

Introduction to Organic Contaminants in Soil: Concepts and Risks

L. Valentín, A. Nousiainen, and A. Mikkonen

Abstract This chapter introduces an overview of the main aspects of soil contamination: the types of contaminants, the threats to soil biota and quality, the effects on humans and animals and legislation concerning contaminants, with a focus on European laws and regulations. Although soil is a non-renewable natural resource, humans have increasingly used it as a contaminant sink ever since the Industrial Revolution. Pollution endangers natural soil mechanisms that allow the soil to keep itself in balance and compromises the supply of soil-based goods and services. Detrimental effects of contaminants on soil microbiota may be directly related to loss of biodiversity and functions such as the recycling of nutrients. However, this direct negative effect is still debated among microbial ecologists because microbial communities may be surprisingly resilient (i.e. able to recover from contamination effects) and/or functionally redundant. Likewise, the potential toxicity of soil contamination to humans is controversial as investigations on the mix of different contaminants are very limited. Due to accumulated evidence of the potential toxicity of single contaminants on human health and animals, mostly based on in vitro or in vivo assays, international guidelines, such as the Stockholm Convention on Persistent Organic Pollutants, have established a list of priority contaminants. Despite worldwide concern about soil contamination, Europe still lacks a common soil legislative tool because the proposed Soil Directive Framework is currently under negotiation. The lack of a European directive is nevertheless compensated by national policies at the member state level.

L. Valentín (✉)

Department of Chemical Engineering, School of Engineering, Universitat Autònoma de Barcelona, 08193 Bellaterra, Barcelona, Spain
e-mail: lara.valentin@uab.es

A. Nousiainen

Finnish Environment Institute, Hakuninmaantie 6, 00430 Helsinki, Finland

A. Mikkonen

Department of Environmental Sciences, Environmental Ecology, University of Helsinki, Niemenkatu 73, 15140 Lahti, Finland

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Contents

1	Soil as a System and Resource	2
2	Soil Contamination as the Main Threat to Soil Quality	4
2.1	Contaminants in Soil	5
2.2	Effect of Organic Contaminants on Soil Biota and Quality	12
3	Health Effects of Organic Contaminants on Animals and Humans	15
3.1	Emerging Endocrine-Disrupting Compounds	16
3.2	Potential Toxicity of the Application of Biosolids in Agricultural Land	18
4	Legislative Framework for Soil Protection and Sewage Sludge Use	19
4.1	European Environmental Policies on Soil Protection	19
4.2	Regulations for Use of Treated Sewage Sludge on Agricultural Land	21
5	Concluding Remarks	24
	References	24

1 Soil as a System and Resource

The quality of water and air is of immediate concern for most people because we all consume these natural resources on a daily basis. The importance of soil, the generally thin layer of unconsolidated material on bedrock, is more difficult to grasp for an average citizen or politician. Nonetheless, soil is the “the biogeochemical engine of Earth’s life support system” [1]. It provides us with food, fodder, fibre and fuel. In addition to these readily rateable agriculture and forestry goods, soils deliver ecosystem services that cannot be easily traded in markets. These life-supporting functions include, for example, recycling of carbon and essential nutrients of all living materials, filtering and storage of water, regulation of the atmosphere and biological control of pests [1, 2].

Continuing urbanisation, desertification intensified by global change and short-sighted agricultural practices threaten the natural soil capital [3]. In the next few decades, a decreasing land area is still expected to deliver soil-based goods and services to nine billion people [4]. The severity of this discrepancy is exacerbated by the fact that soils must be considered to be a largely non-renewable natural resource [3, 5]; the full functionality of land where the thin surface soil layer is lost by erosion or sandstorm, or severely degraded by persistent anthropogenic pollutants, will not be restored within one human generation. Although native people worldwide have traditionally valued and nurtured soil or “Mother Earth,” the policy makers of the modern world have only rather recently identified the endangered status of many soils, much later than was the case for water and air resources. The EU Thematic Strategy for Soil Protection currently identifies erosion, organic matter decline, salinisation, compaction, landslides, contamination and sealing as the major threats to soils [6]. However, the long-awaited binding EU Soil Directive is still at the proposal level [5].

There is an ongoing debate in agricultural policy on whether intensified agriculture on restricted sites or wildlife-friendly farming on larger land areas would better secure delivery of soil-based goods and ecosystem services for the growing population [4]. The possibility of reverting to traditional agro-ecological or biological fertilisation strategies, such as the use of legumes with nitrogen-fixing symbiotic root nodule bacteria or symbiosis between crops and rock phosphate-leaching mycorrhizal fungi, is receiving increasing interest. Additionally, conventional (industrial) agriculture can only be sustainable if the soils are not over-exploited, meaning that the stripped natural soil capital, such as nutrients and carbon, must be replenished [1, 7]. In any case, more efficient recycling of nutrients from waste and by-products will be essential in the future [8]. The production of inorganic nitrogen fertilisers through the energy-intensive Haber–Bosch process will become more expensive due to the increasing price of energy. Moreover, readily utilisable phosphorus, available in a few geographically unevenly distributed and non-renewable phosphate rock deposits, may wane even faster than fossil fuel resources [8].

The protocols of conventional agriculture, especially tilling, deplete soil organic matter content, and climate change seems to intensify this negative development [3, 7]. Sufficient organic C correlates positively with essential soil physicochemical properties such as structure and water holding capacity [9]. Biologically, organic C is the common currency of soil, feeding the entire soil food chain, from microbial decomposers to higher organisms [7]. Accordingly, replenishing stocks of soil C by organic fertilisation in the form of manure or sludge is largely beneficial.

To understand, predict and manage the functioning of soil, it is necessary to stop perceiving it merely as dirt or an abiotic surface for the growth of vegetation. Soil is an intricate three-phase system composed of a variety of solids, water and dissolved substances, as well as gases in pore air [10]. The constituents are organised into three-dimensional structures that resemble fractals and change dynamically over time. Intriguingly, changes in soil structure are biologically mediated and take place in a coordinated manner [11]; soil could thus be called the most complex biomaterial on Earth [12]. In addition to the maintenance of soil structure, the majority of other essential soil functions are also biological by nature [13, 14].

Although the role of fauna such as earthworms cannot be neglected [15], the majority of soil properties can be traced to the activity of soil microbiota, especially bacteria, fungi and archaea [13, 16, 17]. It is estimated that approximately 90% of the energy flow in soil passes through microbial decomposers [18]. Moreover, the metabolic agility of soil microbes is not limited to the consumption of various carbonaceous compounds by heterotrophs. Many bacteria and archaea (i.e. prokaryotes) are able to grow autotrophically. Phototrophs such as soil surface cyanobacteria derive energy from light. Chemolithoautotrophs can literally consume rocks and simultaneously perform biogeochemical transformation processes traditionally considered to be within the field of soil chemistry [19]. This wide diversity of energy sources and living strategies is reflected in the phylogenetic diversity of the organisms: estimates of the number of different bacterial species in just one gram of soil are in the range of 10^4 – 10^7 [20]. The total number of prokaryotic cells in that one

gram may reach 10^{10} , but due to their micron-scale sizes, they only cover approximately the same percentage of soil particle surfaces, $10^{-6}\%$, as the percentage of the surface of the Earth covered by humans [12].

2 Soil Contamination as the Main Threat to Soil Quality

Humans have invented many means to make life more comfortable. Excavating fossil fuels for energy and the advent of agricultural chemicals and pharmaceuticals have facilitated the improvement of the quality of life for many people. Unfortunately, many of these inventions have a downside: chemicals needed for such improvements may have adverse health effects and impacts on the environment and humans. Careless manufacturing and application of industrial and agricultural products together with the lack of suitable waste disposal has caused chemicals to end up where they were not originally meant to be, causing contamination of soil, groundwater, sediments and the food chain itself. In this sense, a contaminated site may be defined as “a site with confirmed presence of dangerous substances caused by man to such level that they may pose a significant risk to a receptor in such a way that action is needed to manage the risk” [21]. Contaminated sites are not equally distributed. Many Western European countries and the United States experienced the early years of industrialisation, and therefore, historically contaminated point source sites, such as polychlorinated biphenyls (PCBs) and dioxin manufacturing facilities, are often found in these countries. Currently, many emerging economies seem willing to pay the price of environmental pollution for rapid development and an increase in the gross domestic product.

If soil contamination is classified according to the source of contamination, point sources are distinct from diffuse sources. A point source of contamination is frequently related to industrial discharges, improper waste disposal or accidental spills during the transportation or handling of hazardous substances. Domestic examples of point contamination are the careless use of septic tanks and leaking underground oil tanks. Diffuse contamination is associated with certain agriculture and forestry practices, transportation and improper waste and wastewater management. Another diffuse source of contamination is the atmospheric deposition of low-volatile compounds that may affect pristine areas at Arctic and Antarctic latitudes due to the “cold condensation effect” [22]. Soil contamination is often associated with groundwater contamination. Soil porewater moves vertically, at a rate largely determined by soil texture, when excess rain is absorbed into the deeper layers, thereby generating groundwater. By contrast, horizontal groundwater flow is driven by lakes and river systems. Vertical and horizontal groundwater flows are the means of transport for many water-soluble contaminants. Because groundwater pollution is very difficult and expensive to manage, it is imperative to prevent the leaching of contaminants into groundwater. On the other hand, non-water-soluble chemicals threaten the function of primary producers living in the soil. Non-water-soluble chemicals also affect higher organisms because poorly biodegradable lipophilic substances tend to accumulate in the food chain.

Despite the difficulties of evaluating the true extent of contamination, the latest estimations in Europe in 2006 set a number of 3.5 million potentially contaminated sites [23]. Of these, approximately 0.5 million were expected to require urgent treatment. The National Priorities List of the 2012 US Environmental Protection Agency (EPA) identified 1,305 superfund sites, which are defined as abandoned hazardous waste sites [24].

2.1 *Contaminants in Soil*

Since the beginning of industrialisation, a great variety of anthropogenic chemical compounds have been synthesised for countless uses. Some chemical groups, such as organochlorides and nitroaromatic compounds, are purposefully synthesised, while the production and incineration of some other commodities, such as polyvinyl chloride (PVC) plastic, create undesired toxic by-products. After the chemical products have served their purpose, they often end up in the environment. The microbes responsible for recycling all matter are seldom well equipped to degrade the new types of molecules, which are therefore biodegraded slowly, if at all. The final destination of persistent contaminants is often the soil, or if they pass through a water treatment plant, either sewage sludge or sediment at the bottom of rivers, lakes or the sea, where they may accumulate, thereby rendering the environment hazardous to life.

The increase in environmental awareness and the acute effects of some toxic compounds have raised questions over the safety of using many chemicals invented for agricultural and industrial applications. A great deal of current research addresses the management and remediation of old contaminated sites. Recent concerns regard the safety of consumer chemicals, especially nanomaterials; the effect of pharmaceuticals on ecosystems; and the combined effect that chemical cocktails have on human and ecosystem health.

In the following sections, the origin and fate of different hazardous and recalcitrant chemicals are considered. Many of the compound groups have been synthesised for several decades around the world, and therefore, in many cases, comprehensive inventories of the production rates of these chemicals are limited. Emission inventories are collected for scientific and administrative purposes, with great differences in their reliability, as well as in their temporal and spatial coverage [25]. Attempts to collect detailed official emission databases have been undertaken by the United Nations under different conventions, such as the Convention on Long-Range Transboundary Air Pollution [26] with the additional Aarhus Protocol [27] and the Stockholm Convention on Persistent Organic Pollutants (POPs) [28]. Scientific studies often require data on other features beyond those deposited in the official databases, and therefore, many efforts have been undertaken to estimate source emission levels, environmental occurrence and final sinks [29–32]. To understand the current state of soil contaminated with hazardous, persistent chemicals, we have attempted to utilise both scientific and official sources, but the reader should bear in mind that these numbers are rough

estimates at best. Descriptions, source emissions and the types of emerging contaminants frequently found in sewage sludge are discussed in [33–39].

2.1.1 Hazardous Compounds Originating from Oil Products

Crude oils are heterogeneous mixtures of hydrocarbons formed underground under high pressure from the remains of organic material. They can be refined into a multitude of products. The main use of oil is as an energy source in traffic, heating and electricity production, as approximately 34% of the global energy demand is met by oil products [40]. Crude oil is also used as a raw material in many man-made materials, such as plastics, paints and solvents. Oil is produced globally in staggering quantities, as global oil demand is foreseen to be 92.9 megabarrels per day in 2015, with an increasing demand reaching 110 megabarrels in 2035 [40]. Crude oil is perhaps globally the most exploited non-renewable natural resource. Accordingly, substances deriving from crude oil are the most common polluters of the environment.

Fate of Fuel Oil

Most fuel oil ends up in its intended place of use, as an energy source in motor vehicles or heating. Burning oil products increases the global levels of atmospheric CO₂, the most important greenhouse gas. Impurities in the oil and incomplete combustion generate nitrous oxides, polycyclic aromatic hydrocarbons (PAH) and acid rain from sulphur dioxide because sulphur is a trace element found in many crude oils. Crude oil refining often includes steps in which oxygenated compounds, such as methyl tert-butyl ether (MTBE), are added for enhanced combustion. If the fuel oil ends up in soil, the water-soluble additives often leach into groundwater, rendering it unfit for drinking.

Crude oil is only found in a number of locations on Earth, and its uneven distribution requires a vast transportation network. Dramatic oil spills that are a consequence of oil transportation and events such as the explosion at the Deepwater Horizon oil rig attract much media attention because their effects on the environment are directly visible. The most common type of petroleum contamination in the environment, however, is from sources of smaller volumes. Leaking heating oil containers, gasoline station tanks and lines; improper handling of waste; and small accidental spills comprise most of the oil pollution in soil, waterways and groundwater. The information on the amount of petroleum products contaminating our soils is fragmented, but thorough estimates of oil contamination in the oceans have been attempted in several studies starting in the 1970s. Natural seeps are the largest contributor of oil in the sea, at 600 kilotons of oil each year. Oil release to the sea by human activities is nearly equivalent, at 480 kilotons each year [41]. As for soil, the European Environment Agency estimated in 2006 that crude oil was the most important pollutant of the investigated contaminated sites, at 33.7%, which was second only to heavy metal pollution (Table 1).

Table 1 Type and source of the most relevant group of contaminants in European soils

Contaminants	Example of compounds	Source of contamination ^a	Estimated percentage ^b	References
Heavy metals	Cu, Zn, Cd, Pb, Hg, Cr	Application of animal manure (D) Military facilities (P) Gasoline stations (P) Sawmills and wood preservation sites (P) Mining and metallurgical industry (P,D)	37.3	[21, 42]
Oil hydrocarbons	Alkanes, alkenes, cycloalkanes	Oil industry (P,D)	33.7	[23]
Chlorinated compounds	PCP, PCBs, PCDD/Fs	Manufacture of pesticide and herbicide (D) Wood preservation sites (P) Pulp and paper production (P) Municipal waste incineration (P,D) Plastics, fire-retardants manufacture (P,D)	Chlorinated phenols – 3.6 Chlorinated hydrocarbons – 2.4	[43, 44]
Monomeric aromatic hydrocarbons	Benzene, toluene, ethylbenzene, xylene (BTEx)	Oil industry (P,D) Gasoline stations (P) Manufactured gas plants (P,D)	6	[43]
PAHs	Benzo[a]pyrene, chrysene, fluoranthene	Oil industry (P,D) Gasoline stations (P) Manufactured gas plants (P,D) Wood preservation sites (P) Municipal waste incineration (P,D) Automobile exhaust (D)	13.3	[43, 45]
Nitroaromatics	TNT, nitrobenzene, nitrophenols, atrazine	Manufacture of aniline, dyes, drugs (P,D) Explosive industry, military facilities (P, D) Manufacture of pesticides and herbicides (D)	^c	[46]

^aP = point contamination; D = diffuse contamination^bAccording to the European Environmental Agency, the estimated percentage is based on the frequency with which a specific contaminant is reported to be the most important in the investigated site [23]^cInformation not available

Fate of Plastic Products

Because plastic products are made of hydrocarbons, they can be burned. However, certain chlorine-rich plastic products, such as PVC, form dioxins when incinerated. Because oil-based plastics are not biodegradable, most man-made plastic that is not burned still exists today. Plastic waste is created in staggering numbers: by 1988 in the United States alone, 30 million tons of plastic were produced annually [47]. Plastic goods most often end up in municipal dumpsites and landfills. Plastic is an inert material and therefore not toxic, but the problem arises from the fact that it does not degrade [48]. Due to careless waste management, massive amounts of plastic are found floating on sea surfaces. Plastic litter comprises most worldwide marine litter, with fishing, merchant and recreational ships as the major sources of plastic litter [49]. Sea currents transport floating material to certain areas, where plastic litter converges as “plastic gyres” found in the Pacific Ocean [50] as well as the Caribbean Sea and the North Atlantic Ocean [51]. In these gyres, up to 580,000 plastic pieces per square kilometre have been reported. Plastic litter is harmful to marine organisms in several ways. For example, marine animals ingest plastic particles that can block their guts, and marine animals can become entangled in plastic debris. Floating plastic can also act as a vector for hazardous compounds or change the ecological balances in the oceans by transporting or providing a good breeding ground for invasive species [49].

Plastic products are known to eventually break down into smaller and smaller pieces (nanoparticles) until they are small enough to enter the cells of living organisms. Because the amount of discarded plastic is so substantial, nanoplastic particles pose an emerging environmental concern. The health effects of nanoplastics are not thoroughly understood, but polystyrene particles up to 240 nm in diameter have been proven to be transportable through placental cells [52].

Fate of BTEX Compounds

The monoaromatic compounds benzene, toluene, ethylbenzene and xylene, commonly found in crude oil, are often jointly called BTEX compounds. The most harmful of these compounds is benzene, which is a known carcinogen. BTEX compounds occur naturally near natural gas and petroleum deposits and are detected in the fumes of forest fires. Most of the highly volatile BTEX compounds released by human activity originate from fuel use and end up as pollutants in the air. Inhaling BTEX-polluted air is also the greatest hazard to humans by these compounds. BTEX compounds are water-soluble, and therefore, improper handling can also cause groundwater contamination.

Future of Petroleum Hydrocarbons

Although technologies for using alternate energy sources exist, most of the transportation infrastructure is still based on the consumption of refined crude oil.

It seems unlikely that alternate energy sources will surpass crude oil-based fuels in the near future. Therefore, effective methods for cleaning up oil-contaminated environments are required. Because of their high carbon concentration, oil products are often readily utilised by environmental microbes. Thus biological treatment methods are typically effective at oil-polluted sites, and many promising, large scale studies confirm that bioremediation is a feasible, cost-effective method for cleaning up oil contamination in situ. Such is the example of the clean-up approach applied to tackle the Deepwater Horizon oil spill in the USA. The oil was dispersed via the direct application of a dispersant that enhanced the natural biodegradation of the oil [53].

2.1.2 Polycyclic Aromatic Hydrocarbons

PAHs are not produced for commercial purposes. They are naturally formed during volcanic eruptions and forest fires. However, most PAHs originate from anthropogenic sources, such as the incomplete combustion of fossil fuels, wood and waste; automobile exhaust; and petroleum derivative spills [54]. Diffuse contamination of PAHs occurs via adsorption to airborne solid particles [55]. Wind transports the particles to distant locations where they are deposited directly onto the soil or indirectly to soil through vegetation. It is estimated that soil receives 0.7–1 mg/m² of PAHs by atmospheric emissions [56, 57]. In 2004, Zhang et al. estimated the total global atmospheric emission of the 16 PAHs listed by the US EPA to be 520 Gigagrams per year [58]. Due to their low solubility, PAHs tend to be deposited into sediments and soil. Once in the soil, PAHs may be degraded or transformed, which will determine their transport, distribution and concentration. PAHs bound to organic matter have reduced mobility but also have a higher resistance to biodegradation. The binding affinity of PAHs to soil organic matter is determined by the octanol–water partition coefficient (K_{ow}). PAHs with high molecular mass, and consequently high log K_{ow} , tend to have a higher affinity for soil organic matter.

2.1.3 Nitroaromatic Compounds

The production of nitroaromatic compounds is one of the largest chemical industries today. These compounds are used in explosives, as starting materials in the pesticide and pharmaceutical industries and in dyes, among many other applications. They are identified by one or more functional nitro groups attached to the aromatic ring structure. Some nitroaromatic compounds are formed naturally, with the reactions catalysed by sunlight or radicals. Certain compounds of this group, such as nitroaromatic antibiotics produced by members of the genus *Streptomyces*, are of biological origin; therefore, pathways for their degradation exist [59]. Despite this, many man-made nitroaromatic compounds have been identified as toxic, mutagenic, carcinogenic and persistent against degradation [60].

Aniline, which is used not only to synthesise drugs, pesticides and explosives but also as a building block for materials such as polyurethane foams, rubber, azo dyes, photographic chemicals and varnishes, is manufactured at a quantity of approximately three million tons each year [61]. The toxic effects of aniline include increased nitration of proteins in the spleen [62].

The most famous explosive is trinitrotoluene, or TNT, which was mainly used in warfare in both world wars, as well as in mining and building. TNT is still widely used and produced. Most of the current problems with TNT and nitroarene compounds are found in sites where ammunition was handled, stored or manufactured. TNT is a persistent contaminant, but its microbial degradation is possible both aerobically [63] and anaerobically [64].

Even though some nitroaromatic compounds are purposefully spread in the environment as pesticides, the majority of their environmental releases are accidental. For example, in the United States alone, 5.1 tons of nitrobenzene were released in soil in 2002 [65]. The greatest known industrial releases have occurred in China; in 2005, an explosion at a chemical factory resulted in the accidental release of 100 tons of benzene and nitrobenzene to the Songhua River [66].

2.1.4 Chlorinated Compounds

Chlorinated compounds have been and still are produced for many purposes. Many cleaning agents, pesticides and pharmaceutical products rely on the chemical properties of the chlorine atom attached to a hydrocarbon backbone or ring structure. Natural degradation pathways do exist for many of these compounds because chlorinated organic compounds are common in certain more complex and biologically active molecules. Some chlorinated compounds are more readily degraded than others, and their degrees of toxicity vary.

In 1994, US PVC manufacturers used 4.26 billion kg of chlorine to produce 4.95 billion kg of PVC [67]. PVC production is the most important reason for man-made organochlorides. The manufacture of the precursor for the plastic, vinyl chloride, is the main reason for dioxin pollution in the United States [68]. The US EPA lists accidental fires and burning of municipal waste containing PVC plastic as other major sources of dioxins [69]. Dioxins are slowly degradable, and they tend to accumulate in sediments. Another important source of organochloride production is the dry-cleaning industry, where the main compound used is tetrachloroethylene (TCE). Although the use of TCE has declined throughout the 1990s due to its classification as a hazardous compound by the US EPA, it is still used in dry-cleaning facilities. For example, in 2001, US plants produced approximately 148 million kg of TCE [70].

Of the 16 POPs listed in the 1998 Aarhus Protocol [27], 11 are organochloride pesticides, which have now been banned in several countries. Most concerns regarding these products relate to their toxicity, with health effects to humans ranging from lung damage and neurological problems to death. Many organochloride pesticides are lipophilic, and they accumulate in the adipose tissues.

Due to these properties and their biochemically stable molecular structures, they are not easily biodegraded in the environment. Organochlorides are transported globally by natural processes and have been observed to accumulate in the Arctic [71]. All pesticides are tested for human toxicity before they are given permission for use. They are often not acutely toxic, at least not in minor concentrations. However, due to their chemical properties, some pesticides are bioaccumulative and are enriched in the food chain to much larger concentrations than the manufacturer intended. The most famous example of this is dichlorodiphenyltrichloroethane (DDT), which was first synthesised in the 1940s. DDT has been banned in many countries, but totally phasing out its use is difficult because it is efficient in preventing malaria vectors, and it is still produced at 4–5 tons each year [72]. Organochlorides of low molecular mass are readily water-soluble and thus can easily contaminate groundwater. Due to the hydrophilic nature of the chlorine atom, organochlorides are efficient compounds in cleaning agents. TCE is used by 90% of dry-cleaners in the United States today. It is toxic to humans and a suspected carcinogen.

Perhaps the most problematic chlorinated compound group includes PCBs, which have been in use since the 1920s for a period of 70 years in hydraulic oils, insulating fluids in transformers and sealants, among other substances, until their toxicity and persistence against degradation were observed. Breivik et al. [30] estimated that the global historical production and consumption of 22 PCB congeners was 1.3 million tons between the years 1930 and 1993 [73]. PCB contamination seems to be unevenly distributed, as many of the highest contamination levels can be found in urban areas [74].

Dioxins are a large group of very toxic chemicals formed when organic matter is burned in the presence of chlorine. Polychlorinated dibenzo-*p*-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs) are among the most studied dioxins. Certain dioxins have in fact been coined as the most toxic compounds ever made by man. Dioxins found contaminating the environment are largely the result of human activity. The highest concentrations of dioxins are often found in soils and sediments near the facilities where they were produced or used. Today, the commercial production of many dioxins is banned, and point sources have been closed down. Currently, the largest source of dioxins is the incineration of chlorine-containing waste, which creates dioxin air pollution. Dioxins are lipophilic compounds that tend to accumulate in the adipose tissues of higher organisms. Human exposure to dioxins is mainly by consumption of dairy products, meat, fish and eggs. Dioxins are also found as impurities in PCB products or wood preservatives. A group of dioxins called chlorophenol herbicides, such as 2,4,5-trichlorophenoxyacetic acid (2,4,5-T), are commercially produced in large quantities. Large areas of land were contaminated with this compound when it was sprayed in central Vietnam as a component of Agent Orange, a defoliant sprayed in quantities of hundreds of kilograms during the Vietnam War in the 1970s.

Chlorinated phenols have been traditionally applied in the production of wood preservatives, insecticides and disinfectants. Common chlorinated phenols found in wood preservatives are 2,3,4,6-tetrachlorophenol (TeCP), 2,4,6-trichlorophenol

(TCP), and pentachlorophenol (PCP), in order of abundance. Minor amounts of other trichlorophenols and dichlorophenols may also be present, as well as recalcitrant polychlorinated phenoxyphenols (PCPPs) and PCDD/Fs as impurities [75, 76]. In Finland, approximately 30,000 tons of CP products were used between 1934 and 1988, when they were banned because of their potential toxicity to humans and the environment [77, 78]. The careless manufacturing and application of wood preservatives together with the lack of suitable waste disposal caused massive contamination of river sediments and sawmill sites. For example, the river Kymijoki in southern Finland was identified as the largest source of dioxins accumulating in fish in the entire Baltic area. Similar products were used in other European countries, especially Nordic countries with a large forestry industry, such as Sweden [79].

2.2 Effect of Organic Contaminants on Soil Biota and Quality

Environmental contamination, either from diffuse or point sources, may compromise the ability of ecosystems to provide society with those goods and services that we require. Contamination is also linked to other widely recognised anthropogenic threats to sustainable functioning of our planet, such as the loss of biodiversity. As many soil properties and processes are conferred by soil biota, it is currently widely agreed that biological characteristics should be taken into account when evaluating the quality, or health, of soil [13, 16].

Microbial communities can respond to disturbances, such as contamination, in many different ways; any of these responses may result in perceived stability or the continuation of essential soil functions [80]. The key species may show resistance to perturbation, meaning that the pollutants have no negative (or positive) effect on them. If the initial reaction is negative but the key species are able to regain their numbers and functionality, the community is said to be resilient. If the key species are irreversibly affected but are replaced by other indigenous species that are able to perform the same task under the new conditions, we see redundancy. Only if all these backup strategies fail will the deleterious effects of contamination on soil functions be observed.

Some specific processes, such as the degradation of recalcitrant chlorinated compounds or nitrogen fixation in symbiosis with leguminous plants, can only be performed by a few specialised microbial genera. If these key populations are compromised, these soil functions may be completely lost. However, for the majority of general soil processes, there is functional redundancy, with a plethora of diverse microorganisms able to perform the same actions under slightly differing conditions [17]. For example, the decomposition of plant material is performed by both soil bacteria and fungi, with the former dominating in neutral or alkaline soils and the latter dominating under acidic conditions [81]. The perceived ecological relevance of biodiversity lies in this ability of other species to take over a task if the original agent is disturbed or eliminated (insurance theory). Biodiversity, generally referred to as richness (i.e. number of different species) from the point of view of conservation, is thus assumed to ensure ecosystem stability [16, 17].

The microbial diversity of soil is vast: up to ten million species with a collective prokaryotic genome ten thousand times the size of the human genome have been found in a mere handful of dirt. In addition to rapid microbial mechanisms of genetic reorganisation, and 3.7 billion years of evolution, this diversity is predominantly produced and maintained in soil by spatial isolation of dispersed cells and small colonies [82, 83]. Although the majority of soil bacteria or archaea will never interact, even with their neighbouring cells just a few millimetres away [10, 17], such a wide biodiversity can be expected to convey a very high level of functional redundancy in microbially mediated soil processes. The true relevance of the natural soil microbial species richness, especially because many species are found in very low abundance, is still a highly disputed topic among microbial ecologists [17]. For example, a high richness does not seem to be linked to higher rates of general soil processes such as degradation of organic C. On the other hand, high diversity has been connected to more efficient degradation of hydrocarbons [84] and a reduced persistence of invader species [85]. In addition, a severe decrease in microbial diversity seems to be associated with an increased susceptibility of soil processes to further perturbation [17].

Soil contamination with inorganic or organic pollutants commonly reduces the diversity or evenness (even distribution of species) of soil bacteria [16, 17, 85]. Generally, a combination of multiple stressors, such as different pollutants or contamination and drought, exerts especially high pressure on soil communities, and the combined negative effect may not be additive but rather synergistic [86]. In the case of soil microbes, this general ecological principle does not seem to hold; prior stress has been associated with both an increase in sensitivity and an increase in community resistance or resilience [16]. In the latter case, the explanation may lay either in similar physiological mechanisms of resistance to multiple stressors or in community adaptation through increased numbers of generally more resistant species. The production of persistent resting forms such as bacterial endospores under stressful conditions can result in increased resilience [16]. Dormancy in general, meaning minimal metabolic activity associated with minimal interaction with the environment, can deliver the same advantages and seems to be a common survival strategy for soil bacteria [83].

The apparent resistance of soil microbial communities to contaminants may not be caused by insensitivity of the exposed organisms but rather by the fact that the pollutants simply are not bioavailable in the specific environment to the organisms under observation on the time scale of the observation. This holds especially true for organic contaminants with high K_{ow} values [87]. Aromatic and halogenated compounds introduced into soil in sludge tend to remain adsorbed in sludge solids such as organic material or fine inorganic particles [88]. If the compounds are released due to degradation of the sludge-derived organic material, pollutant molecules may further be adsorbed on or absorbed in more recalcitrant soil organic matter [87]. Such sorption may be either reversible or irreversible, but in any case, the mobility of low-concentration organic contaminants with poor aqueous solubility in soil is very restricted. As soil microorganisms are often located in micropores or inside aggregates, their spatial separation from pollutants can efficiently reduce their exposure.

If an organic pollutant in soil is sufficiently bioavailable to exert toxic effects, it is generally also bioavailable to organisms able to degrade it. However, the opposite may not hold true because degradative bacteria often have specific mechanisms to improve access to and uptake of organic compounds [89]. The evolutionary rationale for acquiring such mechanisms is that the bacteria degrading organic pollutants are often able to use these as sources of energy, C and N [90]. Because the degradation capacity thus provides a combined competitive advantage in the form of both protection and cell building blocks, microbes have evolved pathways to catabolise seemingly any organic compound [91]. Such organisms are also widely spread. Hydrocarbon degraders can be detected in any environment contaminated with crude or refined oil [92], but degraders of many emerging contaminants [34] belong to bacterial taxa common in the soil environment [93]. Horizontal transfer of the degradation genes from a degrader to another bacterial species, genus or even family further increases the capacity of the microbial community to cope with contamination [16]. On the other hand, some of the newer compounds, especially halogenated aromatic molecules, may be thermodynamically and biochemically so challenging to catabolise that optimal degradation pathways are still under evolutionary development [94]. For such compounds, the degraders are not necessarily widely spread in nature yet. Moreover, the concentrations of such emerging contaminants in the environment may not be sufficient to support the development or maintenance of specialised degrader communities, whereas more abundant and readily utilisable pollutants such as oil typically cause a rapid increase in the number of degraders [95].

In addition to various persistent halogenated aromatics, the introduction of pharmaceutical compounds in the environment has received attention. The ecological effects of antibiotics have particularly been studied because they can disturb microbially delivered functions in various environments such as wastewater treatment plants or agricultural soils. Moreover, the risk of development and positive selection of antibiotic-resistant bacteria is a cause of wide concern. Such concerns may seem exaggerated for soil microbial ecology because any soil contains a diversity of microbes that can produce antibiotics or are resistant to them [85]. In fact, many antibiotics were originally found in soil-inhabiting Actinobacteria, and the search for new drugs from similar sources with modern technologies is ongoing [96]. However, if a significant concentration of an antibiotic could be introduced to soil via sewage sludge, the steep concentration gradient can cause an even more rapid development of antibiotic resistance in the heterogeneous soil environment than in more homogeneous aquatic habitats [97]. Another microbial risk related to sewage sludge is the potential introduction of human pathogens into soil. Diverse soil microbial communities can often outcompete invading species such as human or plant pathogens [14]. However, if the sludge contains both a contaminant that compromises the indigenous soil community and a pathogen already acclimatised to the contaminant, the risk of the pathogen becoming established and persisting in the soil environment increases sharply.

To conclude, a review of recent literature on the connections between soil contamination, microbial biodiversity and ecosystem functioning perhaps raises

more questions than answers. Although it is not evident how diversity (and what type of diversity) is related to soil ecosystem service efficiency and stability, a conservative attitude should be maintained because soil is a non-renewable natural resource. Moreover, soil clay and organic matter contents correlate positively with biodiversity and resilience [82] but negatively with pollutant bioavailability [87]. Thus, coarse-textured mineral soils that have the greatest need for improvement by organic fertilisers are also the ones most vulnerable to the negative effects of co-introduced contaminants.

Although the role of bacterial, archaeal and fungal communities in soil health is indisputable, macrobiota have their own important functions, even in intensively managed agricultural soil. The production of soil-based goods – food, fodder, fuel and fibre – obviously depends on plant growth, and primary production is the final driver of ecosystem services [7]. Unfortunately, plants may be, in general, more sensitive to soil contamination by organic pollutants than by bacteria. The exposure and response of plants to emerging contaminants thus deserves much more attention.

3 Health Effects of Organic Contaminants on Animals and Humans

The Stockholm Convention on POPs lists 22 priority chemical substances that pose potential risks of causing adverse effects to human health and the environment. Since the convention was enacted in 2004, evidence for the toxic effects of POPs such as DDT, dichlorodiphenyldichloroethylene (DDE), PCBs, PCDD/Fs and other halogenated compounds has been demonstrated for both humans and wildlife.

Due to their lipophilic nature, organic chemicals with high molecular mass tend to accumulate in the adipose tissues of living organisms. Thus, even though they are commonly present at low concentrations, adverse effects associated with chronic exposure are of a particular concern. Some POPs are capable of acting as endocrine disrupters that harm the reproductive system and development of wildlife [98–100]. For example, reproduction abnormalities, immune function impairments and thyroid deficiencies have been detected in Baltic grey seals and ringed seals due to PCB intake from food [98]. Exposure to PCBs has also caused immune dysfunction, reproductive failure, increased pup mortality, deformations and adult mortality in minks and ferrets. Other effects in mammals (e.g. seals, dolphins, porpoises and whales) linked to chlorinated compounds such as PCBs, hexachlorobenzene (HCB), 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD), toxaphene and DDT include immunotoxicity, dermal effects, carcinogenicity, vitamin and thyroid deficiencies and mass mortalities by infectious diseases [98, 101]. Water bodies contaminated by effluents from wastewater treatment plants and industries have reduced the viability of larvae of several species of fish; increased blood vitellogenin (i.e. a precursor of egg yolk protein formation) in male trout, carp, flounder and perch; and

caused thyroid damage in salmon species [98, 101]. In invertebrates, exposure to PCBs and tributyltin causes masculinisation in different species of female marine gastropods. In birds, among different reproductive effects, the most evident is DDE-induced egg-shell thinning. In reptiles, feminisation and increased developmental abnormalities of turtles and alteration of sex organ development and function in alligators have been associated with exposure to chlorinated compounds [98].

Although the effects of chronic exposure of humans to low levels of POPs are difficult to predict, some biological effects have been described. For example, exposure of children to PCBs and PCDD/Fs may be linked to an elevated risk for infectious diseases. Exposure of pregnant women to PCDD/Fs may cause lower fertility in their male offspring. The adverse effects to human health of acute and chronic exposure of high concentrations of POPs, especially among industrial workers exposed to daily intakes of chemicals, are more evident. Elevated concentrations of DDE and TCDD have been associated with the development of cancers such as breast cancer, leukaemia and thyroid cancer. Dioxin exposure may also be associated with immunotoxicity, reproductive diseases and neurotoxicity. Extreme exposure to chlorinated compounds has resulted in death [101].

In addition to recognition of the toxic properties of the Stockholm POPs, PAHs are also a significant concern; therefore, 16 PAHs are listed by the US EPA as having a possible carcinogenic nature. However, PAHs with a “bay” or “fjord” region in their molecular structure are the most likely carcinogens. For instance, when entering an organism, benzo-*a*-pyrene (BaP) is activated by a series of metabolic reactions that lead to the final carcinogenic metabolite, a reactive diol epoxide, which may bind covalently to DNA, leading to mutations and tumours [102]. Only BaP is classified by the International Agency for Research Cancer (IARC) as carcinogenic to humans due to extensive evidence of the induction of different tumours by BaP in in vitro and in vivo studies in mice and mammalian cell cultures [103, 104].

3.1 Emerging Endocrine-Disrupting Compounds

Despite the evidence concerning chlorinated compounds and PAHs, a general correlation between human diseases and exposure to other organic contaminants has yet to be proven. This is especially true for new emerging contaminants at low levels of exposure. The reasons for the lack of knowledge are insufficient field or semi-field studies, a lack of data concerning residual levels in the body, ecological background, dose–response relationships and contradictory scientific results. Frequently, the main effect associated with emerging contaminants is the alteration of functions in the endocrine system, that is, the contaminants act as endocrine disrupters. The most common endocrine disrupters found in groundwater, bodies of water, wastewater effluents and sewage sludge are triclosan; tributyltin; 17 β -estradiol; bisphenol A; nonylphenol; the synthetic musks galaxolide and tonalide;

the pharmaceuticals paracetamol, ibuprofen, naproxen, diclofenac and fluoxetine; polybrominated diphenyl ethers (PBDEs); and perfluorinated compounds (PFCs) [88, 105–108]. In the following section, we have focused on three types of endocrine-disrupting agents with particular interest due to the extent of the research conducted on them: bisphenol A, PBDEs and PFCs. For the other potential endocrine-disrupting chemicals listed above, see [108–111] and the references therein.

3.1.1 Bisphenol A

Scientific results for bisphenol A toxicity are contradictory. In experiments with rodents, maternal exposure during pregnancy or early post-natal exposure of pups to low doses of bisphenol A (up to 2.5 mg/kg/day) showed developmental or reproductive effects in the offspring [112]. On the contrary, in a long-term study with minnows, the NOEC (no observed effect concentration, which is defined by the US EPA as “the highest tested concentration of an effluent or a toxicant at which no adverse effects are observed on the aquatic test organisms at a specific time of observation”) related to survival, growth and development parameters ranged from 16 to 1280 µg/L. This concentration range is markedly above the measured concentrations in North American and European fresh waters (ranging from 0.081 to 0.47 µg/L and 0.01 to 0.05 µg/L, respectively) [113]. The authors concluded that the likelihood that bisphenol A in surface waters would cause an effect in fish, even if exposed for multiple generations, is low [114]. In humans, bisphenol A has been detected in serum, breast milk and urine due to environmental or direct exposure during production, use and disposal of bisphenol A-containing products [112, 115]. Following the scientific results on the toxicity of bisphenol A in animals, the European Food Safety Authority (EFSA), the World Health Organization (WHO) and the Food and Agriculture Organization of the United Nations (FAO) declared that the actual effects of bisphenol A on human health need further research. The lack of scientific evidence of its toxicity at the current levels of exposure and major methodological flaws were the main reasons for their declaration [116]. Nevertheless, a global concern has been raised regarding the potential effect of bisphenol A on reproduction and neural and behavioural development in foetuses, infants and children. One of the most important worldwide actions concerning bisphenol A was to ban the manufacturing of baby bottles containing bisphenol A in the EU [117], in some states of the United States [118] and in Canada [119].

3.1.2 Polybrominated Diphenyl Ethers

PBDEs are a class of brominated flame retardants (BFRs) used in textiles, plastics and electronic products. The effects of BFRs are associated with three commercial mixtures of PBDEs: decaBDE, octaBDE and pentaBDE. In laboratory animal experiments, the toxicity of PBDEs was linked to damage to liver function and,

in the case of octaBDE and decaBDE, to an alteration of thyroid hormones and developmental neurotoxicity. Importantly, bacterial tests indicated that these three groups of PBDEs are not mutagenic [120]. Epidemiological studies on humans have focused on three main health effects: endocrine disruption, neurotoxicity and reproductive toxicity. Despite the lack of correlation between thyroid hormone levels and exposure to PBDEs, serum concentrations of PBDEs may be associated with alterations of hormones, as PBDEs may interact as antagonists or agonists at androgen, progesterone and oestrogen receptors [121]. Moreover, PBDEs may be inversely associated with thyroid-stimulating hormone (TSH) or cause a reduction in thyroid hormone T4, which may result in developmental neurotoxicity [120]. In fact, neurotoxicity is the greatest concern regarding PBDEs because there is enough evidence from animal data that suggests that pre- and postnatal exposure may cause behavioural alterations, particularly in motor performance and cognition [121].

3.1.3 Perfluorinated Compounds

Due to their persistence in the environment, perfluorooctanoic acid (PFOA) and perfluorooctane sulfonate (PFOS) are the two major classes of PFCs found in the environment. Their use in a wide range of products has been reduced due to accumulating evidence of their toxicological effects and because they are now included in the Stockholm Convention. Regardless of industrial efforts to moderate their use, PFCs still remain in the environment. Consequently, serum concentrations in humans at levels proven to cause toxicological effects to laboratory animals have raised concern about their effect on human health [122–124]. A recent study has detected PFCs in human newborn cord blood at levels ranging between 30% and 79% of the maternal plasma, which demonstrates that PFCs pass, at least partly, the placental barrier [125]. Laboratory animal studies have demonstrated that hepatotoxicity (e.g. liver enlargement and induction of peroxisome proliferation), immunotoxicity and reproductive and developmental alterations are the main toxicological effects of PFOA and PFOS [123, 124].

3.2 *Potential Toxicity of the Application of Biosolids in Agricultural Land*

Epidemiological studies have frequently focused on the exposure to a single compound, usually at a higher concentration than that measured in the environment. Only a few studies exposing animals to a mixture of chemicals at low concentrations have been conducted. Even research using real contaminated environmental samples (e.g., wastewater, soil, sewage sludge) is negligible. To the best of our knowledge, only the studies by Bellingham and colleagues have been conducted with grazing animals exposed to sewage sludge applied to pasture [126, 127]. In their first study

[126], sheep foetuses were exposed to sewage sludge via maternal ingestion of pasture grass. The foetuses presented lower expression of genes of the gonadotrophin-releasing hormone (GnRH) and galanin systems in the foetal hypothalamus and pituitary gland [126, 127], both having an important role in the regulation of reproductive function. In a similar study [127], foetal and postnatal exposure of rams to sewage sludge caused a reduction in germ cell numbers in a significant fraction of the sheep, indicating sperm production alterations. The results of these studies are difficult to extrapolate to humans because direct exposure to sewage sludge applied to soils is insignificant. Although there is insufficient animal epidemiological data, the effects of the application of biosolids on pasture raise concerns about farm animal health, welfare and productivity [100].

4 Legislative Framework for Soil Protection and Sewage Sludge Use

Whereas water and air have been traditionally more protected, awareness of the need for soil protection, despite the fundamental role of soil in providing important ecosystem services, has been scarce. European experts argue that monitoring all the compounds with potential to enter the soil system is not feasible, and they propose a list of priority substances to be regulated instead. The list is based on the substances that may enter the soil at such concentrations that they pose a risk to human health, crops, and soil biological function and diversity. Several heavy metals (cadmium, copper, lead, zinc, mercury, arsenic, nickel and chromium) and organic contaminants [PAHs, PCDD/Fs, PCBs, hexachlorocyclohexane (HCH), DDT and dichlorodiphenyltrichloroethylene (DDE), among others] are included in the list. A concise description of the most relevant organic contaminants in European soils and their origins is provided in the second section of this chapter.

4.1 European Environmental Policies on Soil Protection

One of the main obstacles for effective protection of soil in Europe is that such a policy is spread across many EU laws and regulations, which are mainly focused on the protection of other environmental media or cover other objectives (e.g., air and water legislation and agriculture legislation) [128]. Because these policies are not directly oriented towards soil protection, soil has not been the subject of specific legislation or regulation for many years. A major legislative breakthrough occurred in 2002, when the preliminary communication by the commission “towards a thematic strategy on soil protection” created a common framework for soil protection. The strategy considered many stakeholders and different threats to soil quality and functions, including soil contamination [129]. The first proposal of the soil thematic

strategy was reflected in the sixth Environment Action Programme (EAP), published by the commission in 2002. In the sixth EAP, the main objectives regarding soil protection were the prevention of soil degradation, the preservation of its functions and the restoration of degraded soil [130]. The next step was the creation of extensive consultation processes during a 2003–2004 division into five working groups. Each working group was composed of experts from the public and private sector, research institutes, the European Environment Agency (EEA) and agricultural, industrial, environmental and consumer organisations [21]. The results from the contamination and land management technical group were launched in June 2004 as a set of recommendations for policy, monitoring and research focused on the priority objectives and targets of the soil thematic strategy. The targets were (1) the sustainable use of soil, (2) the preservation of soil as a resource and (3) the remediation of degraded soils. Having examined the results of the contamination technical group, the commission recognised the need for a Soil Framework Directive to be transposed to the national legislation of each member state [6]. The commission recommends that each member state create an inventory of contaminated sites based on a common definition of contaminated sites, as well as a common list of potential contaminating activities. Additionally, each member state must adopt a national remediation strategy on how to manage contaminated sites and declare a timeframe for carrying out remediation plans. Additionally, a list of potentially dangerous substances is to be compiled by each member state to prevent diffuse (non-point) contamination. The directive sets the obligation to provide a soil status report by the owner of the contaminated soil to the administration.

One year after the proposal of the Soil Framework Directive, the European Parliament adopted its first reading. However, in 2010, a few countries impeded the continuation of the process on the basis of excessive cost, administrative burden and subsidiarity. To date, the proposal remains on the council's table [131].

Nevertheless, since adoption of the strategy, the awareness of soil protection has risen, and as a consequence, numerous European projects and networks have been created, such as the CLARINET network¹ (contaminated land rehabilitation network for environmental technology in Europe) and the NICOLE² (network for industrially contaminated land in Europe). Other networks related to soil protection are the SNOWMAN network,³ working as a funding body for sustainable use of soil and water, and EURODEMO+,⁴ which encourages the demonstration of sustainable and cost-effective technologies for the treatment of contaminated soil and groundwater. The web portal EUGRIS⁵ disseminates information related to soil and water management in Europe.

¹ <http://www.eugris.info/DisplayProject.asp?ProjectID=4420>

² <http://www.nicole.org/>

³ <http://www.snowmannetwork.com/>

⁴ <http://www.eurodemo.info/>

⁵ <http://www.eugris.info/>

At the member state level, some countries, such as the Netherlands, a pioneer in the protection of soil, have their own national policies and regulations for the management of contaminated soils that were adopted before the Soil Framework Directive [132]. Protection guidelines vary from country to country, and specific legislation for soil contamination only exists for some member states, including the Netherlands, Italy, Austria, France, Belgium, Germany, the UK, Denmark, Spain and Finland [128].

4.2 Regulations for Use of Treated Sewage Sludge on Agricultural Land

Sludge is the solid residue originating from the process of domestic or urban wastewater treatment. The EU encourages the use of sewage sludge in agriculture through the Sewage Sludge Directive 86/278/EEC because of its rich organic matter content and the presence of other essential elements such as nitrogen and phosphorous [133]. The directive requires the pretreatment of sludge before its discharge to agricultural soil to provide protection to potential receptors (soil, vegetation, animal and human) against pathogens. Without any other specifications, the directive requires biological, chemical or thermal pretreatment. The pretreatment must be efficient enough to prevent the application of sludge to soil from being hazardous. For this reason, the sewage directive requires concentration limits for certain heavy metals (cadmium, copper, mercury, nickel, lead and zinc). It also prohibits the application of sewage sludge to “soil in which fruit and vegetable crops are growing or grown” and limits the application to “less than 10 months before fruit and vegetable crops are to be harvested.”

The sewage directive was adopted over 20 years ago, and it was based on the existing knowledge of that time. Currently, the EU recognises the need for revision of the directive in light of new scientific evidence about potential risks to human health, the environment and soil quality. The proposal for the revision of the directive in the “3rd draft of the working document on sludge” sets stricter limits on heavy metals depending on the pH of the soil and includes chromium in the analysis [134]. The draft suggests that each treatment plant carry out a minimum number of chemical and biological analyses regarding the quantity of sludge produced per year. The proposal also includes an analysis of some organic contaminants that were not included in the directive (Table 2) [134]. Moreover, the EU is currently reviewing the possibility of analysing halogenated organic compounds, nonylphenol, linear alkylbenzene sulphonates, di(2-ethylhexyl) phthalate (DEHP), PAHs, PCBs and PCDD/Fs in sludge applied to agricultural land. Regardless of the debate on the type of organic compounds and their limits, no current guidelines exist for these compounds. Similarly, no regulation takes into account an analysis of new emerging contaminants in sewage sludge. Current biological and physicochemical technologies are unable to completely eliminate

Table 2 Differences between the main elements of the Sewage Sludge Directive 86/278/EEC [133] and the 3rd draft of the working document on sludge of the European Commission (2000) [134]

Element	Directive 86/278/EEC (1986)	Working document on sludge 3rd draft (2000)
Pretreatment technology	No specification of type, temperature and duration of the treatment: biological, chemical or heat treatment, long-term storage or any other appropriate process.	<p><i>Advanced treatments:</i></p> <ul style="list-style-type: none"> – Thermal treatment at $>80^{\circ}\text{C}$ – Thermophilic aerobic stabilisation: $\geq 55^{\circ}\text{C}$ for 20 h – Thermophilic anaerobic digestion: $\geq 53^{\circ}\text{C}$ for 20 h – Thermal treatment of liquid sludge (70°C for 30 min) followed by mesophilic anaerobic digestion (35°C with mean retention time of 12 days) – Lime conditioning: $\text{pH} \geq 12$ and $\geq 55^{\circ}\text{C}$ for 2 h – Lime conditioning: $\text{pH} \geq 12$ for 3 months <p><i>Conventional treatment:</i></p> <ul style="list-style-type: none"> – Thermophilic aerobic stabilisation: $\geq 55^{\circ}\text{C}$ with mean retention time of 20 days – Thermophilic anaerobic digestion: $\geq 53^{\circ}\text{C}$ with mean retention time of 20 days – Lime conditioning: $\text{pH} \geq 12$ for 24 h – Mesophilic anaerobic digestion: 35°C with mean retention time of 15 days – Extended aeration at ambient temperature (time adjusted to climatic conditions) – Simultaneous aerobic stabilisation at ambient temperature (time adjusted to climate conditions)
Limit values of heavy metals in sludge for use in land (mg/kg dry matter)	<p>Cd: 20–40</p> <p>Cu: 1,000–1,750</p> <p>Ni: 300–400</p> <p>Pb: 750–1,200</p> <p>Zn: 2,500–4,000</p> <p>Hg: 16–25</p> <p>Cr: not considered</p>	<p>Cd: 10 or 250 mg/kg P^a</p> <p>Cu: 1,000 or 25,000 mg/kg P</p> <p>Ni: 300 or 7,500 mg/kg P</p> <p>Pb: 750 or 18,750 mg/kg P</p> <p>Zn: 2,500 or 62,500 mg/kg P</p> <p>Hg: 10 or 250 mg/kg P</p> <p>Cr: 1,000 or 25,000 mg/kg P</p>

Pathogens	Not considered	No <i>Salmonella</i> spp. in 50 g of sludge (wet weight) At least 6 Log ₁₀ reduction (or at least 2 Log ₁₀ in the case of conventional treatments) in <i>Escherichia coli</i> to less than 5·10 ² CFU/g of sludge.
Limit values of organic contaminants in sludge for use on land (mg/kg dry matter)	Not considered	AOX (500) ^b LAS (2,600) ^c DEHP (100) ^d NPE (50) ^e PAHs (6) ^f PCBs (0.8) ^g PCDD/Fs (100 ng TE/kg dry matter)
Emerging contaminants	Not considered	Not considered

^aLimit values are different if they are related to phosphorus content of the soil (mg/kg of P) [134]

^bSum of adsorbable organic halogens

^cLinear alkylbenzene sulphonates

^dDi(2-ethylhexyl)phthalate

^eNonylphenol and nonylphenolethoxylates with 1 or 2 ethoxy groups

^fSum of acenaphthene, phenanthrene, fluorine, fluoranthene, pyrene, benzo-*b*/*j*/*k*-fluoranthene, benzo-*a*-pyrene, benzo-*ghi*-perylene, indeno-1,2,3-*cd*-pyrene

^gSum of the congeners 28, 52, 101, 118, 153, 180

low-biodegradable emerging contaminants from wastewater streams. As these contaminants are often hydrophobic, they directly accumulate in the sludge [88].

Despite increasing concerns related to potential human toxicity, evidence of adverse effects to the environment and endocrine-disrupting properties, more knowledge is required about the occurrence and detection of emerging contaminants in sludge as well as their degradability and actual risk. In this context, the following chapters of this book provide an overview of the current analytical methods for determining emerging contaminants in sewage sludge samples [33] and the different biological treatment processes available for degrading emerging contaminants in sludge [34–39].

5 Concluding Remarks

As the world population increases and clean sites become scarce, new technologies are needed to provide a clean and healthy environment for humans. The chemical industry produces tons of new, potentially hazardous chemicals every year in addition to those substances that are already known to be toxic. These chemicals are designed by humans for specific purposes that have no analogue in the biological world. However, many anthropogenic chemicals have structural resemblances to biologically produced molecules. Microbes inhabiting our soils, sediments and waters are often starved of nutrients and will readily develop ways to use emerging compounds in their metabolism. Microbial evolution is rapid, and for this reason, researchers are finding new genetic pathways for breaking down many anthropogenic chemicals that have not existed for more than a few decades. In this sense, microbes may be a useful resource for cleaning up contaminated environments.

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