

Occurrence of herbicides and their transformation products in sewage sludge: a review

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Abstract: The beneficial reuse of sewage sludge in agricultural soils is limited by the accumulation of micropollutants of emerging concern, which may pose significant environmental and human health risks. This review summarises recent advances in understanding the occurrence, persistence, and fate of herbicides and their transformation products in sewage sludge. Data from various geographic regions are discussed, with a focus on implications for the safe reuse of biosolids in agriculture. Most available studies have been conducted in European Union countries, where land application of biosolids is a common practice. Twelve groups of herbicides and their transformation products have been identified in sewage sludge, including glyphosate and aminomethylphosphonic acid (AMPA), phenylureas, phenoxy acids, chloroacetamides, triazines and their metabolites, triazinones, phenylcarbamates, isoxazolidinones, benzoic acids, dinitroanilines, benzofurans, phenyl ethers, and other herbicides. Among these, triazines and their metabolites were the most frequently detected, with concentration ranges of 0.01–277 ng/g and not detected (n.d.)–237 ng/g, respectively. Glyphosate and AMPA were found at particularly high concentrations (n.d.–35 000 ng/g). Phenylurea herbicides (e.g., diuron and isoproturon) were detected in a limited number of studies, with concentrations ranging from not detected to 102 ng/g. Substantial concentrations of phenoxy herbicides (2,4-D, 2,4-DB, and 2,4,5-T) were also reported in sewage sludge, ranging from 50.5–864 ng/g. The available scientific literature on the occurrence of herbicides in sewage sludge focuses mainly on older, often already banned compounds, while data on currently approved herbicides remain scarce. This review highlights the need for more comprehensive global assessments of herbicides and their transformation products in sewage sludge to ensure the safe agricultural use of biosolids and minimise risks to plants and other organisms. The current lack of systematic monitoring and documentation represents a critical knowledge gap in evaluating environmental exposure and associated risks.

Keywords: contaminants of emerging concern; herbicide metabolites; pesticides; biosolids; wastewater; potential risk

Sewage sludge has long been applied to agricultural soils as a soil amendment and fertiliser because of its high content of organic matter, macronutrients such as nitrogen and phosphorus, and micronutrients including essential trace elements (Barakat et al. 2017). The agricultural use of sewage sludge can therefore reduce the demand for commercial

fertilisers (USEPA 1999, Nikolopoulou et al. 2023). Land application has been practised for decades in forestry, mine reclamation, and on other managed lands, such as parks and golf courses (Barakat et al. 2017).

In recent years, sewage sludge production from wastewater treatment plants has increased across

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European Union member states, with approximately 35% of the total being directly applied to agricultural soils (Campo et al. 2021, Rede et al. 2024). In several countries, including the Czech Republic, Lithuania, Ireland, and Hungary, more than half of the generated sludge is composted or used for land application (Ivanová et al. 2018, Eurostat 2020, Grabic et al. 2022). Similarly, about 47% of sewage sludge in the United States and 27% in China is utilised for land application (Steele et al. 2022).

Herbicides represent the most extensively used class of pesticides, accounting for approximately 54% of the 346 000 tons that comprise the total annual pesticide market (TBRC 2020, Eurostat 2022). They are applied in both agricultural and non-agricultural sectors, including residential areas, gardens, and irrigation systems (Atwood and Paisley-Jones 2017, USEPA 2022). Globally, about 62% of herbicides are used in agriculture, while the remainder is applied for domestic, urban, and industrial purposes (Atwood and Paisley-Jones 2017). The extensive use of herbicides has raised increasing concern regarding their potential environmental and human health impacts (Singh and Singh 2014). After application, herbicides undergo a variety of transformation processes. Within plants, herbicides are metabolised through oxidation, hydroxylation, dealkylation, and conjugation reactions. These plant-derived metabolites may subsequently enter soils and aquatic systems through plant residues, leaching, or runoff, contributing to the environmental load of transformation products. Other degradation pathways of herbicides include biotic (primarily microbial) and abiotic mechanisms. Microbial degradation is often the dominant pathway in soils and sediments, involving N-dealkylation, hydroxylation, deamination, ring-cleavage, and conjugation reactions. Abiotic pathways such as photodegradation, hydrolysis, and chemical oxidation-reduction reactions can also generate persistent degradation products. Many of the resulting transformation products are sufficiently stable to persist in soils, surface waters, and wastewater streams, and in some cases exhibit equal or greater toxicity compared to their parent herbicides (Kolpin et al. 2004). In this manuscript, the term "metabolite" refers to a transformation product generated through biological processes, such as microbial or enzymatic reactions. The term "degradation product" refers to a transformation product formed through abiotic processes, including thermal, chemical, or photolytic degradation. We use these terms to distinguish between biologically mediated and non-biological transformation pathways. The term

"transformation product" is then used as an umbrella term encompassing both of these.

Numerous studies have investigated the occurrence of herbicides in various environmental matrices and their associated risks to ecosystems and human health (Kolpin et al. 1998, Loos et al. 2009, Ouyang et al. 2019, Bodur et al. 2020, Rose et al. 2022, Wang et al. 2023). However, only a limited number of studies have examined the presence of herbicides and their transformation products in sewage sludge. Given their persistence and potential phytotoxicity, these contaminants of emerging concern warrant greater attention, as they may negatively affect plant growth and soil health following sludge application. Therefore, the objective of this review is to address current knowledge gaps concerning the occurrence, concentration levels, and potential risks of herbicides and their transformation products in sewage sludge.

MATERIAL AND METHODS

Information for this review was collected from peer-reviewed literature available in the Web of Science and Science Direct databases. The primary search used the keyword phrase "herbicides in sewage sludge" in combination with at least one of the following terms: sewage sludge, biosolids, herbicides, herbicide metabolites, pesticides, soil contamination, or emerging contaminants.

Additional secondary searches were conducted using specific herbicide classes and compounds, including glyphosate and aminomethylphosphonic acid (AMPA), phenylureas, phenoxy acids, chloroacetamides, triazines, and their transformation products.

Search results were screened by matching the selected keywords against the title, abstract, and keyword fields of each record. Irrelevant studies were excluded, and the remaining eligible full-text articles, reports, and book chapters were reviewed and used as sources for this study. Data were found for 40 herbicides and their transformation products, and the reported concentration range on a dry-weight basis was recorded for each compound. For consistency and clarity, the compounds were classified according to their chemical families to facilitate comparisons of contamination levels across geographic areas. Twelve herbicide groups were identified: glyphosate and aminomethylphosphonic acid, phenylureas, phenoxy acids, chloroacetamides, triazines and their transformation products, triazinones, phenylcarbamates, isoxazolidinones, benzoic acids, dinitroanilines, benzofurans, phenyl ethers, and other herbicides.

RESULTS AND DISCUSSIONS

Sources and occurrence of herbicides and their transformation products in sewage sludge

Many organic contaminants, including herbicides and other pesticides that accumulate in sewage sludge, can be transferred to agricultural products or leach into the environment following the land application of sludge. During wastewater treatment, hydrophobic organic contaminants are effectively removed from the aqueous phase through sorption to sludge, which represents the primary removal pathway for these contaminants. Additionally, volatile compounds such as benzene have been detected in sewage sludge due to absorption processes (Harrison et al. 2006).

The fate of herbicides in soil or sludge depends on several parameters, including adsorption, absorption, volatilisation, and degradation through microbial and chemical processes (Sonida 2014). Numerous analytical methods have been developed for the monitoring of organochlorine pesticides in sewage sludge because of their persistence in the environment (Tadeo et al. 2010). However, relatively few studies have focused on determining and developing analytical methods for herbicides and their transformation products in sewage sludge.

The limited documentation on herbicide occurrence is likely due to the complex matrix of sewage sludge and the typically low concentrations of these compounds, which require extensive extraction and cleanup procedures before chromatographic analysis. The current literature review identified only a small number of studies reporting the presence of herbicides in sewage sludge from different regions. The concentrations of the detected herbicides and their transformation products reported in these studies are summarised in Table 1.

Glyphosate and aminomethyl phosphonic acid. Glyphosate is the most widely used organophosphorus pesticide globally, including within the European Union (Venditti et al. 2023), where it is currently approved until 2033 (Regulation (EU) 2023/2660). It is a post-emergence, broad-spectrum, and non-selective herbicide (Singh et al. 2024). Glyphosate is commonly detected in various environmental matrices, particularly in soil.

Ghanem et al. (2007a,b) evaluated and quantified the accumulation of glyphosate and its primary metabolite, AMPA, in urban sewage sludge from wastewater treatment plants in France. These studies reported high concentrations of glyphosate

not detected (n.d.)–20 300 ng/g and AMPA (n.d.–35 000 ng/g). Similarly, Charbonneau et al. (2024) detected elevated levels of glyphosate (690 ± 530 ng/g) and AMPA ($6\ 260 \pm 1\ 930$ ng/g) in sewage sludge samples collected in Canada. In Sweden, Olofsson et al. (2013) also reported substantial concentrations of glyphosate and AMPA ranging from n.d.–700 ng/g and n.d.–10 000 ng/g, respectively.

The environmental persistence of glyphosate and AMPA is influenced by their relatively long half-lives in soil, ranging from 0.8–151 days for glyphosate and 10–98 days for AMPA. Degradation occurs through both abiotic (chemical and photolytic) and biotic (microbial) processes. However, due to the strong adsorption of glyphosate onto soil particles, it can persist in the environment and may enter the human body indirectly through contaminated food, air, or water (Singh et al. 2024). AMPA soil residues are considered significantly less phytotoxic than glyphosate, with no observed effects on emergence, growth, biomass, or seed germination at concentrations of 0.7 g/L (Ganie and Jhala 2021).

Overall, the widespread detection of glyphosate and its metabolite AMPA in sewage sludge highlights their persistence and strong affinity for solid phases during wastewater treatment. Their presence at considerable concentrations suggests that conventional treatment processes are insufficient for the complete removal of these contaminants. Given their persistence in soils and possible transfer through the food chain, glyphosate and AMPA represent key indicators of agrochemical contamination in biosolids. Further monitoring and improved analytical approaches are essential to assess the environmental behaviour of sewage sludge and ensure its safe reuse in agricultural applications.

Phenyl urea. Phenylurea herbicides are widely used to control annual and perennial weeds in crop fields as well as non-crop areas and are commonly applied as pre-emergent treatments in fruit crops (Liu et al. 2023). They are also extensively used in both urban and rural environments and have been frequently detected in wastewater and sewage sludge across Europe (Ghanem et al. 2008). Given their persistence, their degradation products can also be expected to occur in sewage sludge.

Phenylurea herbicides such as diuron and isoproturon have been reported in wastewater effluents in numerous studies (Nitschke and Schüssler 1998, Köck-Schulmeyer et al. 2013, Mukhopadhyay et al. 2022). Nitschke and Schüssler (1998) found that

Table 1. Herbicides and their transformation products are found in sewage sludge.

Compound	Range (ng/g on a dry weight basis)	Location	Reference
Glyphosate			
Glyphosate	400–20 300	France	(Ghanem et al. 2007a)
	100–3 000	France	(Ghanem et al. 2007b)
	n.d.–700	Sweden	(Olofsson et al. 2013)
	690 ± 530 ng/g	Canada	(Charbonneau et al. 2024)
Aminomethylphosphonic acid (AMPA)	2 000–35 000	France	(Ghanem et al. 2007b)
	n.d.–10 000	Sweden	(Olofsson et al. 2013)
	6 260 ± 1 930 ng/g	Canada	(Charbonneau et al. 2024)
Phenyl ureas			
Diuron	6.6–84.0	France	(Ghanem et al. 2007a)
	n.d.–44.25	Spain	(Campo et al. 2013)
Diuron	6.6–84.0	France	(Ghanem et al. 2007b)
	0.6–44	Switzerland	(Kupper et al. 2005)
Dichlorophenylmethylurea (DCPMU)	n.d.	Nigeria	(Nikolopoulou et al. 2023)
Isoproturon	n.d.	France	(Ghanem et al. 2007a; 2008)
Isoproturon	1.00–101.76	Spain	(Campo et al. 2013)
	< 50	Sweden	(Olofsson et al. 2013)
Phenoxy acid herbicides			
2,4-dichlorophenoxyacetic acid (2,4-D)	300	USA	(EPA 1996)
2,4-dichlorophenoxybutyric acid (2,4-DB)	864	Denmark	(Nanusha et al. 2024)
2,4,5-Trichlorophenoxyacetic acid (2,4,5-T)	50.5	USA	(EPA 1996)
Chloroacetamide			
Acetochlor	n.d.	Spain	(Campo et al. 2013)
Metolachlor	n.d.–2.24	Spain	(Campo et al. 2013)
Triazines and their metabolites			
Triazines	0.01–0.28	Spain	(Masiá et al. 2015)
	0.25–277.44	Spain	(Campo et al. 2013)
Ttriazine-desisopropyl	n.d.	Nigeria	(Nikolopoulou et al. 2023)
Atrazine	3.90–36.90	Spain	(Campo et al. 2013)
	0.01–0.28	Spain	(García-Galán et al. 2010)
Atrazine-deisopropyl (DIA)	14.55–41.79	Spain	(Campo et al. 2013)
	0.28	Spain	(García-Galán et al. 2010)
Atrazine-desethyl (DEA)	6.42–158.37	Spain	(Campo et al. 2013)
	0.25	Spain	(García-Galán et al. 2010)
Propazine	1.53–277.40	Spain	(Campo et al. 2013)
	0.05–0.11	Spain	(García-Galán et al. 2010)
Simazine	4.55–37.79	Spain	(Campo et al. 2013)
	0.06	Spain	(García-Galán et al. 2010)
Terbutriazine	2.60	Spain	(Mena et al. 2003)
	< 100	Sweden	(Olofsson et al. 2013)
	2.15–35.54	Spain	(Campo et al. 2013)
Terbutylazine-desethyl (DET)	3.04–80.77	Spain	(Campo et al. 2013)
	0.03	Spain	(García-Galán et al. 2010)

n.d. – not detected

Continuous Table 1. Herbicides and their transformation products are found in sewage sludge

Compound	Range (ng/g on a dry weight basis)	Location	Reference
Terbutylazine-2-hydroxy (HTBA)	0.94–176.79	Spain	(Campo et al. 2013)
Sebutylazine	0.46–2.26	Spain	(García-Galán et al. 2010)
Cyanazine	0.01	Spain	(García-Galán et al. 2010)
Terbumeton	0.25–49.92	Spain	(Campo et al. 2013)
Terbumeton-desethyl	0.46–236.83	Spain	(Campo et al. 2013)
Prometon	0.13	Spain	(García-Galán et al. 2010)
Terbutryl	5.00–182.87	Spain	(Campo et al. 2013)
Terbutryl	7.4	Denmark	(Nanusha et al. 2024)
Triazinone			
Hexazinone	< 30	Sweden	(Olofsson et al. 2013)
Phenyl carbamate			
Phenmedipham	< 200	Sweden	Olofsson et al. 2013
Isoxazolidinone			
Clomazone	67.9	Denmark	(Nanusha et al. 2024)
Benzoic acids			
2,6-dichlorobenzoic acid, (degradation product of dichlobenil)	22.6	Denmark	(Nanusha et al. 2024)
Dinitroaniline			
Trifluralin	< 5	Sweden	(Olofsson et al. 2013)
Pendimethaline	< 100	Sweden	(Olofsson et al. 2013)
Benzofurane			
Ethofumesate	< 50	Sweden	(Olofsson et al. 2013)
Phenyl ether			
Diflufenican	< 60	Sweden	(Olofsson et al. 2013)
Other			
Aclonifen (nitrophenyl ether)	< 60	Sweden	(Olofsson et al. 2013)
Chlorpropham (isopropyl carbamate)	< 100	Sweden	(Olofsson et al. 2013)
Chloridazon (pyridazinone)	< 50	Sweden	(Olofsson et al. 2013)
Metamitron (triazinone)	< 300	Sweden	(Olofsson et al. 2013)
Methazachlor (chloroacetamide)	< 300	Sweden	(Olofsson et al. 2013)
Propyzamide (benzamide)	< 60	Sweden	(Olofsson et al. 2013)
Prosulfocarb (thiocarbamate)	< 30	Sweden	(Olofsson et al. 2013)

n.d. – not detected

diuron accounted for more than 80% of the total herbicide load in effluents from urban wastewater treatment plants in Germany. A recent study by Cajas-Salazar et al. (2025) reported the presence of diuron in 81% of wastewater samples in Costa Rica, likely due to its widespread use in urban weed control (Liu et al. 2023).

Phenylurea herbicides exhibit high environmental stability and potential toxicity, with several compounds identified as endocrine disruptors (Ghanem et

al. 2008). This led to the regulatory ban of Diuron in the EU in 2007 (Commission Decision 2007/417/EC) and isoproturon in 2016 (Commission Implementing Regulation (EU) 2016/872). The half-life of diuron in soil is approximately 81 days (Rouchaud et al. 2000). Its persistence and bioactive properties emphasise the need to monitor its occurrence in sewage sludge. Data compiled in this review show that diuron was detected in sewage sludge at concentrations ranging from n.d.–44.3 ng/g in Spain (Campo et al. 2013),

6.6–84.0 ng/g in France (Ghanem et al. 2007a, b), and 0.6–44 ng/g in Switzerland (Kupper et al. 2005). However, none of these studies reported the detection of diuron's degradation product, dichlorophenylmethylurea (DCPMU).

Isoproturon was also detected in sewage sludge, with concentrations ranging from 1.00–102 ng/g in Spain (Campo et al. 2013) and up to 50 ng/g in Sweden (Olofsson et al. 2013).

In summary, phenylurea herbicides were frequently detected in sewage sludge across different regions, reflecting their widespread use and environmental persistence. The absence of data on their transformation products, such as DCPMU, and on the presence of those still in use, including chlortoluron and metobromuron, indicates a significant knowledge gap in current monitoring efforts. Considering their potential endocrine-disrupting properties and phytotoxic effects, continuous surveillance and the development of more sensitive analytical methods are crucial for evaluating their environmental risks and ensuring the safe reuse of biosolids in agriculture.

Phenoxy acid herbicides. Phenoxy acid herbicides are widely used for weed control and are selectively applied to manage dicot weeds in crops such as corn, wheat, and rice (Guo et al. 2019). However, studies investigating the occurrence of these compounds in sewage sludge are scarce. According to the current literature survey, only two studies were identified, one conducted in the United States in 1996 (EPA 1996) and another, a more recent investigation in Denmark (Nanusha et al. 2024).

In the U.S. study, 2,4-dichlorophenoxyacetic acid (2,4-D) and 2,4,5-trichlorophenoxyacetic acid (2,4,5-T) were detected in sewage sludge at concentrations of 300 ng/g and 50.5 ng/g, respectively (EPA 1996). The Danish study by Nanusha et al. (2024) reported a high concentration of 2,4-dichlorophenoxybutyric acid (2,4-DB) at 864 ng/g in sludge samples collected from wastewater treatment plants.

Laboratory batch studies investigating the fate of 2,4-D in sewage sludge have shown that, under both aerobic and anaerobic conditions, mineralisation can exceed 90% over 28 days (ATSDR profile). Comparable sludge experiments have demonstrated measurable degradation of 2,4-D (Zipper et al. 1999). These findings suggest that, although occurrence data are scarce, transformation processes do occur in sludge matrices. The U.S. Environmental Protection Agency cancelled all remaining uses of 2,4,5-T in 1979 due to concerns

over its potential oncogenic, fetotoxic, and teratogenic effects, primarily attributed to contamination with dioxin (TCDD). Many EU member states banned it individually during the 1980s, and it was effectively removed from the EU market by 2003 following its non-inclusion in Annex I of Directive 91/414/EEC. Therefore, the detection of 2,4,5-T decades after its prohibition suggests either its remarkable persistence or possible contamination from legacy sources, emphasising the need for continued environmental monitoring. 2,4-D remains one of the most commonly used herbicides (Zipper et al. 1999).

Chloroacetamides. Chloroacetamide herbicides are widely applied to agricultural soils to control annual grasses and dicot weeds. Herbicides such as metazachlor are widely used in the cultivation of oilseed rape. Their extensive use over recent decades has raised significant environmental concerns due to the persistence of their residues (Chen et al. 2024). Acetochlor is a highly effective, long-lasting, soil-active herbicide commonly used in maize, with a reported soil half-life ranging from 3 to 9 weeks (Ju et al. 2020). Acetochlor was banned in the EU in 2008 via non-inclusion in Annex I of Directive 91/414/EEC.

Within this group, Campo et al. (2013) investigated the presence of acetochlor and metolachlor in sewage sludge samples collected in Spain. Metolachlor was detected at concentrations ranging from n.d. to 2.24 ng/g, whereas acetochlor was not detected in any of the analysed samples. We found no information on the analysis of metazachlor in sewage sludge. Overall, the limited detection of chloroacetamide herbicides in sewage sludge suggests that these compounds may undergo substantial degradation or transformation during wastewater treatment. However, their persistence in soils and potential for the formation of transformation products remain environmental concerns, particularly in regions with intensive maize and cereal cultivation.

Triazines and their transformation products. Most studies have focused on determining triazine herbicides and their transformation products due to their widespread use in agricultural and urban environments for weed control and biocidal applications. Triazines are key components in many commonly used herbicide formulations in Europe, and their frequent detection in soils, groundwater, and surface waters worldwide demonstrates their high environmental persistence (García-Galán et al. 2010). Atrazine and diuron are among the most frequently detected herbicides in wastewater effluents from

treatment plants (Wang et al. 2022, Cajas-Salazar et al. 2025). Consequently, many investigations have examined the potential accumulation of atrazine and related compounds in sewage sludge.

Triazines have been detected in sewage sludge at concentrations ranging from 0.01 to 277 ng/g. The most commonly identified compounds include atrazine, simazine, propazine, terbutylazine, se-butylazine, prometon, terbumeton, and terbutryn. Metabolites of atrazine – such as deisopropylatrazine (DIA) and desethylatrazine (DEA) – and of terbutylazine – such as terbutylazine-2-hydroxy (HTBA) and desethylterbutylazine (DET) – have also been reported. Within the triazinone group, hexazinone was detected in sewage sludge collected in Sweden at concentrations below 30 ng/g (Olofsson et al. 2013). Numerous studies on the occurrence of triazine herbicides and their metabolites in sewage sludge have been conducted in Spain, with additional investigations in Greece, France, Sweden, Denmark, Nigeria, and the United States. However, most available data originates from European countries, where sewage sludge is both a waste management concern and a potential resource for agricultural fertilisation. To our knowledge, no data have been reported on the occurrence of terbutylazine – the only currently approved triazine herbicide in the EU – in sewage sludge.

Atrazine was once one of the most widely used herbicides globally, particularly in maize cultivation, for controlling broadleaf and grassy weeds. Until 1993, it was also applied for weed control in non-cropping and fallow land. The reported half-lives of atrazine in soils vary from 4 to 57 weeks, and the half-life of terbutylazine ranges from 30 to 70 days, depending on temperature, application frequency, and soil characteristics (Ju et al. 2020). Atrazine was banned in the European Union in 2004 due to its persistence in water resources, and several other triazine herbicides have since been phased out. For instance, simazine and atrazine were banned in the Czech Republic in 2005, prometryn in 2003, terbutryn in 2007, acetochlor in 2013, hexazinone in 2007, and linuron in 2017 (Kosubová et al. 2020).

The continued detection of triazine herbicides, decades after their ban, provides clear evidence of their environmental persistence and strong affinity for soil and sludge matrices. These findings underscore the importance of ongoing surveillance of legacy herbicides and their transformation products in sewage sludge, facilitating a deeper understanding of their long-term ecological and human health implications.

Other herbicides and their transformation products.

In addition to the major herbicide groups discussed above, several other compounds and their transformation products have been reported in a limited number of studies conducted in Sweden and Denmark. These include herbicides belonging to the triazinone, phenylcarbamate, isoxazolidinone, benzoic acid, dinitroaniline, benzofuran, and phenyl ether families.

In sewage sludge collected in Sweden, phenmedipham (phenylcarbamate) was detected at concentrations below 200 ng/g (Olofsson et al. 2013). The same study also reported the presence of ethofumeate (benzofuran) and diflufenican (phenyl ether) at concentrations of less than 50 ng/g and 60 ng/g, respectively. In Denmark, clomazone (isoxazolidinone) and 2,6-dichlorobenzoic acid (benzoic acid) – a degradation product of dichlobenil – were detected at 67.9 ng/g and 22.6 ng/g, respectively (Nanusha et al. 2024). Olofsson et al. (2013) further identified several additional herbicides that did not fall into specific chemical groups, including aclonifen, chlorpropham, chloridazon (triazinones), metamitron (triazones), methazachlor (chloracetamid), phenmedipham, propyzamide, and prosulfocarb. The concentrations of these compounds ranged from 30 to 300 ng/g in sewage sludge samples collected in Sweden.

Although these herbicides were detected at relatively low concentrations compared to the major herbicide groups, their presence in sewage sludge demonstrates the wide diversity of agrochemical residues entering wastewater treatment systems. The detection of multiple chemical classes, including transformation products such as 2,6-dichlorobenzoic acid, suggests that even compounds used infrequently or in specific applications can persist through treatment processes. These findings emphasise the importance of expanding monitoring programs to improve our understanding of the cumulative environmental impact and potential risks associated with agrochemicals used in sludge reuse in agriculture.

Uptake and phytotoxicity of herbicides from sludge-amended soils

Under European Union legislation (Article 32, Regulation (EC) No. 396/2005), the European Food Safety Authority established a maximum Residue Level (MRL) for pesticide levels in food as 0.01 mg/kg (EFSA 2025). Residual herbicides and their transformation products present in sewage sludge can

be absorbed by crop roots from soil pore water or irrigation water and subsequently translocated to plant tissues (Ju et al. 2020). The phytotoxic effects of sludge-amended soils depend largely on the concentration and type of pollutants present in the sludge. Herbicide uptake and translocation are influenced by physicochemical properties, including hydrophobicity ($\log K_{ow}$), water solubility, and plant lipid content (Ju et al., 2020). Once absorbed, these compounds can be distributed within plant tissues, potentially affecting physiological functions and posing risks to food safety and human health (Brauns et al. 2018, Ju et al. 2020). However, the magnitude of these effects varies depending on crop species, contaminant concentration, and environmental conditions.

Ghanem et al. (2006) investigated the fate of glyphosate, diuron, and nonylphenol in sludge-applied agricultural soils. Their results demonstrated that these organic contaminants are mobile and can be partially transferred to soil leachates and plant seedlings, indicating potential indirect exposure risks for humans and other organisms. Soares et al. (2023) investigated the non-target phytotoxicity of glyphosate in soil on tomato plants. They reported significant inhibition of growth and physiological stress responses at a glyphosate concentration of 10 mg/kg of soil. Glyphosate is known to adsorb strongly to soil components but can persist long enough to exert toxic effects before microbial degradation occurs (Soares et al. 2023). In contrast, Ju et al. (2020) observed no visible phytotoxic symptoms in wheat seedlings exposed to acetochlor and atrazine at concentrations ranging from 1 to 10 mg/L. These contrasting results highlight that phytotoxicity is highly compound and species-specific.

Recent studies have increasingly emphasised that glyphosate contamination can cause toxicity to non-target plants and substantially hinder their growth and productivity (Gomes et al. 2017, Zhong et al. 2018). Therefore, addressing non-target phytotoxicity arising from herbicide-contaminated sludge is essential for protecting agricultural crops and maintaining ecosystem health. Effective management strategies should aim to limit the transfer of herbicide residues into soils and crops, ensuring the safe use of biosolids within sustainable agroecosystems. In summary, the uptake and accumulation of residual herbicides and their transformation products from sludge-amended soils present a significant pathway of contaminant transfer into plants and, ultimately, the food chain. Although the degree of phytotoxicity varies with compound type,

crop species, application method, and environmental conditions, evidence from multiple studies suggests that persistent herbicides, such as glyphosate and diuron, can be absorbed by crops at concerning levels.

Regulatory framework and monitoring practices

The persistence of herbicides and their transformation products in sewage sludge raises critical concerns about their potential toxicity to plants, soil organisms, and humans. Chronic exposure to herbicide-contaminated sludge can disrupt soil microbial communities, inhibit seed germination and plant growth, and lead to the accumulation of residues in crops and food products. Moreover, the leaching of herbicides from sludge-amended soils poses a risk of groundwater contamination, as demonstrated in several studies (Nitschke and Schüssler 1998, Kolpin et al. 1998, 2004, Ouyang et al. 2019, Ghanem et al. 2006, Wang et al. 2023). Therefore, establishing robust regulatory frameworks to control soil, food, and water contamination is essential for preventing long-term ecological and human health impacts.

Herbicides are generally well-recognised and regulated contaminants; some of their transformation products or recently detected residues in unconventional matrices, such as sewage sludge, may be considered contaminants of emerging concern due to limited environmental data or absence from routine monitoring programs. Existing regulations governing the agricultural use of sewage sludge primarily focus on pathogen reduction and heavy metal content, with limited attention to organic contaminants. Only a few countries have introduced monitoring requirements or threshold limits for persistent organic compounds such as dioxins, polychlorinated biphenyls (PCBs), nonylphenol, and polycyclic aromatic hydrocarbons (PAHs) (Harrison et al. 2006, Olofsson et al. 2013). The United States, Japan, and China permit the agricultural use of sewage sludge under strict regulatory control, particularly with respect to heavy metal concentrations (Zhao et al. 2023). In the European Union (EU), the growing production of sewage sludge has prompted greater attention to the sustainability of its land application (Ghanem et al. 2006). The EU Directive 86/278/EEC sets concentration limits for heavy metals in sewage sludge applied to agricultural soils, aiming to protect human health and the environment. Although this directive has been amended multiple times, most recently in 2022, the revisions have continued to focus on metals, without adding limits for organic

contaminants. A 2000 draft document, the Working Document on Sludge, proposed the inclusion of certain persistent organic pollutants such as PAHs, PCBs, nonylphenol, and polychlorinated dibenzo-p-dioxins – but did not address other contaminants of emerging concern, including pesticides, UV filters, perfluoroalkyl substances (PFAS), and halogenated flame retardants (CEC 2000).

Despite the absence of formal limits for pesticides and other organic contaminants, awareness of their potential risks is growing. Regular monitoring and risk assessment of these substances in sewage sludge are crucial for evaluating their environmental behaviour and safeguarding public health (Tadeo et al. 2010). In response to ongoing concerns about contamination, some European countries and agricultural organisations have advocated for alternatives to land application. Switzerland and the Netherlands, for instance, have banned the use of sewage sludge in agriculture and instead promote incineration or other disposal methods to minimise risks to ecosystems and human health (Ghanem et al. 2008).

In conclusion, the application of sewage sludge or biosolids to agricultural soils can introduce a wide range of contaminants of emerging concern, including herbicides and their transformation products. Despite the global predominance of herbicide use compared to other pesticides, their occurrence in sewage sludge has received relatively little attention, largely due to the complexity of the sludge matrix and the typically low concentrations in which these compounds occur.

Among the compounds reviewed, glyphosate and its metabolite AMPA were detected at the highest levels, ranging from hundreds to tens of thousands of ng/g dry weight, whereas atrazine and diuron were generally observed in the low to mid ng/g dry weight range. The available scientific literature on the occurrence of herbicides in sewage sludge primarily focuses on older, often already banned compounds, such as diuron or atrazine, while data on currently approved herbicides (e.g., aminopyralid or clopyralid) remain scarce.

Given these findings, establishing a coordinated global monitoring program is essential to evaluate the risks associated with herbicide residues in sewage sludge and their potential for indirect environmental contamination. Further research should aim to identify the sources of these compounds, distinguishing between currently used and legacy herbicides, and to improve detection and quantification techniques in complex sludge matrices. Moreover, future studies should investigate the

effects of herbicides present in sewage sludge on plant health, microbial communities, and key soil functions. The overall knowledge of the occurrence and behaviour of herbicides in sewage sludge remains limited, and the current lack of systematic data represents a significant gap, making it difficult to fully assess the environmental and agricultural risks associated with sludge reuse. Addressing these knowledge gaps is crucial for ensuring the safe and sustainable management of biosolids in agricultural systems worldwide.

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