from monitoring of suspended matter of Rhine River. All annual average values in Bq/kg dry weight.

Radionuclide	Activity range	Number of positive samples	Mean ± s.d.
^{67}Ga	0–59	7	30 ± 21
^{85}Sr	0–83	21	25 ± 22
^{131}I	0–258	94	5.8 ± 5.6
^{153}Sm	0–183	6	105 ± 65
^{169}Er	0–1,550	1	1,550
^{177}Lu	0–390	92	82 ± 117
^{177m}Lu	0–3	4	3.0 ± 0.1
^{186}Re	0–1,034	1	1,934
^{223}Ra	0–33	8	16 ± 8.2

All values in Bq/kg dry weight.

Table 7. Development of yearly mean activities in suspended matter from 1982 to 2016.

that this nuclide was applied instead of ^{177}Lu, when there were supply difficulties for ^{177}Lu. ^{177m}Lu has a long half-life of 161 days and should therefore not be regularly used for pharmaceutical applications. It remains much longer in the environment, where it can cause damage. Other radionuclides, such as ^{67}Ga, ^{153}Sm, or ^{85}Sr, were found sporadically. Here, different sources (hospitals), connected to the Rhine River catchment, are possible. Since 2015, ^{223}Ra can regularly be found in the suspended matter. Overall, over these years, there were observed no violation of the immission limits for rivers according to the Radioprotection Ordinance. These limits are defined for activities of the river water. In suspended matter, these radionuclides are highly enriched by the collection process of the suspended matter. Supposing a total adsorption of the radionuclides to the suspended particles, the enrichment factor is 1000 and more. Nevertheless, there is only poor knowledge about the low dose effects of radiation on aquatic organisms.

6. Conclusion

Our monitoring programmes for radiopharmaceuticals show that radioactivity is permanently released to the environment despite rigorous treatment and cleaning of the radioactive wastes from hospitals. The limits for radionuclides in rivers and lakes are observed. Nevertheless, little is known about the low dose effects of radiation on aquatic organisms, which may occur well below these limits. Overall, the permanent monitoring of radionuclides in the environment of cities remains an important task.

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Municipal Sewage Sludge Variability: Biodegradation through Composting with Bulking Agent

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Additional information is available at the end of the chapter

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Abstract

Municipal sewage sludge is a waste with high organic load generated in large quantities that can be treated by biodegradation techniques such as composting to reduce its risk to the environment. This research studies the physicochemical variability of sewage sludge from treatment plants in the south of Galicia (Spain) and determines if it is possible to establish a protocol for the use of bulking agent depending on the composition of the sludge and the development of the composting process. Therefore, physicochemical analyses of 35 sewage sludge from different municipalities and 10 samples from the same treatment plant are discussed. Three different mixtures bulking agent:sewage sludge (3:1, 2:1, 1:1, v:v) were carried out in 30 L reactors in triplicate. Finally, proportion 2:1 was replicated six times in a 600 L reactor. High inter-sludge variability was observed specially in key parameters such as moisture and C/N ratio. Intra-variability was lower, and 2:1 proportion was the most suitable mixture since extending the thermophilic phase of the composting process at a greater degree. However, repeatability of the process at a higher scale showed different responses in the temperature evolution. Variability of sewage sludge makes difficult to establish treatment protocols although minimum requirements are necessary for proper composting.

Keywords: stabilization, compost quality, bulking agent, organic matter, sanitation

1. Introduction

As a result of the usual human activities, a large amount and volume of wastes from different sources that vary in composition and toxicity are generated. An important fraction of this waste is organic biodegradable material that has different characteristics that depend, fundamentally, on its origin: agricultural, forestry, agro-industrial, or urban. In general, the uncontrolled dumping of this fraction into the soil is not advisable because its decomposition and / or the presence of hazardous pollutants can generate harmful effects that contaminate the soil, air and water. These biodegradable wastes have non-stabilized organic matter, so they present a high level of phytotoxicity and, frequently, a high load of pathogens, such as viruses, bacteria, fungi, and parasites, both for humans and for animals and plants and may become in a risk to the environment and health. In this way, the organic waste must be stabilized and conditioned reducing the possible effects previously mentioned before its disposal to the soil.

Municipal wastewater treatment plants (WWTPs) produce different solid and semisolid residues during the treatment of the wastewater. Sludge is the semisolid waste generated during the primary (physical and/or chemical), the secondary (biological), and the tertiary (additional to secondary, often nutrient removal) treatment [1]. Sludge is by far the largest waste in volume, amount to about 11 million dry tons per year in the EU, which needs suitable and environmentally accepted management before the final disposal [2]. Since these residues are a source of nutrients and organic matter, it is reasonable to return them to the soil in optimal conditions to improve fertility and continue the natural cycle of nutrients. These organic wastes can undergo biodegradation processes, that is, the breaking of the most complex components into simple compounds through the action of living organisms. Likewise, the action of organisms converts simple molecules into more complex molecules of greater stability. Composting is one of the biological treatments that can be applied for the stabilization of municipal sewage sludge.

Composting is a controlled bio-oxidative process, in which a heterogeneous organic substrate undergoes a thermophilic stage and a transient release of phytotoxins, and produces final products: carbon dioxide, water, minerals and stabilized organic matter called compost (**Figure 1**) [3]. Due to the high microbial activity during the composting process, the temperature increases and accelerates the degradation and mineralization of the organic matter. Changes in temperature throughout the process allow differentiating four phases [4]:

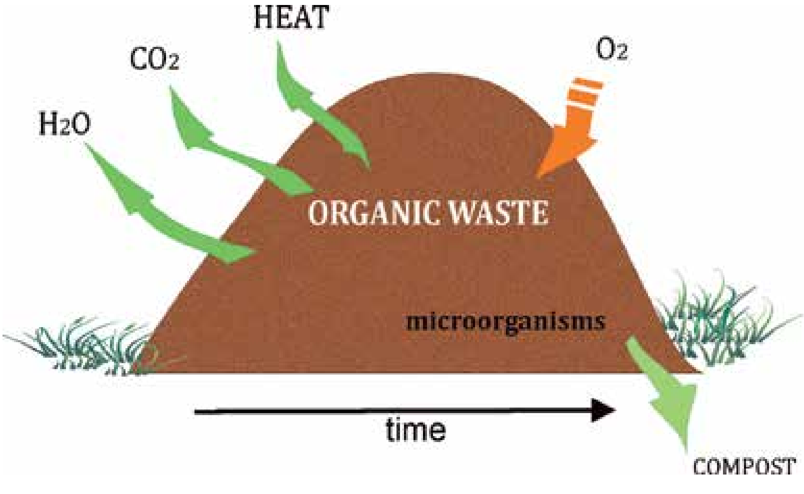

Figure 1. Simple scheme of the composting process where a pile of organic material undergoes the transformation to compost by the action of aerobic microorganisms resulting in the production of heat, carbon dioxide, and water vapor.

- Mesophilic phase: Mesophilic microorganisms proliferate when they feed on easily assimilable organic compounds, which produce an increase in temperature from values close to the ambient until reaching approximately 45°C.
- Thermophilic phase: At temperatures above 40°C, the mesophilic activity drops, and the degradation begins a thermophilic stage reaching values of 60–70°C. This phase is crucial since temperatures of this magnitude destroy the pathogenic microorganisms and seeds of invasive plant species, so this ensures the sanitation of the compost.
- Cooling phase: Because easily degradable materials are consumed during the mesophilic phase and mainly in the thermophilic phase, there is a microbial activity decrease, and the temperature drops to environmental values returning to the mesophilic stage.
- Maturation phase: At this phase, complex secondary condensation and polymerization reactions occur, which results to the compost as the final product. It is necessary that this phase has the duration such that the material acquires the maturity and stability of an organic amendment of agricultural application.

1.1. Factors that affect the composting process

The physical, chemical, and thermodynamic characteristics of the starting material determine the composting evolution, the process efficiency, and the compost quality. Some parameters must be taken into account before sewage sludge composting such as:

1.1.1. Particle size and free air space (FAS)

The composting matrix is a mass of solid particles that must contain enough pores and interstices to enable the development of the aerobic process, so that air circulates inside the mass providing an optimum concentration of oxygen, removing carbon dioxide and excessive moisture, and limiting excessive heat accumulation [5]. Sewage sludge cannot be composted alone due to its compactness and high water content, and bulking agents must be added to provide the structural support to create interparticle voids [6]. In general, organic materials such as agroforestry waste are used as bulking agents because, in addition to providing structure, they have the capacity to absorb water and facilitate the colonization and development of microbial populations [7]. The porosity or air spaces in the composting matrix can be estimated by different methods, and one of the most used is the measurement of free air space (FAS). The minimum values of FAS to ensure biological activity are around 30%, while values of 60–70% seem to be excessive to reach thermophilic temperatures in waste with low content of biodegradable organic matter [5, 8]. The mixture of bulking agent and sewage sludge improves FAS values for composting, although these agents also affect nutrient and moisture balances. Some research has been carried out to study the bulking agent:sludge ratio, as well as the type of bulking material and its particle size, in order to determine their influence on the sewage sludge composting (**Table 1**). The optimum bulking agent:sludge proportion will depend on factors such as process conditions (composting system, volume, time, etc.), origin of the bulking agent, type of bulking (fresh or recirculated), particle size, mixture conditions (FAS, C/N ratio, moisture), etc.

Bulking agent	**Proportion (bulking:sludge)**	**Particle size**	**Composting system**	**Reference**
Wood chips	1:1, 2:1, 4:1 (v:v)	20, 10, 5 mm	4.5 L Dewar® vessels 100 L reactors	[9]
Acacia spp. trimming residues	1:0, 1:1, 1:2, 1:3 (w:w)	40 mm	35 kg reactors	[10]
Six different bulking agents	4:1 (v:v)		170 L reactors	[11]
Recycled and fresh wooden pallets	3:1 (v:v)	<20 mm and >20 mm	47 L cylindrical reactors	[12]
Sawdust	1:1, 3:1 (v:v)		3 m^3 piles	[13]

Table 1. Some research references about the bulking agent, typology, and bulking agent:sludge ratio of the composting of sewage sludge.

According to Diaz et al. [14], the particle size depends on the physical nature of the waste, and sizes of 1–5 cm are suitable for materials that do not compact easily. Haug [5] states that wood chips about 5 cm in size are the most commonly used bulking agent. However, it is logical that the greater the volume of waste under treatment, the larger the size of the bulking agent, that is, in small-capacity research vessels, the use of small particles is recommended, but when industrial reactors or piles are considered, the particle size of bulking agent increases. Thus, an industrial pile with limited turnings will require large particle sizes of bulking agent to facilitate natural aeration.

1.1.2. Moisture

Since composting is a biodegradation process, the available water content must be sufficient to the physiological requirements of the microbiota. Water not only transports the soluble substances for microbial feeding but also eliminates the waste products resulting from cellular metabolism. The optimum moisture content at the beginning is around 55–60% for sewage sludge composting [5]. Higher moisture contents can cause water to fill the micropores of the mixture and hinder the oxygenation, while lower contents cause the decrease in biological activity. Sewage sludge moisture is corrected with bulking agent that absorbs water, as long as porous and unsaturated bulking agents are used.

1.1.3. C/N ratio

The microorganisms overall use about 30 parts of carbon for each part of nitrogen for their metabolism, carbon for energy source and component of cells and nitrogen for protein and nucleic acid synthesis. It is widely known that the composting matrix is more adequate when it has an initial C/N ratio between 25 and 35. High ratio, as in agroforestry waste with high carbon content, involves a decrease in biological activity due to a lack of nitrogen for the metabolism and, therefore, a slowing down of the composting process. Low C/N values, as in municipal sewage sludge, involve an excess of nitrogen that can be lost through volatilization or leaching. Bulking agents improve this ratio by providing organic carbon to the sewage sludge mixture. Even though, the optimal C/N ratio is conditioned by the nature of the bulking agent, so if the carbon is part of compounds that are difficult to break down, such as lignin, it will only be slowly available for microorganisms [15].

Sometimes, it is not possible to condition the waste in the most suitable way in industrial compost facilities. Nutrient levels, specifically the C/N ratio, may not reach the values considered optimal, so the process must be controlled to reduce nutrient losses as much as possible.

Once the parameters related to the nature of the substrate have been established and corrected, the process must be monitored and controlled within appropriate values for each phase of composting, including temperature and oxygen.

1.1.4. Temperature

Temperature is one of the key factors that define the composting process in a way that a solid mixture reaches thermophilic temperatures that, sustained over time, make it possible to obtain compost free of parasites and weed seeds. The European Commission [16] proposes that temperatures must be maintained above 55°C for 15 days in windrow composting or 60°C for 1 week in in-vessel composting to achieve sanitation in biowaste. Excess temperature above 70°C is not convenient since it can cause the death of most microorganisms, delay colonization in later phases and, as a consequence, delay the degradation of the waste. Thus, the temperature during the process must be controlled to ensure that thermophilic temperatures are reached and sustained long enough to guarantee sanitation but not exceeding 70°C.

1.1.5. Oxygen

The maintenance of oxygen levels is a key factor for the development of an aerobic biological process. Oxygen concentration in the composting mass should not be less than 5% [17], since it would cause a succession toward anaerobic microorganisms and, therefore, toward undesirable fermentation processes and the generation of odors. To keep the oxygen levels in proper values during composting, the aeration of the mass must be controlled by forced and natural ventilation or turnings. In addition to supplying the oxygen demand for organic decomposition, aeration also favors the regulation of excess water and helps maintain the temperature at suitable values [5].

1.2. Composting systems

In general, the choice of a composting system or technology in an industrial facility depends on several factors such as type and quantity of waste, economic considerations, legal aspects, location, environmental aspects and product quality, and others [17]. **Table 2** shows some of the most common systems, classified according to their relationship with the environment and the mixing or change of position.

Diaz et al. [14] established a differentiation of composting systems into two groups: "windrow," which refers to the accumulation of the material to be composted in more or less elongated piles or rows, and "in vessel" where the material is confined within a reactor.

	Open systems	Semi-open systems	Closed systems
Statics	Piles/windrows with passive or forced aeration	Piles/windrows with aerated semipermeable cover	Containers/aerated tunnels
Dynamics	Turned piles/windrows/trenches	Turned piles/windrows/trenches in closed buildings	Dynamic tunnels drums

Table 2. Classification of the most commonly used composting systems [4, 14, 17].

From an operational point of view, it is considered that the composting process can be differentiated only in two stages. A bio-oxidative stage that corresponds mainly to the first two phases of the composting process, initial mesophilic phase and thermophilic phase, is characterized by high temperatures, elevated oxygen consumption, and the production of gaseous and liquid emissions [5]. This bio-oxidative stage is conditioned by the intensive organic matter decomposition and is usually developed with a specific technology and duration ranging from a few days to months in the industrial composting facilities. The second stage corresponds to the cooling and maturation phases. It usually lasts longer than the bio-oxidative stage although the dwell time is conditioned by the starting material characteristics and environmental and operating conditions of the facility [18]. The bio-oxidative stage is generally carried out using one of the technologies in **Table 2**, while the maturation period is carried out in piles or windrows, with more or less intervention depending on the idiosyncrasy of the facility or space available. In particular, most composting facilities that use "in-vessel" systems as technology involve the use of windrows to mature the compost [14]. A vessel system requires more investment but presents a greater control of the process: gas treatment, leachate collection system, data collection system of basic variables, watering, etc. The common dwell time in reactors or tunnels is around 14 days. Static reactors allow the monitoring of the process and, therefore, have been used in experimental research.

1.3. Research objectives

An industrial facility that periodically receives municipal sewage sludge should establish a working protocol which will optimize the composting process, ensuring the waste treatment under suitable conditions and time to obtain the highest quality compost. Obviously, it is crucial to know its initial characteristics since sewage sludge composition can be variable. For this reason, this work aims to (1) determine the inter- and intra-variability of municipal sewage sludge in physicochemical parameters, (2) establish the importance and effect of the bulking agent in the composting process of the municipal sewage sludge, and (3) check the reproducibility of the composting of sewage sludge from the same WWTP under the same conditions.

2. Sewage sludge characterization and composting

2.1. Inter-sludge variability

Municipal sewage sludge is characterized by its pasty or liquid consistency resulting from its high water content and small particle size. Physicochemical composition depends on the nature of the initial wastewater and on the technical characteristics of the treatments carried out on wastewater [19]. These treatments concentrate the compounds present in the wastewater, so sewage sludge contains a wide variety of dissolved, settled and suspended substances. It is not only a source of organic matter, nitrogen, and phosphorus but also accumulates substances with potential contamination such as heavy metals, pathogens, and organic pollutants (personal hygiene products, pharmaceutics, etc.).

This study compiles the physicochemical analysis of 35 samples of sewage sludge from different WWTPs of municipalities in southern Galicia (Spain) with populations between 1000 and 35,000 inhabitants. These facilities have secondary treatments for the wastewater with subsequent dewatering of sewage sludge produced. **Figure 2** shows the different aspect of the sampled sewage sludge.

All the parameters reflected those found in the literature for sewage sludge with similar characteristics (**Table 3**) [1, 20]. Moisture contents were lower than that observed by these authors; however, the values were homogenous despite being sampled from different WWTPs and seasonal periods. Sewage sludge composting requires moisture contents around 55–60% [5, 15] so the addition of bulking agents with low moisture allows not only reaching more adequate values of this parameter but also maintaining the structure and porosity of the mixture.

The content of organic matter is similar to the established ranges for untreated sludge despite they are sludge digested secondarily [1, 20]. Their high amount of organic substrates together with their high microbial load (inherent to their origin and the treatment with activated sludge) discourages direct disposal into the soil. Sewage sludge not enough stabilized incorporates pathogens and can cause rapid and uncontrolled biodegradation with the release of toxic substances. However, the high organic content makes these wastes suitable for treatment by biological techniques.

These sewage sludge had a pH close to neutrality that was not incompatible with microbial development, although acidic pH affects the availability of heavy metals because heavy metal cations are generally most mobile under acid conditions [19]. The electrical conductivity presented an important variability, but harmful values for the microbial development were not reached.

Total carbon correlated positively with the content of organic matter ($r = 0.76$, $p > 0.0001$), but this parameter presented greater variability with high values in some of the samples indicating

Figure 2. Municipal sewage sludge from two WWTPs in the south of Galicia (Spain).

	Mean	Median	Percentile 5–95%
Moisture (%)	84.0	85.3	76.8–87.4
Organic matter (%)	71.7	73.6	55.7–81.5
pH	6.8	6.8	5.9–7.9
Electrical conductivity (mS cm^{-1})	0.63	0.59	0.09–1.41
Total carbon (% dw)	35.8	36.1	28.1–40.1
Total nitrogen (% dw)	5.23	5.5	3.3–6.7
C/N ratio	7.2	6.5	5.7–12.2
P_2O_5 (% dw)	3.5	3.6	1.6–5.1
N-NH_4^+ (g kg^{-1} dw)	7.3	6.0	0.7–19.5

Table 3. Physicochemical composition of 35 sewage sludge samples in Galicia, Spain.

an insufficient digestion. Since the ideal ratio for composting is around 20–30 parts of carbon per part of nitrogen, the addition of a carbonated material is necessary to avoid excessive loss of nitrogen. The addition of crushed wood is widely used in industrial facilities for sewage sludge improvement in several aspects: increase C/N ratio, increase in porosity, and moisture control, and with this, the distribution of the oxygen is necessary for the development of the aerobic microorganisms inherent to the composting process. However, the excessive use of bulking materials or co-substrates is not desirable in a treatment facility as the treatment of a larger volume of waste is prioritized in order to optimize costs and resources.

It is well known the harmful nature of sewage sludge when certain compounds, such as heavy metals, reach concentrations above a specific threshold. The most important toxic heavy metals include chromium (Cr), cadmium (Cd), lead (Pb), zinc (Zn), copper (Cu), nickel (Ni), and mercury (Hg). Concentrations of heavy metals in sewage sludge may vary widely, depending on the sludge origins. The content of heavy metals in wastewater, especially those originated in industrial zones and large metropolitan areas, can impose a serious problem since the sludge tends to accumulate heavy metals that exist in wastewater [21]. The mobility of trace metals, their bioavailability, and related eco-toxicity to plants depend strongly on their specific chemical forms or ways of binding [1]. There is a general consensus in the scientific literature that aerobic composting processes increase the complexation of heavy metals in organic waste residuals and that metals are strongly bound to the compost matrix and organic matter, limiting their solubility and potential bioavailability in soil [22]. All heavy metals analyzed (**Figure 3**) showed a wide variability with values, without considering the outliers, of 18 times in copper, 20 times in lead, and 15 times in mercury, for example. However, these values are typical in sewage sludge [1].

The content of heavy metals in sewage sludge is frequently related to industrial density as a consequence of discharges to public sanitation. However, diffuse sources such as urban runoff and small household operations can contribute to contaminated discharges from an imposed residential area [23]. Also, high population agglomerations usually cause higher contents of

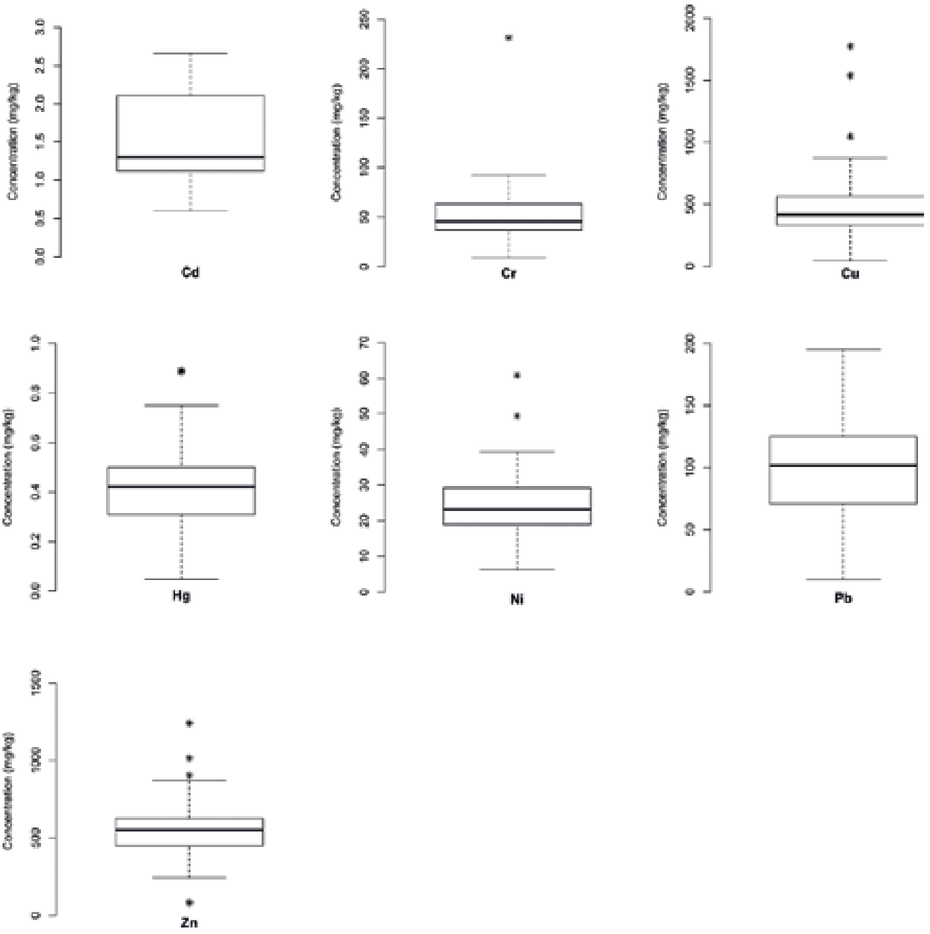

Figure 3. Distribution of heavy metals in sludge samples as revealed in the box plot diagram.

heavy metals in the wastewater. Sewage sludge samples analyzed in this study came from municipalities with different populations, from 1000 to 35,000 inhabitants, although no correlation was found between the population and the contents of heavy metals. The atypical values observed in Cr, Cu, Hg, Ni, and Zn can be attributed to point pollution, and it is considered that the sewage sludge do not present a high pollutant load. However, organic pollutants that are common in wastewater (antibiotics, hydrocarbons, detergents, etc.) have not been analyzed in this study. Aerobic composting has been extensively documented to reduce the concentrations of organic compounds via biological degradation [24–26].

2.2. Intra-sludge variability

To determine the variability of the physicochemical composition of the same sewage sludge, ten samples from the same WWTP were analyzed in a period of 5 years (**Table 4**). Although variability was observed in the parameters analyzed, this was lower than the inter-sludge

	Mean	Percentile 5–95%		Mean	Percentile 5–95%
Moisture (%)	85.5	84–87	Cd (mg kg^{-1} dw)	1.3	1.0–2.1
Organic matter (%)	75.0	71–79	Cr (mg kg^{-1} dw)	40.6	27.1–48.8
pH	6.8	6.2–7.4	Cu (mg kg^{-1} dw)	330	244–402
Electrical conductivity (mS cm^{-1})	0.55	0.1–1.1	Ni (mg kg^{-1} dw)	20.9	14.9–27.7
Total carbon (% dw)	36.3	33–40	Pb (mg kg^{-1} dw)	89.8	65–122
Total nitrogen (% dw)	5.75	5.2–6.6	Zn (mg kg^{-1} dw)	502	443–590
C/N ratio	6.3	5.8–6.8	Hg (mg kg^{-1} dw)	0.48	0.3–0.8
P_2O_5 (% dw)	4.6	3.9–5.3			
N-NH_4^+ (g kg^{-1} dw)	5.5	0.4–13			

Table 4. Analysis of physicochemical parameters of 10 sludge samples from the same WWTP for 5 years.

variability. It is important to highlight the greater homogeneity in the C/N ratio and moisture, while organic matter, total carbon, ammonium, and electrical conductivity had important oscillations. As the WWTP did not have operational alterations in the treatment process over the sampling time, it is assumed that the variability is a consequence of the input wastewater. Heavy rainfall can dilute wastewater, while water consumption in municipalities tends to decrease in the rainy season. However, no appreciable seasonal differences were found in the parameters studied, with more sampling being necessary to corroborate this observation.

The distribution of heavy metals corresponds with the lower quartile (values lower than the median) of inter-sludge heavy metal analysis, so it is a waste with low degree of contamination. Although the WWTP treats the wastewater of 25,000 inhabitants, the level of industrialization of the municipality is low, and the services sector dedicated to tourism is predominant, so the presence of heavy metals in the wastewater corresponds to domestic and residential operations with low inorganic pollution.

In industrial composting facilities, the sewage sludge is subjected to preconditioning which generally consists of mixing with bulking agents and other co-substrates and which must be based on the composition of the input waste. As observed, this composition is variable, and therefore it is necessary to know if this variability influences the development of the process in a significant way.

2.3. Bulking agent proportion

Using crushed wood it is possible to improve both the physical and chemical parameters of sewage sludge, so that the distribution of oxygen and macronutrients are more suitable for aerobic microbial growth necessary for the process. For the determination of the balance between bulking agent and sewage sludge, mathematical formulas or proportional rules can be used trying to reach the desired humidity, FAS, or C/N ratio [5, 17, 27]. The objective of this experience was to determine the proportion of bulking agent most suitable for the development of sewage sludge composting, taking as reference to the self-heating capacity of the waste and the capacity to maintain the thermophilic conditions. As sewage sludge is obtained after secondary treatment, some of the more readily available compounds have already been consumed, so the biodegradation process may be weakened or slowed down. Composting must guarantee maximum sanitization reaching high temperatures and presenting an extended thermophilic phase. In this way, organic matter is stabilized, and the content of pathogens inherent in wastewater is reduced or eliminated.

Therefore, a composting test was carried out on 12 static reactors of 30 L each one with aeration control using three different proportions in volume 3:1, 2:1, and 1:1 and bulking:sludge in triplicate (**Figure 4**). Sewage sludge characterized in **Table 4** was used. As a bulking agent, crushed wood with a size between 0 and 10 mm was used. This particle size has been the ideal one for a pasty residue and for the volume and characteristics of the reactors according to previous experiences. The main characteristics of this bulking material were moisture 32% and organic matter 90%. Composting in reactors facilitates the control of temperature (maximum 60°C), oxygen levels (minimum 5%) and the time and aeration regime (continuous and depending on the tracking parameters). Likewise, this system allows exhaust gases to be directed to a biofilter for odor control and the collection of leachates.

From an empirical point of view, the sludge and bulking mixture were done with difficulty due to the pasty character of this waste which tended to form clumps. In particular, the 1:1 ratio was the most complex mixture to make because some areas were not structured enough and converted the mixture into a dense mass that affected the compaction inside the reactor and produced possible anoxic areas. In contrast, the 3:1 ratio had a porous and looser structure, and most of the sludge was surrounded by wood particles. Oxygen levels remained over 8% in all proportions. **Figure 5** shows how the microbial activity and therefore the temperature responded to the conditions of the experiment. The municipal sewage sludge presented the adequate nutritional conditions for microbial growth according to what was observed in the evolution of temperature. This evolution was significantly different depending on the proportion of bulking agent ($p < 0.0001$). Although the lowest proportions experienced quick

Figure 4. System of 12 composting reactors of 30 L, each one inside a wooden box for the maintenance of adiabatic conditions (left) and mixture of bulking agent with sewage sludge in 3:1 proportion in volume (right).

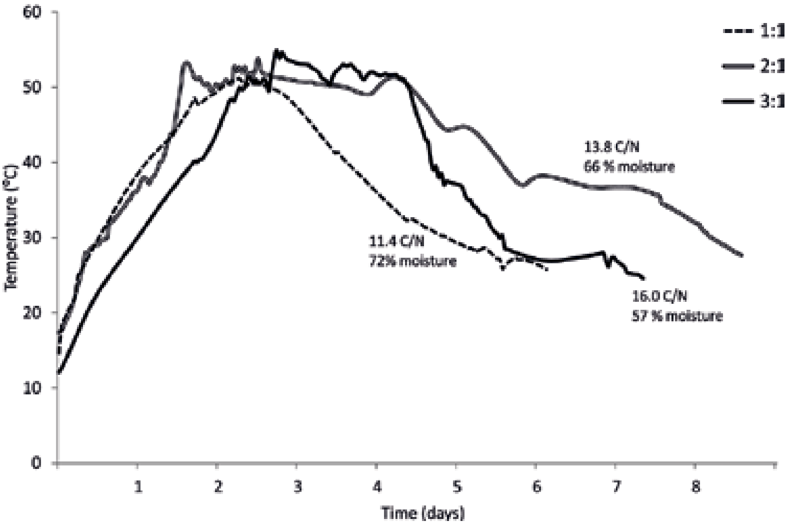

Figure 5. Evolution of the average temperature of the three proportions bulking agent:sludge inside the 30 L composting reactors.

self-heating, the 3:1 ratio was possibly slowed down as a result of the higher content of more recalcitrant carbonated substances that were difficult to break down. The maintenance period of thermophilic temperatures was higher in the 2:1 ratio (4 days), followed by 3:1 (3 days), and finally the 1:1 ratio (1.5 days). It is logical that the higher the content of sewage sludge in the mixture, the greater the content of substances that are easier to break down and the greater the amount of treated sewage sludge per unit volume. However, the 1:1 ratio maintained lower microbial activity that, in line with what was observed during mixing, can be a consequence of its greater compaction and the presence of preferential aeration channels in the mass that prevent a correct distribution of air. After reaching temperatures lower than 35°C, the process was completed, and a high colonization of fungi was observed in some reactors (**Figure 6**). The mass balance after 9 days of the process showed organic matter losses of 10% (2:1), 4.5% (3:1), and 1.6% (1:1). Although 3:1 ratio reached the maximum temperature, there

Figure 6. Development of fungi in reactors with a 2:1 ratio (left) and emptying of a reactor with a 3:1 ratio (right).

was a quick thermal decline after the thermophilic phase which, added to the slight loss of organic matter, indicates that the more porous structure of the mass caused a rapid cooling that prevented the support of temperature and biodegradation at an intensive level.

The bulking:sludge ratio more suitable from the point of view of temperature, in the short term considered in this experiment, was the ratio 2:1, although its initial moisture content was not considered optimal and its C/N ratio could facilitate the loss of nitrogen. This proportion allows greater treatment of sewage sludge per unit volume than the 3:1 ratio in an industrial treatment facility.

2.4. Composting reproducibility

The following experiment consists of the comparison of composting experiences on a larger scale that have a purpose to verify the reproducibility of the sewage sludge process with a 2:1 ratio (bulking:sludge). In this way, the same sewage sludge as in sections 2.2. and 2.3. (**Table 4**) was sampled six times. Crushed wood was used as a bulking agent, but the particle size was adapted to reach a 30% FAS in the mixture [5] and to the highest reactor volume (600 L), considering wood particles between 0 and 30 mm as optimal. Each mixture bulking:sludge was introduced into the reactor (**Figure 7**), the temperature and oxygen levels were controlled by forced aeration, and processes were finished when the temperature dropped to environmental values after the thermophilic phase.

Compared with the previous experience, the initial C/N varied remarkably (8–16), especially due to the wide fluctuations of the initial carbon. Also, moisture contents were higher than in the previous experiment. Regarding the development of the process (**Figure 8**), the evolution of the temperature was significantly different ($p < 0.001$), and two groups can be differentiated: a group of reduced thermophilic phase constituted of sewage sludge reactors 1, 2, and 3 (SS1, SS2, and SS3) and a group of prolonged thermophilic phase constituted of sewage sludge reactors 4, 5, and 6 (SS4, SS5, and SS6). Notable differences were observed in terms of high-temperature conditions: from 3 days under thermophilic conditions in SS1 to 18 days in SS6. Thus, it was observed that the higher the C/N ratio, the greater the capacity to maintain the thermophilic conditions (SS5 and SS6), while the influence of this

Figure 7. Composting reactor of 600 L equipped with a fan, recorder, and control of process parameters and biofilter (left) and colonized mixture of bulking agent with sewage sludge in 2:1 proportion in volume after process time (right).

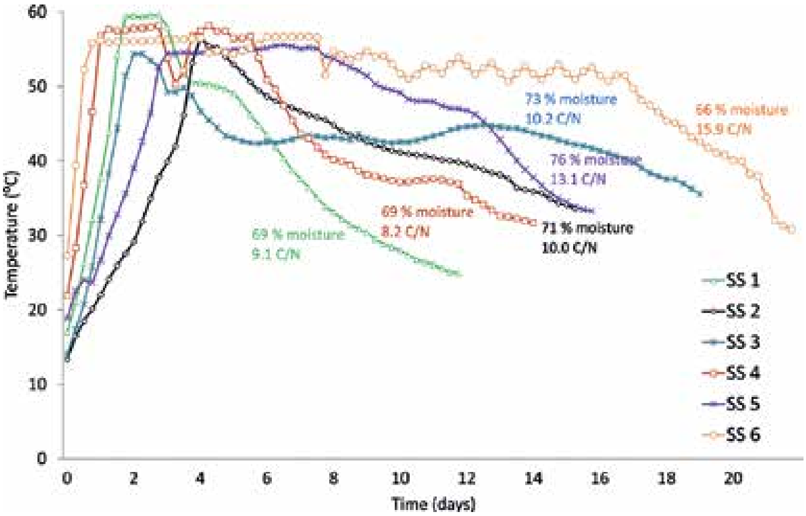

Figure 8. Evolution of temperature during the reactor phase of sewage sludge from the same WWTP at different sampling periods mixed with bulking agent.

parameter on the initial self-heating capacity was not observed. However, the time to reach thermophilic values slowed down with high moisture contents (> 70% moisture), contrary to the experience in 30 L reactors.

As a result of the research, it can be extrapolated that a ratio of 2:1 (bulking:sludge) does not reach the ideal moisture for the composting process, but if the C/N ratio exceeds 10 and the moisture is below 70%, the maintenance of the thermophilic conditions seems to be prolonged. In an industrial compost facility, it is very complicated to establish an ideal mixing protocol for a specific sewage sludge since the variability of the input material causes important variations in the development of the composting process.

2.5. Compost analysis

After emptying the reactors from the reproducibility test, the pre-composted materials were turned and kept in piles for 90 days to mature, and next, compost analyses were performed (**Table 5**). Variability can be observed in the general characteristics established by the legislation on fertilizer products [28] and other important parameters of stability and maturation of compost [29, 30].

It is important to note that organic matter is high in some samples as a consequence of the short periods under thermophilic conditions and that the finest fraction of the bulking agent becomes part of the compost after sieving, increasing this parameter. However, the organic matter is reasonably stabilized with low respiratory activities (less than mg O_2 g^{-1}SV h^{-1}) and poor self-heating of the compost with maximum rating for this test (classes IV and V). Likewise, the germination indexes were high (> 80%) which allows the use of compost without harming the plant growth. The pathogens were within the values for the use of compost, and all experiences allowed sanitation although the group of reduced thermophilic phase (SS1, SS2, and SS3) presented the highest values of *Escherichia coli*.

	Range	Spanish Fertilizers Law [28]		
Moisture (%)	51–66	< 40		
Organic matter (%)	66–75	> 35		
pH	5.4–6.2	—		
Electrical conductivity (mS cm^{-1})	0.9–1.2	—		
Total carbon (% dw)	33–38	—		
Total nitrogen (% dw)	2.9–3.4	—		
C/N ratio	10–14	< 20		
P_2O_5 (% dw)	3.3–3.5	—		
Basal respiration (mg kg SV h^{-1})	100–330	—		
Self-heating test	IV–V	—		
Germination index (%)	96–108	—		
Salmonella spp. (in 25 g)	Absence	Absence		
Escherichia coli (ufc/g)	<10–800	<1000		
		Class A	*Class B*	*Class C*
Cd (mg kg^{-1} dw)	0.8–1.6	0.7	2	3
Cr (mg kg^{-1} dw)	38–52	70	250	300
Cu (mg kg^{-1} dw)	240–300	70	300	400
Ni (mg kg^{-1} dw)	21–26	25	90	100
Pb (mg kg^{-1} dw)	54–84	45	150	200
Zn (mg kg^{-1} dw)	300–480	200	500	1000
Hg (mg kg^{-1} dw)	0.3–0.4	0.4	1.5	2.5

Maximum values allowed in the Spanish fertilizers law for compost are included

Table 5. Maturity and stability parameters in sewage sludge composts from the same WWTP sampled in different times and composted in 2:1 ratio bulking:sludge in static reactor and followed by pile maturation.

The Spanish legislation on compost, Royal Decree 506/2013 of 28 June on fertilizers [28], classifies compost into three categories according to the heavy metal content: classes A, B, and C. The content of Cd, Ni, Pb, Zn, and Cu assumes that all composts are classified as class B. So, low inorganic pollution in input sewage sludge allows meeting the quality criteria for the use of compost as an organic amendment. Although the sewage sludge evolved differently inside the reactor, maturation in a pile for 90 days seems to assimilate the composition of the composts.

3. Conclusions

The development of cities and the centralization of sanitation services mean that the sewage sludge produced in wastewater treatment plants has a growing presence in our society.

Composting is a viable alternative for sludge management, but initial characteristics of the waste must be determined for process optimization. The municipal sewage sludge presents high inter- and intra-variability in key parameters for the evolution of the composting process such as moisture and the C/N ratio. The levels of heavy metals in specific samples of sewage sludge are not useful information if there are no periodical analyses to detect point pollution or seasonal changes. The addition of bulking agent is necessary for the development of the composting process, but its size and proportion must be adapted to the waste composition, the composting system used, and the volume of treatment. The variability in sewage sludge composition makes it difficult to establish treatment protocols in industrial composting facilities, although the establishment of minimum process conditions is necessary, for which the use of a minimum proportion of bulking agent:sludge 2:1 in volume is recommended. Despite the different evolution of the composting process, if the initial sewage sludge presents average composition, the compost achieves adequate quality parameters.

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Wastewater treatment and sludge disposal are important for protecting receiving rivers, lakes, and other water bodies, and vital for human health. Since excessive discharge may cause eutrophication and deterioration of aquatic systems, the US EPA and other national agencies have set guidelines for wastewater discharge standards. Conventional technologies are well developed and widely applied worldwide for wastewater treatment; however, new ideas and new technologies are gaining additional interest for the sake of water and energy reuse. While water is essential in arid regions, wastewater reuse and recycling have been playing an important role in human life. Although there are no universal standards for industrial and agriculture reuse, balancing wastewater treatment and public health protection presents challenges and opportunities.

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