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Persistent Organic Pollutants

Edited by Stephen Kudom Donyinah

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Meet the editor

Dr. Stephen Kudom Donyinah is currently a senior lecturer in the Department of Petroleum Engineering, KNUST, Kumasi. He holds a PhD in Environmental Science and Engineering (2004) and Postgraduate Training in Computer Simulation and Applications to Petroleum Engineering, Geology and Related Subjects in the Oil and Gas Industry (2001), both from the China University of Geosciences, PR China. He also holds a BSc (Hons) in Geological Engineering from KNUST, Kumasi (1990), and an MSc in Petroleum Engineering, Oil and Natural Gas Exploration (1996). In October 1995, Dr. Donyinah was a visiting scholar to Stanford University, CA, USA. In 2002, he was awarded the "Who is Who Award for Achievement in Science" by the International Biographical Center based in Cambridge, England. Dr. Donyinah has also participated in short courses in PetroSkills Training in Houston, Texas, USA, in 2010, 2012, and 2013, respectively. He is an associate member of the American Association of Petroleum Geologists and the Ghana Institution of Engineers. He speaks French and Mandarin Chinese fairly well. He was one of the pioneer lecturers in the Petroleum Engineering Program that was introduced into KNUST in September 2004. He has over 36 years of working experience with KNUST but is now retired and doing a post-retirement contract with the university. During his active lecturing years, he offered courses to students in chemical engineering, geological engineering, physics, and science departments.

His research interest is in deep-sea geology, environmental science, and engineering.

Contents

Preface

Persistent organic pollutants are organic compounds that for their persistent nature require scientific attention and study. It is with this in mind that authors with different backgrounds and specialties have written a number of interesting articles that are now compounded in this book. It is hoped that readers will find it useful and interesting.

The originality of the articles is ascertained and the work has gone through strict standards that make for interesting reading.

Acknowledgment

The work could not be completed without the assistance of the following:

First of all I wish to thank the Almighty God for the opportunity to edit this book on persistent organic pollutants. I also wish to thank Ms. Marijana Francetic, Author Service Manager, for her guidance and patience in assisting me to carry out the editing of the articles sent by the authors. I also wish to thank Ms. Lily Vugah of the Department of Geomatic Engineering of KNUST for her assistance with IT in editing this work.

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Introductory Chapter: Persistent Organic Pollutants (POPs)

Stephen Kudom Donyinah

Additional information is available at the end of the chapter

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1. About POPs

According to the World Health Organization (WHO), persistent organic pollutants (POPs) are chemicals of global concern due to their potential for long-range transport, persistence in the environment, ability to biomagnify and bioaccumulate in ecosystems, as well as their significant negative effects on human health and the environment. The WHO further indicates humans are exposed to these chemicals in a variety of ways: mainly through the food we eat but also through the air we breathe, in the outdoors, in the indoors and at the workplace. The WHO further explains that many products used in our daily lives may contain POPs, which have been added to improve product characteristics, such as flame retardants or surfactants. This property renders POPs to be found virtually everywhere on our planet in measurable concentrations [1].

2. How POPS are manifested chemically in life

According to the WHO report, the most commonly encountered POPs are organochlorine pesticides, such as DDT, industrial chemicals, most notably polychlorinated biphenyls (PCB), as well as unintentional by-products of many industrial processes, especially polychlorinated dibenzo-p-dioxins (PCDD) and dibenzofurans (PCDF), commonly known as ‘dioxins’ [1].

3. Characteristics of POPs

The WHO report further indicates that POPs biomagnify throughout the food chain and bioaccumulate in organisms. The highest concentrations of POPs are thus found in organisms

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at the top of the food chain. Consequently, background levels of POPs can be found in the human body [1].

4. The human risks to POP exposure

Human exposure—for some compounds and scenarios, even to low levels of POPs—can lead, among others, to increased cancer risk, reproductive disorders, alteration of the immune system, neurobehavioral impairment, endocrine disruption, genotoxicity and increased birth defects [1].

POPs as could be seen from above summary are indeed environmental threats that need to be addressed with all seriousness. Their mode of transmission is by atmospheric, and they can find their ways in all aspects of the environment (air, water and soil), and what is making it more dangerous is their persistent nature and most of them being non-biodegradable [2].

Health risk is the most important thing to note and pay particular attention to avoid contraction of example carcinogenic diseases that are life-threatening. It is no wonder that some of the chemicals such as DDT have been banned from usage in modern times. In places where they are found such as in lake sediments and other areas are difficult to remediate and difficult to repair when any damage has been done [3].

There is therefore the urgent need to give the maximum attention and try not to contaminate fresh waters and further spread it in the environment. People should be forewarned about its imminent dangers and try to avoid the dissipation of these dangerous chemicals into the environment.

There is the need to further research into possible areas suspected to be already contaminated such as farmlands where pesticides have been applied and their possible spread around. Taking note also of the fact, some of these dangerous pesticides could reach far more areas than could be imagined, and the strict adherence to the banning of some of them should be observed [4].

Scientists should be encouraged to publish their findings from research and data compiled. The research should target specific environments and the problems well addressed to ascertain what POPs have done to those environments.

The following areas of attention need to be concentrated:

- Dissemination of POP chemicals into the food chain
- Effects of POPs on rural drinking water
- Atmospheric transfer of POPs into the environments
- Harmful effects of POPs
- Managing common sources of POPS

- Anthropological effects of POPs
- The environmental effects of POPs from application of pesticides

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Dissemination of Endosulfan into the Environment

Claudia Rosales Landeros,
Carlos Eduardo Barrera Díaz and Bryan Bilyeu

Additional information is available at the end of the chapter

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Abstract

Organochlorine pesticide pollution of surface water, groundwater, soil, sediments, and air has been recognized as a major problem in many countries because of the persistence in different environments and the consequent potential adverse health effects. This report presents a review of literature on organochlorine insecticide of endosulfan, which has been used extensively for agricultural purposes. It summarizes information on nomenclature, physical-chemical properties, production, metabolism, degradation, distribution in the environment, toxicity, regulation, and technologies for the treatment of water and soil contaminated with this pesticide.

Keywords: persistence, pesticide, pollution, toxicity

1. Introduction

Although pesticides are economically advantageous in agriculture, increasing crop yields, they do generate environmental problems [1]. Some of the most problematic pesticides are the organochlorinated ones, where chlorine is incorporated in organic molecules. Organochlorinated pesticides are highly effective and long lasting. However, these properties lead to environmental persistence and resistance to degradation, thus they are classified persistent organic pollutants. Typical organochlorinated pesticides include DDT, aldrin, dieldrin, endrin, heptachlor, endosulfan, and others.

Endosulfan has been used on a variety of crops including broccoli, potatoes, coffee, cotton, peaches, apples, nectarines, prune, lettuce, tomatoes, grapes, melons, cauliflower, carrots, cabbage, rape, strawberry, alfalfa, beans, cereals, cucumber, tobacco, tea, oil crops, and some

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ornamental flowers to attack pests [2–4]. It typically enters the atmosphere through agricultural application and can be transported long distances in the air. The levels in the air vary substantially depending on the location. Rural areas tend to have higher levels. Endosulfan half-life in soils is estimated to range from 60 to 800 d, while its half-life in groundwater and sediments may increase up to 6 years [5–8].

In this chapter, a complete physicochemical description of endosulfan is presented. The degradation sub-products, toxicity, and environmental impacts are described. Finally, some technologies that have been recently applied to treat the residues are described.

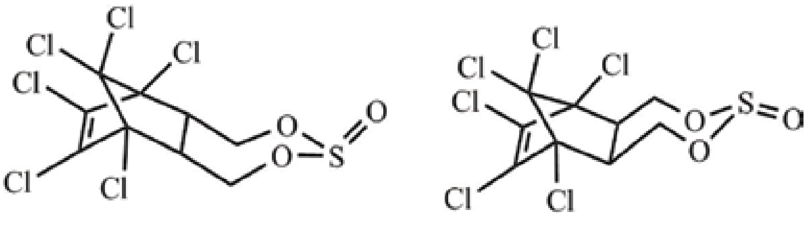
2. Chemical aspects

Endosulfan is an organochlorine insecticide (6,7,8,9,10,10-hexachloro-1,5,5a, 6,9,9a-hexahydro-6, -9-methane-2,3,4-benzo-dioxathiepin-3-oxide) with a CAS Number 115-29-7 that has a cyclodiene structure. It contains a sulfite diester group that is relatively reactive and infers persistence in the environment. The condensed chemical formula is $C_9H_6Cl_6O_3S$.

This pesticide has been widely used since its introduction in the 1954 by Farbwerke Hoechst because it has a broad spectrum of activity. The commercial grade of endosulfan is a mixture of α- and β-endosulfan isomers (**Figure 1**), in a 7:3 ratio, respectively. Its main degradation product is endosulfan sulfate, which has similar properties to the compounds of origin [9–11].

3. Trade names, formulations, and use

Some of the trade names that have been given to endosulfan are Cyclodan, Thiodan, and Thiosulfan, among others that can be found elsewhere [12]. The trade formulations of endosulfan are emulsifiable, microencapsulated, powder, wettable powder, granules, technical powder, technical solid, and technical liquid, with a concentration for agricultural use of 350–500 d of active ingredient (AI)/L or kg and for industrial use the concentration is 940–970 (AI)/L or kg [13].



α endosulfan

β endosulfan

Figure 1. Structure of isomers α and β endosulfan.

4. Physicochemical properties

Table 1 shows some physicochemical properties of α-endosulfan, β-endosulfan, and endosulfan sulfate [14, 15].

Some of the environmental fates of the endosulfan are related to its physicochemical properties. For instance, the aqueous solubility of the α-isomer is higher than the β-isomer and endosulfan sulfate. Compounds whose solubility is less than 25 mg L^{-1} tend to be immobilized in soils and living organisms. The three molecules have partition coefficients octanol-water > 1. Therefore, they are easily absorbed through biological membranes and accumulate in fatty tissues.

Another important characteristic is the vapor pressure. Endosulfan sulfate is the least volatile with a vapor pressure of 10^{-7} mm Hg, so is more persistent in soil and water. The isomers of endosulfan are semi-volatile, with similar vapor pressures to other chlorinated pesticides, making them susceptible to volatilization to the atmosphere with subsequent atmospheric transport and deposition.

One of the criteria for designing of a chemical as a persistent organic pollutant (POP) is that it has log Kow > 5, both endosulfan isomers and endosulfan sulfate do not exceed this value but are close to it, suggesting a potential for bioaccumulation. The relatively high Koc values indicate a propensity for partitioning to the organic carbon fraction in soils and sediments for both endosulfan isomers and the sulfate [3, 15].

Properties	α-Endosulfan	β-Endosulfan	Endosulfan sulfate
Water solubility pH 5, 25°C, mg/L	0.33	0.32	0.22
Henry constant atm m^3/mol. 25°C	1×10^{-5}	1.91×10^{-5}	2.61×10^{-5}
Vapor pressure at 25°C mm Hg	1×10^{-5}	1×10^{-5}	1.0×10^{-11}
Log. octanol-water partition coefficient (Kow) pH 5.1	3.83	3.62	3.66
Log. octanol-air partition coefficient (Koa)	10.29	10.29	5.18
Log. octanol-carbon partition coefficient (Koc)	3.5	4.1	No data
LD_{50} rats (mg/kg)	76	240	160

Table 1. Physicochemical properties of α-endosulfan, β-endosulfan, and endosulfan sulfate.

5. Production of endosulfan

The global production of endosulfan was approximately 18,000–20,000 t annually from 1958 to 2000 with a cumulative global use of 300,000 tons. Approximately one third of this was generated in India, but it had agreed to phase out its use in 2017. China produced approximately 5000 tons per year, and the remaining endosulfan was produced by Israel, Brazil, and South Korea [16]. Regarding the consumption of endosulfan, India was the main consumer 113,000 t from 1958 to 2000, followed by the United States with 26,000 t from 1954 to 2000. In China, annual use is estimated to average 2800 t/y during the period 1998–2004 [3]. Endosulfan is prohibited in 80 countries; some countries have registered only a few commercial products containing endosulfan, other countries have registered dozens of commercial products from various formulators. Endosulfan is now still produced and widely used in the crop fields in most of the developing countries, due to its effectiveness and low application cost [17].

6. Distribution of endosulfan in the environment

Endosulfan is widely distributed in the environment and can be detected in all media, soil, sediments, air, water, and vegetation, over long distances from the application source. Levels of endosulfan in the air samples are very variable depending on the location. Recent measurements indicate that around 320 d is the half-life in the atmosphere [18].

Endosulfan is one of the most abundant organic pesticides in the atmosphere and is capable of reaching remote locations such as the Arctic. The presence of endosulfan in the Arctic at concentrations between 3 and 8 pg m^{-3} has been detected. Endosulfan concentration was obtained using an XD-based passive sampler with samples collected in monitoring stations.

It has been suggested that the transport of endosulfan occurs when the compound volatilizes from warmer regions, experiences long-range atmospheric transport, and condenses again, permitting an accumulation of the substance in temperate regions, higher mountains, and the Arctic. Endosulfan residues in snow and ocean waters in the Artic indicate that atmospheric deposition of endosulfan is taking place, and it can promote bioaccumulation in zooplankton and various species of fish. For some biota, a biomagnification factor for α-endosulfan from fish to seal is also occurring [3, 19–21].

7. Degradation of endosulfan

Figure 2 shows the oxidation pathway of endosulfan; it has been reported that even though some hydrolysis takes place, at environmental conditions, the most common product is endosulfan sulfate [2, 16, 22]. After initial oxidation, four intermediates are detected until endosulfan lactone is reached. In further oxidation, the complete mineralization can be obtained. Endosulfan is relatively resistant to photodegradation but its metabolites, including endosulfan sulfate, are susceptible to photolysis [23]. **Figure 2** shows the main pathways of endosulfan degradation.

In aquatic systems, the α-isomer is converted more readily to endosulfan sulfate than the β-isomer. Various studies that have observed the degradation of endosulfan in aqueous phases identified hydrolysis as the dominating abiotic degradation process resulting in the

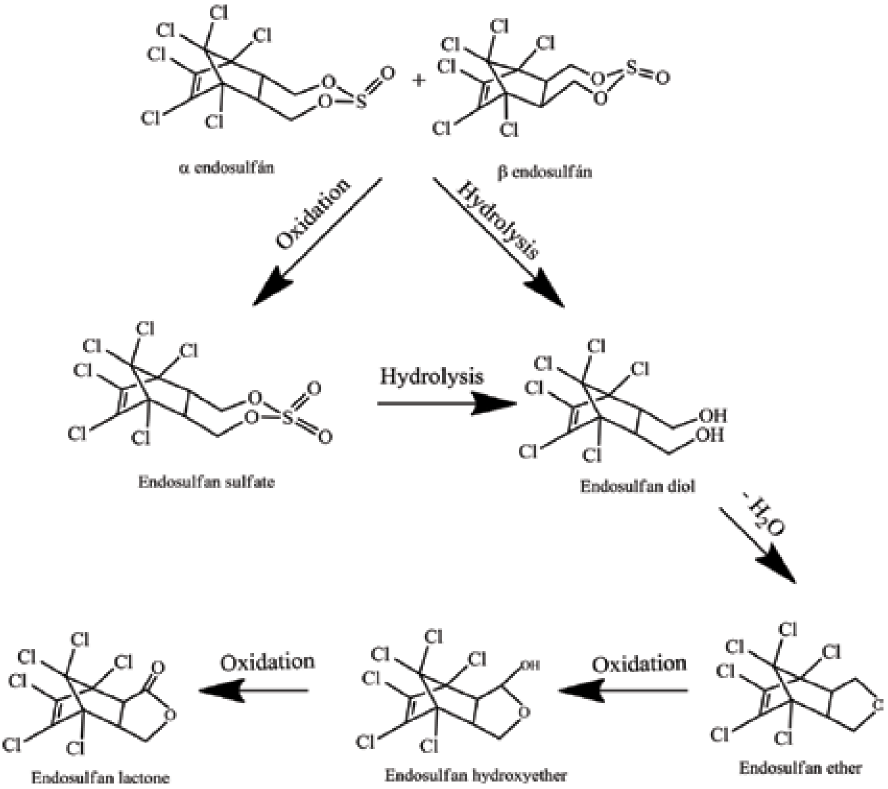


Figure 2. Degradation of isomers α- and β-endosulfan.

formation of endosulfan diol. A positive correlation between hydrolysis rate (khydro) and pH, with base-driven hydrolysis, a predominant degradation process in seawater conditions, allows a rapid degradation of endosulfan into endosulfan sulfate, whereas it takes longer in pure water.

Furthermore, hydrolysis of endosulfan sulfate to endosulfan diol is markedly slower compared to the hydrolysis of α-endosulfan.

The biodegradation of endosulfan has been reported in anaerobic conditions; these conditions predominate in sediments and the results can contradict the interpretation of the isomer deposition in freshwater sediments. At neutral pH and aerobic conditions, the degradation of endosulfan by biological oxidation has also been reported, being sulfate of endosulfan, the compound with the heaviest concentration.

It has been reported that the decomposition of endosulfan in aqueous solution can take place, but some natural environmental factors lead to the formation of sulfate indicating that some oxidation pathway is followed. The values are much lower than the persistence criteria designated for a POP, although in the colder marine waters at high latitudes, base-driven hydrolysis half-lives for endosulfan are likely to be greatly extended, compared to warmer waters in temperate or tropical regions [3, 15, 23].

There are relatively few studies that have examined the persistence of endosulfan in soil under field conditions. Degradation rates strongly depend on the soil conditions (particularly soil water content and ambient temperature).

The Environmental Protection Agency (EPA) indicates that concentrations above 0.22 $\mu g\ L^{-1}$ (acute) and 0.05 $\mu g\ L^{-1}$ (chronic) have adverse impacts on the health of aquatic organisms. To avoid intoxication from water consumption, fish or shellfish from water bodies near fields where the pesticide is used, concentration limits need to be established. For air concentrations, the limit recommended by the National Institute for Occupational Safety and Health (NIOSH) is 0.1 $mg\ m^{-3}$ [22, 24].

8. Regulation of endosulfan

Health authorities and legislators have implemented strategies for the use of pesticides due to the thousands of deaths reported every year due to the indiscriminate use of these substances. In 1985, the code of conduct on the distribution and use of pesticides by the United Nations Food and Agriculture Organization (FAO) was published to regulate the use and availability of pesticides. For a safe use of pesticides, several actions need to be undertaken; in the case of farmers, education on the application of products needs to be provided, government inspectors require to check the application of pesticides in the crop fields within the framework of FAO's Integrated Pest Management System [25].

9. Stockholm convention

This convention that deals with persistent organic pollutants (POPs) is an international treaty for the protection of human health and the environment from the effects of chemical compounds that remain for long periods in the environment, are widely distributed, and accumulate in the fatty tissues of humans and animals. The exposure to these compounds can result in serious health problems, such as some cancers, birth defects, and deficient immune and reproductive systems, among others [12].

The POP Review Committee (POPRC) is a scientific body created to review the chemical compounds that are proposed for inclusion in the text of the Annexes A, B, or C of the convention. Endosulfan was presented for inclusion in Annex A by the European Union in November 2007. The Committee of Review issued the decision POPRC-4/5, it specifies that "the selection criteria for endosulfan have been met" and a working group was established to elaborate a draft risk profile in accordance with Annex E of the Convention [12].

The information was requested from Parties for Annex F as well as the review of additional information on the adverse effects of endosulfan on human health [12, 15]. After evaluating the risk profile and finalizing the risk management evaluation, the POPRC, at its sixth meeting held in Geneva from October, 11 to 15, 2010, decided to recommend to the Conference of the Parties the inclusion of technical endosulfan, its α- and β-isomers as well as the main degradation product, the sulfate of endosulfan in Annex A of the Stockholm Convention for global elimination with possibility of specific and temporary exceptions [15].

10. Rotterdam Convention

This exchange under the Rotterdam Convention on "prior informed consent" applies to banned or restricted chemicals and to the severely hazardous pesticide preparations listed in Annex III. Currently, there are more than 30 chemical products to which the PIC procedure applies. At the fifth meeting of the Conference of the Parties to the Rotterdam Convention that took place in Geneva, Switzerland, between June 21 and 24, 2011, it was agreed to include the endosulfan pesticide in Annex III of the Convention.

Previously, the seventh meeting of the Chemical Review Committee, held in Rome from March 28 to April 1, 2011, recommended the inclusion of a number of new chemicals in this Annex, including the pesticide endosulfan that had recently added to the list of the Stockholm Convention of chemical substances that must be eliminated [26].

11. Recent technologies to treat endosulfan present in water and soil

Nowadays, there is a concern for the development of alternatives for the elimination of endosulfan in both water and soil. In this context, advanced oxidation processes (AOPs) are considered a highly competitive technology for the removal of those organic pollutants not treatable by conventional techniques. All AOPs produce •OH radicals, they are very reactive, attack most organic molecules, and are not highly selective. The generation of •OH radicals is through different reagent systems, which include photochemical degradation processes (UV/O_3, UV/H_2O_2), photocatalysis (TiO_2/UV, photo-Fenton reactives), chemical oxidation processes (O_3, O_3/H_2O_2, H_2O_2/Fe^{2+}), and electrooxidation (BDD electrodes) [27].

Others treatments for pesticides are biodegradation and bioremediation; both of these are based on the conversion or metabolism of pesticides by microorganisms. The difference between these two is that the biodegradation is a natural process, whereas bioremediation is a technology. One disadvantage of these processes is that they require a long time to degrade the pesticide [28].

One of the technologies most resorted to eliminate pesticides present in water is adsorption with activated carbon, as it can be applied at a large scale. Good characteristics of activated carbon include large surface area and well distributed porosity [29].

Table 2 shows some technologies that have been developed to degrade endosulfan present in water and soil.

Treatment	**Matrix**	**Conditions**	**Efficiency**	**Reference**
Electrooxidation by boron-doped diamond anode	Water	Concentration of endosulfan: 6 g/L Supporting electrolyte: NaCl (1 g/L) Current density: 60 mA cm^{-2} Reaction time: 2 h pH: 6	81% removal COD	[30]
Ozonation	Water	Concentration of endosulfan: 10 mg/L Ozone dosage: 57 mg/min Reaction time: 60 min pH: 10	93% removal endosulfan	[31]
Fenton	Water	Concentration of endosulfan: 7.5 mg/L $FeSO_4$ dose: 50 mg/mL H_2O_2 dose: 236 mg/mL Reaction time: 1 h pH: 3 Temperature: 30°C Continuous shaking: 130 rpm	83% removal endosulfan	[32]
Adsorption with sawdust carbon	Water	Concentration of endosulfan: 20 mg/L Adsorbent: 0.2 g Contaminated water: 200 mL pH: 7 Contact time: 250 min Agitation rate: 200 rpm	95% removal endosulfan	[33]
Biodegradation by *Aspergillus niger*	Soil	Concentration of endosulfan: 400 mg/ml Soil: 5 g Incubation time: samples were taken at 12 h interval up to 144 h Temperature: 30 ± 2°C Rotary shaker: 120 rpm pH: 6.8	Complete disappearance of endosulfan	[34]
Photocatalytic degradation with the elution of surfactants	Soil	Concentration of endosulfan: α- and β-endosulfan 12.03 and 6.87 mg/kg, respectively. Soil: 25 g Photocatalyst: nitrogen-doped anatase TiO_2 under visible-light irradiation. Eluents: Tween 80, SDS and Na_2SiO_3 Reaction time: 240 min Temperature: 25 ± 2°C in dark Rotary shaker: 200 rpm pH: 6.23	Complete degradation	[35]

Treatment	Matrix	Conditions	Efficiency	Reference
Nano-phytotechnological using zero-valent iron nanoparticles	Soil	Concentration of endosulfan: 1139 µg/Kg of soil Plants: *A. calcarata, O. sanctum, C. citrates* Temperature: 30 ± 3°C and natural light Contact time: 28 d nZVIs: 1000 mg/kg	The maximum % removal endosulfan was with *Alpinia calcarata* 94.9%	[36]

Table 2. Technologies for degradation of endosulfan present in water and soil.

12. Conclusions

One of the most important economic activities worldwide is agriculture. Form the early 50s and owing to population growth, intensive agriculture practice has been carried out. In this kind of massive production, an excess of chemical substances was used, among them, pesticides. Endosulfan has been one of the most used pesticides due to its wide spectrum of activity; nevertheless, it has very negative consequences on the environment. The physicochemical properties of endosulfan favor bioaccumulation and biomagnification, and it is considered a persistent organic compound; thereby, in 2007, it was proposed to be included in the Stockholm agreement, aim that was reached in 2010. Thanks to the information gathered, a large number of countries have banned the use of endosulfan; however, many other countries still use it on their fields. It has been found that endosulfan is transported to zones considerably far from the application fields, as an example, endosulfan has been detected in the Arctic. Although a large number of countries have opted not to make use of this pesticide, research continues in order to find out how to eliminate it from soil, sediments, water, and a proper disposal of the product that that will be no longer used [37–39].

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Degradation Pathways of Persistent Organic Pollutants (POPs) in the Environment

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Additional information is available at the end of the chapter

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Abstract

Persistent organic pollutants (POPs) are resistant to most of the known environmental degradation processes. Because of their persistence, POPs bioaccumulate in animal tissues and biomagnify along food chains and food webs with potential adverse impacts on human and wildlife health and the environment. Although POPs are resistant to most of the environmental degradation processes, there are some environmental processes mostly microbial degradation that can degrade POPs to other forms that are not necessarily simpler and less toxic. The Stockholm Convention on Persistent Organic Pollutants adopted in 2001 was meant to restrict the production and use of these toxic chemicals in the environment.

Keywords: degradation, POPs, bioaccumulation, biomagnification, Stockholm convention

1. Introduction

Persistent organic pollutants (POPs) are toxic organic compounds that are resistant to most of the degradation processes in the environment, and therefore they tend to persist in the environment, thus bioaccumulating in organisms and biomagnifying along the food chains and food webs in ecosystems. POPs pose a risk of causing adverse effects to human and wildlife health in particular and the environment in general. POPs include a wide class of chemical species with different physicochemical properties and toxicologies. The priority list of POPs consists of pesticides such as dichloro diphenyl trichloroethane (DDT), hexachlorocyclohexanes (HCHs), and hexachlorobenzenes (HCBs), industrial chemicals such as polychlorinated biphenyls (PCBs), and unintentional by-products of industrial processes such as

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polychlorinated dibenzo-*p*-dioxins and dibenzofurans (PCDDs/PCDFs) and polycyclic aromatic hydrocarbons (PAHs). The first priority list of POPs consisted of 12 compounds commonly referred as the dirty dozen by the Stockholm Convention that was adopted in 2001.

Over the last decade, the priority list of POPs has been updated to include such compounds like brominated flame retardants (BFRs), such as polybrominated diphenyl ethers (PBDEs), listed under the Stockholm Convention in 2017 [1], and hexabromocyclododecanes (HBCDDs), currently under consideration for listing. A further group of recently recognized halogenated POPs are the perfluorinated alkyl substances, of which perfluorooctane sulfonate (PFOS), its salts, and perfluorooctane sulfonyl fluoride were also added to the Stockholm list in 2017. Other compounds in the new list include endosulfan, lindane, pentachlorobenzene, chlordecone, and hexabromocyclododecane (HBCD).

POPs have a tendency to persist in the environment for long periods, are capable of long-range transport, bioaccumulate in human and animal tissue and biomagnify in food chains and food webs, and have potential significant adverse impacts on human health and the environment. Exposure to POPs can cause serious health problems including certain cancers, birth defects, dysfunctional immune and reproductive systems, greater susceptibility to disease, and even diminished intelligence. Of all known POPs so far, the organochlorine compounds, including polychlorinated dibenzo-*p*-dioxins (PCDDs), polychlorinated dibenzofurans (PCDFs), and polychlorinated biphenyls (PCBs), have received the most attention due to their persistence in the environment, bioaccumulation, biomagnification, and hazard effects to biota.

2. Sources of POPs in the environment

There are many ways that release POPs to the environment. POPs such as pesticides are released, as a result of plant protection efforts. The main sources of pesticide pollution include

Figure 1. Emission of dioxins from industrial wastes. Source: Marie Sedillo et al. 2010.

their use, transportation, storage, and disposal of obsolete pesticides. Some other chemicals [polychlorinated biphenyls (PCBs), pentachlorophenol] are used as oils, as dielectric and cooling fluids in capacitors and transformers, for wood preservation, etc., and are released into the environment as a result of spills and evaporation. A number of substances like dioxins/furans, polycyclic aromatic hydrocarbons (PAHs), and hexachlorobenzene are by-products of many industrial processes, mainly, thermal (fuel combustion and waste incineration, ferrous industry, coke and aluminum production, road transport, chemical synthesis of chlorinated substances, etc.) and are emitted directly into the air (**Figure 1**) [2].

3. Why are POPs resistant to most of the environmental degradation processes?

In the initial list of the Stockholm Convention, POPs are typically polyhalogenated organic compounds which exhibit high lipid solubility. For this reason, they bioaccumulate in fatty tissues of animals. Halogenated compounds also exhibit great stability reflecting the nonreactivity of C-Cl bonds toward hydrolysis and photolytic degradation in the environment. The high electronegativity of halogens compared to carbon gives the carbon-halogen bond a significant polarity/dipole moment. The electron density is concentrated around the halogen, leaving the carbon relatively electron poor. This introduces ionic character to the bond through partial charges ($C^{\delta+}Cl^{\delta-}$). The partial charges on the chlorine and carbon exert electrostatic attraction between them, contributing to the unusual bond strength of the carbon-halogen bonds. The carbon-halogen bonds are known to be "the strongest in organic chemistry," because halogen forms the strongest single bond to carbon [3, 4]. The bond also strengthens and shortens as more halogens are added to the same carbon on a chemical compound.

The stability and lipophilicity of persistent organic compounds often correlate with their halogen content; thus, polyhalogenated organic compounds are of particular concern. They exert their negative effects on the environment through two processes, long-range transport, which allows them to travel far from their source, and bioaccumulation, which reconcentrates these chemical compounds to potentially dangerous levels in animal tissues [5].

4. Health effects of POPs

POP exposure may cause developmental defects, chronic illnesses, and death. Some are carcinogens, possibly including breast cancer. Many POPs are capable of endocrine disruption within the reproductive system, the central nervous system, or the immune system. People and animals are exposed to POPs mostly through their diet, occupationally, or while growing in the womb [6]. For humans not exposed to POPs through accidental or occupational means, over 90% of exposure comes from animal food products due to bioaccumulation in fat tissues and bioaccumulation through the food chain. In general, POP serum levels increase with age and tend to be higher in females than males [7].

4.1. Effect on endocrine disruption

Exogenous substance/mixture that alters the function(s) of the hormonal system and consequently causes adverse effects in an intact organism or its progeny or its subpopulation is called endocrine disruptors. The majority of POPs are known to disrupt the normal functioning of the endocrine system. Low-level exposure to POPs during critical developmental periods of the fetus, newborn, and child can have a lasting effect throughout its lifespan. A 2002 study [8] synthesizes data on endocrine disruption and health complications from exposure to POPs during critical developmental stages in an organism's lifespan. The study aimed to answer the question whether or not chronic, low-level exposure to POPs can have a health impact on the endocrine system and development of organisms from different species. The study found that exposure of POPs during a critical developmental time frame can produce a permanent change in the organism's path of development. Exposure of POPs during non-critical developmental time frames may not lead to detectable diseases and health complications later in their life. In wildlife, the critical development time frames are in utero, in ovo, and during reproductive periods. In humans, the critical development time frame is during fetal development [9].

4.2. Effect on the reproductive system

The same study in 2002 with evidence of a link from POPs to endocrine disruption also linked low-dose exposure of POPs to reproductive health effects. The study stated that POP exposure can lead to negative health effects especially in the male reproductive system, such as decreased sperm quality and quantity, altered sex ratio, and early puberty onset. For females exposed to POPs, altered reproductive tissues and pregnancy outcomes as well as endometriosis have been reported [9, 10].

4.3. Effect on gestational weight gain and newborn head circumference

A Greek study in 2014 investigated the link between maternal weight gain during pregnancy exposure and PCB level in their newborn infants, their birth weight, gestational age, and head circumference. The lower the birth weight and head circumference of the infants was, the higher POPs levels during prenatal development had been, but only if mothers had either excessive or inadequate weight gain during pregnancy. No correlation between POP exposure and gestational age was found [11]. A 2013 case-control study conducted in 2009 in Indian mothers and their offspring showed prenatal exposure of three types of organochlorine pesticides (HCH, DDT and DDE) impaired the growth of the fetus, reduced the birth weight, head circumference and chest circumference [12].

5. Environmental effects of POPs

POPs can travel long distances in the environment by air or in water so that they are found in ecosystems in which they have never been used and far from their source. Animals of the Canadian Arctic have significant levels of PCBs, organochlorine pesticides (like DDT), and metals, and this poses a health risk to the human population that relies on these animals as a food source. The long-range transport of POPs leads to global pollution (**Figure 2**) [13].

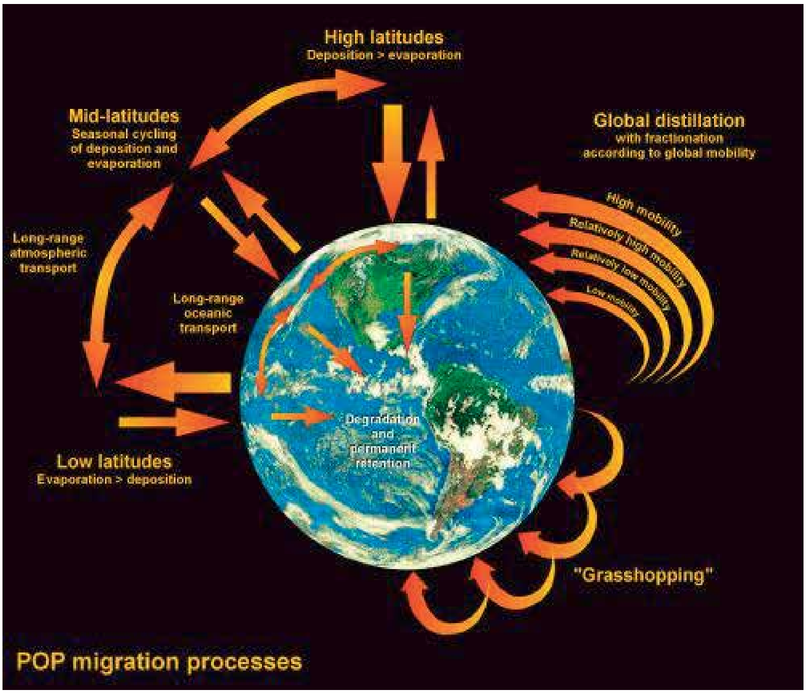


Figure 2. Transboundary movement of POPs. (Source: Ref. [13]).

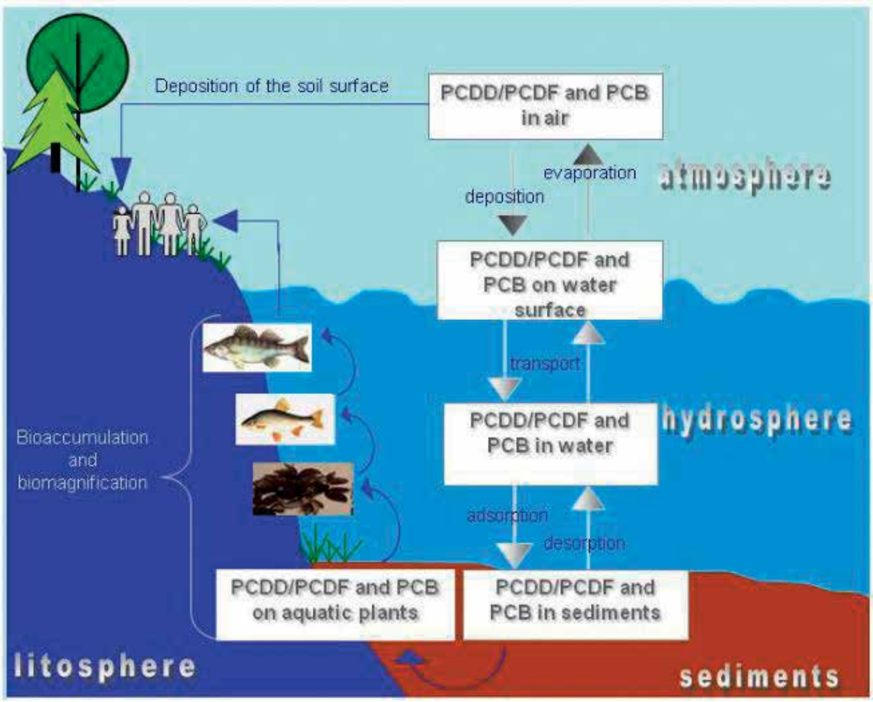


Figure 3. Transport and circulation of PCDDs/PCDFs and PCBs in the environment. (Source: Ref. [14]).

The slow decomposition of PCDDs/PCDFs and PCBs in the environment and the hazards they pose for living organisms make them large-scale environmental degraders, especially because their toxicity can be further enhanced by their ability to accumulate in the soil and sediments and their bioaccumulation and biomagnification within aquatic and land food chains (**Figure 3**) [14].

6. Degradation pathways of POPs in the environment

Despite the fact POPs are resistant to most of the degradation processes in the environment, some molecular alterations are possible in the environment that does not necessarily lead to simpler and less toxic compounds. Some of POP metabolites are equally complex and even more toxic than the parent molecules. Most of the degradation processes of POPs in the environment are assisted by microorganisms. Nevertheless, the half-lives of biodegradation processes of POPs are significantly long, thus accounting for their persistency in the environment. Some representative examples of POP degradations are as presented below.

6.1. Degradation of heptachlor

Heptachlor is known to undergo oxidative dechlorinating in the soil to form 1-hydroxychlordene and by the influence of soil microorganisms to form heptachlor epoxide with a half-life of up to 112 days [15] as shown in **Scheme 1**.

6.2. Degradation of DDT

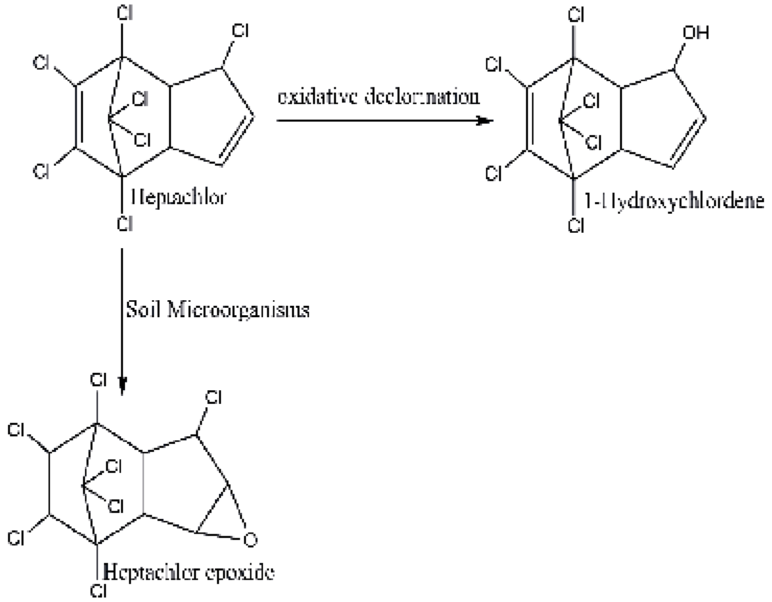
p,p′-DDT can be broken down in the soil by *Enterobacter aerogenes* microorganisms in the presence of UV light and/or iron catalyst to reduced dehydrochlorinated compounds, DDE, and DDD as well as oxidized derivatives which ultimately form *p,p′*-dichlorobenzophenone (**Scheme 2**). *o,p′*-DDT degrades in the same way as *p,p′*-DDT [16].

6.3. Degradation of endosulfan

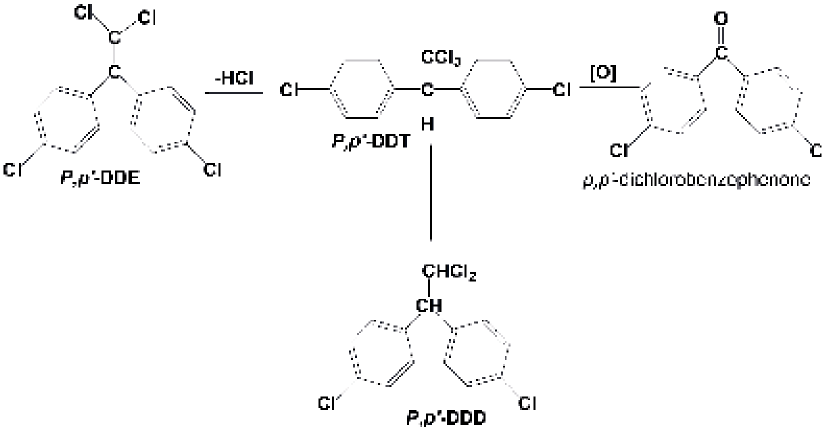
The technical grade of endosulfan consists of two isomers, alpha and beta in the ratio of 70:30. In the environment, endosulfan is photolytically degraded to yield endosulfan sulfate in soil and endosulfan diol in aquatic environment. Endosulfan sulfate is equally toxic as the parent molecule (**Scheme 3**) [16].

6.4. Degradation of hexachlorobenzene

In anaerobic condition, biodegradation of HCB in an arable soil takes place with several dechlorination steps, indicating the following main HCB transformation pathways: HCB → pentachlorobenzene (QCB) → 1,2,3,5-tetrachlorobenzene (TeCB) → 1,3,5-TCB → 1,3-dichlorobenzene(DCB), with 1,3,5-TCB as the main intermediate dechlorination product [17] (**Scheme 4**).



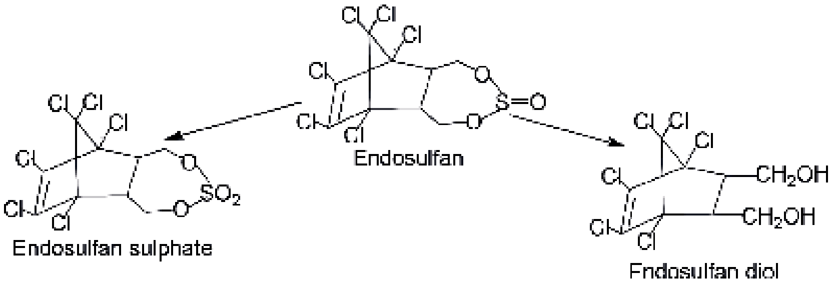
Scheme 1. Degradation pathways of heptachlor in the soil.



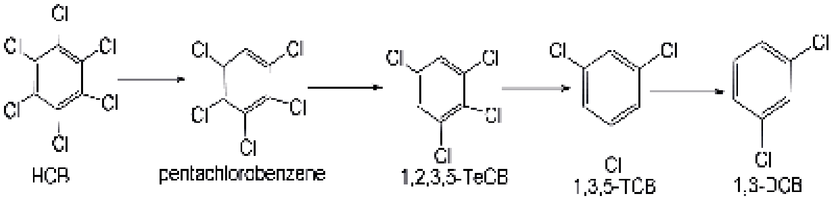
Scheme 2. Degradation of *p,p′*-DDT in the environment.

6.5. Degradation of aldrin/dieldrin

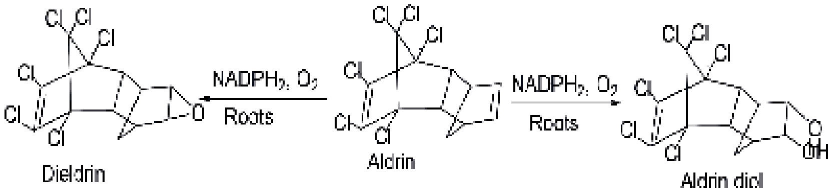
The NADPH$_2$-dependent enzymatic oxidation of aldrin to dieldrin and aldrin to aldrin-diol by two enzyme systems is present in excised roots. The enzymatic oxidation of aldrin in plants is known to be more species specific than the oxidation by microorganisms [10] (**Scheme 5**).



Scheme 3. Degradation of endosulfan in the environment.



Scheme 4. Degradation of hexachlorobenzene.



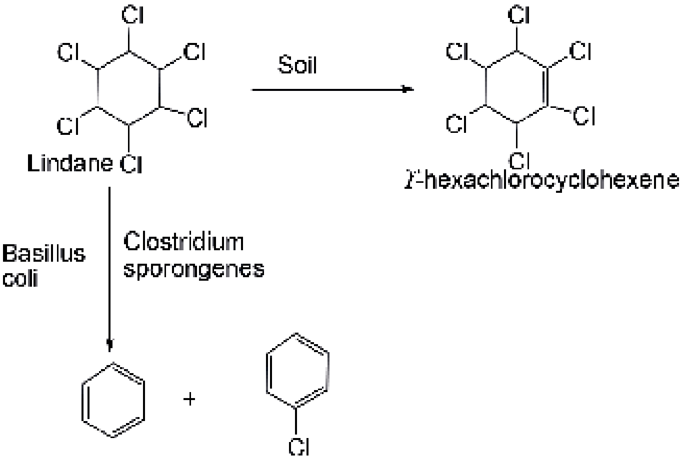
Scheme 5. Degradation of aldrin in the environment.

6.6. Degradation of lindane

Dehydrohalogenation of lindane to γ-hexachlorocyclohexane takes place in moist soil and is attributed to the soil microorganisms such as *Bacillus coli* and *Clostridium sporogenes*. Also these bacteria produced trace amount of benzene and monochlorobenzene from lindane (**Scheme 6**) [18].

6.7. Degradation of PCBs

Various microorganisms are involved in a two-stage process of degradation of PCBs, which happens in aerobic and anaerobic environments. Degrading PCBs is similar to the degradation of biphenyl. However, the chlorines on PCBs prevent them from being utilized as a substrate of biphenyl degradation. Due to high chemical stability, PCBs cannot be used as energy sources. However, due to the chlorination, PCBs can be used as electron acceptors in anaerobic respiration to store energy, which is also the first stage of the degradation pathway, reductive dechlorination. Once the PCBs are dechlorinated to a certain degree, usually lower than five chlorines presenting in the structure and one aromatic ring has no chlorine, they can



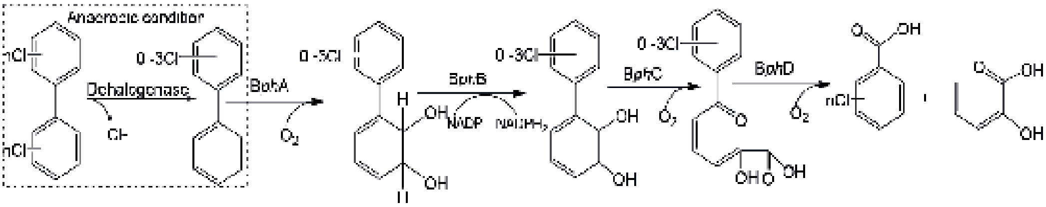
Scheme 6. Degradation of lindane in the environment.

undergo the biphenyl degradation pathway (BP pathway) to be degraded to accessible carbon or CO_2 in the aerobic environment. BP pathway is a pathway that utilizes series of enzymes (BphA, B, C, D, E, F, G) to convert biphenyl to TCA cycle intermediates (pyruvate and Acyl-CoA) and benzoate. However, there are few microorganisms that can dechlorinate substrate under natural conditions. Even with selective media, the accumulation of PCB-dechlorinating microorganisms is still slow, which is one reason for the slow degradation rate. As a result, PCBs usually go through a co-metabolism pathway that involves different microorganism species [7, 14, 17, 25] (**Scheme 7**).

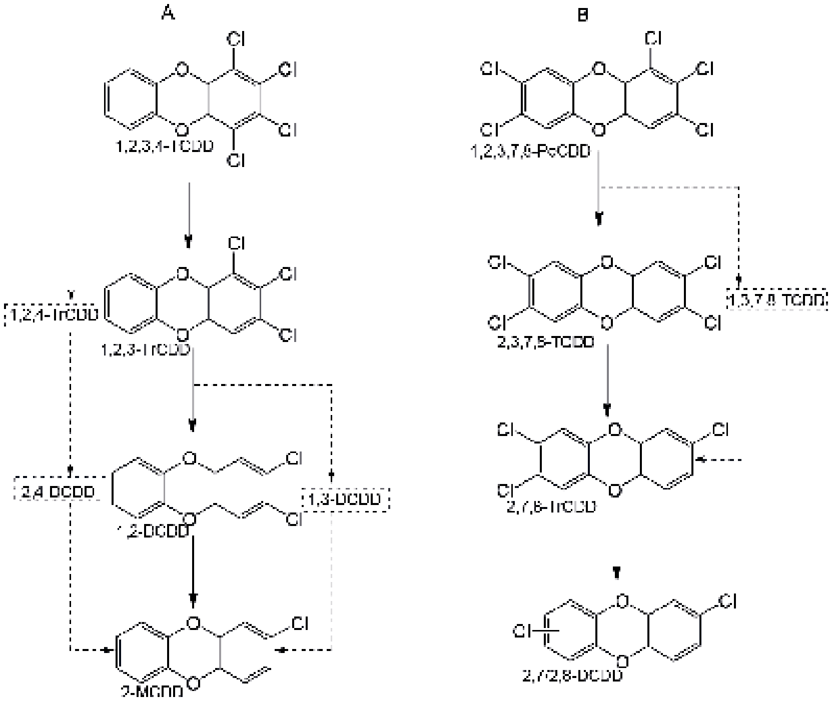
6.8. Degradation of dioxins by reductive dehalogenation

It has been well reported that several species of strictly or facultatively anaerobic bacteria are capable of de-halogenating chlorinated aliphatic and aromatic compounds. Some of these dehalogenation processes have been shown to couple to ATP synthesis via a chemiosmotic mechanism. The reductive dehalogenation linked to energy conservation is called "halorespiration" or "dehalorespiration." For example, a sulfate-reducing bacterium, *Desulfomonile tiedjei* strain DCB-1, has been shown to conserve energy for growth from reductive dehalogenation of 3-chlorobenzoate by an uncharacterized chemiosmotic process. Bacterial dehalorespiration with tri- or tetrachlorinated benzene as a terminal electron acceptor is also known to take place. Gibbs free energy of formation of various PCDDs/PCDFs and redox potentials for PCDD/PCDF substrate/product couples indicate that the reductive dehalogenation of PCDDs/PCDFs is an exergonic reaction, and this implies that microorganisms acquire energy via anaerobic electron transport with PCDDs/PCDFs as terminal electron acceptors.

Despite its physiological and ecological importance, the biological reductive dehalogenation of PCDDs/PCDFs as well as of PCBs has been studied much less than the aerobic biodegradation of dioxin-related compounds. This biological reaction has so far been studied mostly in sediments, sludge, and soils containing anaerobic microbial consortia. Earlier work related to this subject showed changes in PCDD-/PCDF-congener distribution patterns and the resultant accumulation of less-chlorinated forms in sediments. More intensive studies on microbial dehalogenation of PCDDs/PCDFs in the environment started appearing in the past decade. Microbial dehalogenation of PCDDs/PCDFs takes place by removal mainly at positions 1, 4, 6, and/or 9 and led to much more toxic congeners, including 2,3,7,8-TCDD, in some cases. The maximum yield of cell protein coincided with the production of less-chlorinated DD isomers, where no methanogenic activity was detected. Experiments with sediment microcosms spiked with the much less toxic congener 1,2,3,4-TCDD revealed that reductive dehalogenation occurred at the lateral positions with 1,2,4-TrCDD as the main intermediate, leading to 2-MCDD as the final end product. The available information indicates that MCDDs/MCDFs are not dehalogenated further [14, 19–21] (**Scheme 8**).



Scheme 7. Degradation of PCBs in the environment.



Scheme 8. Possible degradation pathways of reductive dechlorination of 1,2,3,4-TCDD (A) and 1,2,3,7,8-PeCDD (B) by *Dehalococcoides* sp. strain CBDB1.

7. What can be done to control or remove POPs in the environment?

The Stockholm Convention on POPs clearly provides suggestive solutions by restricting the production and use of POPs in the environment. The Convention requires that production and use of POPs be stopped and their stockpiles destroyed so that the resulting products are no longer POP. Article 6 of the Convention addresses the identification and management of POP waste. The Convention requires that such wastes be managed in a safe, efficient, and environmentally sound manner and that the disposal be done such that the POP content be destroyed or irreversibly transformed so it is no longer a POP.

Stockpiles of POPs are well documented worldwide, which include obsolete pesticides, PCBs discarded from use (PCB oils and liquids), and heavily contaminated soil (e.g., soil surrounding landfills and deep wells containing POPs). To eliminate these stockpiles of POPs from the environment, two basic POP destruction technologies are suggested, namely, combustion technology and non-combustion technology.

The combustion technologies (hazardous waste incinerators, rotary kilns, furnaces, boilers, IR incinerators, etc.) are usually believed to be the most economically appropriate way for concentrated POP waste treatment. This is why in industrialized nations POP wastes are routinely burnt in incinerators, and for most countries combustion technologies still remain the most economically acceptable way to treat POP waste on the macroscale. Modern waste incinerators are designed to satisfy the required emissions levels.

Over the last 15 years, a number of non-combustion technologies have been demonstrated to effectively treat POP wastes in countries such as Canada, the USA, Australia, and Japan. Some methods, particularly for PCBs, are outlined by the UNEP. However, even developed non-combustion technologies can hardly be competitive with incineration. Other non-combustion technologies lack in research or technical development, and most of them have a scarce commercial operation history.

Current studies aimed at minimizing POPs in the environment are investigating their behavior in photocatalytic oxidation reactions. POPs that are found in humans and in aquatic environments the most are the main subjects of these experiments. Aromatic and aliphatic degradation products have been identified in these reactions. Photochemical degradation is negligible compared to photocatalytic degradation. A method of removal of POPs from marine environments that has been explored is adsorption. It occurs when an absorbable solute comes into contact with a solid with a porous surface structure. Current efforts are more focused on banning the use and production of POPs worldwide rather than the removal of POPs [20, 22–24].

8. Conclusion

POPs pose one of the most challenging problems in environmental science and technology. Their fate, transport, and biodegradation in the environment occur via complex networks, involving complicated interactions with other contaminants and with slow biodegradation and various physiological, chemical, and biological processes. Those processes can be used and modified in order to diminish their environmental concentration. There are more promising results of such activities performed by various researchers worldwide. Nevertheless, the still existing challenge is to develop a bioremediation strategy that involves and integrates different types of solutions, on the scale of the whole ecosystem, in order to optimize the effectiveness of pollutant removal from the environment. For POP stockpiles, the combustion technologies remain by far the most effective and economic method of removing them from the environment.

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Chapter 4

Lake Sedimentary Environments and Roles of Accumulating Organic Matter in Biogeochemical Cycling Processes and Contaminants Loading Are Invasions of Water Hyacinth in Lake Victoria from 1989 a Concern?

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Additional information is available at the end of the chapter

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Abstract

Sediments accumulated in lake basins consist of various organic and inorganic materials, mostly utilized as proxies for climatic changes and as historical records of the lake connectivity to terrestrial ecosystems and anthropogenic activities. In-lake production, aerial wet and dry deposition and transported materials in running water are the main sources of lake deposits, which may be permanently deposited as bottom sediments or remobilized through erosive forces and turbulence, resuspension, tunneling by organisms, and pore-water exchanges with the overlying water mass. Examination of the sediment biodiversity, quality, composition, and stratigraphy is part of the approaches in understanding ecological and climatic changes and other anthropogenic impacts in lakes. There are no detailed studies on the spatial distribution of sediment characteristics within the Nyanza Gulf, especially after the establishment of water hyacinth. The first observations on the nature of the bottom of Lake Victoria were made during 1927–1928 survey, with subsequent detailed geochemical core studies concentrated in the main lake. Roles of sediment organic matter are explained, and data from surficial sediments collected, from about 32 sampling sites between 1994 and 2012, are used to characterize the sediments. Lastly, the potential influences from increased urbanization, eutrophication, presence of water hyacinth (*Eichhornia crassipes*), and associated floating macrophytes since 1989 and current cage aquaculture in *L. Victoria* are explored.

Keywords: Lake Victoria, sedimentary environments, sediments, organic matter, contaminants, organic carbon, depositional basins

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1. Introduction

Lakes are important land features forming linkages with the hydrological systems at local and transboundary scales, while providing water sources, supporting fisheries, and providing livelihoods to many surrounding communities and different ecosystem services. Small and large lake depositional basins continuously accumulate dissolved or particulate inorganic and organic materials produced within the lake water column (autochthonous) or transported from the catchment area (allochthonous). However, besides lake production, human developments and urbanization around surface waters (lakes and rivers) are also a source of various solid and nutrient-rich materials depositing and accumulating on the lake sediments. When autochthonous matter is dominant, lake sediments may either be either carbonate-rich or silica-rich due to the accumulation of siliceous diatoms, or they may be mostly organic. In the latter case, the organic carbon content may reach 20–25%, but in peat bogs it may be even higher [1, 2]. Particulate matter scavenges chemical species (organic and inorganic pollutants) and, with other geochemical barriers, influences their mobility in the secondary environments. Therefore, understanding the sediment-chemical species associations has given more insights to the chemical element availability for metabolic processes and toxicity under certain environmental conditions. Knowledge of lake bottom dynamics and sedimentological processes is essential in matters related to geographical distribution and potential ecological effects of contaminants and in many practical issues, such as choice of adequate dumping sites for dredging deposits and choice of sampling sites from aquatic pollution control. Sediment accumulation areas prevail where fine materials, medium silt with grain size less than 0.006 mm, can be deposited continuously; sediment transportation zones appear where there is discontinuous deposition of fine particles/aggregates, and sand erosion zones prevail where there is no deposition of fine materials [3]. The sediments within areas of transportation, for natural reasons, are generally very variable (from sand to loose mud); areas of erosion are most frequent in shallow waters and characterized by hard or consolidated deposits (from bare rocks, gravel, and sand to glacial clays), and the deposits from areas of accumulation are always comparatively loose, with high water and organic contents and sometimes with a high content of pollutants [3]. The Lake Victoria (Kenya) gulf waters are eutrophic, and it is continuously fed by several large and small rivers which traverse the fertile agricultural highland areas and transport high levels of eroded materials. Information from sedimentological studies in *L. Victoria* exists but is inadequate due to lack of new studies. The chapter examines the significance of sediment organic matter (SOM) in freshwater aquatic environments, besides other sediment factors, and uses the spatial concentration of total organic carbon determined in surficial sediments of Lake Victoria (Kenya) to explore whether water hyacinth invasion has any significant influence on SOM. It also gives an opportunity to reflect on the potential environmental impacts which can possibly emanate from the new cage aquaculture developments in most of the shallow African inland lakes, such as *L. Victoria* which has a huge potential for cage culture.

1.1. Lake Victoria

Lake Victoria, the world's second largest freshwater lake (68,800 km^2 in surface area and mean depth of 35 m) supports the world's largest inland fishery and is a transboundary ecosystem with the Nyanza Gulf, on the extreme eastern edge forming the Kenya portion (**Figure 1**). The gulf connects to the open lake via Rusinga Channel. River water inflows

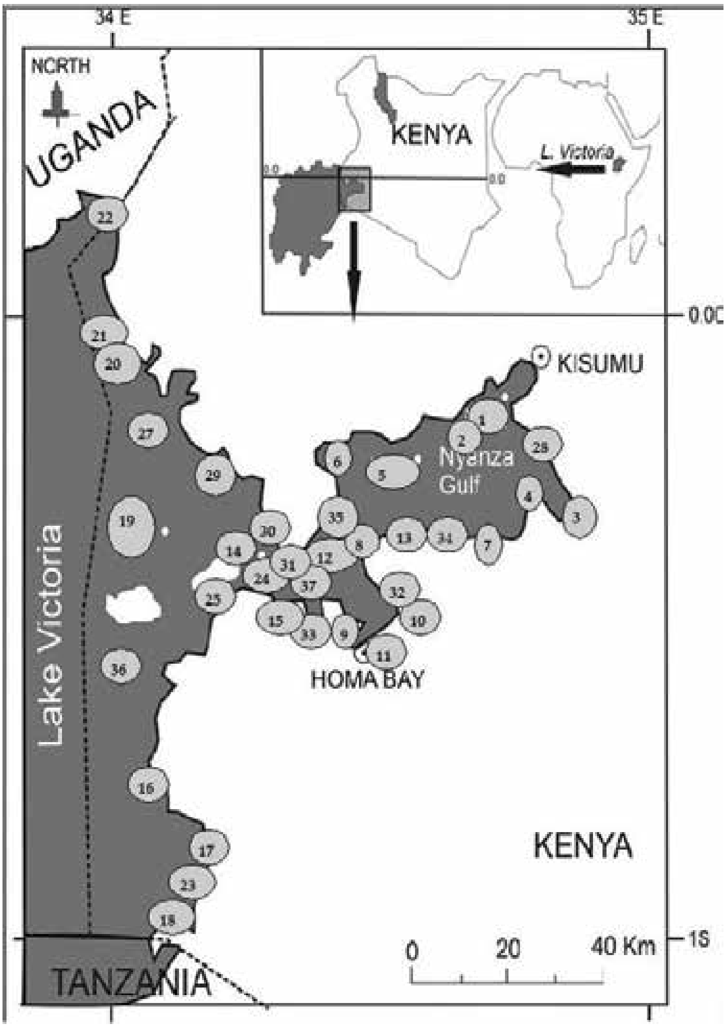

Figure 1. The map of Lake Victoria (Kenya) showing sampling sites.

account for about 20% of the total water inputs into the main lake. The catchment area and the drainage basin are covered by grassland savanna, wetland vegetation, agricultural crops, and forested highland and mountain areas. It is characterized by high tropical temperatures and heavy rainfall in the highlands, described in a long (April–June) and short (October–December) wet season and a dry season. The lake hydrology, physicochemical environment, and changes in primary production of the lake and gulf areas are well-described by various authors [4–13].

Morphometric characteristics from early investigations in L. Victoria and its main gulf areas are provided by Crul [10]. Seismic reflection profiles confirm the origin of the lake as a result of regional tilting and provide an estimated age of 400,000 years for the lake basin [14]. The Nyanza Gulf deepens towards the western direction, as shown by bathymetric map after Kendall [15] and Scholz [16]. Some information on the lake bottom and sediments in the Nyanza Gulf is provided by Mothersill [17] and Mothersill et al. [18].

Nyanza Gulf, a relatively shallow gulf compared to the main lake basin, is composed of numerous inner bays and receives inflowing water from several major rivers. This makes it a distinctly important habitat for several fish species, which are known to breed in the various vegetated bays and river-mouth areas. The gulf is greatly influenced by catchment activities through river inflows and nearby urban human activities. Besides this, an invasive water weed, the water hyacinth, is commonly found in the whole lakeshores and bays. The plant was first reported from Lake Victoria in 1989, and it began to increase in the early 1990s, until it infested some 200 km^2 by 1998 [19]. Its early spread and nourishment were thought to be triggered by nutrient enrichment, and the plant floating mats have persisted up to today.

2. Sources of organic matter sources in lake sediments

Lake basins are receptors of different types of dissolved and suspended materials transported by inflowing water, above lake precipitation, and blowing wind. In-lake productivity processes also contribute a significant amount of organic matter and mineral elements, which enter the lake biogeochemical cycles.

Organic matter in aquatic ecosystems ranges from dissolved organic compounds to large aggregates of particulate organic matter and from living to dead materials [20]. Nearly all of the organic carbon in natural waters is in the form of dissolved organic carbon (DOC), colloidal organic carbon (COC), and dead particulate organic carbon (POC). Metabolism of the organic matter and interactions of this material chemically and biologically are, to a significant extent, governed by the size and chemical composition of the organic matter [20]. The productivity of aquatic macrophytes of the wetland and littoral land-water interface zones constitute a major source of organic matter input for a majority of the lakes of the world [20]. A central role in the underwater light climate is played by dissolved organic matter which is present in all aquatic ecosystems. Chromophoric dissolved organic matter (CDOM) originates from the degradation process of organic materials, usually macrophytes and planktons. Recently, using fluorometer data, Alexander and Imberger [21] characterized phytoplankton patchness in the Nyanza Gulf as indicators of phytoplankton diversity and CDOM, while Loiselle et al. [22] determined the spatial dynamics of CDOM of three major bays on the Kenyan and Ugandan shores of Lake Victoria and developed a model to estimate its flow from these bays to the lake.

Lake sediments are comprised mainly of clastic material (sediment of clay, silt, and sand sizes), organic debris, chemical precipitates, or combinations of these. The relative abundance of each depends upon the nature of the local drainage basin, the climate, and the relative age of a lake. Sediments are deposited at different rates in different aquatic environments. Deposition rates vary from site to site, but typical values for the rate at which sediments accumulate in freshwater lake sediments are 1 mm/year (or 1 m per 1000 years). When a watershed drains into a lake, accumulated sediments have the potential to yield information about historic rates of sedimentation that can be used to evaluate the effectiveness of previous erosion control measures [23].

The active lake sediment layer (top layer) forms the exchange zone between sediments and overlying water column. It plays an important role in the biological system; however, it can become anoxic in deeper areas, hence influencing the chemical equilibria and transformations.

Degradation of decaying organic matter and organic rich waste discharges can lead to decreases in DO concentrations as a result of the increased microbial activity (respiration). In severe cases of reduced oxygen concentrations (whether natural or man-made), anaerobic conditions can occur (i.e. 0 mg l^{-1} of oxygen), particularly close to the sediment–water interface as a result of decaying, sedimenting material. Dissolved oxygen levels influence the redox potentials (Eh) and different chemical processes in the aquatic habitats and the distribution of fish species. This is explained by Njiru et al., [24] who explored the impacts of hypoxic conditions to the fishery in Lake Victoria, where, from acoustic data, Nile perch catches increased with increase in DO concentrations and no fish were caught when DO was below 2.5 mg/L^{-1}.

Organic matter constitutes a minor but important fraction of lake sediments. It is made-up of a complex mixture of lipids, carbohydrates, proteins, and other biochemicals contained in the tissues of living benthic micro-organisms and contributed from the detritus of organisms formerly living in the lake and its watershed. Humic substances are diagenetically formed from these biochemical starting materials and constitute the major part of the complex mixture of organic materials [25]. Some natural organic compounds significantly affect the quality of water for certain uses, especially those which depend on organoleptic properties (taste and smell). During chlorination for drinking water disinfection, humic and fulvic acids act as precursor substances in the formation of trihalomethanes such as chloroform. In addition, substances included in aquatic humus determine the speciation of heavy metals and some other pollutants because of their high complexing ability. As a result, humic substances affect the toxicity and mobility of metal complexes [2]. Therefore, measurement of the concentrations of these substances can be important for determining anthropogenic impacts on water bodies. Humus is formed by the chemical and biochemical decomposition of vegetative residues and from the synthetic activity of micro-organisms. It is operationally separated into fulvic and humic acid fractions, each being an aggregate of many organic compounds of different masses. Fulvic acid has molecular masses mostly in the range 300–5000, whereas the dominant masses in humic acid exceed 5000. The relative content of fulvic acid in the dissolved humic substances present in freshwaters is between 60 and 90%. Humic and fulvic acids are fairly stable (i.e. their BOD is low). However, these substances are chemically oxidizable and, therefore, can readily affect the results of COD determinations [2].

Organic matter also forms part of the palaeolimnological record preserved in lake sediments. The different types of biota populating a lake and its watershed produce organic matter having distinctive biochemical compositions. Changes in the community structure of these biota create variations in the amounts and types of organic matter deposited at different times in the history of a lake. Organic matter is consequently a dynamic biogeochemical component of sediments [25].

2.1. Roles of lake sediment organic matter

The most important determinants of chemical-sediment association are composition or grain-size distribution, pH, salinity, DO_2, mineralogical content (clay mineral composition, hydrous iron-manganese oxides, carbonate contents), organic matter, and redox potential.

Concentrations of some inorganic and organic contaminants (PAH, PCBs, OCs, Hg, and alkylated metal forms) can become increasingly high and important sources of exposure, with transfers along lake food chains in the long term. Contaminated sediments are therefore a concern to lake managers of surface lake waters receiving significant amounts of anthropogenic wastes, hence the development and use of sediment quality guidelines in protecting the aquatic fauna and flora. Managing contaminated sediment in place requires a complete chemical, biological, and physical understanding of the fate and mobility of contaminants. Most of them adsorb onto suspended and deposited particles at the bottom, where they form important secondary sources. Soils and sediments are important "sinks" for such contaminants because of their enormous quantities and their abilities to pick up, or sorb, large amounts of a wide variety of contaminants. It is essential to understand the mechanism by which the contaminant is sorbed to soil and sediment [26]. Compared to other natural environmental substrates, sediments have a greater capacity to bind Hg more than 90% of total Hg in sediment-water system which is sorbed or held in sediments [27].

Stable isotope signatures ($^{\delta 13}$C and $^{\delta 15}$N) of organic matter in lake sediment cores have been used as indicators of historic lacustrine productivity [28, 29] and past nitrogen sources [28, 30], respectively. Total carbon (TC) to total nitrogen (TN) ratios of OM can be used to assess the relative contributions of higher plants versus phytoplankton to sediments [31–34]. In *L. Victoria* (Tanzania), the potential to discriminate between input sources of organic material into lakes using stable isotope signals in sediment and suspended particulate matter was demonstrated, where stable C and N ratios showed that inshore areas in bays without pronounced fluvial input were dominated by autochthonous planktonic organic matter; conversely, for bays receiving significant fluvial inflows, the composition of organic matter depended on the extent of preservation of shoreline vegetation [35].

Sediment metabolism (e.g. measured as sediment oxygen uptake) is highly varied and depends on the individual characteristics of a lake. Profundal sediments may have a high organic carbon content (up to 25%) and are more homogenous compared with littoral sediments, with a resultant high sediment metabolism [36]. Organic matter degradation is influenced by the presence of benthic fauna, which enhance the oxidation of the sediments and organic matter cycling by increasing oxygen supply during respiratory pumping [37]. Benthic animals and microbes depend on organic matter for their nutrition. Because many components of organic matter are relatively easily oxidized forms of reduced carbon, the dissolved oxygen concentration of sediment porewater is controlled largely by the availability of oxidizable organic matter below the sediment–water interface [25]. Organic matter so resuspended is re-exposed to oxidation in the water column. Resuspension is usually greater in large, well-mixed lakes than in small lakes. Bioturbation, or biological mixing, of surface sediments also prolongs the exposure of organic matter to oxidation and adds to this the degradation due to the nutritional needs of benthic fauna [25].

2.2. Chemical adsorption to sediments and soil

Sorption to soils and sediments is probably the most influential factor on the transport and fate of organic contaminants in the environment. The extent of the sorption to soil and sediment affects not only the contaminant level in an ecosystem but the movement and fate of the contaminant as well. For example, in a hydrogeologic system, the increased sorption of a contaminant to soil and sediment reduces its level in the adjacent water column and thus decreases its exposure and transport to other parts of the ecosystem, such as fish and plankton [26]. The way in which contaminants are sorbed into soil or sediment varies with the nature of the contaminant and the makeup of the soil and sediment [38, 39]. The composition of soil and sediment includes both mineral matter and organic matter as the primary constituents. Under relatively dry conditions, the soil/sediment mineral matter acts as an adsorbent, where the sorbed organic compounds are held on the surface of the mineral grains. The soil/sediment organic matter (SOM) acts as an absorbent or a partition medium, where the sorbed organic compounds dissolve (partition) into the matrix of the entire SOM. The soil or sediment, then, is characterized as a dual-function sorbent, in which the mineral matter sorbs the contaminant by adsorption, while the SOM sorbs the contaminant by a partition process [40–42]. Because so many environmental contaminants are transported by groundwater and surface water, it is important to understand the unique function of the soil organic matter within these aquatic systems and how the partition processes affect the fate of common environmental contaminants.

The organic carbon partitioning coefficient, K_{oc}, data of both carbon tetrachloride (CT) and 1,2-dichlorobenzene on most normal soils from shallow depths are shown to be quite invariant, suggesting that soil organic matter at such depths from diverse geographic sources maintains a comparable polar-to-nonpolar balance and possibly a comparable composition [26]. However, soil samples are genuinely different from bed-sediment samples in terms of their K_{oc} values. The average K_{oc} values for nonpolar solutes on bed sediments are about twice those on soils, suggesting that sediment organic matter is in general less polar in nature than soil organic matter. This unique geochemical disparity has not been documented until now [26]. The observed difference in K_{oc} between the soil and bed-sediment samples must be taken into account in future studies. Because it has now been shown that K_{oc} values for soils are largely consistent worldwide, just as K_{oc} values for sediments are largely consistent worldwide, K_{oc} values can be used to assess the sorption of nonpolar contaminants to the organic matter of different soils/sediments. This finding should result in considerable savings in cost and time for contamination studies [26].

Although suspended sediment as a whole can be examined as a transport mechanism for trace metals, additional insight can be gained from a knowledge of the particle-size distribution. The most significant factor controlling sediment capacity for retaining trace metals is grain size, according to Jenne et al. [43]. The correlation between decreasing grain size and increasing trace-metal concentrations is significant. This correlation is a result of factors, both physical and chemical, that most notably are related to the large surface area per unit weight of fine particles (such as clays) compared to larger particles. According to Horowitz [44] the increase commonly is more than a hundredfold.

A recent view of the role of clays as metal concentrators implies that clays function as substrates for the precipitation and flocculation of organic matter and secondary minerals such as hydrous iron and manganese oxides. Those secondary minerals, in turn, become substrates for the accumulation of trace metals rather than the clays themselves, according to Jenne [45]. There is some debate whether accumulation takes place by organics and secondary minerals or whether there is direct physical and chemical interaction with the clays. However, there is general agreement that the largest concentrations of metals are present with the clays and that the following clay minerals have a decreasing order of association with trace metals: montmo rillonite>vermiculite>illite, chlorite>kaolinite.

2.3. Methane production

Besides methane emissions from wetland areas [46], freshwater anoxic areas are notably important sources. Freshwater bacteria are at the hub of biogeochemical cycles and control water quality in lakes [47]. Methane is oxidized in lakes by a group of bacteria that convert methane and oxygen to cellular material and carbon dioxide [48]. In deeper lakes, methane oxidation occurred mainly within a narrow zone at the boundary of the seasonally mixed layer and the permanently anoxic monimolimnion [49]. Reduction of carbon dioxide and the decomposition of organic sediment material contribute to methanogenesis. Methanogenic bacteria directly reduce the dissolved carbon dioxide near and in the sediments. Simultaneously, methane is formed from organic matter by acetate fermentation. Only three key functional groups of micro-organisms of limited diversity regulate the fluxes of methane on earth, namely, the aerobic methanotrophic bacteria, the methanogenic archaea, and their close relatives, the anaerobic methanotrophic archaea [50]. The anaerobic methanotrophic archaea appear to gain energy exclusively from the anaerobic oxidation of methane, with sulphate as the final electron acceptor according to the net reaction:

$$CH_4 + SO_4^{2-} \rightarrow HCO_3^- + HS^- + H_2O \tag{1}$$

A great deal of biogeochemical research has focused on the causes and effects of the variation in global fluxes of methane throughout earth's history, but the underlying microbial processes and their key agents remain poorly understood [50]. This is a disturbing knowledge gap because 85% of the annual global methane production and about 60% of its consumption are based on microbial processes [50]. Furthermore, wetland ecosystems are vulnerable due to increasing demand for agricultural lands, yet they act as important filters and C sinks. Nutrient concentration gradients were observed between the deep and seasonally stratifying main lake basin and the large, shallow river-influenced Nyanza Gulf, which are connected by the relatively deep and narrow Rusinga Channel [51]. Since the gulf as a whole is P limited, continued P input to this semi-closed part of the lake will result in increased algal blooms and increased eutrophication and therefore negatively affecting the water quality [52, 53]. Increased availability of nutrients in the water helps sustain the healthy water hyacinth, the persistent alien-invasive floating macrophyte species in the Nyanza Gulf. Increased eutrophication [11, 12, 54] process and changes in productivity have been recorded in the lake from several studies and coupled with increased allochthonous material, there is a potentially higher probability of continued degradation of the lake environment.

3. Studies on sedimentary environments in Nyanza Gulf of Lake Victoria (Kenya)

More detailed observations on the sedimentary environments on diatom records and sediment bottom structures in Lake Victoria were made by Stager et al. [55–59] and Scholz et al. [16], with more insights on sediment chronology, accumulation rates, and stratigraphic patterns of biogenic silica accumulation in deepwater cores in the main lake basin determined by Verschuren et al. [60]. Mfundisi [61] analyzed the impact of wetland drainage on soil and plant carbon pools in Yala Swamp. In the developing countries, wetlands are a source of great support to the rural communities, which derive a significant proportion of their livelihood from these areas [62]. However, land cover changes and degradation are often associated with increasing demand for agriculturally fertile soils in the drainage basins. P washed down from the catchments has been identified in the basin and finds its way into the lake especially in areas where macrophytes have been cleared. Upon decomposition of the vegetation matter, the nutrients are released to the bottom mat and sludge [63]. Several studies in lake sediments have tried to explore their potential as sources of labile phosphorus nutrient [64–66] and eutrophication. Other authors have tried to utilize stable isotopes of C and N to understand different sources of OM and processes operating in the C and N cycles [67–69].

3.1. Why study sedimentary organic matter

Sedimentary records are valuable indicators of the short- and long-term in-lake ecosystems. Long-term effects of anthropogenic activities are better understood when linked to the slower sedimentary processes, especially in large deeper basins. However, such efforts are hampered by the lack of expensive C analysers in most laboratories. The use of the inexpensive and rapid LOI method allows generation of useful information on sediment organic matter contents and is a widely accepted method. Several sediment studies apply this approach [70] in trying to find relationships between organic matter and organic carbon determined from dry combustion. Apart from comprehensive palaeolimnological research efforts made possible by new sediment cores collected in 1995 and 1996 and (eutrophication related changes in the pelagic phytoplankton community of *L. Victoria* as archived in the offshore (in the deepest parts of the lake basin) sedimentary record of biogenic silica, no other detailed information on the spatial distribution of the surficial sediment organic matter on the extreme eastern gulf (*L. Victoria*, Kenya) has been provided. Information gathered in two separate surveys is used to show the spatial distribution of some of the surficial sediment characteristics.

3.2. The physicochemical environment of Nyanza Gulf of Lake Victoria (Kenya)

In the gulf, most of the sampling sites are nearshore zones of less than 10 m deep (sites of greater 10 m are LS_37 of 11.0 m and LS_14 of 13.8 m), when compared to the deeper sites sampled in the main lake (except for the shallow river-mouth areas in the northern area). Surficial sediments in the gulf were observed to consist of dark/gray to brown fine mud and slightly sandy to sandy muds. Observed sediment characteristics are shown in **Table 1** for each site.

Table 2 shows the mean and range values of the sampled water depth, surface water turbidity, transparency, and chlorophyll-a concentrations. Surface water conditions during the survey and previously collected data are shown in **Figures 2–4**. Although all the three parameters were not determined during all the surveys, available data show a similar trend in water transparency and surface water turbidity. The lake water turbidity showed a high spatial variation during all the sampling surveys. The range values of surface water turbidity were 6.08 NTU to 561 NTU (a maximum value omitted in the graph, at site LS_ 21 during May 2000). In February 2001 and January–February 2004, surface water turbidity values ranged from 6.45 NTU to 74.8 NTU and 5.08 NTU to 56.6 NTU, respectively.

Gulf sites	Nearshore/offshore zones	LS_1 (brownish muddy sediment); LS_2, LS_5, LS_6, LS_8, LS_34, LS_13, LS_37, LS_30, LS_31, LS_15, LS_9, LS_32, LS_33, LS_24, LS_14, (dark/gray fine muddy sediment, with large and small empty shell remains)
	Off river-mouth zones	LS_4, LS_7, LS_10, LS_3, LS_28 (sandy brown/gray muddy sediment with empty shell remains)
Open lake sites	Off river-mouth zones	LS_23 (slightly sandy brown muddy sediment); LS_22 (fine dark brown sandy muddy sediment); LS_21 (fine brown muddy sediment with small to slightly larger bivalve shells); LS_20 (muddy sediment with discrete fine sandy particles with small to slightly larger bivalve shells)
	Nearshore/offshore zones	LS_18, LS_16, LS_17, LS_25 (dark/gray fine muddy sediment); LS_36 and LS_19 (fine greenish watery muddy sediment signs of algal deposits)

Table 1. Visual descriptions of collected surficial sediments during June–July 2012 survey.

	Mean (±SD)	**n**	**Min. value**	**Max. value**
June–July 2012				
Water depth (m)	9.1 (11.3)	30	0.87	54
Transparency (m)	0.88 (0.85)	24	0.2	3.2
January–February 2004				
Water depth (m)	8.2 (7.4)	25	2.5	40
Transparency (m)	1.1 (0.5)	25	0.4	2.2
Turbidity (NTU)	17.98 (15.32)	26	3.0	56.6
Chlorophyll-a ($\mu g l^{-1}$)	10.68 (3.73)	25	6.01	22.73
July 2003				
Water depth (m)	8.6 (7.5)	25	2.5	40
Transparency (m)	0.99 (0.58)	25	0.35	2.85
Chlorophyll-a ($\mu g l^{-1}$)	20.62 (10.69)	23	8.0	48.02
August 2001				
Water depth (m)	6.4 (4.0)	24	1.9	18
Transparency (m)	0.96 (0.49)	24	0.3	2.60
Chlorophyll-a ($\mu g l^{-1}$)	16.2 (8.9)	24	5.5	38.5
February 2001				
Water depth (m)	7.2 (3.4)	19	2.3	12.6
Transparency (m)	0.89 (0.35)	19	0.45	1.6
Turbidity (NTU)	19.16 (16.5)	19	6.45	74.8

	Mean (±SD)	n	Min. value	Max. value
December 2000				
Water depth (m)	6.7 (3.5)	21	2.4	14.8
Transparency (m)	0.92 (0.43)	21	0.2	1.86
September 2000				
Water depth (m)	8.0 (6.1)	19	2.5	26.0
Transparency (m)	0.99 (0.43)	19	0.4	2.0
Chlorophyll-a (μgl^{-1})	7.70 (3.21)	19	1.26	13.08
May 2000				
Water depth (m)	5.6 (3.6)	20	2	14
Transparency (m)	0.83 (0.35)	19	0.32	1.5
Turbidity (NTU)	49.9 (122.2)	20	4.86	561

Table 2. Changes in recorded mean and range values of the sampled water depth, surface water turbidity, transparency, and chlorophyll-a concentrations in *L. Victoria* (Kenya).

Water transparency values also followed a similar trend as the turbidity in each sampling site. In May 2000, September 2000, December 2000, February 2001, August 2001, July 2003 January–February 2004, and June–July 2012, the values ranged from 0.32 m to 1.5 m, 0.2 to 1.86 m, 0.45 m to 1.6 m, 0.3 m to 2.6 m, 0.35 m to 2.85 m, 0.4 m to 2.2 m, and 0.2 m to 3.2 m). In most of the sites, the values were below 1.5 m (the maximum values were recorded at deeper sites in the open lake).

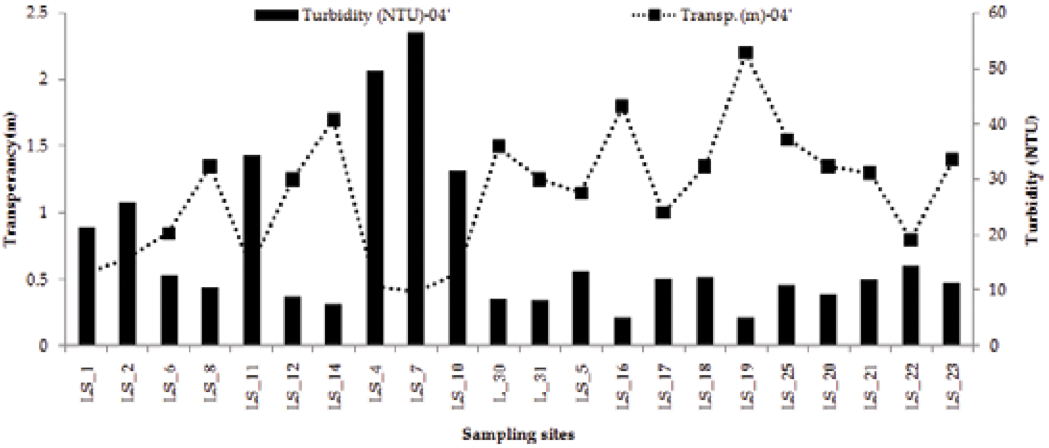

Figure 2. Water turbidity and transparency variations during January–February 2004 survey.

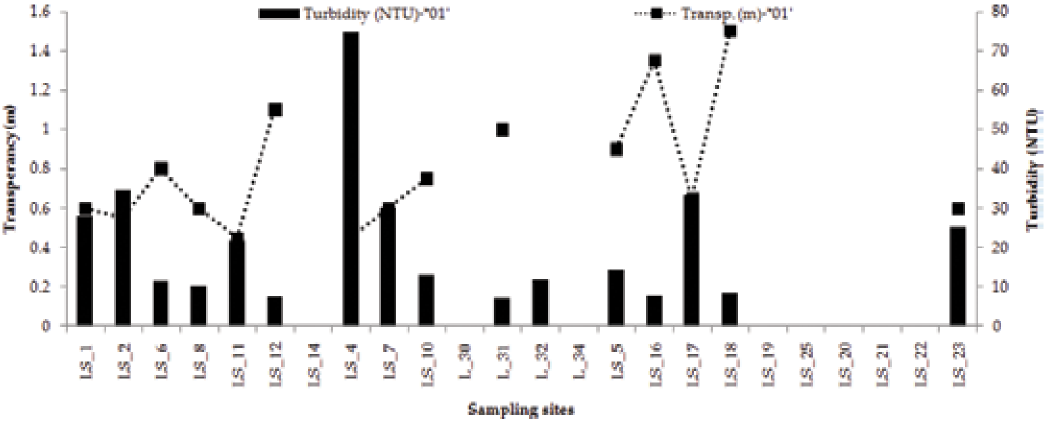

Figure 3. Water turbidity and transparency variations during February 2001 survey.

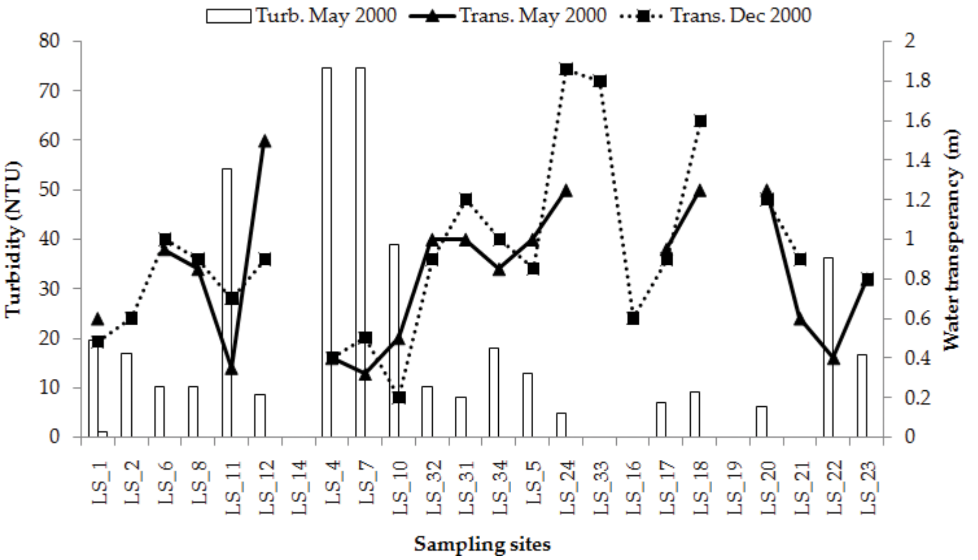

Figure 4. Surface water turbidity and transparency variations during may 2000 and December 2000 surveys.

Changes in spatial variations in chlorophyll-a concentrations have been reported previously, but only a few measurements were available from the various survey data discussed (**Figure 5**). In September 2000, August 2001, July 2003, and January–February 2012, the values ranged from 3.48 μgl^{-1} to 13.08 μgl^{-1}, 5.4 μgl^{-1} to 38.5 μgl^{-1}, 8.95 μgl^{-1} to 48.02 μgl^{-1}, and 6.01 μgl^{-1} to 22.73 μgl^{-1}, respectively. Although the values showed high spatial variability, relatively higher concentrations were evident in the gulf waters during May 2000 and July 2003. However, most of the chlorophyll-a concentrations showed insignificant and negatively correlated with water depth and water transparency. Significant correlations of the chlorophyll-a concentration with water transparency were observed during February 2001 ($r = -0.679$, $p < 0.01$, $n = 19$). Similarly, in January–February 2004, the concentrations of chlorophyll-a were negatively and significantly correlated with surface water turbidity ($r = -0.770$, $p < 0.01$, $n = 26$).

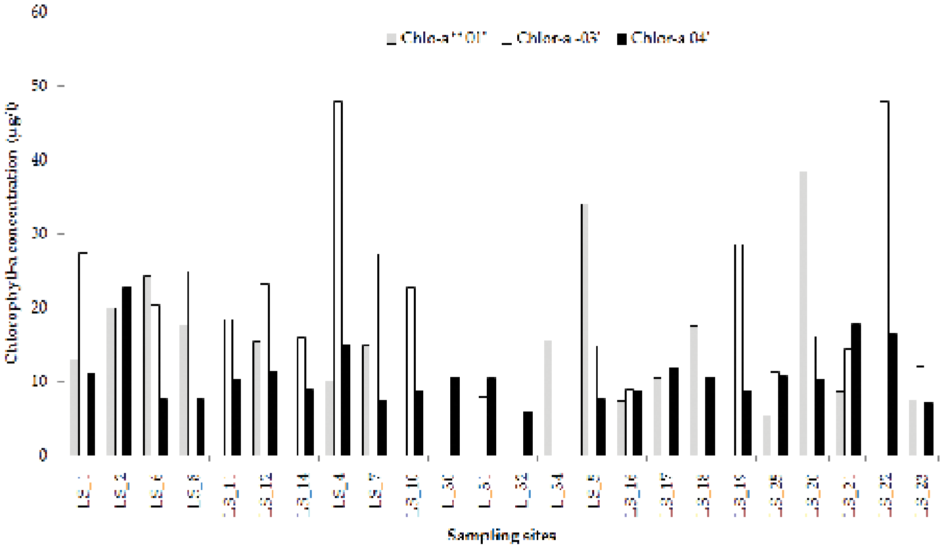

Figure 5. Chlorophyll-a concentration variations during August 2001**, July 2003, and January–February 2004 surveys.

The months of May 2000, December 2000, and June–July 2012 fall within the wet season, whereas the rest of the sampling surveys were conducted during the drier season experienced around the lake basin. Calculated correlations showed strong positive correlations between water transparency and water depth with a significant Pearson r coefficient ($p < 0.01$ level) of 0.817 (2012 survey, n = 24); 0.717 (2004 survey, n = 26); 0.828 (2003 survey, n = 25); 0.792 (August 2001, n = 24); 0.478 ($p < 0.05$; February 2001, n = 19); 0.496 ($p < 0.05$, December 2000, n = 21); 0.631 (September 2000, n = 19), and 0.541 ($p < 0.05$, May 2000, n = 20).

The surficial sediments were characterized by a relatively high water content, with over 89% of the samples containing water contents of greater than 75%. The values ranged from a minimum of 27.34% to a maximum value of 91.55%. Sediment organic matter contents (1 hour drying values) were more variable (**Figure 6**) and ranged from 1.90% to 33.47%. Lake sites with notably low sediment-water contents were LS_20, LS_21, and LS_23, whereas lower contents (less than 20%) of organic matter were found in sites LS_20; LS_23; LS_34, LS_13, LS_1, and LS_ 32; LS_11; LS_17; LS_14; LS_22; and LS_9 and LS_10.

The overall mean (± standard deviation) carbonate content (**Figure 7**) was 2.26 ± 1.48% (n = 29). Surficial sediment mean carbonate contents ranged from 0.21 ± 0.01% to 8.09 ± 0.36% for all the stations in 2012. The distribution of calcium carbonate contents in surficial sediments (**Figure 10**) shows a relatively low range when compared to values obtained in 2003/2004 which ranged from 0.5% to 21.8% (n = 29), with a mean (standard deviation) of 8.9 ± 6.6%. The differences are mainly attributed to the method of determination used. Current sediment carbonate concentrations are based on the gravimetric method as opposed to the wet digestion method used for the data of 2003/2004. Shell remains in surficial sediments seem to contribute to the variable concentrations found, although most of the samples contained relatively low amounts. These values are lower when compared to bottom sediments from more calcareous formations, although the contributions of other possible biochemical sources have also not been assessed.

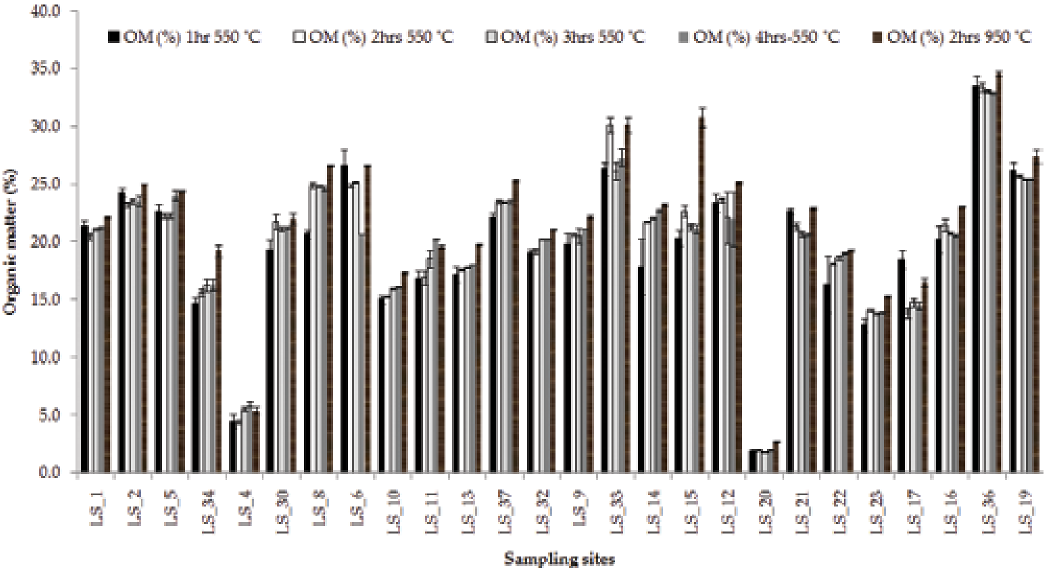

Figure 6. Mean (±SD) sediment organic matter variations at different drying durations and temperature using 2012 survey sediment samples.

Relationships between some of the sediment characteristics determined are shown in **Figures 8** and **9**. The organic matter content shows a strong positive correlation with water content and water depth at 0.01 level of significance (two-tailed test). Calculated bulk density values (**Figure 9a** and **b**) were within a narrow range from 0.0205 gcm^{-3} to 0.0875 gcm^{-3}, with higher values in sediments of relatively low percentage of OM and water contents. The sediment bulk density relationship with the sediment OM and water contents was best described by an exponential relationship ($r^2 = 0.900$ and $r^2 = 0.630$), with a strong negative correlation coefficient. The water content of surface sediments varies from about 30–50% in minerogenic deposits from areas of erosion to approximately 95–99% in highly organic sediments [3]. Part of the sediment

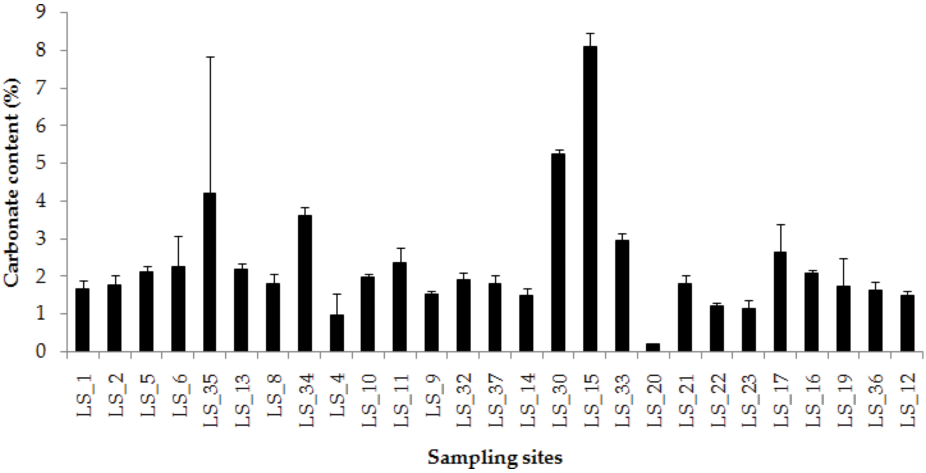

Figure 7. Mean (±SD) sediment carbonate content variations during June 2012 survey in *L. Victoria* (Kenya).

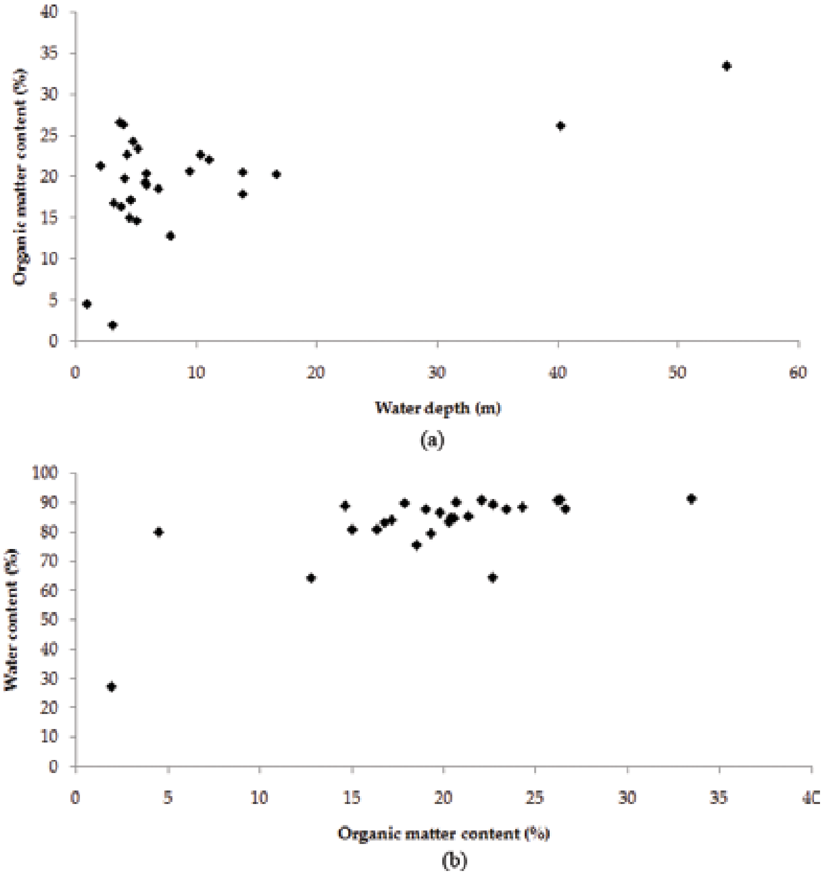

Figure 8. (a) The relationship between surficial sediment organic matter and water depth (r = 0.533, n = 27). (b) the relationship between surficial sediment organic matter and water content (r = 0.661, r^2 = 0.437; n = 27).

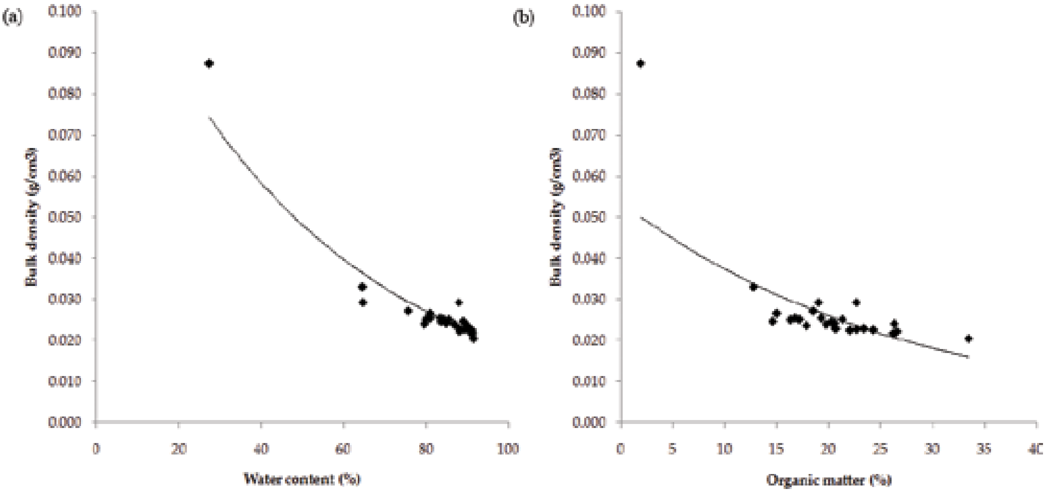

Figure 9. (a) Relationship between the sediment-water content and bulk density. (b) Relationship between the sediment organic matter content and bulk density.

water is bound to crystals in chemical structures or forms film tightly adsorbed to sediment particles, and the rest constitutes the mobile medium, which surrounds the sediment particles and takes part in exchange processes between the particulate and dissolved phases, as well as in exchange processes between sediments and lake water [3].

Surface and bottom lake water temperature show about 2°C range (surface 23.9°C to 25.9°C, bottom 23.0°C to 25.2°C) and a difference of about 0.9°C to 0.7°C. There are no large variations of the gulf water temperature when compared to the whole lake surface and > 50 m depth mean temperatures reported in 2009 ([13], 25.88 ± 0.86°C surface and 24.89 ± 0.23°C > 50 m) and 1927 ([71], 24.69 ± 0.71°C surface and 23.32 ± 0.29°C > 50 m). Studies from main lake [72] show that between 1927 and 2008 the lake's temperature increased by 0.99°C at the surface and by 1.34°C at depths >50 m, with the rate of warming increasing most rapidly between 2000 and 2008 in the whole lake. In February 2000 there were marked thermal discontinuities in the water column at a number of deep stations, with marked oxyclines at depths ranging from 30 to 50 m and with all stations being anoxic from 50 m downwards [72]. In contrast, in February 2007 the lake's temperature had risen, especially at the bottom, and both the thermal discontinuities and oxyclines were much reduced, only one station recording a dissolved oxygen concentration of <2.0 mg l^{-1} at 50 m [72].

Lake waters are more towards neutral alkaline (pH values of 7.59–8.51) and of high oxygenation levels in the surface layers, and sometimes appreciable oxygen levels occur even in deeper waters (above 3.45 mgl^{-1} in 2012). In July 2003, the dissolved oxygen in bottom water stations was above 2 mgl^{-1} in all stations. However, in some instances, very low to anoxic conditions have been reported in deep sites. Sitoki et al. [13] reported mean dissolved oxygen of 2.55 mgl^{-1} at stations of greater than 40 m depth (**Figure 10**) from lakewide surveys in 2000 and 2001 (February to March) and 5.75 mgl^{-1} (August to September). But less deoxygenation of lakewide bottom was reported at the same stations in February–March and August–September of 2006 to 2009 surveys with mean DO concentrations of 6.13 mgl^{-1} and 5.80 mgl^{-1}, respectively.

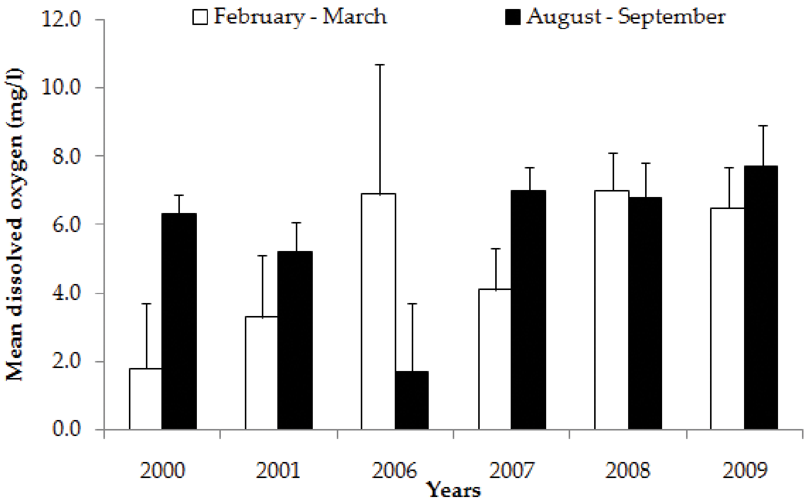

Figure 10. Mean dissolved oxygen concentration (mgl^{-1}) at greater than 40 m lake water depth during February–march and August–September lakewide surveys in different years (values adapted from Sitoki et al.) [13].

In Lake Victoria, thermal stratification, leading to hypoxia, was observed in the late 1920s [4]. Hypoxia conditions were restricted to the deeper waters (>60 m) and for shorter periods during the rainy season [6]. Lake Victoria has three phases of thermal stratification; moderate stratification occurs between September and December, stable stratification in January to March/April, and deep strong mixing in June to July [6, 73]. Stratification of the water column isolates the bottom water from exchange with oxygen-rich surface water and the atmosphere, while decomposition of organic matter in the isolated bottom water consumes dissolved oxygen [24]. For lakes, factors affecting vertical water mixing such as wind and temperature can lower DO in bottom waters to anoxic levels. Increase in deepwater temperatures, increases thermal stratification stability [74]. Thermal stability makes the lake less able to mix effectively and promotes low oxygen conditions in deepwaters during stratification period between September and April [73].

Low dissolved oxygen or hypoxic conditions can be due to natural causes such as algal respiration, seasonal flooding, stratification, and anthropogenic causes. Low dissolved oxygen environments vary in temporal frequency, seasonality, and persistence [75–77]. Hypoxia occurs naturally in habitats characterized by low mixing or light limited, heavily vegetated swamps and backwaters that circulate poorly, stratify, and have large loads of terrestrial organic matter [78, 79]. Levels of hypoxia are mainly determined by primary productivity, depth, and temperature of the aquatic body [77]. Increasing and widespread deepwater anoxia in Lake Victoria might put at risk the entire fishery [80]. In Lake Victoria, severe hypoxic conditions (<1.0 mgl^{-1}) now persists at depths below 40–50 m which cover about 35% of the lake's total bottom area [81]. Water hyacinth is notably a persistent floating macrophyte in Lake Victoria. Shading of the water by the hyacinth curtailed photosynthesis, while microbial breakdown of decaying plant material used the available oxygen. The waters below water hyacinth recorded DO as low as 0.1 mgl^{-1} making it inhabitable to most fish [82]. Additionally, the weed affected the distribution of fish by blocking migratory routes of those escaping low DO and predation [83]. However, studies by Njiru et al. [82] found the hyacinth to have led to recovery of the native species which were more hypoxia tolerant such as catfishes, lungfish, and tilapia. Hypoxia is physiologically stressful for fish, shellfish, and invertebrates with prolonged exposure to anoxia being fatal to most aquatic fauna [76, 84]. Njiru et al. [24] explored the impacts of hypoxia on the fishery of Lake Victoria. Hypoxia exposure can prompt both lethal and sublethal effects in fishes, leading to reduced feeding, reproductive, growth, metabolism, and slower reaction time. These effects vary across fish species [84] but also depend on the frequency, intensity, and duration of the hypoxic events [76]. In shallower lake areas, with permanent cover of macrophytes, especially large extensive floating water hyacinth, deoxygenated waters may influence the distribution of low oxygen-intolerant fish species in the lake.

3.3. Sources of organic matter in Lake Victoria sediments

Sediments accumulated in lake basins consist of various organic and inorganic materials mostly utilized as proxies for climatic changes and as historical records of the lake. The gulf's bottom deposits are mainly a combination of the several externally transported materials, surface runoffs, and shoreline-eroded materials and slowly settling suspended loads. An equally important source is the autochthonous organic matter which is aerially derived materials. The first observations on the nature of the bottom of Lake Victoria were made by Graham and

Worthington during their survey in 1927–1928 [71]. They stated that nearly all the bottom of the lake was covered with a fine greenish-black mud which was almost entirely composed of the dead shells of diatoms [10]. First palaeolimnological records of bottom sediments in the northern part of the main Lake Victoria (outside the Nyanza Gulf) were provided by Kendall [15]. Scholz et al. [16] study revealed that fine-grained late-Pleistocene and late-Holocene sediments having a maximum open-basin thickness of about 8 metres overlie older desiccated lake sediments, alluvial materials, Precambrian crystalline, and tertiary volcanic rocks depending on the position in the lake. The distribution of these sediments mimics bathymetry. Thicker sediment layers may be found near bathymetric heights and inshore waters. Analyses of the composition of oven-dried samples of mud revealed 24–64% silica, 4–25% carbon, 1.5–4.8% iron, 0.6–2.2% nitrogen, 0.5–2% sulfur, 0.04% phosphate, 0.3% Ca, 0.07% Mg, 0.05% K, and 0.03% Na [10]. Talbot and Livingstone [85] used geochemical analysis of organic matter in sediment cores from Pilkington bay, Ugandan area of *L. Victoria* in 1971 (depth of 32 m and 66 m) to provide a history of lake level fluctuations. The core sediments were characterized by moderate to low organic contents and very low hydrogen index. Very low HI from sediments rich in algal remains indicates severe degradation of the organic material. At 6.9 m and 9.8 m downcore Ibis core 1, the TOC values were 18.6 and 2.6%, respectively [85]. Similarly, at 7.3 m and 10.3 m downcore Ibis core 3, the TOC values were 7.9 and 2.1%, respectively [85]. TOC and HI both decline as an exposure surface is approached, mainly due to the selective removal of unstable components by bacterial respiration and inorganic oxidation. The carbon isotopic composition of the organic matter shows significant variations through the core $\delta^{13}C_{org}$ values were > −20‰ at and below the discontinuity surfaces and < −20‰ above the upper shell bed. According to Talbot and Livingstone [84], variations in the carbon isotopic composition of the bulk organic matter may reflect mainly changes in the relative contributions from different plant communities, which are also related to changes in the lake. Although all aquatic algae and many vascular plants have carbon isotopic compositions in the range from −22‰ to −30‰, plants using the C_4 photosynthetic pathway have range from −9‰ to −16‰ [86, 87]. Variations in the bulk organic matter isotopic composition of organic matter in Lake Victoria are likely principal to reflect varying contributions from plant communities with different proportions of C_3 and C_4 plants. In particular a sediment dominated by inputs of aquatic algae or forest trees is likely to have a $\delta^{13}C$ between −20‰ and – 30‰, while substantial inputs from C_4 graminoid plants from either marshes or terrestrial grassland will tend to produce a $\delta^{13}C_{org}$ between −10‰ and – 15‰. Characterization of stable isotope signatures of various organisms from the lake shows varied values, but the information is limited spatially. Studies on sources of carbon in the *L. Victoria* ecosystem reported mean (±SD) values of stable C isotope values for organisms collected at deep site and littoral site in Napoleon Gulf in 1995 [69] for δ13C were gastropods (−19.0 ± 1.7), bivalves (−18.0 ± 0.7), *Rastrineobola argentea* (−16.9 ± 0.8), and *Lates niloticus* (−18.9 ± 0.2). The δ13C of plants ranged from −8.8‰ to −24.6‰, while in fishes the values ranged from −18.6‰ to −24.5‰, suggesting assimilation of mostly C_3 sources for the fishes [67]. According to Gichuki et al. [68], aquatic macrophytes from wetland ecosystems in Nyanza Gulf had $\delta^{13}C$ isotopic ratios ranging from −8.92 to −29.18, and for the dominant macrophytes, they observed most enriched $^{\delta 13}C$ values for *Cyperus papyrus* and most depleted $\delta^{13}C$ values for *Eichhornia crassipes*. Fractionation of carbon isotopes during photosynthesis is a key parameter for understanding organic carbon isotope signatures in aquatic ecosystems. Photosynthetic fractionation of carbon isotopes can occur at the diffusion, dissolution, and carboxylation step [88]. During photosynthesis, plants preferentially acquire the lighter carbon isotope, ^{12}C. Consequently, plant organic matter has a lighter isotope ratio than the source inorganic carbon [88]. More recently, on the Tanzanian portion of the lake, Machiwa [35] demonstrated the potential to discriminate between input sources of organic material into lakes using stable isotope signals in sediment and suspended particulate matter. Variations in $\delta^{13}C$, $\delta^{15}N$, and C/N ratios in SPM and sediments in inshore areas were due to differences in the proportions and sources of autochthonous or allochthonous matter. Watershed characteristics, such as urbanization, and lake characteristics, such as algal blooms, also immensely influenced the stable isotope signal of the organic matter in sediments [35]. Although this study did not incorporate isotopic studies, it clearly shows that interpretation of such information demands more spatial and temporal information on isotopic patterns to understand within lake variations in allochthonous inputs, considering the high seasonal variability in a tropical type of climate experienced in the lake region.

Short cores from the open lake document a shift in lake conditions beginning in the 1930s that progressed to the major ecosystem collapse of the early 1980s [14]. The coincidence of the shift in sediment properties in the 1930s with the beginning of rapid expansion of human population and agricultural activity suggests cause and effect. It is conceivable that the lake experienced similar conditions due to natural causes between about 9800 and 7500 years ago [14]. From core studies, deep rift lake basins [89], with anoxic depths below 250 m, contains thick sequence of biologically undisturbed, finely laminated muds and silts. Similar low oxygen conditions to anoxic conditions reported in deep sites of Lake Victoria a relatively shallow basin can possibly promote accumulation of significant amounts of organic matter after deposition, depending on type of sedimenting materials, the extents of bioturbation processes, and redox conditions. There are no experimental studies on downward flux measurements of particulate carbon in the gulf areas. In shallower areas, downward fluxes of particulate organic matter may be highly variable, and the remobilization of deposited sediments through resuspension caused by physical mixing processes may contribute to variations in sediment composition and low-sediment organic matter.

Understanding sources, dispersion pathways, and sinks of sedimentary materials can improve our understanding of various geochemical cycles in the lake. In aquatic environments dissolved phosphate is consumed during growth of phytoplankton and is regenerated during bacterial decomposition of organic matter. The regenerated phosphate may be released to the overlying water, reprecipitated within the sediment as authigenic phase or adsorbed by other constituents of sediment [90]. Development of anoxia in sediments will lead to reduction of iron oxides and release of sequestered P. Adsorption on oxidized surface sediment affects the flux of phosphate from the sediment to the overlying water [91].

Besides the sediment physical factors, iron-manganese oxides, clay minerals, organic matter, and reactive Fe are among the sedimentary geochemical factors controlling chemical partitioning and bioavailability. Linnik and Zubenko [92] showed that the release of heavy metals from bottom sediments was promoted, for example, by a deficit in dissolved oxygen, a decrease in pH and redox potential (Eh), and an increase in mineralization and in dissolved organic matter concentration. Compared with other natural environmental substrates, sediments have a greater capacity to bind Hg. More than 90% of the total Hg in sediment-water system is sorbed or held in sediments [27]. Sediments therefore serve are useful long-term records of the material influx and provide historical records for evaluating past and other ecological changes occurring in the lake. However, very few studies have been concentrated in the gulf, as the best depositional basins for provision of long-term records are in the main lake. Therefore, continuous provision of data on the sedimentary environment is valuable in understanding processes within these areas and their influences on the above water quality, considering the fact that the area receives significant inputs from the inflowing rivers and nearby human activities.

The six coring stations, representative of the main lake depositional basin, were located at a water depth range between 48 and 68 m [60], but none was located in the Nyanza Gulf, where the depths are below 60 m. Accumulation of fine-grained Holocene sediments in offshore regions of Lake Victoria is restricted to the deep east-central basin floor [16, 59]. However, surficial sediment deposits the deep gulf, and open stations contain similar organic rich muds. Verschuren et al. [60] noted that with increasing distance from the depositional centre, progressively thinner sheets of Holocene sediments occur, for example, about 5.4 m at station V95-1G and 3.6 m at V96-1MC (eastern central basin), reflecting bottom dynamics that become less and less favorable for undisturbed sediment accumulation. According to Verschuren et al. [60], in the transect of stations examined, greater physical biological sediment mixing at shallower depths is evident in the lack of flocculent surface muds in cores V96-1MC and V96-8MC (western central basin). In these shallow sites, organic matter decreases from 32% at the top of the short sediment core surface, to 23% at bottom of core compared to a change of 14% (top of core) to 10% (end of core). The deepest site short cores at 58 m and 68 m water depth had a sub-oxic sediment–water interface (0.0 mgl^{-1} to 0.7 mgl^{-1}), with high and near constant organic matter contents along the sediment core (35–38% near top surface of the core and 33–35% end of core). The core closer to the extreme western side of the open lake portion of the Nyanza Gulf contained 27% (top) and 25% (end of core).

3.4. Sedimentation and nutrients in Lake Victoria

Rivers contribute a significant load of suspended materials annually into the lake. Although it is not possible to provide current rates of resuspended loads, the inputs of organic matter into the depositional areas seem significant from the productive water column (autochthonous sources). Johnson [92] summarized published sedimentation rates for several lakes. There is surprisingly little difference between the sedimentation rates observed in tectonic versus glacial lakes, even though the relief, and hence, the sediment supply rate per unit area of drainage basin should be higher around tectonic lakes. Verschuren et al. [60] established average recent sedimentation accumulation rates of 0.032 ± 0.001 to 0.028 ± 0.001 gcm^{-2} $yr.^{-1}$ from ^{210}Pb dating of sediment cores in deep depositional sites in the main lake. The rates are lower but comparable with other variable rates reported for other temperate lakes [93]. Variable sedimentation rates are reported in different types of lakes, but the mean values reported by Verschuren et al. [60] for the lake appear to fall within the low end values for other lakes. In L. Erie, sedimentation rates [94, 95] estimated from 35 stations varied from less than 20 $mgcm^{-2}$ $yr.^{-1}$ to greater than 1000 $mgcm^{-2}$ $yr.^{-1}$ with an average of 230 $mgcm^{-2}$ $yr.^{-1}$.

Although soil types and land uses vary in different drainage basins, the surrounding gulf areas are under the same typical tropical wet climate. Lindenschmidt et al. [96] in a neighbouring rural catchment of *L. Victoria* found out that less loading will occur from riverine systems that have lower discharges, consist of nonagricultural land, and have low basin slope. Soil erosion and leaching in this tropical region increase dramatically as slope incline increases. A sediment core was taken 55 m water depth off western Kenya (core at station 103) and the diatom and chemical stratigraphy analyzed [9]. The dry weight sedimentation rate increased after 1960 to 90 gm^{-2} $yr.^{-1}$ from 57 gm^{-2} $yr.^{-1}$ before then. There is an interpretable sequence which begins with increasing production of *Cyclostephanos* concurrent with an increase in C and N deposition early in the century [9]. These trends continued until the decade of the 1960s when P and biogenic Si deposition began a rapid increase. By the late 1960s, *Melosira* spp. was nearly gone largely replaced in the diatom community by *Nitzschia*. By the late 1970s, modern rates of C, N, P, and Si deposition were established as was the modern diatom community [9]. The increased deposition rates of N beginning in the 1920s and P beginning in the 1950s were likely results of watershed and airshed disturbance [9]. Primary production was extremely high as lake level rose in its first 500 years, nourished by the high input of nutrients from the flooded landscape [14].

Concentrations of P in the gulf lake water (2000–2002) were found to be different from those in the main lake with phosphorus fractions, soluble reactive P, and total P being significantly higher in the main lake than in the gulf [53]. Well-oxygenated conditions in the gulf keep the PO_4-P strongly bound to mineral particles, whereas in the main lake, where deeper depths allows for development of anoxia, it is released into solution [53]. In 2005 and 2006, an assessment of the potential for sediments to contribute to the water column P concentrations in Lake Victoria showed that sediment total TP, apatite phosphorus, inorganic phosphorus, and organic phosphorus increased in sediments along the gulf towards the main lake, while the non-apatite inorganic phosphorus (NAIP) increases were less defined [65]. The longitudinal gradient of sediment TP and its fractions in Nyanza Gulf is a result of high rates of terrigenous input and resuspension and transport of the light, phosphorus-rich inorganic and organic matter towards the main lake [64]. The non-apatite inorganic P concentration on the western end of the gulf is exceptionally high, >1500 $mgkg^{-1}$ [66]. Total P in the sediment ranged from 812.7 to 1738 $mgkg^{-1}$ dry weight and was highest in the Rusinga Channel, the exchange zone between the gulf and the main lake. In the gulf and the Rusinga Channel, the less bioavailable apatite phosphorus dominated, whereas in the deeper main lake, organic P was the major fraction illustrating the importance of anaerobic release of P from sediments and acceleration of internal P loading in the main lake [65].

Chemical processes within the sediments play an important role in the P fluxes within and from sediments. In aquatic environment dissolved phosphate is consumed during growth of phytoplankton and is regenerated during bacterial decomposition of organic matter [91]. Much of the regeneration takes place in the water, but in relatively shallow environments such as lakes, estuaries, and continental shelves, sediments may play an important role in the regeneration of phosphate [97]. The regenerated phosphate may be released to the overlying water, reprecipitated within the sediment as authigenic phase or adsorbed by other constituents of sediment. Adsorption on metal oxides in the sediment has been identified as one of the principal reactions involving phosphate [90]. Mortimer [98] has described the oxidized surface layer as a trap for phosphate. The reactions that release phosphate to the porewater are desorption of phosphate from surface sites on sediment particles, mineralization of organic matter, and reduction of iron oxides in the anoxic zone of the sediments [99].

3.5. Inferences from stable isotope signatures in lake sediments and their applications

Organic rich sediments have been reported in sediments from depositional basins of the main Lake Victoria [100, 101]. Previous studies show a slight variability in SOM contents (**Figures 11** and **12**). Mean sedimentation rates, and organic carbon (total core length mean) of sediment core 103 (core recovered at 56 m water depth in 1990 by Hecky) [9], 96–5 MC (core recovered at 68 m water depth in 1996 by Verschuren et al. [102], and Itome (core recovered at 25 m water depth in 1995 by Campbell et al. [103] were 100, 320, and 276 gm^{-2} $yr.^{-1}$ and 168, 204, and 184 mgg^{-1} dry weight, respectively. A similar trend in sediment organic matter emerged in surficial sediments in the relatively shallower Nyanza Gulf, with significant spatial differences especially in the zones with significant influence of externally derived riverine inputs. According to Hecky et al. [100], the isotopic analysis of all the three sediment cores recovered by Hecky [9], Verschuren et al. [102], and Campbell et al. [103] recorded an increase in the isotopic signature of the sedimentary organic matter (from a baseline −22‰ to −21‰ in the deepest core and no clear trends for inshore Itome core, which was significantly $\delta^{13}C$ enriched). According to Hecky et al. [100], a Mwanza-Port Bell (southern shore-northern shore) surface water transect in October 1995, of main *L. Victoria*, show highly correlated POC and PN (r = 0.96) with a mean molar C/N ratio of 7.2 with higher ratios nearshore (up to 8.4). These low, near Redfield ratios, values for C:N are characteristic of Lake Victoria [104] and are indicative that the particulate matter sampled was of algal origin. Isotopically depleted PC occurred offshore, and $\delta^{13}C$ was increasingly enriched nearer the coasts as depth shoaled. The $\delta^{15}N$ of the PN showed an inverse pattern with highest $\delta^{15}N$ values observed offshore.

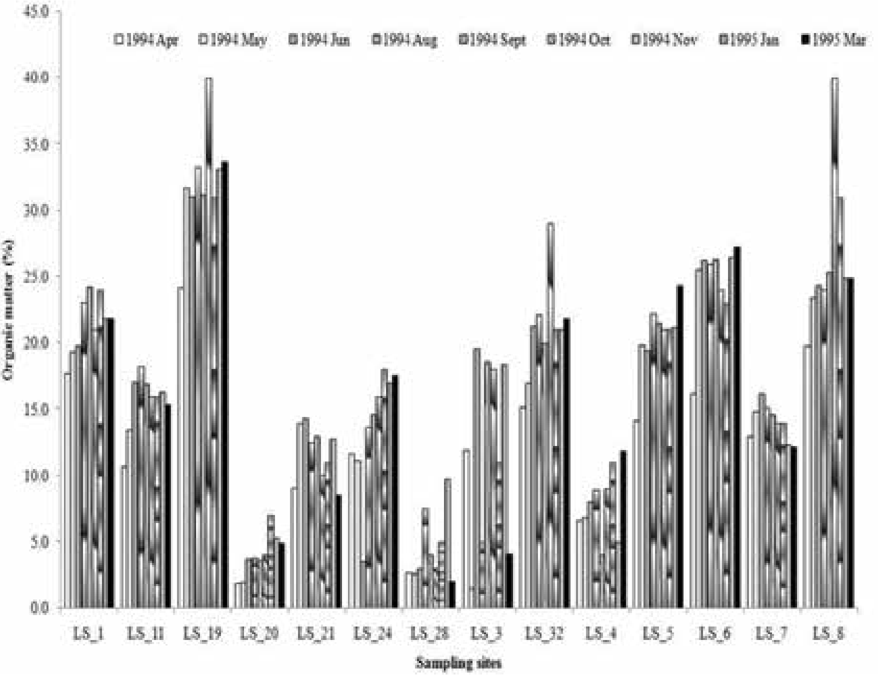

Figure 11. Monthly sediment organic matter contents in surficial sediments.

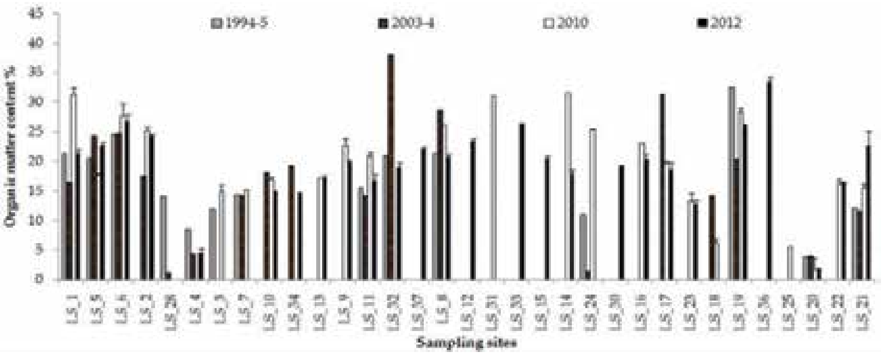

Figure 12. Mean sediment organic matter contents (±SD) in surficial sediments.

Consequently, there was a strong inverse relationship between $\delta^{15}N$ and $\delta^{13}C$, with the former decreasing at high algal abundances and the latter increasing as PC increased. The scatter of the isotopic signatures with increasing algal abundances indicates that these relationships are dynamic in nature responding to the availability and demand for CO_2 and DIN [100]. The Nyanza Gulf is more active in terms of exchanges between the land and the lake, when compared to the offshore depositional basins. Again, exports of organic rich waters from urbanized areas act as important modifiers of sedimentary organic matter derived from in-lake productivity and higher plant production.

3.6. Significance of floating water hyacinth mats in Lake Victoria on sediment organic matter accumulation

A major portion of the organic matter in freshwater systems originates from the terrestrial environment. The bulk of allochthonous organic matter consists of structurally complex polysaccharides, lignocelluloses, and other complex organic compounds [105]. Autochthonous production is also an important source of organic matter in lakes and is generally less refractory than allochthonous carbon [106, 107]. Autochthonous organic matter is primarily derived from phytoplankton and macrophytes, but, in shallow clear lakes of Nyanza Gulf from April 1994 to March 1995 from different surveys conducted in Nyanza Gulf between April 1994 to 2012 where light penetrates to the bottom, benthic micro-algae can also be an important source of detritus [106].

Littoral sediments are often heterogeneous because of the presence of rooted macrophytes and the resuspension of particles in shallow water during windy periods, and the net sedimentation of organic matter is small because of alternating sedimentation and resuspension episodes [36]. In addition there can be a significant downward transportation of material along the lake bottom resulting in deposition of organic matter in the profundal sediments [36]. Submerged aquatic macrophytes are generally soft in nature, moderately rich in protein, and are preferred by different herbivorous fish. The production of littoral and pelagic phytoplankton and of the dominant biomass of submerged macrophytes and epiphytes in littoral zone contributes to the total sediment organic matter accumulated over time.

Much of the organic matter produced by these larger aquatic plants remains in the wetlands and littoral zones of lakes and undergo decomposition [20]. During senescence and after death of organisms, much of the organic matter is released as soluble compounds. The particulate components decompose at various rates depending on their location, composition, and environmental conditions, particularly those of temperature and oxygen availability. When decomposing tissue falls to the sediments in detrital masses, the environmental of the aggregates rapidly becomes anaerobic. Under these reducing conditions, rates of decomposition are decreased greatly [20].

Water hyacinth has contributed to several to various socio-economic impacts in the lake fishery, such as lake transportation, artisanal fishing. Also, Ofulla et al. [108] study on associations between aquatic macrophytes and vector snails for schistosomiasis illustrated that *B. sudanica* and *B. africanus*, the two most common snail hosts of schistosomiasis in the Nyanza Gulf, were found associated with the aquatic macrophytes in the lake waters. Besides this, a form of ecological succession (the progressive displacement of one or more species of plants by other species) has been observed in Lake Victoria, in which stationary mats of water hyacinth along the shores and banks of rivers were replaced by other aquatic plants such as hippo grass (*Vossia cuspidata*) and other aquatic sedges such as *Cyperus papyrus* and climbing plants such as *Ipomoea aquatica* [109–113], creating concern among stakeholders in the region. The dispersal and continuous presence of water hyacinth is therefore still a concern in *L. Victoria* since the 1990s. Kisumu Bay, Homa Bay, Asembo Bay, Luangwa Gembe, off Sondu-Miriu river-mouth, off Kibos river-mouth, and Dunga are in-lake areas commonly found associated with macrophytes, including water hyacinth as observed by Ofulla et al. [109]. Besides this, large *Cyperus papyrus* swamps are found around major river-mouths of Sondu-Miriu, Nyando, Kisumu Bay, Kibos river-mouth, and Dunga areas. Persistence of extensive floating mats of water hyacinth and other macrophytes in major bays of Nyanza Gulf (**Plates 1a, 1b,** and **2a**) has the potential to introduce a lot of plant debris and decaying particulate organic materials into the lake sediments (**Plates 2b** and **2c**).

3.7. Are future potential impacts from cage culture on lake sediments of concerns?

In recent years, aquaculture production has increased worldwide, mainly due to the increasing demand from aquaculture produce and the need for improved food security. These developments are supposed to improve income and livelihoods but can generate negative

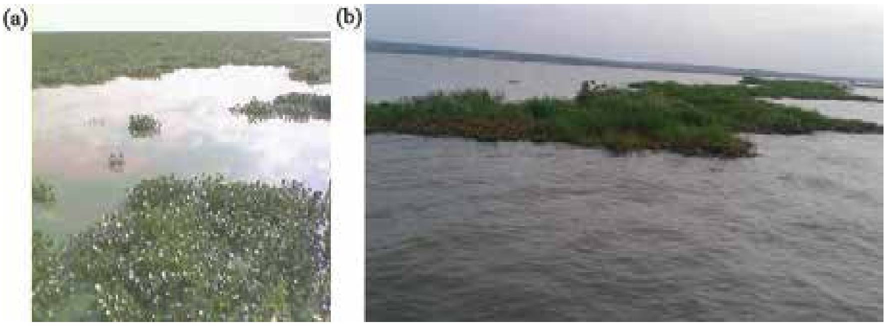

Plate 1. Water hyacinth and other macrophytes in Nyanza gulf of Lake Victoria in July 2012 (a) and June–July 2017 (b).

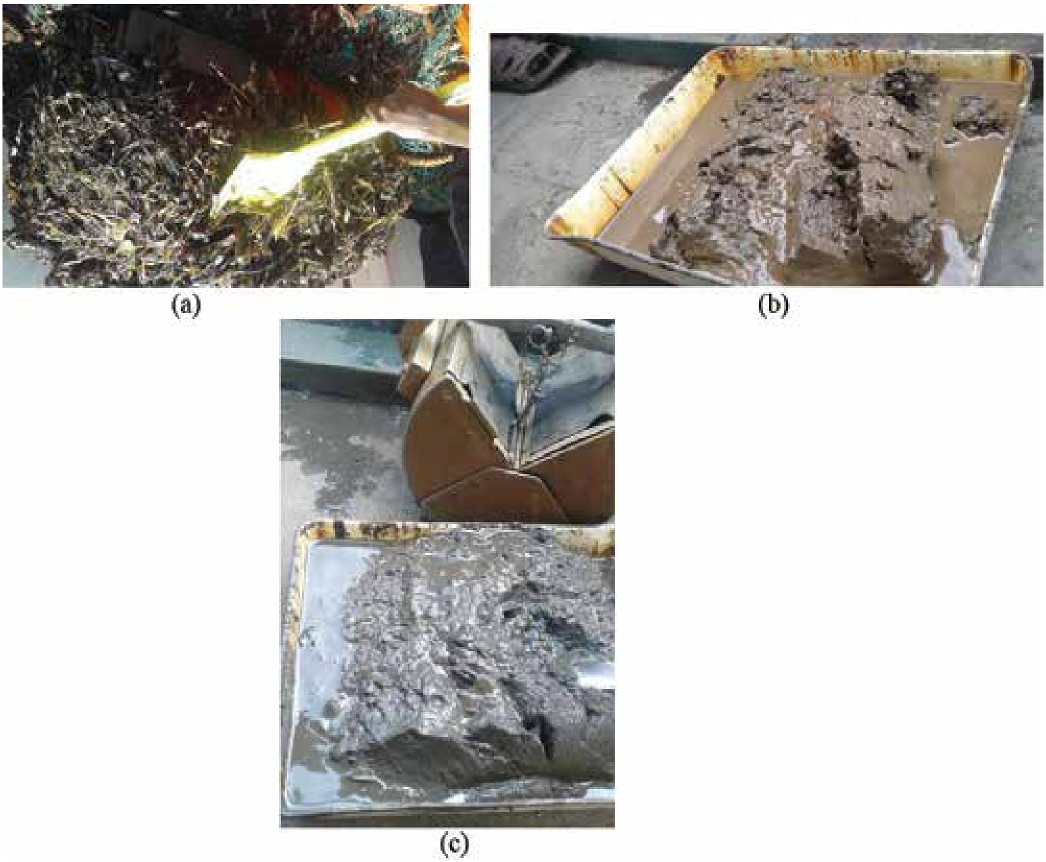

Plate 2. Undegraded water hyacinth and other macrophytes (a), retrieved from a trawl net and freshly retrieved surficial sediments from shallow riverine zones (b) and from deep open lake areas (c) using a Ponar grab sampler, in Nyanza gulf of Lake Victoria in June–July 2017.

impacts such as pollution, landscape modification, or biodiversity change, if best aquaculture practices are not followed. However, it should be recognized that to date the majority of aquaculture practices have had few adverse effects on ecosystem [114]. First studies on impact of fish cage operations on surrounding water environment in L. Malawi [115, 116] were minimal despite substantial discharges from the cages, due to dispersion by water currents and aggregation of wild fish species feeding on the wastes. Experimental studies on cage culture from Uganda and Tanzanian side of *L. Victoria* found no consistent environmental changes using water quality parameters, phytoplankton and macro-invertebrates [117, 118]. Effect of nutrient discharge on DO was not pronounced. Nevertheless, some cases of environmental degradation in coastal areas have occurred due to, for example, intensive cage culture operations in Europe and shrimp farming practices in Southeast Asia and Latin America [114, 119].

Fecal contamination implies a high risk of contracting waterborne diseases if the water is used for drinking purposes without pretreatment. *Escherichia coli* (*E. coli*) is used as an indicator for human and animal fecal pollution of water. Urban sewage and industrial effluent [120] around Kisumu and Homa Bay areas are considered more vulnerable to fecal contamination, than open lake sites. Safe water quality implies low risk from bacteriological pollution and acceptable properties in terms of chemical, oduor, and taste [121]. Under the World Health Organization (WHO) guidelines, the bacterium *E. coli* should not be detected in a given 100 ml sample of drinking water [122]. Increased nutrients from atmosphere, land and fecal contamination, fuel the growth, and proliferation of algal blooms in surface water. Cyanobacteria are potentially toxic to humans and animals and can also degrade the ecological and esthetic values of water. From previous phytoplankton surveys in Kisumu Bay of the Nyanza Gulf of *L. Victoria* (Kenya), cyanobacteria were the most dominant, contributing 50% to the total phytoplankton biovolume. The highest MC concentrations were recorded between November and March coinciding with the wet season when rainfall and nutrient enrichment from the catchment increased [13]. Algal blooms were thicker and more frequent in Murchison Bay than Napoleon Gulf. Highly toxic blue-green algal scums (*Microcystis* and *Anabaena* spp.) and water hyacinth (*Eichhornia crassipes*) congregated along the shores of the city of Gaba (Uganda) water intake sites. Microcystin levels were between $<0.5\ \mu gL^{-1}$ and $3\ \mu gL^{-1}$ [123]. In bays of *L. Victoria* (Tanzania), the level of water exchange from individual bays to the main basin is an important factor influencing eutrophication and microcystin production in nearshore habitats [124]. Microcystins were found in closed bay sites, and concentrations ranged from 0.4 to $13\ \mu g\ l^{-1}$ microcystin-LR equivalent and coincided with high abundance of *Microcystis* spp.

Particulate matter fluxes into the bottom sediments remove and incorporate particulate-bound metals from the water column, where they can become permanently buried or reintroduced back through sediment resuspension, especially in shallower areas. Similarly types of feed and sources are important factors which can contribute to accumulation of non-essential metals and other organics in aquatic food chains and caged fish. Supplementary fish diets improve fish nutrition. However, understanding how dietary MeHg affects its bioaccumulation in caged fish fed from marine based feeds is unknown but of importance. Variations in sediment metal contents have been reported in the lake from different surveys in 2010, 2012, and 2013. Total mercury concentration in sediments fell within the range of values recorded elsewhere but with low ng/l concentrations in the water. There is paucity of data on Hg contents in biota from the gulf, apart from initial results by Campbell et al. [103]. Recent research indicates that heavy metals do tend to accumulate in the sediments below fish farms. However, most studies have found that concentrations are within acceptable environmental guidelines even at farms that have been in production for many years [125]. Toxic metals that bioaccumulate and magnify along food chains are a concern to human health worldwide. Improvement in feed formulations is expected to decrease Zn loading to the marine environment, as many manufacturers are adding lower amounts of a more available form, zinc methionine [126]. Recently moderate to high levels of sum of seven PCB concentration were provided in sediments and fish, with median values of 2.2 to $96.3\ \mu gKg^{-1}$ dry weight and 300 to $3000\ \mu gKg^{-1}$ lipid weight, respectively. Fish cestode endoparasites biomagnified PCB levels than levels in fish hosts. These levels were found to be comparable with ranges of the PCB values found in other places of the world [127]. In a recent study, Abong'o et al. [128] indicates occurrences of some OCs around island waters of *L. Victoria*, supporting previous reports of use of the same pesticides in the wider catchment by Musa et al. [129]. Antibiotics and therapeutants are administered to recover sick fish, but this has declined in marine aquaculture. Commercially medicated feed is readily available and is commonly used at farms in response to outbreaks. However, the amount of antibiotics released depends upon the fish species, amount of feeding activity, and absorption in the fish digestive tract [125]. The most obvious detrimental effect of extensive use of antimicrobials in aquaculture is selection of fish and shellfish pathogens resistant to multiple antimicrobials. Antimicrobial resistance determinants in piscine pathogens could also be acquired from environmental antimicrobial-resistant bacteria that have been selected by residual antimicrobials in water and sediments [130, 131]. Considerations suggest that excessive aquacultural use of antimicrobials may potentially have major effects on animal and human health as well as on the environment. There are no detailed assessments to provide information on amounts of antimicrobials in use aquaculture and potential effects.

Biofouling adds weight to nets and equipment, and it changes hydrodynamics of fish cage systems. Chemical antifoulants are used to control or eliminate the growth of marine organisms which attach to aquaculture cages, ropes, and structures [125], and hence their toxic effects on other nontarget organisms around fish farms are of concern. Heavy and persistent biofouling impedes water flow through cages, increases BOD in cages, causes net drag, and can shorten the useful life of nets and ropes [132, 126]. Finally, as documented in a recent study by Biginagwa et al. [133], concerns are emerging on the possible effects of microplastics on fish and as sources of organic contaminants in the lake, although there are increasing public awareness campaigns of uncontrolled disposal of all types of plastics in surface waters.

The cage culture industry is at its infancy in Kenya but with a huge interest in the technology. Currently in *L. Victoria*, cage farms are operational. It is expected that increasing investment in cages (in Kenya, Uganda, and Tanzanian sections of *L. Victoria*) will also create a high demand on feeds and seed, with extensive areas under farms in this transboundary ecosystem. In marine aquaculture, there are many lessons learnt with regards to negative environmental impacts from cage farms. Although there are no incidents of contamination from such activities, it is therefore prudent to ensure full implementation of guidelines on best management practices and awareness creation to ensure cage operations and other farm activities promote a sustainable fishery as a whole. This calls for frequent monitoring of the lake environment.

4. Conclusion

Sediments eroded from watersheds are important determinant factors in water quality and integrated water resource management. Increased concentrations in surface water causes increased turbidity, reduced under water light transmission and siltation, and reduced water storage in dams and shallow lakes.

Maintaining good sediment and water quality today is prioritized due to human health related concerns from faecal contamination from untreated and partially treated domestic wastewaters; discharge of industrial chemical effluents; increased use of pesticides, fertilizers, and herbicides for crop production and livestock rearing; and persistent organic pollutants and pharmaceutical residues which are endocrine disruptors and carcinogens.

Bottom lake sediments are important archives of the lake and anthropogenic indicators of their catchment. In *L. Victoria*, although the deeper (> 40 m) depositional areas are in the open lake, visual observations show that most of the offshore sediments consists of muddy deposits plus significant shell remains, with more sandy type of sediments in some of the areas off river-mouths.

The sediment organic carbon contents varied spatial, but there were no significant variations between the different sampling periods. The surficial sediments are organic rich and are characterized by a relatively high water content, with over 89% of the samples containing water contents of greater than 75%. In 2012 survey, sediment organic matter contents were more variable and ranged from 1.90 to 33.47%.

An evaluation of the SOM at different heating durations at constant temperature 550°C and at very high temperatures of 950°C did not show any significant differences. High primary production and greater settling in deeper area contribute to the nature of sediments deposited and also are reflected in the relatively high OC contents.

The importance of sediments in adsorption of contaminant substances and influencing geochemical processes within the lake are also emphasized. It is recommended that continuous monitoring strategies are adopted in view of the new cage culture developments initiated in most of the African tropical lakes, including Lake Victoria, as uneaten feeds and operations may influence water and sediment quality in cases where designed best management practices are not fully implemented. There is a need to prioritize sediment research including the microbial component, porewater exchanges, and sediment fluxes which are rarely incorporated in major projects.

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Conflict of interest

The author wishes to declare that there is no conflict of interest and the data used is from original research unless otherwise adapted from cited sources.

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Chapter 5

The Adaptation Mechanisms of Bacteria Applied in Bioremediation of Hydrophobic Toxic Environmental Pollutants: How Indigenous and Introduced Bacteria Can Respond to Persistent Organic Pollutants-Induced Stress?

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Additional information is available at the end of the chapter

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Abstract

The chapter describes the aspects of bioremediation that are related to survival and metabolism of bacterial degraders in the adverse environment contaminated with dangerous hydrophobic chemicals, polychlorinated biphenyls (PCBs). Successful environment decontamination requires bacterial strains that possess appropriate enzymes and are able to degrade particular contaminants. This chapter deals mainly with the adaptation mechanisms that allow bacteria to decrease toxic effects of the dangerous compounds on cytoplasmic membrane as the first contact point of pollutants and the bacterial cell. Many responses have been observed in bacteria that counteract the effects of toxic environmental organic pollutants: saturation-rigidification of cell membrane, *cis*/*trans* isomerization of fatty acids, increased content of cyclopropane fatty acids, and changes in branched fatty acids and cardiolipin, production of stress proteins, and elimination of toxic compounds using efflux pump. The study of these mechanisms is the first step in selection of appropriate resistant bacterial strains for bioremediation applications. Next steps should include study of degradation potential and efficacy of the most resistant strains. Setting up suitable experimental systems to examine the cell responses to toxic environmental organic pollutants in the adverse environment and optimal conditions for metabolism of bacterial degraders are important issues in the current bioremediation research agenda.

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Keywords: adaptation, bacteria, biodegradation, bioremediation, bioaugmentation, biostimulation, cytoplasmic membrane, environmental stress, fatty acids, persistent organic pollutants, polychlorinated biphenyls, terpenes

1. Introduction

Due to more than 200 years of industrialization and to the use of dangerous substances in many production processes, the countries across the world are facing the problem of soil, sediment, and water matrices contamination. Contaminated sites, namely environmental burdens, generally resulted in past and also arise nowadays from the manufacturing, storage, use, and disposal of hazardous chemicals and materials. It is now widely recognized that polluted sites pose threats to human health and the environment.

Polychlorinated biphenyls (PCBs) represent an environmental concern due to their hydrophobicity and toxicity. Although the production of PCBs has been banned and their use heavily restricted, they still pose an environmental problem due to their presence in old electrical transformers, capacitors, landfills, and in contaminated soil and sediments mainly in the areas around the former production facilities [1, 2]. Their physical and chemical properties such as thermal and chemical stability, resistance to degradation, and general inertness contribute to their persistence in the environment [3]. PCBs represent potential health risks for living organisms due to their lipophilic nature, bioaccumulation, and potential carcinogenic properties [4]. Hydroxylated PCBs (HPCBs), known PCB metabolites, have been detected in human serum samples and wildlife blood samples [5]. Numerous adverse health effects in human have been associated with these compounds. HPCBs are capable of mimicking a thyroid hormone, thyroxin [6], and may generate reactive oxidative species and cause DNA damage. Studies performed with the individual PCB congeners show that PCB toxicity and biodegradability are structure related as well [7].

Many conventional and sustainable remediation techniques have been invented to destroy hazardous organic pollutants [8]. The finding that both Gram-negative bacteria, such as *Achromobacter, Alcaligenes, Burkholderia, Commamonas, Pseudomonas*, and Gram-positive bacteria, such as *Bacillus, Corynebacterium*, and *Rhodococcus*, are able to degrade some PCB congeners opened the door to implement biological technologies. Bioremediation technologies using degradation capacity of microorganisms, mainly bacteria, have been seen ecological and economical alternative approach to physicochemical processes to eliminate diffusive contamination of persistent organic pollutants (POPs) in various environmental matrices, e.g., soil, sediments, and sludges. Bioremediation is an attractive, generally low-cost, innovative technology that is a sustainable approach to clean up organic compounds from contaminated areas. Bioremediation represents a perspective and prospective technique for treatment of polluted environments which involves usage of microorganisms and/or plants for pollutant biodegradation or biotransformation. The technology can be performed as natural attenuation or employed as an assisted bioremediation: biostimulation (addition of nutrients and inducers to fortify and stimulate the growth and metabolism of indigenous microorganisms), and bioaugmentation (introduction of indigenous or suitable exogenous bacteria to enhance biodegradation of relevant pollutant) [9–13]. However, successful soil bioaugmentation requires not only application of the individual bacterial strain or a bacterial consortium with the required degradation ability but also of the microorganisms able to survive in the adverse environment [14–17]. Poor survival of the inoculated microorganisms (usually bacteria) and low bioavailability of the hydrophobic carbon source are usually the main obstacles to the successful inoculum amendment. Moreover, the bottleneck for the successful catabolism of a recalcitrant hydrophobic compound is most often not the nature of the biochemical pathway for its degradation, but the overcoming of the endogenous and exogenous stress associated to the utilizing conditions. Although many bacteria have ability to metabolize, e.g., PCBs, high concentrations of these chemicals act as environmental stress factor and inhibit cell survival and then ability to metabolize these pollutants. If bacterial strains wanted to survive, they had to develop efficient adaptation mechanisms in the adverse environment [18, 19].

For the purpose to select the degradation-effective and adverse environment-resistant bacterial strain from 11 environmental isolates, obtained from the PCB-historically contaminated sediment and identified using molecular-biological methods [20], our research was focused on the study of adaptation mechanisms and responses of bioaugmented bacteria during the biological treatment of water and sediment matrices contaminated with PCBs. Since PCBs are highly hydrophobic, they may efficiently cross cell membrane through free diffusion. The effects of PCBs, chlorobenzoic acids (CBAs, PCB-biodegradation end products), biphenyl, and terpenes (the potential inducers of PCB degradation) on bacterial cytoplasmic membrane were determined [10, 11, 15, 19]. Only the resistant bacteria that possess the appropriate enzymes may play a major role in bioremediation technologies.

2. Response mechanisms of bacterial cells to adverse environment

2.1. Saturation of membrane fatty acids

The most adaptive mechanisms are concerned with maintenance of the cell membrane fluidity and lipid-phase stability [21]. Fluidity of cytoplasmic membrane is a very important characteristic of the membrane structure and is defined as the reciprocal value of its viscosity. It can be modulated by the alteration of fatty acids that build membrane phospholipids. Extreme environmental conditions activate in cells a series of processes that allow microorganisms to minimize their negative impact. Bacteria have developed various mechanisms to eliminate toxic compounds present in the environment. Being at the interface between the cell and the environment, the cytoplasmic membrane is the first site of contact between the cell and contaminant. Hydrophobic organic pollutants change the fluidity of bacterial membrane that can lead to a significant disturbance of physiological function and apoptosis. This is the reason why membrane flexibility and adaptation ability largely determine the survival of the cell [22, 23]. Since fatty acids are the major constituents of membrane phospholipids, modulation of number and position of double bonds of acyl chains by specific fatty acid desaturases plays crucial role in preserving a suitable dynamic state of the bilayer during environmental impact [24]. One of the observed membrane adaptation mechanisms is the increase of saturation of bacterial membrane lipids. The linear acyl chains of saturated fatty acids can be tightly packed leading to lower fluidity (**Figure 1**) that counteracts the fluidizing effects caused by the presence of toxic organic compounds [25]. Although bacterial cell tries to increase membrane rigidity to counteract the effects of organic pollutants, the membrane must be able to perform its physiological functions. Therefore, a part of membrane must stay in liquid-crystalline phase. The mechanism of increase of saturation degree has limitation due to the condition of synthesis of saturated fatty acids. In bacteria, only the energy-dependent *de novo* biosynthesis of saturated fatty acids allows the increase in the degree of saturation, which may also be the reason why alteration in the degree of saturation was only observed in growing cells [26, 27]. Therefore, under growth-inhibiting conditions, lipid biosynthesis is stopped due to stringent response regulation, and that is why, only growing cells can perform such kind of membrane adaptation [25]. A correlation between an increase in the degree of saturation of membrane fatty acids and increased tolerance toward the toxic compounds in *Pseudomonas putida* P8 was described [28]. This phenomenon is thought to be one of the major long-time adaptive mechanisms in microorganisms exposed to toxic aromatic compounds. Due to this, the bacterial membranes become more resistant to the fluidizing action of aromatic compounds, which allows the cells to survive in hydrocarbon-contaminated sites [14, 29].

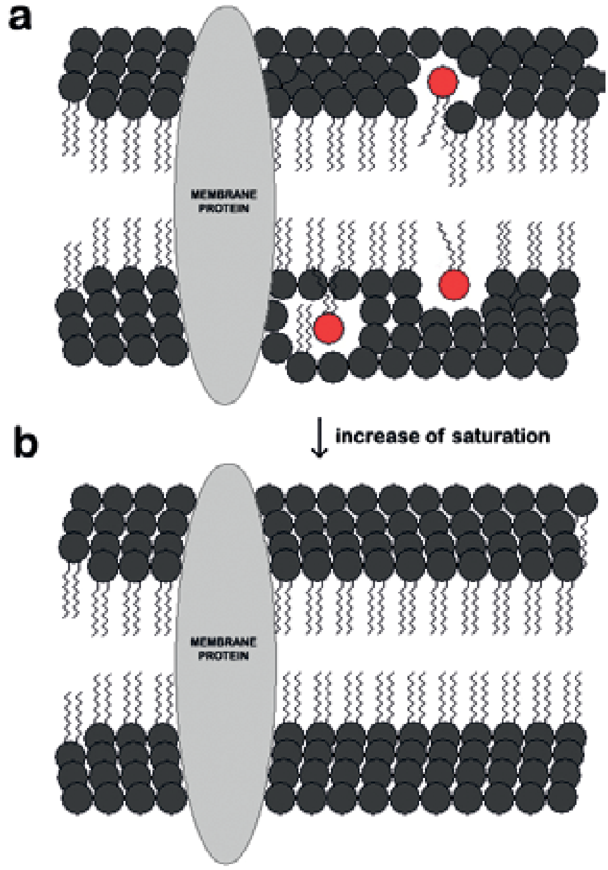

Figure 1. Increase of the synthesis of saturated fatty acids (grey circles) instead of unsaturated fatty acids (red circles) leads to the higher membrane saturation, higher rigidity, and lower fluidity. Modified according to [16].

2.1.1. *Cis/trans isomerization of unsaturated fatty acids (UFAs)*

Various bacterial strains, e.g., *Pseudomonas*, can adapt to the presence of toxic compounds and their fluidizing properties by isomerization of *cis* unsaturated fatty acids to their appropriate *trans* isomers. These two forms of unsaturated fatty acids have different steric structure. The *cis* configuration of the acyl-chain has a nonmovable bend of 30°, which causes steric hindrance and disturbs the highly ordered fatty acid package [30]. In contrast, the steric behaviour of *trans* fatty acids and saturated fatty acids is very similar. Nonmovable bends of *trans* fatty acids have 6°. Both *trans* and long chain saturated fatty acids possess a long-extended conformation. It enables them to adopt a denser packing in the cytoplasmic membrane and allows protecting membrane against the fluidizing molecules. That is the reason why the transformation of *cis* to *trans* fatty acid leads to the decrease of membrane fluidity (**Figure 2**). Another reason for an ordered packing of *trans* fatty acids compared to *cis* isomers is their higher T_M (transition temperature). This mechanism was monitored in growing as well as in growth-inhibiting conditions. *Cis-trans* isomerase is constitutively present, does not require ATP or other cofactors including NAD(P)H and glutathione, and works in the absence of *de novo* synthesis of lipids. The *trans* fatty acids are formed by direct isomerization of the

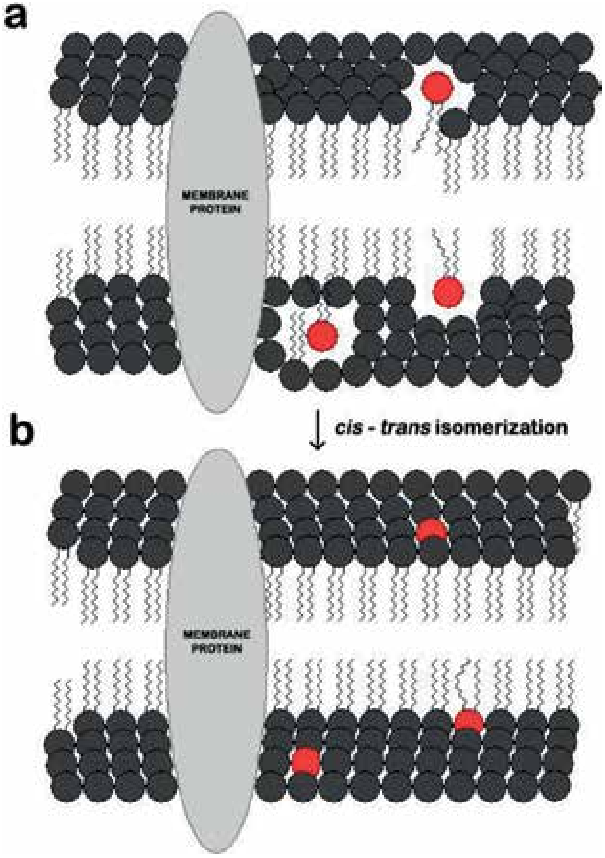

Figure 2. The transformation of *cis* unsaturated fatty acids into corresponding *trans* isomers decreases the membrane fluidity of bacterial cell. Modified according to [16].

complementary *cis* configuration of the double bond without a shift position. Because of the steric differences between *cis* and *trans* configurations, this conversion reduces membrane fluidity and counteracts against the stress [31].

2.1.2. Changes in cyclopropane and branched fatty acids: anteiso-/iso-branching

Changes in cyclopropane and branched fatty acids can be observed in the adverse environment as well. Higher concentration of organic pollutants stimulated production of cyclopropane fatty acids in some bacterial strains [19, 22, 29]. The role of these fatty acids is still not understood in detail. Some authors indicated that cyclopropane fatty acid formation is one of the most important mechanisms that protect bacterial cells against many chemicals [23]. In the presence of toxic compounds or toxic conditions, bacteria increase the production of *iso*-branched fatty acids on the expense of *anteiso-* forms to decrease the membrane fluidity [9, 14, 32]. Transition temperatures of the branched fatty acids are lower for the *anteiso*-fatty acids. This difference together with steric differences causes a remarkable change in the fluidity of the membrane when the species of branched fatty acids are changed from *iso-* to *anteiso-* form. The effect on transition temperature caused by a change from *anteiso-* to *iso*-branching in G^+ bacteria is comparable to the isomerization of *cis* to *trans* unsaturated fatty acids in G^- bacteria. Even the volume occupied with *anteiso*-fatty acids is higher than that occupied with *iso*-FAs. According to the different physicochemical properties of those two species of branched FAs, the bacteria showed a decreased amount of *anteiso*-FAs when grown under adverse conditions to decrease the fluidity of membrane and diminish incorporation of the pollutants into membrane structures [14, 16].

2.2. Changes in phospholipids

Bacteria contain several different phospholipid headgroups in their cytoplasmic membrane. Each of them holds specific function to maintain cell vitality. In the presence of environmental perturbations, cells alter the amount of phospholipids. Changes in phospholipid headgroups on environmental pollution are rarely studied than fatty acid alteration. Weber and de Bont [33] studied the effects of the composition of the phospholipid headgroups on the membrane fluidity. Phosphatidylethanolamine (PE) is the most abundant phospholipid in bacterial membrane that comprises more than 70% of all phospholipids [27]. It provides lateral pressure to bacterial membrane bilayer and keeps the position of amino acids. It is a nonbilayer forming lipid because of its steric conformation (small glycerol group and high acyl-chain volume). Nonbilayer aggregates (preferred hexagonal conformation) of cytoplasmic membrane are important in cell division, membrane fusion, and in the lateral proteins and lipid motion. The ratio between bilayer and nonbilayer forming lipids varies in response to environmental changes. Organic solvents like benzene and toluene can reduce the transition temperature of membrane lamellar gel to liquid-crystalline phase (T_M) and enhance the formation of nonbilayer aggregates with decreasing the transition temperature from cylindrical into inverted hexagonal phase (T_{LH}). Stabilization of the T_M is important to sustain membrane fluidity and stability. T_M of cytoplasmic membrane can be slightly modified by membrane phospholipids (each of them has different T_M), which can affect bilayer stability of membrane. Cultivation of

Pseudomonas putida S-12 with toluene decreased the amount of PE and increased the content of phosphatidylglycerol (PG) and cardiolipin (CL). This alteration could stabilize membrane by lowering the fluidity. However, phospholipids have much higher effects on bilayer stability (T_{LH}) than on membrane fluidity (T_M) because of their ability to form hexagonal or lamellar structures [33]. Based on these facts, the decrease of PE content leads to higher bilayer stability. Nevertheless, bacterial cell tries to keep balance between bilayer and nonbilayer phospholipids to maintain its physiological function. Donato et al. [34] described the effects of DDT on the bacterial strain *Bacillus stearothermophilus*. This compound induced a very significant increase of the PE membrane content with a parallel decrease of PG content. This alteration was accompanied by an increase of straight chains and a parallel decrease of branched fatty acids in cytoplasmic membrane. DDT promoted more ordered membrane with an increase of the T_M temperature to higher values that led to higher membrane rigidity. However, increase in PE and decrease of PG amounts is not a usual response of the bacteria. PG is important in CL synthesis and plays a role in protein translocation across the membrane [35].

Based on their polarity, toxic organic solvents can accumulate in different membrane sites. This affects their ability to change the membrane bilayer stability by formation of an inverted cone (polar pollutants) or cone structures (nonpolar pollutants). Polar pollutants as ethanol can accumulate between the glycerol headgroups. This process can destabilize bilayer-nonbilayer balance. Bacterial cells react to these effects by the formation of a lipid with a small headgroup volume (e.g., monoglucosyldiglyceride). The presence of benzene increases the formation of hexagonal aggregates. Cells counteract this phenomenon by stimulation of production of lamellar phospholipids (e.g., diglucosylglyceride). Similar effects can be observed in the presence of toluene. Toluene can incorporate into the membrane between the acyl chains. The cell responds by production of the higher amount of CL to stabilize the bilayer. CL has a larger headgroup volume compared to PE. The decrease of PE production and increase of CL content will increase the volume of headgroups. This can compensate toluene-induced increase of acyl chain volume and stabilize the bilayer. Moreover, CL has 10 K higher T_M than PE. Due to this fact, CL increases the membrane rigidity, while toluene induces disordering of acyl chains. Some opposite effects occur in the presence of polar ethanol [33, 36]. The regulation of phospholipid headgroups controls the ratio between bilayer and nonbilayer membrane structures and the bilayer surface charge density.

2.2.1. *Adaptation responses of bioaugmented bacteria used in biological treatment of contaminated water and sediment matrices to nonpolar PCBs and polar 3-CBA*

The effects of nonpolar PCBs and polar 3-chlorobenzoic acid (3-CBA, one of PCB-degradation end product) were assessed in our laboratory using four bacterial isolates obtained from the long-term PCB-exposed contaminated sediment (*Ochrobactrum anthropi* and *Pseudomonas veronii*) and soil (*Alcaligenes xylosoxidans* and *Pseudomonas stutzeri*) [37]. About 100 mg L^{-1} of each pollutant was added separately into the minimal mineral media at the beginning of cultivation together with the bacterial inoculum (1 g L^{-1}). Adaptation responses in phospholipid headgroups were analyzed after 6 days of cultivation on the rotary shaker (180 rpm) at 28°C in the dark (**Figure 3**). The differences in adaptation responses toward polar and nonpolar

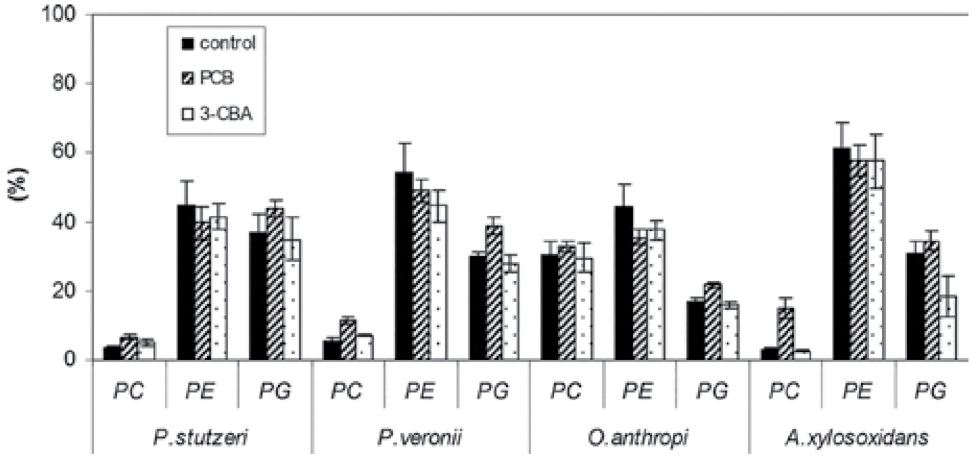

Figure 3. Percentage amount of membrane phospholipids after the addition of nonpolar (PCBs) and polar (3-CBA) toxic pollutants into the minimal mineral medium in the presence of two bacterial strains isolated from a long-term PCB-contaminated soil—*Pseudomonas stutzeri* and *Alcaligenes xylosoxidans, and* two bacterial strains isolated from a long-term PCB-contaminated sediment—*Pseudomonas veronii* and *Ochrobactrum anthropi.* Modified according to [16]. PC, phosphatidylcholine; PE, phosphatidylethanolamine; and PG, phosphatidylglycerol.

contaminants can be seen on the examples of PC and PG. Only a minority of bacterial strains contain PC in their membrane [16]. This phospholipid belongs to a bilayer-forming group similarly to PG [38]. An increase in PC accumulation in membrane was observed after addition of nonpolar PCBs. Polar 3-CBA did not rapidly affect the amount of this phospholipid in the membrane. Only slight increase of PC content was observed in both *Pseudomonas* species after 3-CBA addition. On the contrary, both pollutants caused the decrease of PE amount in all studied strains. As mentioned in previous part, PE belongs to nonbilayer phospholipids. The presence of both toxic pollutants leads to their accumulation in membrane and destabilizes the bilayer conformation. Cells counteract these effects by reducing the nonbilayer phospholipid fraction to increase the membrane stability. This phenomenon was accompanied by an increase in membrane saturation and *cis*/*trans* isomerization to decrease membrane fluidity [19]. Nonpolar compounds are able to accumulate between the acyl chains of phospholipids and stimulate the hexagonal formation and increase T_M. Because of such accumulation, increase of PG content in membrane can be expected [33]. Our results obtained using the PCBs are in accordance with this assumption. The presence of 3-CBA caused the decrease of PG content. This can be explained by the ability of a polar compound to accumulate between the polar phospholipid parts (glycerol headgroups) and by a stimulation of micellar formation (interdigitated phase). PG has a larger headgroup volume; therefore, a decrease of this membrane component increases membrane stability. The addition of PCBs evoked increase of PG and PC membrane incorporation and decrease of PE in bacterial cells. These results are in agreement with the results obtained with other nonpolar toxic compounds [33].

The effects of toxic environment were not confirmed in the case of addition of 3-CBA at the time of inoculation in both strains of *Pseudomonas* genera. We assumed that 3-CBA is extremely toxic when present at the lag phase of the bacterial cell growth. The adaptation mechanisms occurred in the cytoplasmic membrane (increase of *trans*/*cis* ratio) were not efficient enough to counteract the effects of 3-CBA (**Figure 4a**). Such toxic conditions are responsible for the disability of both *Pseudomonas* strains to adapt to polar organic acid. Therefore, a biomass amount decreased below the inoculation amount. The determination of branched fatty acids was performed because of their ability to change membrane fluidity (**Figure 4b**). *Anteiso-*/*iso-*ratio reflected the changes in branched fatty acids. These fatty acids are generally produced to increase the membrane fluidity. *Anteiso-*(3-methyl) fatty acids exert stronger influence on membrane fluidity than *iso-*(2-methyl) isomers due to their steric configuration and different transition temperatures. Under the toxic condition, bacteria increase the production of *iso-*fatty acids on the expense of *anteiso-* forms to decrease the membrane fluidity [9, 14, 32]. The 3-CBA addition to the 3-day-old cultures revealed enhancement of the adaptation mechanism compared to the addition of PCBs with all strains except for *A. xylosoxidans*. Interesting information was observed in branched membrane fatty acids in both studied *Pseudomonas* strains. The amount of these acids increased when the toxic compounds caused a growth inhibition of *P. stutzeri.* This effect was also observed in *P. veronii* after the addition of organic pollutants and in absence of *cis* to *trans* isomerization. Because of lower production of unsaturated fatty acids under these conditions, cell may try to maintain liquid-crystalline phase of at least part of membrane with these fatty acids [33]. *A. xylosoxidans* and *O. anthropi* were confirmed as most adapted to tested chloroaromatics among all studied bacterial strains [37]. Thus, *A. xylosoxidans* and *O. anthropi*, bacterial strains isolated from different contaminated matrices, soil, and sediment, both long-time polluted with PCBs, could be useful in further bioremediation studies.

2.2.2. Increase of phospholipid amount

A unique phospholipid that plays an important role in cell membrane adaptation is cardiolipin (CL). Increase in its synthesis strongly enhances the adaptation ability of bacterial cell to the presence of organic solvents. This mechanism was observed mainly in *Pseudomonas* species [39]. Together with PG, it represents the most abundant anionic lipid component of bacterial membrane. This phospholipid is markedly present in many of G^+ bacteria. It may trap protons in an acid structure and bind to many of unrelated proteins. The molecule consists of two phosphatidic acid residues linked by a glycerol. It contains four fatty acid chains per molecule and possesses one negative charge per headgroup. CL is synthesized with cardiolipin synthase in the cytoplasmic membrane. The synthase catalyzes the transfer of phosphatidyl group between two phosphatidylglycerol molecules. This enzyme reacts with two PG molecules, one acting as phosphatidyl donor and the other as phosphatidyl acceptor. This enzyme does not have strict substrate specificity and may act in the reverse direction and decompose CL. Trace amount of CL occurs in bacterial cells during the exponential growth phase. Accumulation of CL increases at the beginning of stationary phase. It is the most stable of all membrane phospholipids and is essential for the survival upon long-time starvation. Only *de novo* synthesis of CL was described in bacteria [40]. Prokaryotes can change the amount of this lipid depending on their physiological status and growth conditions. Increase of the amount of CL is a known adaptation mechanism in the stress environment. It may reflect a requirement for enhancement of the structural integrity of the cytoplasmic membrane or for the support of stress-related increases in energy transduction [41]. CL stimulates changes in the physical properties

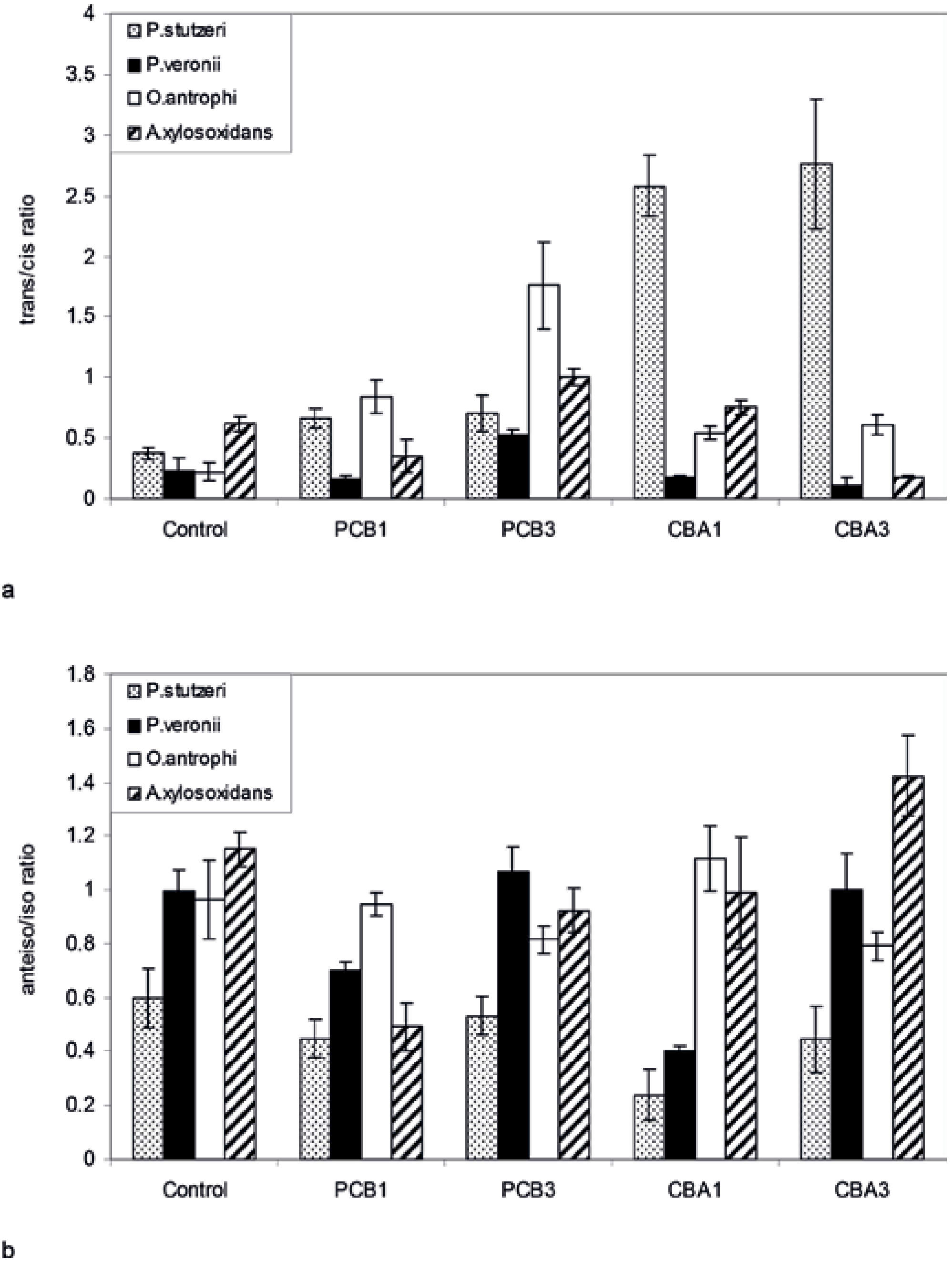

Figure 4. (a) The *trans/cis* ratio and (b) the *anteiso/iso* ratio of phosphatidylethanolamine and in control experiment (without PCBs). PCB1, PCBs added at the first day of cultivation; PCB3, PCBs added to the 3-day-old culture; CBA1, 3CBA added at the first day of cultivation; and CBA3, 3-CBA added to the 3-day-old culture. Modified according to [37].

of cytoplasmic membrane. Even small amounts of CL decrease the lateral interaction within the monolayer leaflet, which decreases the energy required to stretch the membrane and could favor the creation of membrane folds [42]. This is the reason why CL is concentrated in polar and septal regions of the cell. It can form nonlamellar structures that are required for membrane curvature and lead to the formation of clusters. The advantage of its unique conformation enables the nonlamellar structure to pack tightly forming microdomains which are stabilized by membrane proteins [43, 44]. Recent studies confirmed that bacteria with cardiolipin synthase deficiency are more vulnerable to organic solvents [45]. The mutant bacterium that is not able to synthesize CL was used to find out whether the *cis*/*trans* isomerase is able to compensate CL in adaptation mechanisms. The mutant was not able to grow, which indicates that *cis*/*trans* isomerase was not fully able to replace adaptation effects of CL [46].

2.3. Toxic pollutants as substrates for the efflux system

Such elimination of unwanted chemicals takes place by an uncontrolled efflux and accelerates active extrusion of structurally unrelated compounds from the cytoplasm or the cytoplasmic membrane to the external space. Toxic organic pollutants may represent substrates for the efflux system. Several studies indicated the importance of physical properties of compounds (hydrophobicity and molecule charge) for the determination of specificities of this mechanism [47–49]. The efflux system transporters for organic compounds identified in multidrug resistant G– bacteria belong to the resistance-nodulation-cell division family (RND) of pumps that are encoded chromosomally [50]. This system consists of complex transporters, which export toxic compounds through the cell membranes in a single-energy-coupled step. It requires a cytoplasmic membrane export system, which acts as an energy-dependent extrusion pump, a membrane fusion protein, and an outer membrane factor [51]. It was found that primary multidrug efflux system AcrAB-TolC facilitated the efflux of hydroxyl-PCBs out of the cells [46]. These multidrug-resistant pumps may affect the accumulation and degradation of PCBs by bacteria. Moreover, adapted bacteria of *Pseudomonas* sp. accumulated lower amount of trichlorobenzene in cells than nonadapted strains [39]. Similar results were published with toluene [51]. The ability of *E. coli* to eliminate PCBs and hydroxyl-PCBs was studied by Geng et al. [52]. The primary efflux system facilitated the elimination of hydroxylated PCBs (HPCBs) out of the cell. Since AcrAB-TolC is constitutively expressed in *E. coli* and is conserved in all sequenced Gram-negative bacterial genomes, the results suggest that the efflux activities of multidrug-resistant pumps may affect the cellular accumulation and degradation of PCBs in G^- bacteria. The multidrug resistance and the efflux of toxic pollutant by *P. aeruginosa* were determined [53]. Some of efflux pumps act on a restricted range of substrates. An example of such pump is TtfDEF pump from *P. putida* DOT-T1E, which extrudes only toluene and styrene [54]. Other pumps have a broad range of structurally diverse compounds. MexAB-OprM from *P. aeruginosa* can extrude hexane, xylene, and PCBs [48].

2.4. Production of stress proteins

Other known response of bacterial cells to POPs presence is the production and overexpression of stress proteins [55–59]. The production of shock proteins belongs to nonspecific general stress responses. Induction of stress proteins in *E. coli* with benzoate has been reported [60]. Other stress protein is induced by 4-chlorobiphenyl and biphenyl in *B. xenovorans* LB400 [55]. Expression regulation of the stress proteins was reviewed and the role of alternative sigma factor σB in this adaptation was emphasized [62]. This factor controls the production of bmrUR operon in *Bacillus subtilis* necessary for production of multidrug efflux proteins [63]. Toxic environment acts not only on the envelope but usually affects the cell proteome as well. Damaged proteins can be replaced with the newly synthesized. However, this method is not efficient under nutrient limitations. Therefore, the proteome repair is required to maintain cell viability.

Three major mechanisms operate in bacteria after a proteome damage induced by adverse environment [64]. First mechanism includes the chaperones, which assist in proper *de novo* folding of proteins and provide an important means of restoring activity to damaged proteins. Second mechanism describes the existence of enzymatic repair systems that directly reverse certain forms of protein damage, including proline isomerization, methionine oxidation, and the formation of *iso*-aspartyl residues. Third mechanism concerns proteolysis of abnormal proteins, which cannot be repaired. No effect on membrane lipids of *B. xenovorans* LB400 in the presence of 4-CBA and 2-CBA was observed. The primary adaptation was revealed as an overexpression of proteins (mainly the overproduction of catechol-1,2-dioxygenase, belonging to 3-oxoadipate chlorobenzoate degradation pathway). Stress proteins, metabolic proteins, and elongation factors were stimulated as well [56].

2.5. Changes in bacterial cell morphology as a stress response

Cell envelope of microorganisms consists of cell wall and cytoplasmic membrane. These covering compartments protect cell nucleus against outside effects and help in communication with other cells. Most of adaptation mechanisms relate to cytoplasmic membrane as highly selective barrier. Moreover, the first line of cell protection is based on the alteration of the membrane composition that leads to lower fluidity and permeability toward toxic compounds. The surface structure is quite dissimilar in G^+ and G^- bacteria. G^+ bacterial strains have thick murein-containing cell wall convoluted with teichoic acids. The role of murein layer in the exclusion of toxic compounds from cell is improbable because of its structure and properties. Contrarily, G^- bacteria have a very thin murein layer that is linked from the outside part with the outer layer. The predominant component of this addition layer is lipopolysaccharide (LPS) composed of polysaccharide chains with six to seven saturated fatty acid bonds in glucosamine disaccharide structure. Thanks to these tightly packed saturated fatty acids, LPS has a very low permeability to hydrophobic compounds and thus can act as cell protection [51]. LPS chain plays a role in cell resistance as well. The study with *E. coli* mutants unable to synthesize these polysaccharides showed high sensitivity toward hydrophobic detergents [33]. Moreover, changes in LPS composition led to higher o-xylene resistance of *Pseudomonas putida*. LPS molecules with high molecular weight were replaced by a lower weight bands to adapt to *o*-xylene [36]. This concept of a protective function of LPS can be supported by a lower sensitivity of G^- bacteria toward various organic contaminants such as biphenyl, benzene, naphthalene, PCBs, and toluene [19, 29]. The amount and type of LPS molecules present in bacterial cell wall have crucial effects on the bacterial surface properties as hydrophobicity and adhesion with outer surfaces and substrates. The decrease of cell hydrophobicity generally leads to lower cell availability toward lipophilic contaminants and diminished permeability [61]. Some microorganisms that are capable of utilization of hydrophobic contaminants produce biosurfactants to increase bioavailability of such unique carbon sources [65]. Cell survival in adverse environment can be supported also by the addition of divalent ions (Mg^{2+} and Ca^{2+}). It is supposed that these divalent ions can diminish the charge repulsion of adjacent polyanionic LPS molecules with their electrostatic bond. Higher toluene resistance of *Pseudomonas* sp. was observed after the supplementation of cultivation media with divalent ions [33]. Toluene adaptation correlated with lowered surface hydrophobicity [51]. The removal of LPS molecules can lead to the loss of the resistance to toxic contaminants [66]. Although the penetration of external compounds is diminished by outer membrane, large number of small molecules can move through this compartment, thanks to protein canals. Changes in cell morphology in the presence of toxic compounds were observed in G^- [67] as well as in G^+ bacteria [68]. General responses of G^- bacteria to environmental stress were attributed to increase cell size. G^+ bacteria showed filamentous growth, increased cell volume, formation of endospores [63, 69], and production of unusual extracellular capsule [70].

2.6. The presence of terpene-containing plant matrices protected bacteria against the environmental stress and facilitated biodegradation of PCBs

Another efficient way how to cope with toxic compounds is to decrease their toxic effects with their biodegradation or biotransformation. The appropriate degradation enzymes, mono- or dioxygenase, are bonded to the inner part of bacterial cytoplasmic membrane. Bioaccumulation of hydrophobic compounds in cytoplasmic membrane is minimized with hydroxylation of these compounds. The usual degradation pathway begins with the incorporation of hydroxyl group into the pollutant structure [71–75]. However, increase in pollutant's polarity leads to its higher water solubility and higher availability to a microorganism itself. This situation usually leads to higher toxicity of the environment. Therefore, the microorganisms able only to modify toxic compounds probably cooperate with other organisms to achieve complete mineralization of contaminants into CO_2 and H_2O or at least transform the parent compounds into less or nontoxic intermediates [76].

Some compounds present in the nature can help bacteria to degrade the target pollutant [77–80]. The mechanisms of these compounds have not been described in detail yet. However, we observed that some of these compounds can diminish toxic effects of PCBs and their intermediates, namely chlorobenzoic acids, and consequently decrease bacterial adaptation mechanisms relating to membrane fatty acid composition. Then, bacteria were able to degrade PCBs nearly "without adaptation responses" which means that adaptation changes were observed only in a small extent because bacteria were "protected" in the presence of these compounds [81]. Plants rich in terpene contents belong to this group. Many studies including our research described the stimulation effects of ivy leaves, pine needles [82], eucalyptus leaves, tangerine, and orange peel [83–85] on biodegradation of hydrophobic pollutants. Potential use of natural plant matrices containing terpenes in the bioremediation of PCBs was studied in our previous works [15, 19, 81]. Our results clearly indicated the stimulation effects of terpene-containing matrices, namely ivy leaves and pine needles on bacterial growth in the presence of PCBs. The increase of fatty acids (FAs) content that is responsible for the increase of membrane fluidity was observed. Consequently, the smaller extent of necessary adaptation changes (*trans*/*cis* ratio of UFAs, *anteiso*/*iso* of branched FAs) was determined using addition of ivy leaves and pine needles into the defined mineral medium and the real polluted sediment, both contaminated with PCBs during degradation by bacterial isolate *Ps. stutzeri* (**Figure 5a**, **b**) and control strain *B. xenovorans*. More details can be seen in [11]. On the contrary, none stimulated

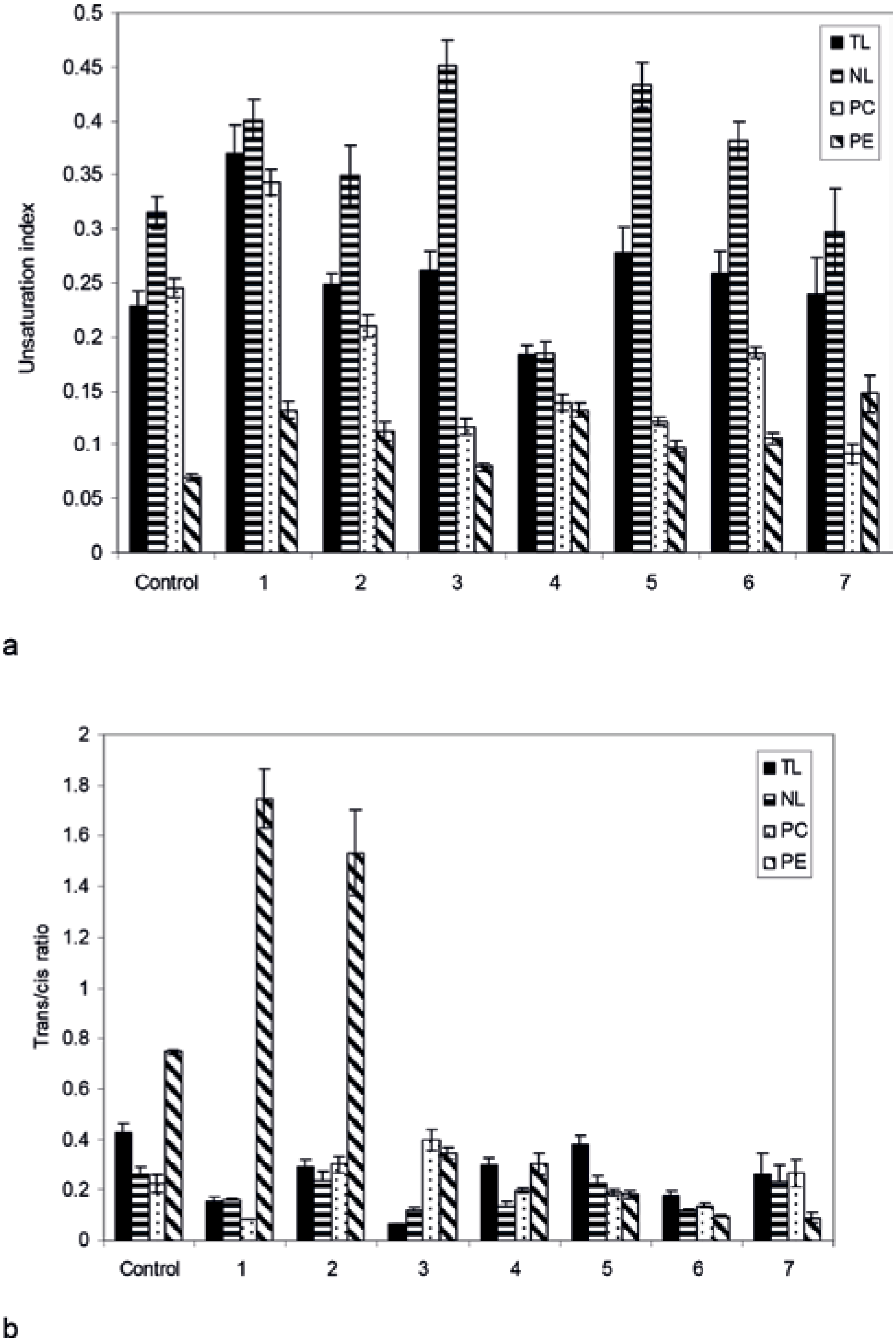

Figure 5. (a) The unsaturation index and (b) *trans*/*cis* ratio of fatty acids in total lipids (TL), nonpolar lipids (NL), and membrane lipid phosphatidylcholine (PC) and phosphatidylethanolamine (PE) of bacterial strain *P. stutzeri*. Experimental sets: Cont, control experiment contains PCBs; 1, PCBs and biphenyl; 2, PCBs and carvone; 3, PCBs and limonene; 4, PCBs and ivy leaves; 5, PCBs and pine-needles; 6, PCBs and orange peel; and 7, PCBs and tangerine peel. Modified according to [81].

and protected effects were observed in the presence of used synthetic terpenes, carvone and limonene, which corresponded with other papers [86–90].

It is important to note that the growth rate of anaerobic indigenous or incorporated bacteria is much slower when compared to that of the aerobic ones. Therefore, the adaptation mechanisms take more time and these bacteria are sensitive to organic compounds, e.g., solvents to a higher extent than aerobic bacteria [25].

2.7. Bioremediation of PCB-contaminated sediment using bioaugmentation (introduction of the adapted resistant bacteria) and biostimulation (addition of the natural plant terpenes)

Bacterial strains with pronounced degradation ability (that possess the *bph* gene encoding biphenyl dioxygenase starting the first step of PCB degradation—hydroxylation of PCB congeners) and ability to adapt and colonize in the adverse environment are the essential elements of successful bioremediation process. The use of the microorganisms to clean up polluted environments using their degradation ability is a rapidly expanding area of environmental biotechnology, namely bioremediation technologies. Bioremediation is an attractive, generally low-cost, innovative technology that represents a sustainable approach to removal of organic and inorganic pollutants. Bioremediation represents a perspective and prospective technique for decontamination treatment that involves application of microorganisms and/or plants for pollutant biodegradation or biotransformation. The two assisted bioremediation strategies—biostimulation and bioaugmentation are usually applied, when natural attenuation is not fast enough or complete enough (natural attenuation means the nonassisted reduction of contaminant concentrations in the environment through physical phenomena, chemical reaction, or biological processes). PCBs are generally subjected to both aerobic and anaerobic metabolism of bacteria. It is generally known that under aerobic conditions, biphenyl dioxygenase attacks biphenyl core and transforms PCB congeners into the respective chlorobenzoate and a pentanoic acid derivative. Under anaerobic conditions, PCB congeners are subjected to reductive dechlorination resulting in the intact biphenyl and some lower chlorinated PCB congeners. Both metabolic pathways are working only when the environmental conditions are optimal for the indigenous or introduced bacteria [91, 92].

Bioaugmentation can be defined as the technique for improvement of the metabolic capacity of the indigenous population to remove pollution by the inoculation, which means introduction of specific competent strains or consortia of microorganisms to the contaminated soil or sediments. Usually, the indigenous (autochthonous) or exogenous (allochthonous) bacteria are used. The basic premise for such intervention is to improve biodegradation of pollutants and save the time of treatment. Biostimulation involves addition of nutrients, trace minerals, electron acceptors, electron donors, or some inducers to improve the growth and then metabolic activity of the indigenous microbial population. Both approaches can be used under aerobic and anaerobic conditions, while the former is the prevailing case [93, 94].

Two strategies of assisted bioremediation, (a) bioaugmentation and (b) combined bioaugmentation and biostimulation, have been applied to degrade PCBs in the river sediment long-term exposed to PCB contamination sampled from the surroundings of a former PCB producer. A PCB-resistant bacterial strain *Ochrobactrum anthropi*, one of the two best evaluated isolates related to adaptation mechanisms in the presence of PCBs with the minor adaptation responses (lower *trans*/*cis* ratio and higher *anteiso*/*iso* ratio) was used. One experimental set represented bioaugmentation treatment (introduction of bacteria 10 mg kg^{-1} of dry sediment into 5 g of contaminated river sediment flooded with 15 ml of defined mineral medium) and the second one combined bioaugmentation (introduction of bacteria 10 mg kg^{-1} of dry sediment) and biostimulation (addition of 15 g of terpenes containing ivy leaves cut into small pieces per kilogram of dry sediment) (for more details see [11]). Bacteria were introduced into the contaminated sediment to enhance the number of PCB degraders. The ivy leaves served as a stimulant agent of indigenous and introduced bacterial growth and as a protective agent against environmental stress caused by the presence of PCBs, as well as a potential PCB degradation inducer as structural analog of biphenyl (due to the toxicity not allowed to the environment as the inducer). Contaminated sediments treated with bioaugmentation and combined bioaugmentation and biostimulation were compared with the nontreated sediment (abiotic control experiment in which activity of the indigenous and introduced bacteria was inhibited by addition of 2.5% sodium azide). During the static 85 day-biodegradation at 28°C in the dark, the evaporated PCB congeners were captured on the sorbent SILIPOR C18 on the apparatus [95] and their amount was deducted from biodegraded one. The evaporation of PCB congeners was highest in the control experiment and lowest in the experiment with the addition of bacterial strain together with ivy leaves due to sorption. The results of specific PCB congener analyses revealed the degradation ability of adapted bacteria *O. anthropi* toward wide spectrum of chlorinated biphenyls. The initial amount of 12 determined PCB congeners was 40 mg kg^{-1} of dry sediment. Both lower (di-, tri-, and tetra-CBs) and higher chlorinated (penta-, hexa-, and hepta-CBs) congeners present in the industrial mixture of PCBs Delor103 were reduced during the bioremediation process. The higher PCB degradation was achieved during combined bioaugmentation and biostimulation (**Figure 6a**). Linearity for the in-time removal of PCB 101 (2,2′,4,5,5′-penta-CB) and PCB 118 (2,3′,4, 4′,5-penta-CB) by *O. anthropi* in bioaugmentation experiment was observed (not shown). The highest degradation in the experiment with ivy leaves was observed within the first 7 days when 5% (PCB 8) to 34% (PCB 180) degradation was achieved. The presence of ivy leaves in sediment led to higher biomass decrease within the first 7 days; however, after 42 days, the number of viable cells increased. Interestingly, the decrease of biomass within first 7 days of cultivation with ivy leaves was accompanied with the highest degradation rate. Ivy leaves could probably induce the activity of PCB degradation enzymes first and, after, the utilization of other carbon substrates present in sediment that they served as energy source. The degradation rate of PCBs removal accelerated after first 28 days in both bioaugmentation, and combined bioaugmentation + biostimulation experiments. The addition of ivy leaves stimulated PCB biodegradation which led to increased removal of PCB congeners (**Figure 6b**). The removal of overall PCBs was significantly higher when the combination of bioaugmentation and biostimulation strategy was used. Total degradation of PCB congeners in the sediment is presented in **Figure 6a**. Lower chlorinated congeners (PCB 4 and PCB 8) underwent transformation to a smaller extent. On the other hand, higher chlorinated congeners (PCB 118, PCB 138, and PCB 153) have been transformed to a higher extent. Low degradation of di-CB compared to the higher chlorinated congeners could be explained with the higher evaporation of di-CB compared to penta- and hexa-CBs that could diminish the amount of di-CB accessible to microorganisms. Addition of the ivy leaves increased mostly the degradation of PCB203, PCB8, PCB101, and PCB28 (18, 17, 15, and 14% increase compared to the PCB removal under the bioaugmentation conditions). At the end of bioremediation process, the highest degradation of PCB 18 (2,2′,5-tri-CB) in both remediation approaches was established (**Figure 6a**). Control experiment with suppressed bacterial

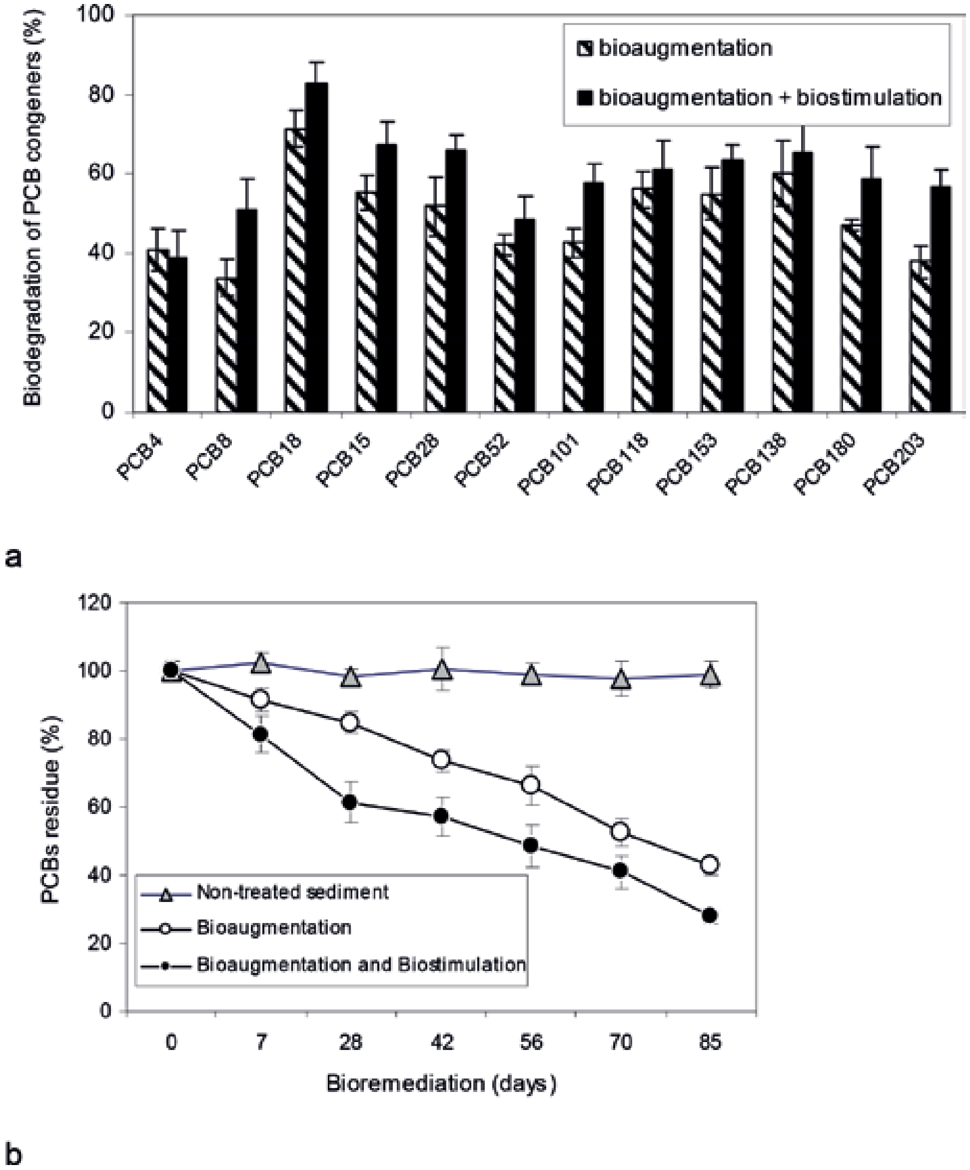

Figure 6. (a) Content of residual PCBs after 85-day bioremediation of PCB-contaminated sediment in the presence of introduced *Ochrobactrum anthropi*; (b) the change in the residual PCB content throughout bioremediation: bioaugmentation with *O. anthropi* and bioaugmentation + biostimulation with the addition of *O. anthropi* and ivy leaves. Control represented nontreated sediment with the inactive biomass. Modified according to [11].

growth revealed none or just very low PCB congener transformation caused probably by the abiotic factors (**Figure 6b**). **Figure 6b** shows also the overall change in the amount of PCB residues in sediment during the duration of remediation process. After 85 days, 27% of the initial PCB amount (40 mg of eight determined PCB congeners per kilogram of dry sediment) remained in sediment treated with a combination of bioaugmentation and biostimulation (with an addition of *O. anthropi* and ivy leaves). Sediment treated only with bioaugmentation (addition of *O. anthropi*) contained 1.5 times higher content of residual PCBs. The performed experiments confirmed the stimulatory effect of ivy leaves toward the bacterial growth and degradation ability of *O. anthropi* as well as on better adaptation to PCBs. The ability of *O. anthropi* to transform higher chlorinated PCB congeners in contaminated river sediment was established as well. These findings could be useful for bioremediation technologies in the decontamination of PCB polluted environment.

3. Conclusions

Many responses have been observed and confirmed in bacteria that counteract the effects of toxic environmental organic pollutants. Rigidification of the cell membrane is a consequence of cell adaptation mechanisms. The alterations in cytoplasmic membrane maintain ratio between bilayer and nonbilayer phospholipids (prevention against the environmentally induced formation of interdigitated structure) and keep the optimal phospholipids ordering to stabilize membrane fluidity. Another mechanism to protect bacterial cell is the efflux of toxic compounds from the membrane compartment. Toxic compounds affect not only cytoplasmic lipids but also cell proteins. This results in the development of special protein repair mechanisms by bacteria. Study of these adaptation mechanisms was the first step in selection of appropriate resistant bacterial strains, usually isolated from the contaminated area, and used for bioremediation application. Successful environment decontamination using biological approaches requires bacterial strains that can degrade particular (one or more) contaminants. Moreover, such strains have to be able to survive and adapt to adverse environment. Next step included the study of degradation potential of the most resistant strains. The resistant strain/consortium possessing appropriate degradation enzymes is the essential element of successful bioremediation. Both assisted bioremediation approaches, bioaugmentation and biostimulation, revealed to be perspective and prospective approaches of PCB decontamination. The degradation studies in artificial precisely defined matrices under the laboratory conditions (microcosms) could be applied in macrocosm and then after verification of strain/consortia degradation efficacy and survival ability and characterization of the optimal conditions for the successful decontamination process used in the field conditions.

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This book consists of four technical articles and an introduction that discusses the characteristics of persistent organic pollutant (POP) behavior, covering organic matter in lake sediments, degradation pathways of POPs and specific pesticides, and the adaptation mechanisms of bacteria.

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