Leachable organic compounds from sewage sludge and their environmental risk potential

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Sewage sludge management is still a major problem in countries where it is not used as a thermal source (Rosiek, 2020) or phosphorus recovery by thermochemical methods is not implemented. The lack of interest in direct application to agricultural soils or as a component in compost production is linked to legislative limits which do not reflect the current needs of ensuring the safety of sludge application in agriculture. The sludge may contain hundreds of toxic organic compounds, e.g., polycyclic aromatic hydrocarbons (PAHs), phthalate esters (PAEs), alkylphenol polyethoxylates, synthetic musk, antibiotics, ultraviolet stabilisers, bisphenol analogues, organochlorine pesticides, polybrominated diphenyl ethers (PBDE), pharmaceuticals, hormones, perfluorinated compounds, and polychlorinated biphenyls (PCB), metals, pathogenic bacteria (Chen et al., 2019), and particles of microplastics. The contribution aims to assess environmental risks from the application of sludge caused by the leaching of organic compounds and micro-pollutants.

The presence of organic pollutants in sludge has been monitored in sludge from the Waste Water Treatment Plant Krnov, which has a capacity of 70,000 equivalent inhabitants. In addition to wastewater from residents, wastewater from the machinery industry and food production (Kofola beverages production, Krnov starch factories) flow to the treatment plant. Determination of organic compounds in sludge dry matter was performed by thermal desorption gas chromatography with mass spectrometry (TD-GC/MS). Organic pollutants in the aqueous leachate were determined by solvent-assisted stir bar sorptive extraction (SA-SBSE). The aqueous leachate was prepared according to the standard EN 12457-4:2003 (ratio 1:10).

Sludge from the processing plant contains plastic particles and additives (plasticisers) used to manufacture plastics. Plastics determined in the sludge contain polystyrene, i.e., a degradation product of styrene. Other organic compounds identifying the presence of plastics include methyl methacrylate, a constituent of the polymethyl methacrylate (PMMA) known as organic glass. Furthermore, dioxolane was identified in the sewage sludge, which is considered non-intentionally added substances (NIAS) in the PET polymer (Franz et al., 2004). Sewage sludge also contains additives used to modify the properties of plastics (softening agents): didecyl phthalate, diethyl phthalate, dibutyl phthalate, di(2-ethylhexyl) phthalate (DEHP), dioctyl terephthalate (Kodaflex DOTP), and bis(2-ethylhexyl) terephthalate with a solubility ranging from 0.27 mg/L to 1 g/L. Phthalates or phthalate esters (PAEs) do not come from cosmetic products because such use is prohibited. PAEs may be a component of the coating of pharmaceutical pills. The determined concentration of DEHP in sludge is 12.5 ± 3.2 mg/kg. The decomposition products of phthalic acids esters (PAE) include phthalic acid and 6-ethyl-3-octyl butyl ester(Amir et al., 2005). In the group of plasticisers, the highest concentrations in the dry matter of the sludge were found for dibutyl phthalate (30.5 ± 6.4 mg/kg) and the lowest concentrations for di-(2-ethylhexyl) adipate – DEHA (1.0 ± 0.2 mg/kg) and phthalic anhydride (0.5 ± 0.1 mg/kg), a precursor for the manufacture of plasticisers.

Chemical compounds from personal care products and cleaning products

Benzophenone is used in personal care products (PCP) such as lip balm and nail polish, laundry, and cleaning products to protect against UV light. In sludge, benzophenone occurs at a concentration of 6.8 ± 1.2 mg/kg. Octocrylene (3.6 ± 0.6 mg/kg) and homosalate (3,3,5-trimethyl-cyclohexyl-salicylate) are present in the 1.6 ± 0.2 mg/kg concentration to prevent any natural chemical degradation that can occur when skincare products are exposed to sunlight for prolonged periods. Also, azobenzene is used in PCP products as a UV blocker (Liu et al., 2018). Azobenzene occurs in sludge at a 3.5 ± 0.8 mg/kg concentration. Isopropyl myristate and palmitate are used in cosmetics as a binding emollient and emulsifier in eye makeup, soaps and detergents, hair care products, nail care products, shaving products, and other skincare products. Isopropyl myristate occurs in sludge at a concentration of 5.0 ± 0.5 mg/kg, and 2.04 ± 0.20 mg/kg for isopropyl palmitate. Silanes and siloxanes are used for improving the state of the hair. Siloxanes are used in cosmetics to soften, smooth, and moisten. The following compounds were identified in the sludge: dichloromethylphenylsilane, 1,1-dimethylsilanediol, phenyltrimethylsilane, and triethylsilanol. Fragrance material

4-methylacetophenone occurs in sludge at a concentration of 1.6 ± 0.4 mg/kg. Other identified fragrances include celestolide (0.40 ± 0.05 mg/kg) and tonalide (2.6 ± 0.6 mg/kg).

Compounds derived from textile washing

Di-2-ethylhexyl adipate (DEHA) is one of the plasticisers. It is part of coated fabrics that is released during washing. Other compounds released from textiles and toys may include DOTP Kodaflex. An antibacterial compound 2,5-Di-tert-butyl-1,4-benzoquinone, which is possibly used as a filler for textiles, is present in the sludge at a concentration of 20.8 ± 4.5 mg/kg.

Compounds derived from industrial wastewater and agricultural activities

In sludge, 2,4,6-trichlorphenol (TCP) was determined at a concentration of 60.8 ± 5.2 mg/kg. The main source of TCP is industrial wastewater from wood processing, paper, and textile industry (Khorsandi et al., 2018). A metabolite of the pesticide chlorpyrifos – 2-hydroxy-3,5,6-trichlorpyridine has been identified in the sludge at a concentration of 5.55 µg/kg. Fungicides in the sludge include zoxamide and soil bactericide nitrapyrine used as a nitrification inhibitor co-applied with nitrogen fertiliser. From very toxic halophenols, sludge contains 4-bromo-2-chlorphenole (25.0 ± 4.2 µg/kg), metabolite of organophosphorus pesticide (profenofos), and 2-bromo-4-chlorphenole at a concentration of 16.5 ± 3.7 µg/kg.

Compounds of unclear origin

Aromatic hydrocarbons, including alkylated benzene compounds, have been determined in the dry matter of the sewage sludge at a concentration of 105.2 ± 32.6 mg/kg. The origin of PAHs is not clear; they are contained in domestic wastewater and industrial wastewater (Sun et al., 2019). Polyaromatic hydrocarbons (16 US EPA PAHs) occur in sludge at a concentration of 245.7 ± 45.7 mg/kg.

Compounds of “unclear origin” – aromatic hydrocarbons and PAHs (350 mg/kg) have the highest concentrations from the contaminants in the sludge from WWTP. Compounds of industrial origin are present at concentrations of 61 mg/kg, followed by plasticizers (45 mg/kg), compounds contained in PCP (27 mg/kg), compounds released during washing (21 mg/kg), and compounds from agriculture (47 µg/kg). PAEs, benzophenone, and homosalate, pesticides – profenofos and halophenols, which are classified as endocrine disruptors, exhibit dangerous properties. Carcinogens include azobenzene, 2,4,6-trichlorphenol, PAHs, and aromatic hydrocarbons. The dry matter of sludge contains compounds with environmentally and medically adverse effects; their environmental hazards increase with leaching. Water leachate from sewage sludge contains 162 organic compounds. Amino acids and proteins have the highest leachability from the solid sludge matrix (42.5%). The lower leachability is characteristic for organic sulfur compounds (22.6%), aldehydes, ketones, and anhydrosaccharides (20.0%), sterols, alkanes, and methylated alkanes. In the aromatic hydrocarbons group, alkylated benzene forms such as 4-ethenyl-1,2-dimethylbenzene have the highest leachability.

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