Chapter 14

Producing sludge for agricultural applications

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14.1 INTRODUCTION

The progressive implementation of the Urban Waste Water Treatment Directive 91/271/EEC (amended by 98/15/EC) in all Member States is increasing the quantities of sewage sludge requiring disposal. When treating municipal wastewater, the disposal of sludge is a problem of growing importance, representing up to 50% of the current operating costs of a wastewater treatment plant. Based on sewage sludge production data from 2002 until 2007, an increase from 5.5 million tons to an annual EU-27 sewage sludge production of 10 million tons is reported (European Commission, 2014). This increase is mainly due to the practical implementation of the Directive as well as the slow but constant rise in the number of households connected to sewers and the increase in the level of treatment.

During the last decades there has been a major change in the ways sludge is disposed. Prior to 1998, municipal sludge was primarily disposed at seawaters or was either used as a fertilizer on agricultural land (Ødegaard *et al*. 2002); alternatives were sludge incineration or simply landfilling. Since 1998 onwards, European legislation prohibits the sea disposal of sewage sludge, in order to protect the marine environment. Moreover, the European Union published in 1999 the Landfill Directive (1999/31/EC), which requires the member states to reduce the amount of biodegradable waste being dumped by promoting the adoption of measures to increase and improve sorting activities at the origin, recovery and recycling. The main article of the Directive 91/271/EEC dealing with sludge is Article 14, this article stipulates that 'sludge arising from wastewater treatment shall be re-used whenever appropriate'. This is a clear priority given to the use of sludge in agriculture, when this use is appropriate considering in particular the quality of the sludge. To emphasize the nutritional value of sewage sludge, the term biosolids is normally used when sewage sludge is applied for agricultural purposes. Accordingly, the agricultural use has become the principal disposal method for biosolids; 37% of the sludge produced is being utilized in agriculture, 11% is being incinerated, 40% is landfilled while 12% is used in some other areas such as forestry, silviculture, land reclamation, etc. The latest trends in the field of sludge management, i.e. wet oxidation, pyrolysis, gasification and co-combustion of sewage sludge with other materials for further use as energy source, have generated significant scientific interest (Fytili & Zabaniotou, 2008).

Since 1986 the utilization of sewage sludge has been subject to provisions stipulated in the EU Directive (86/278/EEC). The Directive sets out requirements with respect to the quality of sludge, the soil on which it is to be used, the loading rate, and the crops that may be grown on treated land (European Commission, 2001a). The Directive seeks to encourage the use of sewage sludge in agriculture. At the same time it regulates its use in such a way that any potential harmful effect on soil, vegetation, animals and human beings is prevented. According to the above principle, the use of untreated sludge in agriculture is prohibited, unless it is injected or incorporated in the soil. To provide protection against potential health risks from residual pathogens, sludge must not be applied to soil in which fruit and vegetable crops are growing or grown, or less than ten months before fruit and vegetable crops are to be harvested. Grazing animals must not be allowed access to grassland or forage land less than three weeks after the application of sludge. The Directive also requires that sludge should be used in such a way that account is taken of the nutrient requirements of plants and that the quality of the soil and of the surface and groundwater is not impaired. Moreover, the term treated sludge is defined in the Directive as the sewage sludge which 'has undergone biological, chemical or heat treatment, long-term storage or any other appropriate process so as significantly to reduce its fermentability and the health hazards resulting from its use' (Directive 86/278/EEC).

All the EU member states have transposed the European limits of Directive 86/278/EEC for sludge use in agriculture into their own regulations. Since its adoption, several Member States have enacted and implemented stricter limit values for heavy metals. The member states imposing more stringent limits than those of the sludge directive are Austria, Belgium, Czech Republic, Denmark (with respect to Zn), Finland, Germany, Netherlands, Slovenia and Sweden. On the contrary, the member states that still have the limits close to those of the sludge directive are Cyprus, Estonia, France, Greece, Hungary, Luxembourg, Ireland, Italy, Latvia and Spain (Mininni *et al.* 2015). The perspective of the revision of Directive 86/278/EEC, which could lead to the implementation of more stringent limit values for heavy metals in sludge, could therefore have an impact in the latter countries, at least on the provisions to be set by national regulations (average heavy metals content in sludge is in most cases well below regulatory requirements) (European Commission, 2001b).

The European Commission is currently assessing whether the current Directive should be reviewed – and if so, the extent of this review. For example, Directive 86/278/EEC sets limit values for only six heavy metals, but some countries have already incorporated limits for other metals (e.g. Se, Mo, As). Table 14.1 shows the limit values of heavy metals for sludge intended to be used in agriculture. Also Table 14.2 shows the maximum heavy metal concentration in soils and the maximum amount of each heavy metal that can be added annually in agricultural land (Directive 86/278/EEC).

On the contrary, the Directive does not have limit values for organic and emerging micropollutants in sewage sludge, which could contaminate terrestrial and aquatic environment when the sludge is used in agriculture. Although there is no uniform approach to set limits for micropollutants several countries (such us: Austria, Denmark, France, Germany and Sweden) have established limits concentrations in sludge for:

(i) *Polycyclic aromatic hydrocarbons (PAH)*: 1–6 mg kg^{-1} DS
(ii) *Polychlorinated biphenyls (PCB)*: 0.1–1 mg kg^{-1} DS
(iii) *PCDD/F*: 30–100 mg kg^{-1} DS
(iv) *Absorbable organic halogens (AOX)*: 400–500 mg kg^{-1} DS
(v) *Linear alkylbenzene sulphonates (LAS)*: 1,300–5,000 mg kg^{-1} DS
(vi) *Nonylphenol and –ethoxylates (NPE)*: 10–450 mg kg^{-1} DS
(vii) *Di(2-ethylhexyl)phthalates (DEHP)*: 50–100 mg kg^{-1} DS

Although in the EU a common norm on the maximum allowed values of pathogenic microorganisms or indicators in fertilizing products does not exist, *Salmonella* and *Escherichia coli* has been proposed as marker microorganisms, in such a way that the sludge produced must not contain *Salmonella* in 50 g (fresh

Table 14.1 Limits of Cd, Cu, Hg, Ni, Pb and Zn for sludge in agriculture (mg/kg DS of sewage sludge).

State	Cd (mg kg^{-1} DS)	Cu (mg kg^{-1} DS)	Hg (mg kg^{-1} DS)	Ni (mg kg^{-1} DS)	Pb (mg kg^{-1} DS)	Zn (mg kg^{-1} DS)	Cr (mg kg^{-1} DS)
Directive 86/278/EEC	20–40	1,000–1,750	16–25	300–400	750–1,200	2,500–4,000	–
Austria	2–10	300–500	2–10	25–100	100–400	1,500–2,000	50–500
Belgium	6–10	375–600	5–10	50–100	300–500	900–2,000	250–500
Bulgaria	30	1,600	16	350	800	3,000	500
Cyprus	20–40	1,000–1,750	16–25	300–400	750–1,200	2,500–4,000	–
Czech republic	5	500	4	100	200	2,500	200
Denmark	0.8	1,000	0.8	30	120	4,000	100
Estonia	20	1,200	20	400	900	2,500	1,200
Finland	3	600	2	100	150	1,500	300
France	20	1,000	10	200	800	3,000	1,000
Germany	2*–10	600*–800	1.4*–8	60*–200	100*–900	1,500*–2,500	80*–900
Greece	40	1,750	25	400	1,200	4,000	500
Hungary	10	1,000	10	200	750	2,500	1,000
Ireland	20	1,000	16	300	750	2,500	–
Italy	20	1,000	10	300	750	2,500	–
Latvia	10	800	10	200	500	2,500	600
Lithuania	PTE regulated throuhg limits in soil						
Luxembourg	20–40	1,000–1,750	16–25	300–400	750–1,200	2,500–4,000	1,000–1,750
Malta	5	800	5	200	500	2,000	800
Netherlands	1.25	75	0.75	30	100	300	75

(Continued)

Table 14.1 Limits of Cd, Cu, Hg, Ni, Pb and Zn for sludge in agriculture (mg/kg DS of sewage sludge) (*Continued*).

State	Cd (mg kg^{-1} DS)	Cu (mg kg^{-1} DS)	Hg (mg kg^{-1} DS)	Ni (mg kg^{-1} DS)	Pb (mg kg^{-1} DS)	Zn (mg kg^{-1} DS)	Cr (mg kg^{-1} DS)
Poland	10	800	5	100	500	2,500	500
Portugal	20	1,000	16	300	750	2,500	1,000
Romania	10	500	5	100	300	2,000	500
Slovakia	10	1,000	10	300	750	2,500	1,000
Slovenia	2	300	2	70	100	1,20	150
Spain	40	1,750	25	400	1,200	4,000	1,500
Sweden	2	600	2.5	50	100	800	100
UK	PTE regulated through limits in soil						
Brazil	39	1,500	17	40	300	2,800	1,000
China	5–20	800–1,500	5–15	100–200	300–1,000	2,000–3,000	–
Japan	5	–	2	300	100	–	500
Jordania	40	1,500	17	300	300	2,800	900
Russia	15	750	7.5	200	250	1,750	500
USA	39–85	1,500–4,300	17–57	420	300–840	2,800–7,500	–
Range in Europe	0.5–40	75–1,750	0.2–25	30–400	40–1200	100–4,000	75–1,750

* Proposed new limits
PTE (Potential toxic elements)
Sources: Adapted from Mininni *et al.* 2015; Healy *et al.* 2016; LeBlanc *et al.* 2008.

matter), and the treatment must induce a concentration reduction of *Escherichia coli* of 6 log10 or the concentration be less than 5 × 102 CFU/g of final product. Some European countries have already set limits for pathogens such as *salmonella spp.*, *fecal streptococci*, *enterovirus*, *helminthes eggs*, *Escherichia coli* and enterobacteria. More detailed information about organic micropollutants and pathogens limits in sewage sludge can be found in Mininni *et al.* (2015).

Table 14.2 Limit values for concentrations of (i) heavy metals in soil and (ii) amounts of heavy metals which may be added annually to agricultural land, based on a 10 year average (Directive 86/278/EEC).

Parameters	Heavy Metals in Soil (mg kg^{-1} DS)	Heavy Metals Added Annually (kg ha^{-1} y^{-1})
Cd	1–3	0.15
Cu	50–140	12
Ni	30–75	3
Pb	50–300	15
Zn	150–300	30
Hg	1–1.5	0.1
Cr	–	–

In general, EU legislation on sewage sludge is based on the pre-cautionary scheme and the limits set for its agricultural use are in general stricter than the EPA's (Environmental Protection Agency, USA). Furthermore, sewage sludge falls under numerous restrictions and it cannot be included in ecological bio-products (as compost), in organic farming fertilizers, etc. Although the EU's policy towards a sustainable use of phosphorus is currently promoted, P recovered from sewage sludge is not yet identified as a possible raw product, due to its 'waste' origin. Sewage sludge cannot be regarded solely as 'waste'; it is a renewable resource for energy and material recovery. From this perspective, legislation on sewage sludge management tends to incorporate issues related to environmental protection, public health, climate change impacts and socio-economic benefits.

Future trends on sludge management are mainly dependent on future alignment of legislation. It does not seem that a new sludge directive is pending (Mininni *et al.* 2015). In fact, the European Union developed the draft of a 'Working document on sludge' (European Commission 2000) to promote the use of sewage sludge in agriculture while improving the safety and harmonize quality standards but the draft was finally withdrawn. Moreover, works in progress have not evidenced a health and environment impact due to sludge agricultural use although some attention is already paid by many member states on organic pollutants and pathogens. Finally, it is expected that stabilized sludge will be used in agriculture in large quantities in the next years in many important member states such as France, Germany, Italy, Spain and the UK (Mininni *et al.* 2015).

14.2 SLUDGE PRODUCTION PROCESSES

The main objective of wastewater treatment is to reduce the pollution load on receiving waters. However, the treatment processes concentrate most of the impurities and the microbial excess biomass in the sludge. Sludge, originating from the treatment process of wastewater, is the residue generated during the primary (physical and/or chemical), the secondary (biological) and the tertiary (additional to secondary, often nutrient removal) treatment (Fytili & Zabaniotou, 2008). The treatment and disposal of sludge should be considered as an integral part of the treatment process; therefore, wastewater treatment should be regarded as a low-solids stream (treated water effluent) and a high-solids stream (sludge).

Table 14.3 shows the main physic-chemical properties of primary and biological sludge and Table 14.4 shows the main physico-chemical properties of mixed sludge.

Table 14.3 Typical chemical composition and properties of primary and activated sludge.

Item/Sludge	Primary Sludge	Activated Sludge
Total dry solids (DS), %	2–8	0.83–1.16
Volatile solids (% of DS)	60–80	50–88
Grease and fats (% of DS)		
Ether soluble	6–30	–
Ether extract	12966	5–12
Protein (% of DS)	20–30	32–41
Nitrogen (N, % of DS)	1.5–4	2.4–5
Phosphorus (P_2O_5, % of DS)	0.8–2.8	2.8–11
Potash (K_2O, % of DS)	0–1	0.5–0.7
Cellulose (% of DS)	8–15	–
Iron (not as sulfide)	2–4	–
Silica (SiO_2, % of DS)	15–20	–
Alkalinity (mg/L as $CaCO_3$)	500–1500	580–1,100
Organic acids (mg/L as Hac)	200–2000	1,100–1,700
Energy content	10,000–12,500	8,000–10,000
pH	5–8	6.5–8.0

Source: Fytili and Zabaniotou, 2008

14.2.1 Sludge production

14.2.1.1 Primary sludge production

Primary sludge is drawn from the primary sedimentation tanks. It contains all the readily sedimentable matter from the wastewater; plus another 1% collected as scum; it has a high organic content (mainly fecal matter and food scraps) and is thus highly putrescible. In its fresh state, raw sludge is grey in color with a heavy fecal odor.

Primary sludge accounts for 50–60% of initial suspended solids in the wastewater inlet stream. Typical solids concentrations in raw primary sludge from settling municipal wastewater are 6%–8% and the portion of volatile solids varies from 60% to 80%. Primary precipitates can be dewatered readily after chemical conditioning because of their fibrous and coarse nature.

14.2.1.2 Biological sludge production

Activated sludge (AS) is the most common secondary biological treatment used to treat sewage and industrial wastewater and was developed around 1912–1914. There is a large variety of designs, however, in principle all AS consist of three main components: (i) an aeration tank, which serves as bioreactor, (ii) a settling tank

Table 14.4 Chemical composition and properties of (i) untreated sludge, (ii) Dewatered anaerobically digested sludge (iii) composted sludge, (iv) thermally dried sludge, (v) biochar and (vi) sludge ash.

Properties	Units	Mixed Sewage Sludge[a]	Anaerobically Digested Sludge[b]	Compost[c]	Dried Sludge[d]	Biochar[e]	Sludge Ash[f]
VS content (db%)	%	43–80	56–76	55–67	64–69	25	<1
Ash content	%	20–57	44–24	32–45	31–36	75	>99
pH		4.5–8.3	8.4	6.5–7.8	6.9–7.2	6.7–9.5	–
EC	mS cm^{-1}	1.1–11.9	2.3	1.2–8.5	1.5–6.2	0.6–1.9	–
CEC	cmol kg^{-1}	9.2	–	–	–	2.3–35	–
RI	mg O_2 g^{-1} VS h^{-1}	2.5–9.5	2–5	1.3–2.1	–	–	–
TOC	g kg^{-1}	360–412	340–412	181	296	179	–
C/N ratio		42562	42560	7.5–13	8.3	9	–
Total N	g kg^{-1}	15–62	39–59	22–39	36–61	22525	–
Total P	g kg^{-1}	15432	34	13–28	13–29	20–42	23–93
S	g kg^{-1}	8.9	8–15	–	–	0.4–1	6.6–8.9
Ca	g kg^{-1}	10–38	19–50	–	–	2–15	66–163 Mg
Mg	g kg^{-1}	4–26	0.3–19.2	–	–	3–15	16–35
Na	g kg^{-1}	0.7–1.5	–	2.5	–	1–2.7	3.6–32 K
K	g kg^{-1}	1.9–6.5	2.3	2.8–5.0	2.2–4.3	1.2–16	42669
Al	g kg^{-1}	8	–	–	–	–	37–67
Cu	mg kg^{-1}	151–800	993	139–743	645–823	400–2100	553–4775
Co	mg kg^{-1}	30	–	15	–	21	42–553
Cr	mg kg^{-1}	54–500	54	30–345	30–217	230	114–1402
Ni	mg kg^{-1}	17–80	64	19–105	42–85	35–740	63–369
Cd	mg kg^{-1}	0.6–3.6	3.2	<0.5–4.4	<0.5–3.6	1.8–9.8	1.7–15.6
Zn	mg kg^{-1}	588–1700	998	600–1385	800–1346	900–3300	384–4303
Pb	mg kg^{-1}	28–3940	78	67–1196	75–3747	130–750	122–999
Mn	mg kg^{-1}	188–395	–	173–241	–	253–667	470–2510
Hg	mg kg^{-1}	0.4–8	–	2.4–2.8	2.7	–	1.1
NPE	mg kg^{-1}	489–2556	513–981	24–363	14–3150	–	–
PCBs	mg kg^{-1}	0.01–0.35	0.023	0.01–0.06	0.01–0.06	–	–
PHAs	mg kg^{-1}	0.1–5.3	1.1	<0.01–16	0.2–7.4	1–100	–
DEHP	mg kg^{-1}	2–164	143	2–120	589138	–	–
LAS	mg kg^{-1}	816–3240	3240	214–2879	331–5572	–	–
PCDD/Fs	ng TEQ kg^{-1}	7–15	7.7	11–55	12–77	–	–

[a]Herzel *et al.* 2016; Hossain *et al.* 2015; Manara and Zabaniotou, 2012; Ponsá *et al.* 2010; Ponsá *et al.* 2009; Ramírez *et al.* 2008; Tarrasón *et al.* 2008.
[b]Ramírez *et al.* 2008; Ponsá *et al.* 2010; Epstein, 2002.
[c]Domene *et al.* 2009; Fernández *et al.* 2007; Ponsá *et al.* 2009; Ramírez *et al.* 2008; Tarrasón *et al.* 2008.
[d]Domene *et al.* 2009; Domene *et al.* 2010; Fernández *et al.* 2007; Ramírez *et al.* 2008; Tarrasón *et al.* 2008.
[e]Hossain *et al.* 2010; Hossain *et al.* 2015; Mayer *et al.* 2016; Cai *et al.* 2013.
[f]Herzel *et al.* 2016; Mattenberger *et al.* 2008; Zhang *et al.* 2002.

('final clarifier') for separation of AS solids and treated waste water and (iii) a return activated sludge (RAS) equipment to transfer settled AS from the clarifier to the influent of the aeration tank.

In a biological treatment processes, biomass growth occurs concurrent with the oxidation of organic or inorganic compounds. The ratio of the amount of biomass-produced respect to the amount of substrate consumed is defined as the biomass yield. In aerobic conditions the growth yield can reach 0.60–0.70, which means that 60–70% of organic biodegradable matter removed in the biological treatment is converted into new cellular biomass (Foladori *et al.* 2010). Due to both biological growth and accumulation of partially degraded solids present in the raw wastewater, excess sludge eventually accumulates beyond the desired mixed liquor suspended solids (MLSS) concentration in the aeration tank. This amount of secondary sludge (called Waste Activated Sludge) is removed from the treatment process to keep the ratio of biomass to food supplied in balance. Typical solids concentrations in secondary sludge from an activated sludge processes are 1–2% and the portion of volatile solids varies from 50% to 85%. Additionally, nutrients from wastewater should be treated before discharging, in this sense, there is a minor production of sludge produced after biological nutrient removal (BNR) processes.

14.2.2 Characteristics of sewage sludge

The characteristics of sludge play an important role when considering the ultimate disposal of the processed sludge, especially in their use for land application. Sludge characteristics can be broken down in three categories: (i) physical, (ii) chemical and (iii) biological.

The important physical characteristics are the solid content and the organic matter content. The total solids content affects the method of land application. Liquid or low-solids sewage sludge will generally be injected into soil to prevent vectors and provide better aesthetics. On the contrary dewatered or semisolid biosolids are usually spread on the surface and subsequently plowed into the soil (Epstein, 2002). The organic matter is an important constituent of biosolids and its use for land application enhances the organic content of soils. In sandy soils the organic matter increases the water-holding capacity, soil aggregation and other soil physical properties. It reduces the soil bulk density and increases the cation exchange capacity (a very important property for supplying plant nutrients). The positive effect of organic matter on the soil physical properties enhances the plant root environment. Therefore, plants are better able to withstand drought conditions, extract water, and utilize nutrients (Epstein, 2002).

Chemical properties affect plant growth as well as the soil's chemical and physical properties. The important chemical characteristics are: (i) pH, (ii) soluble salts, (iii) plant nutrients (macro and micro), (iv) essential and non-essential trace elements to humans and animals and (v) organic chemicals. A detailed list of heavy metals, trace elements, priority pollutants and organic chemicals can be found in Epstein (2002). The pH of most biosolids (whether liquid, semisolid, or solid) is generally in the range of 7–8, unless lime is added during the wastewater treatment process. Plant nutrients are among the most important chemical characteristics of biosolids, the major plant nutrients are nitrogen (N), phosphorus (P) and potassium (K). Other macronutrients are calcium (Ca), magnesium (Mg), and sulfur (S). The micronutrients essential to plant growth are boron (B), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni) and zinc (Zn). It has been recognized for centuries that sewage sludge contain plant nutrients. Table 14.3 and Table 14.4 show nutrient typical values found in raw and treated sludge.

Regarding biological properties, pathogens are the most important biological property of biosolids for land application. Since pathogens survive the wastewater treatment processes (primary and secondary treatment), land application of sewage sludge directly from these processes needs to be avoided or restricted to land management systems. Further treatment, such as digestion, composting, alkaline stabilization, or heat drying, increases the opportunities for land application (Epstein, 2002). The presence of pathogenic microorganisms such as viruses, bacteria and fungi involve a potential risk that may affect soil organisms or plants and produce changes in the microbial community structure and soil properties. A more detailed description of health risks involved in application of sludge in agriculture due to pathogens is found in Section 2.2.6.2 of this chapter. On the other hand, application of sewage sludge in agriculture enhance microbial population, which increases the rate of organic matter decomposition in soils. As a result, there is a significant change in the soil physical properties. This produces a marked improvement in the plant-root environment and better plant growth (Epstien, 2002).

14.3 SLUDGE PRE-TREATMENT PROCESSES

14.3.1 Sludge pre-treatment technologies

Pretreatment, which is aiming to reduce the eventual amount of sludge production, is typically done by the application of external forces and agents in order to destruct sludge solids (Müller et al. 2004). Pretreatment is mostly used for biological sludge, even though it has application for mixed sludge as well. Applied forces lead to rupture of the cell membrane of bacteria in biological sludge resulting in release of organic substances outside the cell (Wang *et al.* 1999). Hence, sludge disintegration achieves solubilization and conversion of slowly biodegradable, particulate organic materials to low molecular weight, readily biodegradable compounds ending up producing much less sludge after stabilization such as digestion.

There are different kinds of pretreatment methods, which are conducted by the application of mechanical (ultrasound, homogenizer, mill, and others), physical (thermal treatment, microwave), chemical (use of ozone, acids, alkali and other chemicals) and biological (with or without enzyme addition) means (Müller, 2001). These methods can be applied individually or one method can be combined with another, (such as thermo-chemical) to disintegrate sludge more effectively. It is known that sludge pretreatment if applied before anaerobic digestion, increases the stabilization and biogas production, decreases the sludge to be disposed, solves bulking and foaming, improves dewatering and disinfects sludge. Below is brief discussion of mechanisms of different pretreatment methods.

Satisfactory results obtained in lab scale tests encouraged many companies to commercialize thermal pretreatment methods. So some of these methods has become a part of the sludge treatment systems in a number of WWTPs. Examples to these are the patented thermal pretreatment systems such as Cambi, Biothelys and Zimpro Processes. There are many full-scale applications of thermal pretreatments processes in Ireland, Denmark, Norway, USA and Sweden. Full-scale application of ultrasonication is not as widespread as thermal treatments and one example at full scale is found in Ulu Pandan Water Reclamation Plant in Singapore. Ozonation pretreatment are not widespread at full scale but some full application can be found in industrial WWTP. An example of Ozone application in municipalities located in the southern part of the Marche region in Italy.

These Pre-treatment technologies have been extensively described in Chapter 12, therefore in the present Chapter only the physic-chemical and biological changes and its implication for soil agricultural application are considered.

14.3.2 Effects of pretreatment on the agricultural use and value of sludge

The nutritional and beneficial value of sludge for land application is highly affected by the process that sludge goes through; more specifically, whether the sludge is pretreated or not; has it gone through a digestion process, or what is the sequence of treatment units for sludge. As mentioned above, sludge pretreatment processes break up the flocs either by physical or chemical means or by different combinations of these. During these processes floc components are solubilized from the solid phase and introduced into the liquid medium. As expected, this affects the quality of solid sludge (the typical form of sludge that is used in land application).

14.3.2.1 Organic Matter Reduction

As previously mentioned, the function of organic matter in land-applied sludge is to enrich the soil and enhance the soil properties such as aggregation and water holding capacity. On the other hand, the main purpose of pretreatment is to advance digestability of sludge and enhance biogas production. Therefore, pretreatment is most commonly applied prior to anaerobic digestion. For systems applying pretreatment and further anaerobic digestion, most solubilized organics are converted to biogas (Braguglia *et al.* 2015). Thus, digested sludge for land application contains much less organic matter. If no digestion exists, the solubilized organics are lost with the liquid fraction obtained in dewatering operations, which also end up producing lower organic content sludge. Despite the fact that pretreatment reduces organic matter in solid sludge, there is still sufficient organics remaining following pretreatment due to the fact that only partial removal of organics is achievable during these processes.

14.3.2.2 Nutrients Solubilization

Most nutrients such as nitrogen and phosphorus have the potential to be solubilized along with other floc components during the pretreatment process. Once they are soluble, they are either uptaken during the digestion process, or released with the liquid fraction discharged from the digesters or obtained in dewatering processes. Zhang *et al.* (2015) showed that about 39% more ammonia nitrogen and about 82% more nitrate nitrogen are lost with centrate when thermal pretreatment and anaerobic digestion are employed together in a full scale WWTP. Srinivasan *et al.* (2015) compared ozone, peroxide, radiofrequency heating and combinations of these methods for their effect on sludge properties. Their results showed that very significant amounts of nutrients are solubilized from sludge solids into the liquid phase. According to their data, solubilized Total Kjeldahl Nitrogen (TKN), NH_4^+, orthophosphate, calcium, magnesium and potassium reach up to 97%, 95%, 96%, 94%, 100%, and 85%, respectively (Srinivasan *et al.* 2015). Dogan and Sanin (2009) report that about 30% more ammonia nitrogen is present in digester effluent when alkali-microwave pretreatment and anaerobic digestion is applied together in a lab scale digester. The study observed no release of orthophosphate phosphorus during these treatments. These findings indicate some nutrients are clear to be lost from sludge during pretreatment due to solubilization effect. Therefore pretreated sludge is expected to have typically lower nutrient contents when compared to untreated sludge.

14.3.2.3 Pathogen and Indicator Reductions

One remarkable effect of pretreatment methods is their achievement of better microbial quality of sludge (pathogen or indicator content reduction). For example after thermal hydrolysis sludge of higher microbiological quality and cleaner sludge is obtained. Levantesi *et al.* (2015) found that thermal hydrolysis (135°C, 20 min) caused over a 3.2 logs removal of *E. coli*, almost 4 logs removal of smatic coliphages, more than 2.5 logs removal in spores and higher than 0.9 logs removal in *Salmonella*. Among a number of pretreatment methods tested, thermal hydrolysis at 130°C provided the highest removal of microorganisms tested, reducing their concentration to non-detectable levels in almost all analyzed samples (Levantesi *et al.* 2015). In the study of Foladori *et al.* (2007), the mechanism of ultrasound on microbial decay was explained by an initial disaggregation of cells clumped in aggregates of different sizes with no observation of death. With increasing ultrasound energy, both permeabilisation and cell disruption start. They found that activated sludge, *E. coli* and *E. feacalis* showed differences in their inactivation by sonication. *E. coli* underwent cell disintegration at lower levels of ultrasonic energy. On the other hand, a complete disaggregation of activated sludge flocs required ultrasonic energy around 80 kJ L^{-1}, while for the damage and death of the released free cells, higher levels of energy need to be applied. Ozonation is also a means of effective disinfection. In the study of Park *et al.* (2008) the fecal coliform concentration was below the limits of detection when the ozone dose was above 0.3 g/g DS. At this dose, the impact of ozone on the inactivation of *Streptococcus* and *Salmonella* was also significant. At an ozone dose of 0.4 g/g DS complete reduction of these organisms was observed. In the study, an ozone dose of 0.3 g/gDS was suggested to fulfill the criteria for the disinfection for class A biosolids in USA.

14.3.2.4 Trace Organic Contaminants Removal

Concerns have been raised due to the presence of numerous trace organic contaminants such as pharmaceuticals, antibiotics, hormones, pesticides, etc. in sludge. From this perspective, pretreatment may bring some relief, since a number of methods used are able to oxidize refractory compounds. Removal of these persistent organics depends on the method applied and the chemical's structure; so the results and success vary from one system to another. Since some of these pretreatment methods have oxidative properties, the toxic organics have the potential to be degraded during these treatments, although if the oxidation is not complete, there is a risk of forming by-products which are even more toxic than the initial molecule. Methods such as ultrasonication, ozone application and thermal treatment are considered among the advanced methods that are able break some bonds of hard to degrade trace organic contaminants. In one study, the ultrasound treatment of sludge was tested on the removal of pesticides. The treatment resulted in a significant reduction in the sludge pesticide content (90% of the total pesticide mass was removed). Investigation into the sono-degradation of three characteristic pesticides (thiabendazole, acetamiprid and imazalil) revealed the formation of transformation products already reported in studies on the degradation of these compounds by advanced oxidation processes, thus confirming that ultrasonication involves hydroxyl radical reactions (Rivas Ibañez *et al.* 2015). The fate of pharmaceutical residues in WWTP sludge was evaluated during mesophilic anaerobic digestion and six treatment technologies (pasteurization, thermal hydrolysis, advanced oxidation processes using Fenton's reaction, ammonia treatment, thermophilic dry digestion, and thermophilic anaerobic digestion) were compared. Advanced oxidation processes using Fenton's reaction affected several compounds, including substances showing general stability over the range of treatments such as carbamazepine, propranolol, and sertraline. Pasteurization, ammonia treatment, and thermophilic dry digestion exhibited relatively modest reductions. Interestingly, only thermal hydrolysis efficiently removed the ecotoxicologically potent estrogenic compounds from the sludge (Malmborg & Magner, 2015). Ak *et al.* (2013) demonstrated that anaerobic digestion of waste activated sludge when coupled with mild ozone treatment (e.g. 1.33 mg O_3/g-VSS), affects enhanced removal of endocrine disrupting compounds (acetaminophen, estrone, benzyl butyl phthalate, progesterone, diltiazem and carbamazepine) sorbed onto the sludge. Anaerobic reactors receiving return activated sludge feed ozonated at different ozone doses indicated substantial pollutant removals as compared to the control. Fate of nonylphenol compounds, (NPEs) were studied in thermally hydrolyzed and anaerobically digested (15 day SRT) sludges. In this study even though the transformation between the target compounds occurred, the total concentrations of NPE did not change between influent and effluent for thermally pretreated and anaerobically digested sludges (Manara & Zabaniotou, 2012).

14.3.2.5 Heavy Metals

Heavy metals, which constitute a historical concern for sludge land application, are conservative and accumulative pollutants. Their fate in pretreated and digested sludge has been an interest. Most of the studies in literature shows much less can be done on heavy metals concerning their removal during pretreatment processes. One mechanism of removal is by solubilization from sludge solids to liquid and therefore they may be removed by physic-chemical technologies. In an example study, sonication time and power density greatly affected the heavy metals solubilization degree. Soluble heavy metals increased almost linearly with sonication time within the first 15 min and then stabilized. A minimum power density of 0.8 W/mL was required for heavy metal solubilization. The study showed that the effect of sonication time on heavy metal release was higher than that of power density. Besides, each heavy metal behaved differently during the ultrasonic treatment. Arsenic and nickel release were easier and the solubilization degree reached 58.4% and 34.9% after 30 min of sonication, respectively. On the other hand, solubilization degree of copper was low. Cadmium was stable and could not be released by sonication. Other studies indicated no solubilization of metals from sludge. Braguglia *et al.* (2015) reported that due to typical weight loss during anaerobic digestion, and conversion of biodegradable matter to biogas, the heavy metal concentrations in the digested samples are expected to be higher with respect to the feed. They observed no removal during the investigated processes (thermal treatment and sonication), and because of the mass loss during the treatments, the effective heavy metal concentration increased at the end. In the study of Yan *et al.* (2015), the effect of hydrothermal treatment at various temperatures (120–200^{o}C) on the properties of sewage sludge derived solid fuel was investigated. Similar heavy metal enrichment in solid particles was found after hydrothermal treatment. These results indicate that the possibility of conservative pollutants such as heavy metals to enrich in sludge can pose risks for land application.

14.4 SLUDGE TREATMENT PROCESSES

The solids resulting from wastewater treatment must undergo further treatment prior to land application. Land application of biosolids requires the disinfection and stabilization of biosolids. The objective is to reduce the level of pathogens, reduce vector attraction and produce a stabilized product - that is, a product that would not decompose very rapidly and produce offensive odors (Epstein, 2002). Studies carried out during the last years, showed that raw sewage sludge in the conditions of its land application can be a significant source of undesirable substances in the soil and plants. The main contaminants of sewage sludge are heavy metals, organic pollutants, pharmaceutical residues and pathogens (Dichtl *et al.* 2007).

Changes in legal requirements for sewage sludge application are planned that will set lower limit values for hazardous substances and higher quality requirements in general. Although direct application of raw sewage sludge to agricultural land is the current most commonly applied management technique in Europe, several technologies focused on minimizing the negative impacts of direct soil application of sewage sludge are used at industrial level or being under development.

An overview of most used processes applied to sewage sludge including biological, drying, thermal and chemical processes and the implications of the application to agricultural soils of its final products (e.g. compost, dried sludge, biochar, ashes) are explained in the following sections:

- *Biological processes*: (i) anaerobic digestion, (ii) composting, (iii) vermicomposting and (iv) bioleaching
- *Drying processes*: (i) thermal drying, (ii) biodrying and (iii) solar drying
- *Thermal processes*: (i) incineration, (ii) pyrolysis (iii) gasification
- *Chemical processe*: (i) lime addition

14.4.1 Biological processes

14.4.1.1 Anaerobic digestion

Anaerobic digestion used to treat primary and secondary sludge resulting from the aerobic treatment of municipal wastewater is a standard technology around the world. The technology is used in thousands of installations as part of modern treatment systems of municipal wastewaters. Anaerobic digestion is defined as a biological process in which the biodegradable matter is degraded or decomposed in the absence of oxygen using specific microorganisms that produce biogas composed mainly of methane and carbon dioxide. Overall, the process converts about 40% to 60% of the organic solids to methane (CH_4) and carbon dioxide (CO_2), as thereby it also reduces the amount of final sludge solids for disposal whilst limiting odor problems associated with residual putrescible matter. The chemical composition of the gas is 60–65% methane, 30–35% carbon dioxide, plus small quantities of H_2, N_2, H_2S and H_2O. Of these, methane is the most valuable because it is a hydrocarbon fuel (giving 36.5 MJ/m^3 in combustion).

In general, mesophilic anaerobic digestion of sewage sludge is more widely used compared to thermophilic digestion. In mesophilic anaerobic treatment, Gantzer *et al.* (2001) reported that pathogens (*Salmonella* and viable pathogen nematode eggs) were still present at concentrations above the sanitation requirements (under the provision of French Decree N. 97–1133). On the contrary, the enhanced hygienization effect of the thermophilic process complies with the EU policy for elimination of pathogens and it has been reported that thermophilic anaerobic digestion of sewage sludge can lead to EPAs class A biosolids, which are suitable for subsequent land application. More information about pathogenic disinfection during anaerobic digestion processes can be found in Epstein (2002).

Epstein (2002) reported data on the nutrient content in 250 sewage sludge samples from 150 wastewater treatment plants. Nitrogen, P, Ca, and S are present in relatively large amounts, whereas K and Mg are found in much smaller amounts. Anaerobically digested sludge showed median and average concentrations of total nitrogen of 4.2 and 5% respectively. Similar values were obtained for aerobic sludge. On the contrary the median concentration of N-NH_4 was four times higher in anaerobic digested sludge compared to aerobically treated sludge.

Although anaerobic treatment itself is very effective in removing biodegradable organic compounds, leaving mineralized compounds like NH_4^+, PO_4^{3-}, S^{2-} in the solution, several organic compounds such as pharmaceutical and personal care products (PPCPs) can persist after the process. Carballa *et al.* (2007) showed removal efficiencies of PPCPs higher than 60% for antibiotics, natural estrogens, musks and naproxen. For the other compounds (e.g. ibuprofen, diazepam, etc.), the values ranged between 20% and 60%, except for Carbamazepine, which showed no elimination.

To be applied in soils, sufficiently stabilized sewage sludge should be used in order to avoid negative effects on plant growth. Ramirez *et al.* (2008) showed a reduction of toxicity of anaerobically digested sludge compared to raw sludge (from two to five times less toxicity) in *B. Rappa, L. perenne* and *T. pratense*. On the contrary digested sludge showed higher ecotoxicity compared to composted sludge (much more stabilized). Anaerobic sludge usually undergoes an aerobic post-treatment (e.g. composting) to improve stability and to decrease its final moisture, facilitating its storage and transport.

14.4.1.2 Composting

Composting is defined as the biological decomposition and stabilization of organic substrates, under conditions that allow development of thermophilic temperatures as a result of biologically produced heat, to produce a final product that is stable, free of pathogens and plant seeds and that can be beneficially applied to land (Haug, 1993). It is the main biological process applied to sewage sludge in Europe and is a generally accepted and highly beneficial method of stabilizing its organic matter (Oleszczuk, 2008). In fact, according to the last Eurostat available data, composting was used to treat 14% of sludge produced in Europe in 2013.

Composting reduces the volume of sludge and its transporting costs, eliminates the risk of disseminating pathogens and removes mal-odorous compounds. Moreover, the addition of compost to agricultural soils has the following positive effects: (i) lead to a slow release of nutrients (95% of N is in organic form),

(ii) has a high binding capacity for organic and inorganic elements (contaminants or nutrients), (iii) improves water storage and soil water content due to its increased water-holding capacity and (iv) aids in the creation of soil agglomerates that can facilitate aeration of plant roots and improve water infiltration into the soil (Sánchez *et al.* 2015). It also prevents soil erosion and runoff. Gantzer *et al.* (2001) among many other studies (Haug, 1993) showed that composting processes achieving thermophilic temperatures (>45°C) were able to fulfil the sanitation requirements of pathogen micro-organism (*Salmonella* and viable pathogen nematode eggs among others).

When composted materials are used as organic amendments in soils, it is of great importance that the material is sufficiently stabilized in order to avoid negative growth effects due to N mineralization, oxygen depletion or the presence of phytotoxic compounds. Ramírez *et al.* (2008) showed that composting is an effective way to reduce phytotoxicity of sewage sludge before being applied to agricultural soils: a strong positive correlation was found between higher values of half maximal effective concentration (EC50) (less toxicity) and the stability degree of their organic matter. Also negative correlations between EC50 and total nitrogen, hydrolysable nitrogen or ammonium content were found. On the contrary, no ecotoxicity correlations were found with heavy metals or organic pollutant content comparing raw and composted sewage sludge. In similar studies, Domene *et al.* (2011) showed that mortality and reproduction of soil microinvertebrates were clearly explained by the stability of wastes (the higher the stability the higher the LC50 and EC50), which was probably related to releases of secondary metabolites, mainly ammonium, during the decomposition in soil of unstable raw sewage sludge.

14.4.1.3 Vermicomposting

Another method used in some countries such as India is vermicomposting. Vermicomposting has been widely used as a method of sludge stabilization because of simple technology. Vermicomposting is a complex mechanical and biochemical transformation of sludge achieved through the action of earthworms. Earthworms have potential both to increase the rate of aerobic decomposition and composting of organic matter and also to stabilize the organic residues and removing the harmful pathogens and heavy metals in the sludge (Sinha *et al.* 2010). Earthworm metallothioneins (MTs) proteins have a very high capacity to bind metals. Numerous studies have documented earthworm's bioaccumulation capability of Cd, Pb, Cu, Ca, Mg, Fe, Zn. Ireland (1983) determined up to 100 mg kg^{-1} Cd and 7600 mg g^{-1} dry weight Pb in tissue of earthworm after vermicomposting of biosolid. Basja *et al.* (2003) suggested that earthworm may not be able to remove toxic substances completely, but at least it changes the 'chemical make-up' of the sludge to rendering it harmless to the soil. They found that vermicomposting complies with 'grade A' standards for biosolid stabilization. Tiger Worm (*E. foetida*), Red Tiger Worm (*Eisenia andrei*), the Indian Blue Worm (*Perionyx excavatus*), the African Night Crawler (*Eudrilus euginae*), and the Red Worm (*Lumbricus rubellus*) are most appropriate for vermicomposting of biosolid under all climatic conditions (Sinha *et al.* 2010).

14.4.1.4 Bioleaching

Bioleaching (bio-acidification process) is the most common metal leaching method and is based on the oxidation of sulfur or iron by chemiolithotrophic bacteria. The most widely used microorganisms in metal leaching are *Acidithiobacillus thiooxidans* (formerly known as *Thiobacillus ferrooxidans*) and *Acidithiobacillus ferrooxidans* (Cho *et al.* 1999). Bioleaching of biosolid before land application can be used to remove a significant fraction of the heavy metals content of the agricultural product (Shanableh & Ginige, 1999). Ghavidel *et al.* (2010) reported that bioleaching is an efficient and powerful tool for removal of heavy metals from biosolid. Researchers were able to remove 24.73% of Fe, 83.96% of Cu, 81.46% of Ni and 38.96% of Pb from biosolid using the bioleaching method. Wen *et al.* (2009) reported that the removal efficiencies of Cr, Cu, Pb, and Zn from biosolid were 43.6%, 96.2%, 41.6%, and 96.5%, respectively. However, Shanableh and Ginige (1999) found that the bioleaching process also reduces the nutrients content of the biosolid.

14.4.2 Drying processes

Drying is a relatively simple technological operation in which thermal energy is provided to sludge to evaporate water. Although usually the ultimate goal of dried sludge is its energy valorization (e.g. via incineration or pyrolysis), it is frequently used directly as soil amendment; therefore, drying processes can be used as standalone sludge post-treatments or be applied prior to further thermal treatment. The most common sludge drying technology is thermal drying. The application of this conventional drying technology can be technically and economically challenging because of the use of high amounts of external energy (e.g. natural gas). Recently bio-drying, extensively described in Chapter 15, has been presented as an economical and energy-saving emerging technology to reduce the sludge content and to evaporate bound water by biologically produced heat (Dufour, 2006). Also, solar drying could be an economic alternative to conventional drying systems, especially in areas with proper climatic conditions (Dichtl *et al.* 2007).

The process of drying sludge reduces volume of the product, making its storage, transportation, packaging and retail easier. Sludge drying also inactivates pathogens and volatile chemicals and leads to a sanitized final product in pellets in relatively short time, with low odours and good handling characteristics (Fernández *et al.* 2007). Gantzer *et al.* (2001) showed that a drying process carried out during 10 h at 108°C was able to fulfil the sanitation requirements of two categories of pathogen micro-organism (*Salmonella* and viable pathogen nematode eggs).

Tarrasón *et al.* (2008) showed that thermal-drying of sewage sludge modifies its behaviour as a source of nitrogen when applied to soil. As consequence, mineral nitrogen concentrations ($N\text{-}NH_4$ and $N\text{-}NO_3$) of soil treated with thermally dried sludge can be high at short time after amendment far before growth of vegetation, increasing the risk of nitrate leaching. Also, soil amended with thermally dried sludge shows a greater degree of carbon mineralization because the organic matter is not stabilized yet (on the contrary than in a composting process) and, as highlighted before, it is of great importance that the organic ammendment applied to soil is sufficiently stabilized in order to avoid negative growth effects. Several authors showed higher ecotoxicity, both in plants and microinvertebrates, of thermally dried sludge compared to composted sludge. For example, in germination tests of *Brassica rapa*, EC50 for composted sludge were 10 times higher (less toxicity) than for thermally dried sludge. Moreover there was no statistical difference between thermally dried sludge and fresh sludge in terms of its ecotoxicty.

14.4.3 Thermal processes

The direct use of sewage sludge in agriculture is controversial because it acts as a sink for pollutants in wastewater treatment plants and it is often contaminated with heavy metals and organic contaminants. Lately, various modern thermal technologies have been introduced, offering an alternative trend to the sewage sludge disposal, especially with the decreasing availability and the increasing price of land for landfilling. The principal goal of thermal processing of sewage sludge is the utilization of the stored energy in sludge and the minimization of environmental impacts at the same time, in order to meet the increasingly stringent standards (Fytili & Zabaniotou, 2008). Processing of raw sewage sludge before thermal treatment, usually by means of a drying process, is often necessary from a technological and economical point of view. Thermal processes generate by-products that can be potentially used in agriculture, if they accomplish with the regulations, such as sludge ashes produced in incineration processes and biochar produced in pyrolysis processes.

14.4.3.1 Incineration

Incineration is the most popular thermal treatment used for the processing and management of sewage sludge. In fact, according to the last Eurostat available data, 23% of sludge treated in Europe in 2013 was treated by incineration. During incineration, organic matter is combusted to CO_2 and other trace gases, with water removed as vapour. The process cannot be considered as a complete disposal option because significant quantities of inorganic incinerated sewage sludge ash remain.

Application of waste ash to agricultural land presents an opportunity for the recovery of essential plant nutrients (Zhang *et al.* 2002). However, the amount of ashes that may be applied to agricultural land is restricted by their heavy metal contents, because concentration of Ni, Cu, Zn, Cd, Sn, Pb are much higher in sludge ashes than they are in soils. From the aspect of liming effect and plant nutrients, the waste ashes can be used as liming agents on acid soil and may also bring agronomic benefits (Zhang *et al.* 2002).

Sludge ash is rich in phosphorus content, ranging between 4% and 9%, and contains amounts of phosphorus comparable to commercial superphosphate. Sludge ash could replace phosphate rock-based products and reduce EU dependence on phosphorus imports (Herzel *et al.* 2016), but its direct utilization is usually not possible because of its content of heavy metals. Therefore, the focus is on alternative sludge ash treatment technologies that gain the most economic and ecological benefit from the sludge's valuables. Different technologies such as (i) BioCon-Process, (ii) SEPHOS-Process, (iii) ASH DEC Umwelt AG or (iv) RuePa-Process have been recently developed for phosphorus recovery from sludge ash (Dichtl *et al.* 2007). Compared to co-incineration, only during mono-incineration phosphorus recovery from sludge ash is possible. The phosphorus concentration in ashes resulting from co-incineration processes is too low so that the recovery of nutrients is uneconomic (Dichtl *et al.* 2007).

14.4.3.2 Pyrolysis and Gasification

Pyrolysis is the process through which, organic substances are thermally decomposed in an oxygen-free atmosphere, at temperatures varying in the range of 300 and 900°C. Gasification is the thermal process during which carbonaceous content of sewage sludge is converted to combustible gas and ash in a net reducing atmosphere. A by-product of these thermochemical processes of sewage sludge is a solid product containing char (mostly carbon) and ash called biochar.

This biochar can be combusted for heat and power, gasified, activated for adsorption applications, or applied to soils as a soil amendment. Biochar has received much attention in the context of carbon sequestration, climate change mitigation, and soil improvement (Mayer *et al.* 2016). For instance, biochar contributes to carbon sequestration when land-applied because the carbon does not readily degrade; the mean residence time of carbon in biochars made at 550°C was estimated to be over 1000 years (Singh *et al.* 2012). Additionally, biochar may act as a soil conditioner, enhancing plant growth and crop yields by supplying and, more importantly, retaining nutrients (reducing nutrient runoff from land via adsorbtion) and by providing other services such as improving soil physical and biological properties. Specifically, the incorporation of the biochar can influence the structure, texture, porosity, particle size distribution and density of the soil, and in this way it potentially alters the air oxygen content, water storage capacity and microbial and nutritional status of the soil within the plant rooting zone (Amonette & Joseph, 2012). Biochar can also neutralize the pH conditions of acidic soils as it has a positive liming effect (Hossain *et al.* 2010). Agrafioti *et al.* (2013) indicated that there is no environmental risk using biosolid biochars as a soil amendment.

Recent studies showed that pyrolysis could also contribute to remove organic micropollutants of wastewater sludge. Pyrolysis carried out at 450°C removed polychlorinated biphenyls (PCBs) by 75% from industrial sewage sludge, and pyrolysis of contaminated sediment at 800°C removed greater than 99% of dioxins and PCBs (Ross *et al.* 2016).

Biochar from sewage sludge also has a high heavy metal content and the amount of char that can be intended for agricultural utilization is therefore also restricted. Liu *et al.* (2013) investigated the biosolid biochar's capability of remedying contaminated soils. They found that pyrolysis increased heavy metals (Cu, Pb, Zn, Cd, and Cr) contents of biosolid biochar, but heavy metal availability of them were lower than those of air-dried biosolid and the plant availability of heavy metals was reduced in polluted soil. Conversely, Van Wesenbeeck *et al.* (2014) found that heavy metals were retained in the biochar during carbonization, whereas Hg, As, Cd, and Se were released and thereby depleted in the biochar. Zhang *et al.* (2015) investigated the immobilization of As (III) of biosolid biochar. According to their results, biosolid pyrolyzed at a higher temperature showed a lower As (III) sorption capacity and sorption of As (III) was faster than that of Cr (VI) but slower than that of Pb (II). Biosolid biochar reduced plant productivity because of increased electrical conductivity associated with the biochar amendment.

As this biochar still contains organic matter, combustion of the biochar is suggested for the full exploitation of sewage sludge. Ash from biochar combustion and gasification is enriched in P, facilitating P recovery. Therefore, the combination of thermochemical processes, such as pyrolysis followed by char combustion or gasification, combined with phosphorus recovery leads to value added products, energy and nutrients, all contributing to a greater use of this waste (Atienza-Martínez *et al.* 2014).

14.4.4 Chemical processes

Sewage sludge tends to increase acidity of the soils as a result of proton release from organic matter decomposition and mineralization of N-NH_4. Increased soil acidity could cause greater solubility of metals and consequently their enhanced plant availability and leaching potential, particularly in soils with poor buffering capacity Increased attention is paid to the sludge stabilization process aiming to minimize the mobility of heavy metals by using various additives due to compliance to more stringent regulations (Samaras *et al.* 2008). Lime is considered as one of the most common amendment materials for sewage sludge stabilization, as it plays significant role in reducing the microbial content of sludge (pathogens), as well as the availability of heavy metals, enhancing the agricultural benefits and lowering the respective environmental risks (Wong & Selvam, 2006). However, the application of lime for the stabilization of sewage sludge depends upon a number of parameters, such as the availability of lime, the associated costs, the required period for stabilization, etc.; thus, alternative materials other than lime such as fly ash should be considered for sludge stabilization.

Samaras *et al.* (2008) showed that sewage sludge amended with stabilizing agents (lime and fly ash) initially provoked strong phytotoxic effects on three examined plant species. On the contrary, samples stabilized for an extended time (35 d) presented negligible seed germination inhibition. For liming treatment various studies have demonstrated the necessity of a stable pH between 12 and 12.6 for 20–60 days for the elimination of *Salmonella* and viable nematode eggs. On the contrary, when these sanitation conditions are not fulfilled, as in the study carried by Gantzer *et al.* (2001) (using quick lime 25% and a retention time of 1 day) the samples analysed contained viable nematode eggs and/or *Salmonella*. In the same study with lime concentrations up to 62%, the sludge was sanitized, six months storage at pH not less than 11.5 were necessary to produce sanitized sludge.

14.5 GENERAL EFFECTS OF BIOSOLIDS ON AGRICULTURE

14.5.1 Effect on agricultural productivity and soil fertility

The reuse of biosolids in agriculture provides the necessary nutrients and micronutrients necessary for plant and crop growth. They may be used as a soil conditioner, improving its physical and chemical properties and reducing the possibility of soil erosion. Their use also addresses EU policy on sustainability and reuse of resources. Numerous studies have documented their efficacy in increasing crop yields and their use in biofuel cropping systems, and in general, biosolids application to land have been found to have a statistically significant impact on crop yields (Latare *et al.* 2014) and soil phosphorus (Shu *et al.* 2016), while having negligible adverse ecological impacts (Adair *et al.* 2014). A selection of recent studies that report impacts of biosolids application on crop growth, soil fertility, water holding capacity, and soil pH (a lowered pH upon biosolids application is known to enhance the uptake of most metals; Carvalho *et al.* 2013) is shown in Table 14.5.

Table 14.5 Impacts of biosolids application on soil fertility and plant productivity.

Country	Area of Study Focus	Biosolids Application Rate	% Increase of Parameter Measured Versus no Treatment (Zero Biosolids Addition)					References
			Biomass Yield	Mehlich P	Organic Matter	Water Holding Capacity	pH	
USA	Switchgrass growth	0 kg N ha^{-1}	0					Liu *et al.* 2015
		153 kg N ha^{-1}	25					
		306 kg N ha^{-1}	37					
		459 kg N ha^{-1}	46					
Turkey	Wheat growth	0 kg N ha^{-1}	0					Sanin *et al.* 2013
		80 kg N ha^{-1}	30					
		160 kg N ha^{-1}	10					
Canada	Soil test phosphorus	0 t ha^{-1}		0				Shu *et al.* 2016
		28 t ha^{-1}		30				
S. Africa	Organic matter, water holding capacity, pH	0 t ha^{-1}			0	0	0	Cele and Maboeta, 2016
		25 t ha^{-1}			157	3	–12	
		100 t ha^{-1}			576	5	–8	

For example, Mantovi *et al.* (2005) in a study carried out during 12 years, showed that biosolids gave crop yields similar to the highest mineral fertiliser dressing. Applied at a normal rate (5 tons DS ha^{-1} y^{-1}), they can completely surrogate mineral fertilisers, giving crop yields similar to that by mineral dressing. However, with a higher sludge (liquid or dewatered) application rates up to 10 ton DS ha^{-1} y^{-1}, excessive N supply was harmful, leading to wheat lodging and poor quality of crops such as sugar beet or wheat. On the contrary sludge compost could be applied at these higher rates without causing negative effects on yield and quality of crops. These results highlights the suitability of compost as a treatment alternative for sewage sludge.

14.5.2 Health risks involved in application of sludge in agriculture

There are several issues associated with the reuse of municipal sewage sludge in agriculture. While many of these are issues of perception, there is considerable concern, which is scientifically based, over the presence of persistent and emerging contaminants in biosolids (Clarke & Cummins, 2014), the risk of contamination of soil and water (Fu *et al.* 2016), the presence of toxic metals and pharmaceuticals in the sludge, which may build up in the soil and enter the food chain following continuous applications to land (Latare *et al.* 2014; García-Santiago *et al.* 2016), and the risk of emission and transport of bioaerosols containing pathogens following land application of biosolids (Jahne *et al.* 2015). The potential impact of land application of biosolids may also be very long lasting: for example, micro-plastics, which have been found in high concentrations in sewage sludge and have been detected on soils 15 years post-application (Magnusson & Norén, 2014).

The risk of indirect exposure to humans can occur through several pathways (consumption of food-crops, animal up-take to meat or milk or drinking water). Risk assessment approaches have been adopted to assess the environmental fate of contaminants in biosolids, with Quantitative Structure Activity Relationships (QSAR) model approaches dominating (Clarke & Cummins, 2015). Studies that have made links between biological effects and individual compounds in field trials are extremely rare (Zhang *et al.* 2015). While most commentators have stated that the risk to human health following dietary intake of organic contaminants from crops grown on biosolids-amended lands is minimal (Verslycke *et al.* 2016), they acknowledge that a certain amount of uncertainty still exists (Oun *et al.* 2014).

As seen before there are considerable differences in national legislation regarding the reuse of biosolids in agriculture related to health risk policies and perception. In some countries, such as Belgium (Brussels and Flanders), Switzerland and Romania, the reuse of biosolids in agriculture is prohibited (Milieu *et al.* 2013), whereas in other countries, such as the Republic of Ireland, restrictions govern their reuse in agriculture (Bord Bia, 2013). Moreover, there are differences governing the application rates of biosolids to land. In Europe, the application of biosolids is based on the nutrient and metal content of the biosolids whereas in the majority of states of the USA, biosolids are applied to land based on the nitrogen requirement of the crop being grown and not on a soil-based test. This means that excessive metal accumulation may build up in soil and plants (Antoniadis *et al.* 2008), or may be lost to surface waters (Oun *et al.* 2014) or groundwater. In the EU, the rate of application of six metals (Cu, Ni, Pb, Zn, Cd and Hg) are currently regulated, but the possibility exists that other potentially harmful, unregulated metals, such as arsenic, selenium and antimony, for which no international standards exist for reuse in agriculture, may accumulate in the soil upon repeated application. In a study of the sludge from a range of wastewater treatment plants in Ireland, Healy *et al.* (2016) measured antimony concentrations from 17 to 20 mg kg^{-1}, which were appreciably higher than recorded in wastewater treatment plant sludge elsewhere (<0.01 to 0.06 mg kg^{-1}; LeBlanc *et al.* 2008) and in non-polluted soils (0.53 mg kg^{-1}; Fay *et al.* 2007).

Losses to surface and subsurface waters may occur in two ways: as short-term (incidental losses) whereby losses occur in a rainfall event immediately following land application of biosolids, or as long-term (chronic losses), which occurs when there is a build-up of contaminants in the soil. Surface and groundwater losses of nitrogen and phosphorus species following land application of biosolids have mainly been reported in the literature (Peyton *et al.* 2016). Research has also focused on the presence of human enteric pathogens (Peyton *et al.* 2016), persistent organic pollutants (POPs), endocrine disrupting compounds (EDCs) and pharmaceutical and personal care products (PPCPs) in biosolids (García-Santiago *et al.* 2016) and their potential for loss in rainfall events. Prior to land application, sludge is treated using techniques such as thermal drying, composting, anaerobic digestion and pasteurisation, but complete inactivation of pathogens is difficult to achieve and even though reductions in wastewater treatment may reduce the densities of pathogens in sludge by a number of orders of magnitude. Depending on factors such as pH, soil texture, temperature, moisture content and competition with other microorganisms, may actually regrow following land application (Erickson *et al.* 2014). As the survival time of pathogens, following land application, may be up to four months (Brennan *et al.* 2012), there is a very high possibility that they may be transported to surface and groundwater in incidental rainfall events after land application. For example, Peyton *et al.* (2016) measured total coliform concentrations of up to 1.0×10^6 MPN (Most Probable Number) per 100 ml in surface runoff 15 days after land applications of three common types of biosolids (thermally dried, lime stabilised and anaerobically digested sludge). Alternatively, it is possible that viable pathogens could be present on the crop surface following biosolid application, or may become internalised within the crop tissue where they are protected from conventional sanitization (Solomon *et al.* 2002). In this case, a person may become infected if they consume the contaminated products. To prevent this risk stric application policies are stablished in current European Legislation (Directive 86/278/EC). However, at the time of writing, there has been no documented case of outbreaks or illnesses that have occurred from exposure to pathogens arising from the landspreading of biosolids.

According to Erbardt and Prüeb (European Commission, 2001a), organic contaminants are not expected to pose major health problems to the human population when sludge is re-used for agricultural purposes. Furthermore, many organic compounds will be biodegraded in the soil, and because of their size, organic compounds are generally not taken up by plant roots and translocated to the above-ground edible crop (Epstein, 2002). The presence of organic environmental pollutants, like dioxins and PCBs in agricultural crops is more the result of atmospheric deposition than direct absorption from contaminated soil. On the other hand, there are environmental reasons for monitoring sludge for detergents like LAS and nonylphenols because they are high volume chemicals with an extensive household and industrial use. They are also more water soluble than the organics previously discussed and therefore more mobile and bioavailable in soils. The impact on human health is low because of a low transfer from soil to human consumers (European Commission, 2001a). The ecotoxicological impacts of some of these organic compounds have been studied: as an example, a low ecotoxicologial risk might be expected for plants and soil invertebrates considering the usual levels of NPE in soils receiving polluted sludge (Domene *et al.* 2010; Domene *et al.* 2009). The environmental impact, however, could be significant through leaks to surface waters. Many detergents are clearly toxic and harmful to aquatic organisms and detergents have been indicated as responsible for changes in aquatic populations (European Commission, 2001a). PAHs have become one of the primary pollutants in sludge: it isessential to reduce their contents before the sludge can be used in agriculture through proper treatment. Paraiba *et al.* (2011) investigated the presence of PAHs in biosolids and in soil with biosolids applied as agricultural fertilizer and simulated a long-term risk of soil contamination by PAH. Their results evidenced that PAH concentration levels found in biosolids might raise potential contamination risks to the soil. It is important to perform a close monitoring of PAHs contents and to conduct a more detailed study of the PAHs migration mechanisms in order to obtain data to make changes in existing legislation to ensure full safety of the procedure of agricultural biosolid use. According to Baran and Oleszczuk (2002), biosolid below 5% with a PAH content up to 6000 $\mu g\ kg^{-1}$, should not disturb to natural soil conditions.

The risk to soil fertility of organic contaminants in biosolid spread on farmland has been designated as 'possible' in Table 14.6 by Smith (2009).

Table 14.6 Assessment of risks to health and the environment from recycling sewage sludge to agricultural land.

Environmental Parameter	Risk Attributed
Human health	P[a]
Crop yields	L[b]
Animal health	L
Groundwater quality	L
Surface water quality	L
Air quality	L
Soil fertility	P[c,d]

(L, low risk[a]; P, possible risk[b])
[a]Risk is designated as 'possible' (P) where there is some reported evidence that current operational practice may result in a potential impact on the environment on the basis that one or more of the following conditions apply.
[b]Risk is designated as 'low' (L) where environmental effects are minimized by current operational practice.
[c]There is uncertainty about the environmental implications of particular sludge components.
[d]Effects may occur under certain extreme 'worst-case' conditions, given the current regulations and codes of practice.
Source: Smith, 2009.

14.6 CASE STUDIES ON AGRICULTURAL APPLICATION OF SLUDGE

Legislation governing the land application of sludge in agriculture is designed to minimize the risk of danger to the public, either through the contamination of soil, surface and groundwater, or through the risk to public health. On account of this, regulations governing the reuse of sewage sludge in agriculture are frequently conservative, overly reactive to issues of public perception and local custom, and are discriminatory between the reuse of human sludge and potentially more dangerous, but more socially acceptable, wastes (e.g. animal wastes such as dairy cattle slurry) in agriculture. Therefore, quantifying the environmental persistence and fate of organic and inorganic contaminants following land application of biosolids is necessary, as it provides a sound scientific basis for management practices governing their use in agriculture and, moreover, it allows the potential risks associated with its reuse to be evaluated against other wastes that are commonly applied to agricultural land. The potential benefits of reuse of treated municipal sludge on land are well known and detailed in Table 14.5, and while the potential risks associated with its reuse, which ultimately govern legislation and practice, are also well examined, the quantification of those risks relative to the reuse of other wastes on land are less frequently examined in the literature. Therefore, for the purposes of this review, issues of concern investigated in case studies will be (i) surface runoff of contaminants relative to equivalent applications of dairy slurry, arguably the common agricultural waste applied to land, and (ii) potential bioaccumulation in the food chain through uptake by crops.

Very few studies have compared surface runoff of contaminants arising from the land application of biosolids to equivalent applications of dairy cattle slurry, but of those studies that have, it has been found that, in general, biosolid applications to land to not pose any greater threat to surface runoff than dairy slurries (or their derivatives, e.g. compost). It is important to note that these studies did not investigate the surface runoff of new and emerging contaminants, which may be present in runoff waters. Peyton *et al.*

(2016) applied three types of biosolids (anaerobically digested, thermally dried and lime stabilized slugde sludge) and dairy cattle slurry to small grassland plots at the same rate (40 kg P ha^{-1}) and measured the surface runoff of nutrients, microbial matter and metals, over three successive rainfall events that occurred within 15 days of application. Soil types, on which the study was conducted, ranged from sandy silt to sandy loam, and did not impact the results. The study found that with the exception of total and faecal coliforms and some metals (Ni, Cu), the greatest losses were from the dairy cattle slurry-amended plots. The study concluded that when compared with slurry treatments, biosolids generally do not pose a greater risk (in terms of losses of the parameters measured) along the runoff pathway. Mamedov *et al.* (2016) also examined the relative impacts of land applications of anaerobic digested biosolids to dairy waste (applied as a compost) on surface runoff in a laboratory-based runoff box study. When they were applied at the same rate (50 t ha^{-1}) to three types of soil (loamy sand, loam, clay), surface runoff of suspended solids from the biosolids-amended runoff boxes was the same as or significantly lower than the composted manure amended-runoff boxes, depending on the soil type (no other organic or inorganic contaminants were measured in that study).

Metal bioavailability and uptake by plants is affected by contamination levels and several soil properties such as pH, organic matter and clay content, element speciation in the soil, absorption of the element onto the root, and translocation into the plant (McGrath & Fleming, 2006). Alkaline soil conditions reduce metal bio-availability, but metal cations are more active under acid conditions, with increases of Mn, Zn, Cu, Ni and Cd content in ryegrass being reported when soil pH is reduced (to around 4) following biosolids application (Smith, 1994). In addition to modifying soil pH, the rate at which biosolids is applied also potentially impacts metal uptake by plants (Antoniadis *et al.* 2008) to a point at which plant phytotoxicity may be likely. Antoniadis *et al.* (2008) measured appreciable differences in Cd, Ni, Pb and Zn concentrations in ryegrass between AD biosolids-amended and un-amended plots. Of the studies that have investigated bioaccumulation of various elements by crops, no field-based study could be found that compared uptake rates arising from the landspreading of biosolids with dairy cattle slurry or indeed any other type of animal waste. The heavy metal transfer factor (TF) is the ratio of heavy metal concentration in the plant to that in the soil and is the slope of the proportional line between plant and soil heavy metal. Sanin *et al.* (2013) found that TFs of Cd, Pb, and Ni for wheat plant have increased due to increasing doses of biosolid and wheat germs had higher Cd, Pb, and Ni concentrations than corn-stalk.

It is important to determine the cumulative and residual effects of repeated applications of biosolid on agricultural land Sigua *et al.* (2005) indicated that successive land application of biosolid for at least three years followed by no sewage sludge application for at least two years may well be a good practice economically because it will boost and/or maintain sustainable forage productivity and at the same time minimize probable accumulation of nutrients, especially trace metals. Land-receiving of biosolid should be periodically monitored to ensure that heavy metal levels in the soil and plants remain within acceptable limits and to assess acceptable biosolids doses and maximum application.

The use of the combinations of biosolid and chemical fertilizers may be more effective than alone application of biosolid (Sanin *et al.* 2013). Erdal *et al.* (2000) found that the combinations of biosolid and triple super phosphate fertilizer significantly increased P content of corn when compared with control. On the other hand, the more amount of biosolid among combinations increased, the less content of P was found for the plant. However, this less amount among combinations (until 80 mg kg^{-1} biosolid treatment) was not significant. According to Erdal *et al.* (2000) the biosolid can be used for supplying some part of phosphorus needs of plant. Li *et al.* (2005) concluded that combined application of sewage sludge and chemical fertilizer could help quickly establishing a self-maintaining vegetation system in the primary process of nutrient demand. Kahiluoto *et al.* (2015) compared biosolid with chemical fertiliser and they suggested that phosphorus was more plant-available from biosolid than from chemical fertiliser. Iron coagulants are sometimes added to sewage to prevent phosphorus from entering waterways and causing eutrophication. However, adding iron brings a risk: iron-bound phosphorus may not be as usable by plants as non-iron bound forms of phosphorus. However, increasing the amount of sludge used reduced the proportion of phosphorus taken up by plants, even though there was a greater amount of potentially available phosphorus. High levels of iron binding were found to prevent take-up of phosphorus.

14.6 CONCLUSIONS

The agricultural use has become the principal disposal method for sewage sludge in Europe, agricultural use accounts for 37% of the total sludge produced and it is expected that stabilized sludge will be used in agriculture in large quantities in the next years in many important EU member states. The sludge utilization in agriculture is subject to provisions stipulated in the EU Directive 86/278/EEC,

The reuse of treated municipal sewage sludge (biosolids) in agriculture provides the nutrients and micronutrients (such as N, P, K but also Fe, B, Cu and Ni among others) necessary for plant and crop growth. The use of sludge in agriculture also enhances the organic content of soils, increases the water-holding capacity, the soil aggregation, reduces the soil bulk density, increases the cation exchange capacity, enhances the plant root environment. Therefore, plants are better able to withstand drought conditions, extract water, and utilize nutrients. However, there are several issues associated with the reuse of municipal sewage sludge in agriculture, the presence of persistent and emerging contaminants in biosolids, the risk of contamination of soil and water, the presence of toxic metals and pharmaceuticals in the sludge and the risk of emission and transport of bioaerosols containing pathogens following land application of biosolid are among the main concerns.

Therefore, sludge treatment aiming to minimize the negative impacts of sludge direct soil application is a key step of sludge management schemes. Several biologic (e.g. anaerobic digestion, composting), thermal (e.g. drying, incineration, pyrolysis) or chemical (e.g. lime addition) treatments are widely applied to sludge aiming to: (i) reduce or even completely eliminate the presence of pathogens (specially thermal and chemical treatments but also biological treatments reaching thermophilic temperatures), (ii) stabilize the organic matter producing products that would not decompose very rapidly (iii) minimize the offensive odours generation (iv) reduce the moisture and therefore improving its storage capacity and reducing its volume and transportation costs and (v) partially eliminate several organic pollutants and emerging contaminants. However, much less can be done on heavy metals concerning their removal during treatment processes.

Numerous studies have shown that biosolids application to agricultural land have a statistically significant impact on crop yields and soil phosphorus, while having negligible adverse ecological impacts. To be applied in soils, sufficiently stabilized sewage sludge should be used in order to avoid negative growth on plants. In that sense, composted sludge have shown less toxicity in both plants and soil biota than raw, anaerobically digested and thermally dried sludge. Also composted sludge can be applied at higher rates than raw sludge without causing negative effects on yield and quality of crops.

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