Application of sludge and environmental safety

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Introduction

Sludge is a waste material of industrial and municipal sewage treatment processes [1]. In Poland, each year over 3 thousand municipal sewage treatment plants produce more than 550 thousands Mg of dry matter and the quantity is constantly growing. From 1st January 2016 in accordance with the Regulation of the Minister of Economy, sending sewage to landfills will be banned. According to the applicable legislation, municipal sludge can undergo recovery by application in: 1) landfarming, understood as cultivation of any agricultural products placed on the market, including crops for production of animal feed; 2) cultivation of plants for the production of compost; 3) cultivation of plants for production of plants not intended for consumption or production of animal feed; 4) for reclamation of land, including land for agricultural purposes; 5) for adaptation of land for specific purposes resulting from waste management plans, spatial development plant or zoning and land development decision under appropriate conditions set out in the Act on waste. A large amount of sludge in Poland is thermally converted in mono-incineration plants or cement plants, however, since recently one of the predominant methods of sludge utilization was their environmental use. Currently, 1/5 of the produced sludge is used directly in the agriculture, while more and more sludge is composted and used for production of so-called organic fertiliser.

With the growth of civilisation and development of new manufacturing technologies, domestic sewage contains more and more new chemical compounds and the properties of sewage sludge are determined by composition of the wastewater flowing into the treatment plant. Therefore, there is still one question we have to answer: whether application of sewage sludge onto soil surface is environmentally safe.

Physical and chemical properties of sewage sludge

Sewage sludge is composed mainly of organic matter – its fertilising properties have been known for a long time. Dehydrated (dry) sludge depending on applied stabilisation process contain on average 50–70% of organic matter and 30–50% mineral part (including 1–4% of inorganic carbon); 3.4–4.0% N; 0.5–2.5% P, as well as some other nutrients, including microelements.

As a result of sewage treatment many pollutants enter the sludge. Among them till recently most important were trace elements, mainly heavy metals (e.g. Pb, Zn, Cd, Cr, Hg, Ni, Fe), metalloids such as As, non-metals as Se, or light metals as Al. However, numerous studies show that total metal content in sludge is decreasing which is confirmed by long-term assessments carried out among others in Germany, Austria and Great Britain. For example, in Germany compared to 1977 a decrease of content of Cd and Cr by over 90%, and Ni by 70%, was observed. This is mainly a result of great decrease of metal concentration in wastewater flowing into the plant, which in turn is a result of introduction of new technologies as well as a pre-treatment of industrial sewage. Moreover, it shall be noted that the total heavy metal content is not a reliable measure of their availability for live organisms, and thus its real toxicity. In order to assess that, it is necessary to determine amount of metals bound by various components (fractions), for which sequential analysis is applied. This method allows identification of compound groups that binds the metal. Heavy metals in sewage sludge can be present in the form of chelates, sulphides, carbonates or can be adsorbed on the surface of minerals precipitating during the treatment – mainly iron compounds. Organic matter also exhibits high affinity towards metals.

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Another group of compounds of high environmental significance are organic pollutants, primarily including group of compounds known as persistent organic pollutants: polycyclic aromatic hydrocarbons PAHs; polychlorinated biphenyls PCBs, dioxins and furans, adsorbable organic halogens (AOX); surfactants and phthalates. Sewage sludge is mainly analysed in terms of content of PAHs. E.g. content of 16 PAHs in studied municipal sludge of former Poznań voivodeship varied in range of 275 – 401 μg/kg of dry matter, of which benzopyrene accounted for an average 6.5% of the content [2]. Another compound group – polychlorinated biphenyls (PCBs) is a mixture of congeners of various number of chlorine atoms and their arrangement in biphenyl molecule. As there can be 209 individual PCBs, the range of contents of analysed PCBs is very wide. Rosinska [3] states that total PCB content in dehydrated sludge varies in range of 20.24–79.95 pg/g of dry matter. Conversions of PCBs during sewage treatment processes can lead to generation of other equally toxic compounds (dioxins, furans). In the recent years, concentration of PCDD/Fs tend to decrease in developed countries, but not to quickly due to the presence of dioxin precursors as triclosan commonly used as antibacterial agent in cosmetics and textile materials.

„New" pollutants and their environmental impact

In the literature, the term Pharmaceuticals and Personal Care Products, PPCPs covers a wide range of compounds exhibiting biological activity. PPCPs include drugs used by humans and animals, additives used in medicine and pharmaceutics (e.g. neutral components and drug carriers), dietary and food supplements (so-called nutraceutics), as well as cosmetics (such as soaps, shampoos, Eau de toilette, repellents, antiseptics and UV blockers). PPCPs in natural waters, sewage, muds and sewage sludge are present in very low concentrations of order ng/dm^3 – μg/dm^3 [4]. However, even such quantities can be very toxic to the environment. Research by Olofsson et al. [5] place this group of pollutants at the second position among pollutants present in sludge produced in Sweden. The authors mention: siloxanes, triclosan (with antibacterial properties); antioxidant – butylated hydroxytoluene (BHT), antibiotics – fluoroquinolones (FQ) and tetracyclines (TCs); detergents (4-nonylphenol) and pesticides (including biocides); as products the occurrence of which in the sewer system is inevitable. At the same time, they estimate that taking into accounts quantity of products containing these substances and placed on the market 63% of FQs, 51% of Tcs, 41% of 4-nonylphenol, 29% of triclosan and 17% of siloxanes enters the sewage sludge. US Food and Drug Agency confirmed presence of 72 components of PPCP in 110 sewage samples from sewage treatment plant in range of 0.002 to 48 mg/kg of dry matter, with the majority of them entering the sludge after the treatment process. However, the list of PPCPs is much longer (Tab. 1). As PPCPs are a group of compounds of various chemical and physical properties, their toxicity, and what follow, their impact on various parts of the environment can also vary greatly. In order to assess PPCP behaviour in the environment, it is necessary to consider their solubility and octanol-water partition coefficient logK_{ow}.

Table 1

Types of PPCPs [4]

Group/class of compounds	Compound
pharmaceuticals	
antibiotics	trimethoprim, erythromycin, lincomycin, sulfamethoxazole, chloramphenicol, amoxicillin
anti-inflammatory and analgesic agents	ibuprofen, diclofenac, fenoprofen, acetaminophen, naproxen, acetylsalicylic acid, fluoxetine, ketoprofen, indomethacin, paracetamol
psychotropic drugs	diazepam, carbamazepine, primidone, salbutamol
lipid metabolism regulators	clofibric acid, bezafibrate, fenofibrate, etofibrate, gemfibrozil
β-blockers	metoprolol, propranolol, timolol, sotalol, atenolol
radiocontrast agents	iopromide, iopamidol, diatrizoate
steroids and hormones	estradiol, estrone, estriol, diethylstilbestrol (DES)
dietary supplements	huperzine A – acetylcholinesterase inhibitor
personal care products	
odourising agents	nitrated, polycyclic and macrocyclic musk; phthalates
UV blockers	benzophenone, methylbenzylidene camphor
repellents	N,N-diethyltoluamide
antiseptics	triclosan, chlorofen

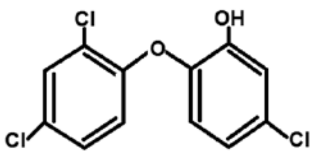

Fig. 1. Structural formula of triclosan (4-chloro-2-(2,4-dichlorophenoxy-phenol)

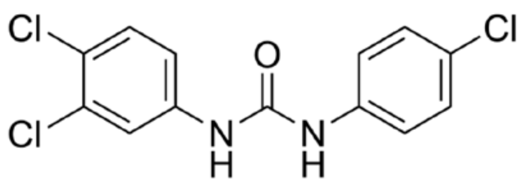

Fig. 2. Structural formula of triclocarban (3-(4-chlorophenyl)-1-(3,4-dichlorophenyl)urea)

Among PPCPs, the greatest interest of the researchers is paid to pharmaceuticals and triclosan. Poland, according to the data of the Office for Registration of Medicinal Products, Medical Devices and Biocidal is sixth drug sales market in Europe in terms of volume. The most often used non-prescription drugs are pain-killers, anti-inflammatory agents, flu remedies, vitamins, minerals, immunity boosting drugs and digestive ailment drugs [6]. Triclosan and triclocarban (Fig. 1, 2) are antibacterial chemical agents used in over 2 thousand of products: soaps, detergents, clothes, toothpastes or even pacifiers for babies. According to the guidelines of the EU Directive on Cosmetic Products 76/768/EEC, triclosan can be used in products in concentration not greater than 0.3% in ready product. Triclosan in aquatic environment can undergo photolysis when exposed to sunlight forming 2,8-dichlorobenzo-p-dioxin and 2,4-dichlorofenol, while in chlorinated water – forming chloroform. Laboratory tests showed that both triclosan and triclocarban caused disruption of hormone path and can stimulate the growth of drug resistant bacteria or superbacteria [7]. Analyses of sewage sludge for triclosan content indicate that its concentration varies in the range of 0.5 – 55 mg/kg [8], while USEPA gives even a level of up to 133 mg/kg [9]. Triclosan introduced with sludge to the soil usually forms Methyl-triclosan (Me-TCS). This compound is not so strongly antimicrobial, however, it has higher lipophilicity and is more persistent that originical triclosan.

According to the universally accepted definition *"Nanomaterial means a natural, incidental or manufactured material containing particles, in an unbound state or as an aggregate or as an agglomerate and where, for 50 % or more of the particles in the number size distribution, one or more external dimensions is in the size range 1 nm-100 nm."* Nowadays, nanoparticels are used almost in all areas of life (Tab. 3) and their presence in the sewage became common. Therefore, it becomes more and more probable that they are released into the environment, where they can have harmful effect on important groups of bacteria and other live organisms.

Table 3

Nanoparticles and their application [10]

Source	Type of nanoparticles	Used quantity	Application
Metals and alkaline earth metals	Ag	high	Antimicrobials, paints, coatings, medical applications, food containers
	Fe	high	Water treatment
	Pt	high	Catalysts
	Sn	unknown	paints
	Al	high	Metallic coatings
	Cu	unknown	microelectronics
	Zr	high	
	Se	low	Dietary and health supplements
	Ca	low	Dietary and health supplements
	Mg	low	Dietary and health supplements
Metal oxides	TiO_2	high	Cosmetics, paints, coatings
	ZnO	low	Cosmetics, paints, coatings
	CeO_2	high	Fuel catalysts, paints
	SiO_2	high	Paints coatings
	Al_2O_3	low	substrate-bound;
Carbon materials	technical soot	high	substrate-bound, but released from used tires
	carbon nanotubes	medium-high	Used in various composite materials
	fullerenes (C60-C80)	medium-high	Used in medicine and care products
various	nanoclays	high	plastic containers
	ceramics	high	coatings
	quantum dots	low	various compositions
	organic nanoparticles	low	Vitamins, drugs, drug and care products carriers, food additives

Antibacterial properties of silver nanoparticles made their application a common thing in various materials, including plastics, textiles, coatings and cosmetics. The newest research showed that silver nanoparticles in sewage sludge used in agricultural land as a fertiliser can be toxic to soil microorganisms. At the same time, scientists taking into account change of silver concentration in sludge and allowable dose of sludge used for soil estimated that silver content in soil can be exceeded within 50 years [11]. Another problem is absorption of nanoparticles by plants and their incorporation in the food chain. Research by Stegemeier et al. [12] indicates that silver ions and silver nanoparticle forms differ in releasing Ag^+ ions from particles Ag-NPS, Ag_2S-NPS and Ag^+. However, the ions bound with plant roots to a similar extent and exhibited similarly limited (<1%) degree of translocation to shoots.

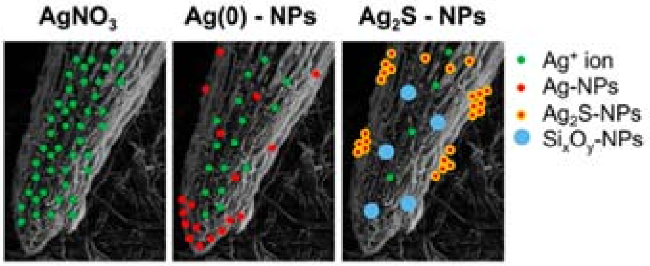

Fig. 3. The adherence of various forms of silver (including silver Nps) to alfalfa roots [12]

Summary

Environmental of the PPCPs is of such an importance that in 2012 Aistar B. A. Boxall et al. in monograph: „*Pharmaceuticals and Personal Care Products in the environment: What are the big questions?*" have described key aspects of assessment of exposure and risks related to the environmental presence of PPCS for humans and animals [13]. The same year, brought to the European Union list of pollutants to be monitored in water introduction of such compounds as: diclofenac, ethinylestradiol and 17-beta-estradiol. In December 2013, US Food and Drug Administration (FDA) has published official notice in the Federal Register requesting from manufacturers of antibacterial soap *"solid evidence for application of triclosan and triclocarban"* as the research proved its harmfulness and ineffectiveness [14]. The Organisation for Economic Co-operation and Development (OECD) also for several years has been working on preparation of number of papers regarding environmental fate of nanoparticles.

Introduction of the new technology is connected with possibility of introduction of new chemical compounds to the environment, also through sewage and sewage sludge (and composts produced from them). Therefore, application of sewage sludge will never become completely safe method of land fertilisation, especially for agricultural purposes. However, there is still a number of soils and lands excluded from cultivation of plants intended for consumptions as well as degraded land, where application of sewage sludge brings so needed organic load.

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