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#### Review

# The presence and fate of priority pollutant metals in animal manure: Legislation, impact and mitigation

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#### ABSTRACT

Animal manure is widely applied as an organic fertilizer to enhance soil fertility and reduce reliance on chemical fertilizers. Raw manure is applied directly to land, creating significant environmental and health risks from metals, which remain unregulated in manure application. This paper reviewed literature published between 2000 and 2024 to: (1) identify under-investigated metals (2) evaluate associated environmental and human health risks, and (3) assess the effectiveness of treatment technologies. A total of 188 peer-reviewed studies reporting metal concentrations in cattle, chicken, pig, and sheep manure were compiled into a dataset. Concentrations were standardized to mg kg-1, and statistical analysis was performed to evaluate differences across manure types and regions. Ecological risks were assessed using risk quotient (RQ) calculations based on Predicted No-Effect Concentration (PNEC). While Zn, Cu, and Pb have been extensively studied, metals including Hg, Tl, and Sb remain largely unexplored despite being classified as priority pollutants. The RQ of several metals, both major and under-investigated, exceed ecological safety thresholds, indicating high environmental risk. Conventional treatments reduce the toxicity of major metals including Zn, Cu, and Pb, but the behaviour of under-investigated metals such as Hg, Sb, and Tl is poorly understood. Many studies also lack proper quality assurance, including the incorporation of blanks and Certified Reference Materials (CRMs), limiting reliability. These findings highlight the need for focused research on under-investigated metals, rigorous quality control, and the development of regulatory guidelines and evidence-based application practices to mitigate environmental contamination and sustainable livestock manure management.

### 1. Introduction

The world population is projected to reach 9.7 billion people by 2050, with the greatest growth occurring in developing nations (United Nations, 2022). This will have a significant impact on food and water security, as the global food demand is estimated to increase for at least the next 50 years (Tripathi et al., 2019). Sustainable agricultural intensification is necessary to enhance food production without significantly expanding farming acreage (Helfenstein et al., 2020; Ickowitz et al., 2019). Several strategies, such as increased use of chemical fertilizers and pesticides, may satisfy the predicted worldwide food demand (FAO, 2022), but may have negative impacts on the environment including the emission of greenhouse gases (GHGs) (Liu et al., 2015), reduction of soil organic matter (Tripathi et al., 2020), acidification and

deterioration of soil quality (Cen et al., 2020), and further contamination of water resources (Srivastav, 2020). It is therefore necessary to adopt sustainable agricultural practices, such as the use of organic fertilizers, taking cognizance of the type and constituents of the fertilizers, to reduce the environmental impacts of the agricultural sector whilst meeting the food demand for a growing population (Gaffney et al., 2019; Möller & Schultheiß, 2015).

Organic fertilizers, derived from raw animal manure through composting or anaerobic digestion (AD), are rich in organic matter (Köninger et al., 2021). In recent years, global livestock manure production has surged to approximately 13 billion tons annually (Zhan et al., 2025), while in the European Union (EU)-27 and the UK alone, raw manure from cattle, chickens, and pigs reached around 1.4 billion tons per year between 2016 and 2019, of which 90 % was applied to soil

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(Köninger et al., 2021). The application of manure as an organic fertilizer improves plant growth and enhances microbial and enzyme activities in soil (McBride et al., 2020), increases the availability of nutrients (Shaji et al., 2021), improves soil health and structure (Rayne and Aula, 2020), and contributes to soil carbon sequestration (Huang et al., 2022). However, it may also introduce various pollutants such as metals, pathogens and antibiotics into the environment, and can also enhance nutrient runoff to the aquatic environment (Nolan et al., 2020; Venglovsky et al., 2018; Wang et al., 2017).

Essential trace metals, supplemented in animal feed, such as zinc (Zn), manganese (Mn), copper (Cu), cobalt (Co), selenium (Se), molybdenum (Mo) and iron (Fe), are necessary to maintain a number of physiological and biochemical processes in animals, plants and humans (Hejna et al., 2018). However, an excess of these essential metals, due to their excretion in animal manure and their application on agricultural land, can cause toxicity to plants and soil microbial communities (Gourlez et al., 2024). Indeed, the presence of other metals such as mercury (Hg), cadmium (Cd), arsenic (As) and lead (Pb), even at low concentrations, can also cause toxicity and adverse impacts on plants, soil, animal and human health, and are considered to be undesirable compounds in livestock feed (Tahir and Alkheraije, 2023). Previous studies quantified the presence of essential Zn, Cu, Mn and non-essential metals such as Pb and Cd in pig (Luan et al., 2021), cattle (Zhao et al., 2014), chicken (Sungur et al., 2016), and sheep manure (Zeng et al., 2018). However, few studies have reported the presence of other potentially toxic metals including Hg, Thallium (Tl) and Antimony (Sb). The presence of these metals may have environmental and human health implications. Mercury and Sb can inhibit plant growth by disrupting photosynthesis and inducing oxidative stress (Sapre et al., 2019; Vidya et al., 2022) and Tl induces leaf chlorosis and reduces plant growth (Chang et al., 2024). The presence of these metals in the human food chain can cause toxic effects as Hg affects the kidneys, nervous and cardiovascular systems (Kim et al., 2016), Sb has been linked to cancer (Lai et al., 2022), and Tl is a potential neurotoxin capable of crossing the placenta, causing premature birth (Fujihara and Nishimoto, 2024). These hazards highlight the need to examine their presence in agricultural systems. The management of animal manure, when used as an organic fertilizer, is therefore necessary in the context of sustainable agricultural practices and the prevention of the risk of build-up of metals in the soil. Although the quality and management of manure when used as composts are regulated by several directives such as the Nitrates Directive (EU, 1991) and the Fertilizing Products Directive (EU, 2019a), the metal content of raw animal manure (without any processing) when applied to agricultural land is not yet regulated under any EU directive (Köninger et al., 2021). While pyrolysis, anaerobic digestion, and composting can reduce the bioavailability of metals (Zhu et al., 2015; Meng et al., 2017), there are currently no means of completely removing metals from manure (Köninger et al., 2021). Therefore, it is important to quantify the concentration of metals in animal manure, as there is the potential for detrimental effects on environmental quality and human health (Provolo et al., 2018).

The aims of this paper are to: (1) identify under-investigated metals (Hg, Sb, Be, Se, Ag and TI), which are also classified as priority pollutants, in various types of manure; (2) examine the environmental and human health risks associated with raw manure and the deficiencies of the existing legislative framework, and (3) evaluate the efficacy of existing mitigation strategies.

## 2. Materials and methods

## 2.1. Data sources and screening

The literature search was conducted in Scopus using the keywords "manure" AND "metal" OR "heavy metal," restricted to peer-reviewed research articles published between 2000 and 2024, in English, with no geographical limitations. A schematic of methodology for the

literature search is presented in Fig. 1. A total of 2769 papers were identified. To refine the results, keywords were further limited in Scopus to "organic fertilizer", "trace metals", "chicken manure", "cattle manure", "pig manure", "swine manure", "slurry", "livestock manure", "fertilizer application", and "soil amendment", a total 1588 publications were identified, which were exported to Mendeley for further analysis. After reviewing the abstracts, 1400 papers were excluded as they did not report metals listed in the priority pollutant lists of the US EPA (2014) and Irish EPA (2011) in raw manure (Table S1). For legislative context, the EU Law Database (EUR-Lex) and the official website of the USDA were also consulted.

### 2.2. Data extraction and visualization

A secondary dataset was compiled based on peer-reviewed literature reporting metal concentrations in livestock manure. Publications from 2000 to 2024 were systematically screened, and data corresponding to four manure types (cattle, chicken, pig, and sheep) were extracted. For each manure-metal combination, the reported mean concentration and standard deviation (when available) were recorded. Under-investigated metals are defined as those reported in less than 50 studies, as shown in Fig. 2. Metals identified in this study as under-investigated were selected from those listed as priority pollutants by the U.S. EPA under the Clean Water Act (US EPA, 2014). Data on other metals, which are widely studied and common to both the U.S. and Irish EPA priority pollutant lists, as well as additional under-investigated metals identified from the Irish EPA list, are provided in the supplementary material (Sections S2 and S3). The concentrations of metals reported in the selected studies were expressed in mg kg<sup>-1</sup>. For studies that reported concentrations in alternative units, values were systematically converted to mg kg<sup>-1</sup> to ensure consistency and comparability across the dataset.

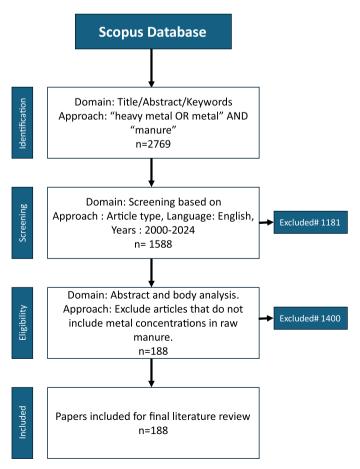
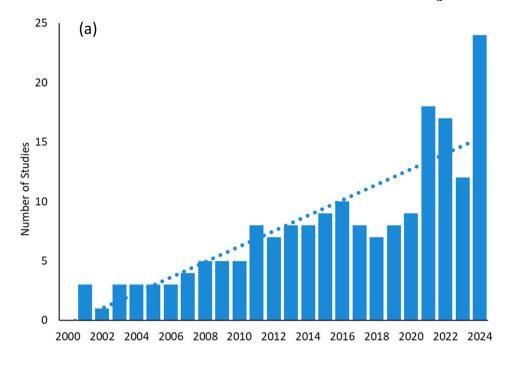


Fig. 1. Literature review strategy flowchart for metals in manure.



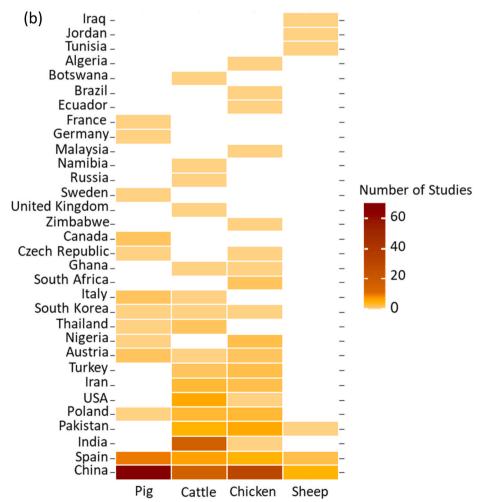


Fig. 2. (a) number of studies reporting metal content in raw manure from 2000 to 2024 (b) Geographical distribution of studies reporting metals in cattle, chicken, pig and sheep manure.

#### 2.3. Data processing and statistical analysis

Statistical analysis were conducted in R using non-parametric methods as data were not normally distributed. For each metal, Kruskal–Wallis rank-sum tests were performed to evaluate differences in mean concentrations among manure types, both across the full dataset and within each continent. Post-hoc pairwise comparisons were conducted using Wilcoxon rank-sum tests with Benjamini–Hochberg adjustment for multiple testing. A comparative analysis was not feasible due to the limited data available for under-investigated metals. Data visualization was performed using the ggplot2 package, producing faceted boxplots to illustrate the distribution of metal concentrations by manure type, metal, and continent.

#### 2.4. Risk Quotient (RQ) calculation

To assess the ecological risk of metals, the Risk Quotient (RQ) was calculated as the ratio of the measured or reported concentration of a given metal in manure (C) to its Predicted No-Effect Concentration (PNEC) using Eq.1.

$$RQ = \frac{C}{PNEC} \tag{1}$$

where C represents the mean concentration of the metal (mg kg $^{-1}$ ) obtained from the compiled dataset, and PNEC is the reference value derived from ecotoxicological thresholds reported in regulatory guidelines from European Chemicals Agency (ECHA, n.d.). The degree of ecological risk was classified based on the RQ values: RQ > 1 indicates high risk,  $0.1 < RQ \le 1$  indicates moderate risk, and RQ  $\le 0.1$  indicates low risk (Mohan and Balakrishnan, 2019).

### 3. Results and Discussion

### 3.1. Publication trends and quantitative analysis

The number of publications reporting the presence of metals in raw manure has increased since 2000 (Figure2a), which may be attributed to the increase in livestock units to meet the demand for food associated with the growing global population (Sheer et al., 2024). Approximately 20 % of studies reported using blanks and Certified Reference Materials (CRMs) for quality assurance. Approximately 70 % of the studies originated from Asia, followed by Europe (20 %), America (north and south) and Africa (Fig. 2b). No reports on metal content in manure have been

reported from Oceania (Australia, New Zealand etc.). In Asia, China has produced the largest number of studies, followed by India, Pakistan and Iran. Most of the studies in China have reported metal concentrations in pig manure, as it accounts for half of the global pig production (Bai et al., 2023). In the EU, most of the studies were from Spain (where most research were conducted on pigs, followed by cattle and sheep), Austria, Poland and Italy. Samples from Asia and Europe display broader distribution ranges and higher median values for several metals, suggesting regional differences in environmental management and regulatory frameworks, while samples from Africa and America show lower or more variable concentrations (Figure S1). Approximately 38 % of the studies have reported the presence of metals in pig manure, followed by cattle and chicken manure (Fig. 3). However, fewer studies have reported metal content in sheep manure. Zinc and Cu are the most frequently reported metals in animal manure, followed by Cd, Pb, Cr, Ni and As (Fig. 3). Zinc, Cu, and other essential nutrients such as Co and Fe are normally incorporated as supplementary nutrients in livestock feeds to enhance their health and production (Hejna et al., 2018). However, other metals such as As, Cd, Pb and Hg are also found in animal feed (Hejna et al., 2018). A comparative analysis of metal concentrations in livestock manure across four continents reveals distinct patterns influenced by species and regional agricultural practices. Chicken and pig manure consistently exhibit elevated levels of Zn and Cu, likely due to feed additives used as growth promoters and disease control agents in intensive farming systems (Hejna et al., 2018), whereas cattle and sheep manure generally show lower concentrations (Figure S2). Species-specific patterns in trace element correlations were observed. Copper and Zn showed significant associations between several species' pairs, indicating that their levels may be influenced by diet, metabolism, or shared environmental exposure. In contrast, other metals, including As, Pb, Ni, and Cr, were not significantly correlated across species pairs (Table S2). These results emphasize that trace element dynamics are both element- and species-specific, highlighting the need to consider individual metal behaviour when assessing livestock trace elements status.

## 3.2. Legislation governing metal content in manure

The application of raw manure to agricultural lands is a widespread practice, yet it raises concerns due to the presence of metals, which can accumulate in soils, transfer to crops, and enter the food chain. Effective legislation is critical to mitigate these risks and protect both environmental and human health. Different countries have established

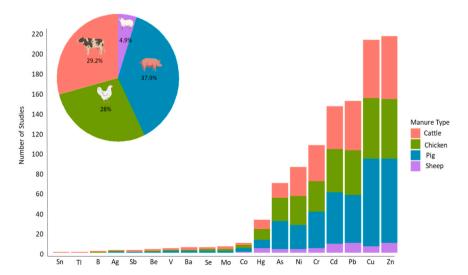


Fig. 3. Distribution of studies (2000–2024) by manure type and reported metals. The pie chart shows the proportion of manure types, and the stacked bar chart shows the number of studies over time by manure type. Studies analyzing multiple manure types are counted in each relevant category.

regulatory limits on metal content in organic fertilizers. However, these limits vary depending on national guidelines, reflecting diverse agricultural practices, environmental concerns, and regulatory frameworks (Table 1). For instance, in the United States, the application of raw manure is primarily regulated under the National Organic Program (NOP, 2018), and it can be applied to land if the crop is not intended to be used for human consumption or when applied for a minimum of 90–120 days prior to harvesting. However, there are no specific federal regulations addressing the permissible metal content in raw manure (NOP, 2018). Similarly, in the EU, raw manure is not directly regulated for metal content (Köninger et al., 2021), though it is classified as an organic fertilizer once processed through composting or AD (EU, 2019a). Despite this, only around 8 % is processed by methods such as composting, which leaves a considerable proportion of untreated manure (92 %) being applied directly to land (Lyngsø Foged, 2011). While limits on metals have been set for organic fertilizers in some countries including China (Table 1) (Luan et al., 2021), these regulations often do not extend to raw manure, leaving a significant regulatory gap. Raw manure can contain elevated concentrations of metals such as Cu, Zn, and Cd, which may accumulate in the environment over time and pose long-term risks. The need for comprehensive legislation governing the metal content in raw manure is increasing, particularly given that in the Shanxi region of China, more than 85 % of manure produced from livestock animals is directly applied to land without any prior treatment (Duan and Feng, 2021). In India, under the framework of the Fertilizer Control Act (FCO (FCO (Fertilizer Control Act, (1985)), the maximum permissible concentrations of metals in organic fertilizers are also specified. These legislations focus primarily on well-studied metals such as Zn, Cu, Pb, and Ni. However, they do not establish limit values for the under-investigated metals, except for Hg. To the best of our knowledge, there are currently no legally established limits for metal content in raw manure in the EU, USA, China, or India. Existing regulations and threshold values apply only to organic fertilizers. In the absence of specific legislation for raw manure, the thresholds established for organic fertilisers can provide a provisional reference for assessing potential environmental and human health impacts. This emphasizes the necessity to extend regulatory frameworks to explicitly address raw manure, including the establishment of metal concentration thresholds and recommended treatment or land application protocols.

### 3.3. Pathways of metal exposure in livestock animals

Livestock are exposed to metals through different pathways (Fig. 4). In animal production systems, feed supplementation is considered the primary route of metal exposure (Afzal and Mahreen, 2024), although industrial and municipal wastewater may introduce toxic metals into soil and water bodies (Afzal and Mahreen, 2024; ElSayed, 2018). The exposure of animals to metals is also linked with husbandry practices such as intensive and extensive production systems (Pšenková et al., 2020). Intensive production systems refer to the production of livestock under a controlled environment by providing nutrition via animal feed, water and the administration of veterinary products (Mpofu, 2020). In intensive systems, the complete (mixture of all dietary requirements) and concentrated feed provided to the animals depends on dietary

requirements, cost, and their availability in national and international markets (Afzal and Mahreen, 2024). Animal feed and feed materials may contain toxic substances such as Cd, Pb, As and Hg during feed processing (Adamse et al., 2017). Indeed, the concentration of these potentially toxic metals has been found to be higher than the permissible limits in animal feed (Table 2). In extensive production systems, the diet of the livestock animals are based on products grown by farmers and can be combined with concentrated feed to meet the animals' nutritional needs (López-Alonso, 2012). Animals are kept under extensive systems especially in Asia, Africa and South America, and are exposed to metals due to industrial activites and inadequate waste disposal techniques (Modernel et al., 2019; Otte et al., 2019). Due to the limited availability of forage during winter, animals are frequently forced to graze on contaminated land and are exposed to polluted water (Afzal and Mahreen, 2024). The use of contaminated water for irrigation and atmospheric deposition are also considered to be sources of metals in soil (Alengebawy et al., 2021). The ingestion of soil and the grazing on forage grown on contaminated soil are considered to be the main route of exposure in livestock animals in extensive farming systems (Collas et al., 2020). Previous studies have reported the presence of metals in different environmental sources of exposure such as water and forage (Table 2).

## 3.4. Presence of under-investigated metals in raw manure

Manure serves as an important source of nutrients and organic matter in agricultural soils, but it may also introduce potentially toxic metals into the environment. Zn, Cu, Pb, Ni, Cd, Cr, and As are among the priority metals of concern for public health because of their high toxicity (Kumar et al., 2021; US EPA, 2014). These metals have been extensively analyzed in previous studies across various types of manure (Section S2 and Table S3). Across all livestock types, Zn and Cu are the most prominent in terms of both concentration (Figure S1) and potential ecological impact, as their RQ is more than 1 for most of the studies examined (Section S2).

In addition to these widely studied metals, several underinvestigated metals including Hg, Sb, Be, Se, Ag, and Tl were identified from the list of priority pollutants under the U.S. Clean Water Act (US EPA, 2014). These metals were evaluated in raw pig, cattle, sheep, and chicken manure across multiple regions to assess their environmental risk (Table 3). In total, 12 under-investigated metals were identified in this study; of these, six are discussed in the main text because they are listed as priority pollutants by the U.S. EPA and exhibit higher toxicological relevance, while data for the remaining under-investigated metals (including those identified from the Irish EPA list) are presented in the Supplementary Information (S4).

#### 3.4.1. Mercury (Hg)

Mercury is considered one of the most hazardous metals due to its negative impact on the environment and has no known biological function in living organisms (Mitra et al., 2022). Various anthropogenic activities, as well as natural sources such as rock weathering and volcanic emissions, release Hg into the environment (Gworek et al., 2020), either as methyl Hg (MeHg) or in the inorganic form (HgCl<sub>2</sub>) (Raj and

**Table 1**The permissible limits of trace metals in organic fertilizers used for land application (mg kg<sup>-1</sup>).

Location				Metals					References
	Cu	Ni	Pb	Cd	Zn	Hg	As	Cr	
EU	300	50	120	2	800	1	40	2	EU (2019a)
China	85 <sup>a</sup>	_	50 <sup>b</sup>	$3^{\mathrm{b}}$	500 <sup>a</sup>	_	$30^{a}/50^{b}$	$150^{b}$	China (2010) <sup>a</sup> ; China (2012) <sup>b</sup>
USA	1500	420	300	39	2800	17	41	1200	US EPA (1994)
India	300	50	100	5	1000	0.15	10	50	FCO (1985)

<sup>&</sup>lt;sup>a</sup> From Technology Code for Land Application Rates of Livestock and Poultry Manure (GB/T 25246-2010, pH < 6.5 for vegetable land in China).

<sup>&</sup>lt;sup>b</sup> From organic fertilizer (NY 525–2012, China).

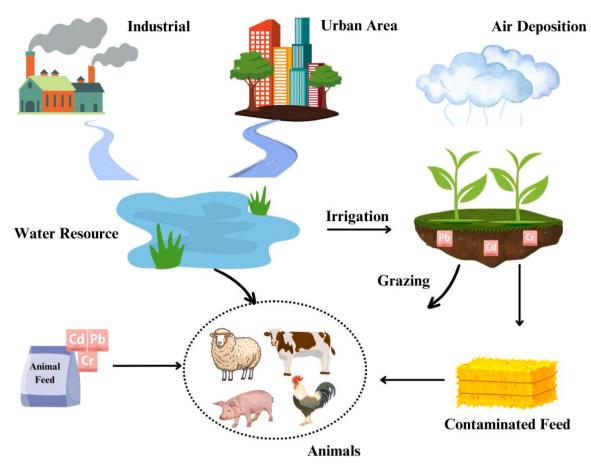


Fig. 4. Pathways of metal exposure in animals from various environmental sources.

Maiti, 2019). Due to its high toxicity potential and capability for bioaccumulation, there are concerns about its presence in agricultural ecosystems (Sánchez-Báscones et al., 2017). Fertilizer application is considered to be the primary source of Hg in agricultural soil (Wang et al., 2016). Although Hg is one of the least studied metals in manure, previous studies have reported Hg concentrations ranging from less than 0.1 mg kg<sup>-1</sup> in pig manure to 14.93 mg kg<sup>-1</sup> in chicken manure (Table 3). According to the European Chemicals Agency (ECHA), the PNEC of Hg in soil is 0.022 mg kg<sup>-1</sup> (ECHA, 2023a). Pig manure has been reported to contain Hg concentrations ranging from 0.1 to 4.6 mg kg<sup>-1</sup> (Moreno-Caselles et al., 2002; Wang et al., 2013), while cattle manure has higher Hg levels, ranging from less than 0.001 in India (Tripathi et al., 2004) to 7.5 mg kg<sup>-1</sup> in Pakistan (Irshad et al., 2013). Chicken manure shows similarly higher Hg levels, with values between  $0.02 \text{ mg kg}^{-1}$ in Turkey (Demirel et al., 2013) and up to 14.93 mg kg $^{-1}$ in China (Yu et al., 2021). In sheep manure, Hg levels were also higher than the PNEC, and concentrations were reported at  $0.04~\text{mg kg}^{-1}$  in Spain (Moreno-Caselles et al., 2002) to 10 mg kg<sup>-1</sup> in Pakistan (Irshad et al., 2013). The RQ from most of the previous studies is > 1, which indicates that the Hg poses a potential ecological or human health risk. The application of Hg-contaminated manure to agriculture soils can cause toxicity in the human food chain. The toxicity of Hg in plants can have a negative impact on different biological processes such as respiration, photosynthesis, and division of cells which inhibit plant growth (Sapre et al., 2019). The previous studies indicate that plants can easily uptake Hg from soil. However, the uptake efficacy depends on the chemical form of Hg present and its bioavailability in the soil (Qian et al., 2018). Under anaerobic conditions, microbial activities can convert the inorganic Hg into the highly toxic methylmercury (MeHg) form (Luo et al., 2023). In general, MeHg species are more readily absorbed by plant roots and translocated to shoots compared to

inorganic Hg (Qian et al., 2018). Mercury can pose significant risk to human health and including kidney damage, defects in central nervous system, cardiovascular disease and impotency (Kim et al., 2016).

## 3.4.2. Selenium (Se)

Selenium is an essential micronutrient for animal and human health; however, exposure to high levels can cause toxic impacts (Gupta and Gupta, 2017). The environmental fate of Se in agricultural soils depends on bioavailability and speciation which can be influenced by soil pH, organic matter, microbial activities and redox potential (Wang et al., 2022). Fertilizers and agrochemicals introduce Se to soils. However, due to the limited uptake capacity of plants, a significant proportion of Se accumulates in the soil, thereby contributing to soil contamination (Yue et al., 2021). Higher concentrations of Se in soil can cause toxicity in plants, primarily due to oxidative stress and the disruption of protein structure and function (Gupta and Gupta, 2017). Exposure to Se can cause cardiovascular problems, mental disengagement, inflammation of the skin and rashes in humans (Nancharaiah and Lens, 2015). Moreover, due to its high mobility, Se has significant leaching potential and can contaminate groundwater, (Comas et al., 2014; Zhai et al., 2019). Pig manure from Spain and Austria contained Se at levels between  $< 1~\mbox{mg kg}^{-1}$  and  $3.37~\mbox{mg kg}^{-1}$ , while cattle manure in Austria and the USA had concentrations up to 0.59 mg  $kg^{-1}$  and 3 mg  $kg^{-1}$  respectively. For chicken manure, Se ranged from 1.40 mg kg<sup>-1</sup> in Austria to  $3.46 \text{ mg kg}^{-1}$  in Ecuador (Table 3), exceeding the soil PNEC of 0.044 mg kg<sup>-1</sup> (ECHA, 2023b). Although there have been limited studies on Se levels in animal manure, the RQ of these studies is > 1, indicating a higher environmental risk. This implies that repeated manure applications may result in Se accumulation, leading to soil toxicity, groundwater contamination, and enhanced bioaccumulation in crops.

The concentration of metals in different feed materials and the permissible limits of undestrable substances in animal feed. Values are given in mg kg<sup>-1</sup> except water which is given in ug L<sup>-1</sup>.

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Animal type	Source					Metals				Location	Reference
		Cu	ij	Pb	po	Zu	Hg	As	Cr		
Sheep	Pasture	16.8	ı	10.41	0.14	62.1	0.28	6.03	1	Spain	Martinez-Morcillo et al. (2024)
Cattle	Forage	4 – 9	ı	209 - 899	$n.d.^{1} - 2$	14.7 - 202	ı	1	ı	Nigeria	Ogundiran et al. (2012)
Cattle	Forage	10.4 - 11.3	ı	ı	0.21 - 0.23	32 - 38	1	2	2.03 - 2.10	Pakistan	Khan et al. (2018)
Cattle	Water	3.4 - 11	ı	0.1 - 2	0.1 - 1.5	13.4 - 54	1	1	ı	Romania	Miclean et al. (2019)
Cattle	Forage	0.1 - 0.4	ı	0.01 - 0.05	0.003 - 0.01	2.4 - 4.3	ı	1	ı	Romania	Miclean et al. (2019)
Cattle & Sheep	Water	1	ı	ı	1	ı	ı	460 - 1880	1	Pakistan	Kazi et al. (2016)
Cattle & Goat	Fodder	0.02 - 25	0.1 - 0.4	0.04 - 5	0.03 - 2	ı	ı	1	0.01 - 8	Pakistan	Iqbal et al. (2021)
Sheep	Forage	1	ı	ı	1	2 - 7	ı	1	1	Pakistan	Ge et al. (2022)
Pig	Complete feed	1	1.5	0.2	0.09	120	ı	1	3	China	López-Alonso et al. (2012)
Pig	Complete feed	n.d. – 392	ı	0.6 - 63	n.d. – 5	16 - 2042	n.d. – 310	n.d. – 17	1 - 200	China	Wang et al. (2013)
Pig	Complete feed	2.3 - 1137	ı	I	n.d. – 32	37 – 598	ı	0.02 - 13	n.d. – 12	China	Zhang et al. (2012a)
Pig & Chicken	Complete feed	1	ı	I	1	ı	ı	0.1 - 68	ı	China	Yao et al. (2013)
Chicken	Complete feed	0.06 - 140	n.d. – 12	n.d. – 4	n.d. – 0.1	0.1 - 121	ı	n.d. – 19	n.d. – 38	China	Hu et al. (2018)
Chicken	Complete feed	4 - 199	ı	0.3 - 35	0.1 - 4	6 - 296	n.d. – 65	n.d. – 6	0.4 - 533	China	Wang et al. (2013)
Chicken	Complete feed	2.8 - 98	ı	ı	n.d. – 8	52 - 151	ı	0.02 - 6	n.d. – 936	China	Zhang et al. (2012a)
Threshold level in complete animal feed		ı	ı	2	0.5	ı	0.1	2	ı	EU	EU (2019b)
		I	ı	ı	≤ 1.25	I	$\leq 0.1$	4	> 2	China	Tao et al. (2020)
MAC-EQS **		1	20	7.2	≤ 0.45	I	0.02	ı	ı	EU	EU (2008a)
Inland surface waters ( $\mu g L^{-1}$ )											

°n.d. is not detected \*\* MAC-EQS is maximum allowable concentration of environmental quality standards

#### 3.4.3. Beryllium (Be)

Beryllium is considered a carcinogenic compound and is widely used for scientific and industrial applications such as nuclear power electronics and missile defense systems (Islam et al., 2022). In soils and sediments, naturally occurring Be concentrations usually vary from 0.1 to 100 mg kg<sup>-1</sup> (Bolan et al., 2023). Humans can be exposed to Be through the inhalation of Be-contaminated air, food and drinking water (Bolan et al., 2023). Exposure to higher concentration of Be in plants can impair growth by reducing seed germination and the uptake of essential nutrients (Tanveer and Wang, 2019). The consumption of Be-contaminated food can lead to the development lymphocyte-mediated hypersensitivity, which may cause lung disease (Bolan et al., 2023; Yi et al., 2021). In the present dataset, Be concentrations were reported only for Austria and the USA, where its levels in pig, cattle, and chicken manure ranged from 0.16 < 0.18 mg kg<sup>-1</sup> (Table 3). These limited findings suggest that Be has not been widely investigated in the context of animal manure, compared to more prevalent metals such as Pb or Cd. Furthermore, since no soil PNEC has been established for Be, RQ calculations could not be performed, highlighting the need for additional toxicological and ecological studies.

## 3.4.4. Antimony (Sb)

Antimony is a non-essential metalloid and has the potential to cause cancer (Tao et al., 2021a). The concentrations of Sb in soil and the aquatic environment are increasing due to both natural and anthropogenic activities such as coal combustion (Tang et al., 2023). Antimony can be present in different oxidation states such as (-III, 0, +III, and +V) and it has been found in different environmental media such as water and soil (Tao et al., 2021a). The long term toxicity of Sb to soil microorganisms and plants is species-dependent, increasing in the order: methylated Sb < Sb(V) < Sb(III), with Sb(III) being the most toxic form (Vidya et al., 2022). Exposure to higher concentrations of Sb can reduce seed germination and inhibit plant growth due to oxidative damage and disruption of the photosynthetic process (Vidya et al., 2022). Humans can be exposed to Sb from crops grown on Sb-contaminated soil (Tang et al., 2022), and exposure to elevated concentrations of Sb can cause cancer in humans due to the disruption of signaling pathways (Lai et al., 2022). Only a limited number of studies have quantified Sb in livestock manure. Reported concentrations ranged from 0.21 mg kg<sup>-1</sup> in pig manure from Canada (Kumaragamage et al., 2016) to 0.25 mg kg<sup>-1</sup> and 0.84 mg kg<sup>-1</sup> in cattle manure from the USA and Botswana, respectively (Ultra et al., 2022; McBride and Spiers, 2001) (Table 3). These values are well below the soil PNEC of 37 mg kg<sup>-1</sup> (ECHA, 2023c), and the corresponding RQ values are < 0.1, suggesting a low likelihood of ecological risk. However, given the scarcity of data, the long-term contribution of manure-derived Sb to soil accumulation remains uncertain and requires further investigation.

## 3.4.5. Silver (Ag)

Silver is used in a variety of commercial and industrial products such as medical devices, conductors, iron and steel production and also arises from the combustion of coal (Padhye et al., 2023), ending up in both terrestrial and aquatic ecosystems (VandeVoort and Arai, 2012). In addition to Hg and Cd, Ag is ranked as one of the most potentially hazardous metals (Ratte, 1999). In recent years, Ag-based nanoparticles (NPs) have been widely used in different industrial activities such as food storage vessels, soaps and disinfectants due to their antibacterial properties (McGillicuddy et al., 2017; Shoults-Wilson et al., 2011). AgNPs are primarily found in wastewater treatment facilities, where the majority adhere to sewage sludge and find their way into soil through the application of biosolids on agricultural land (Shoults-Wilson et al., 2011). The accumulation of Ag in soil can decrease biodiversity and microbial biomass, which ultimately deteriorates soil quality (Natalia et al., 2024). Exposure to high concentrations of Ag or Ag NPs can cause toxicity in plants including reduced root length and oxidative stress (Cvjetko et al., 2017). The exposure of Ag to humans via the food chain

**Table 3** The concentration of different trace metals found in manure. All the values are given in mg kg $^{-1}$ .

Manure Type	Metals						Location	Reference
	Hg	Tl	Ве	Sb	Se	Ag		
Pig	0.173 ± 0.01**	_	_	_	_	_	China	Sha et al. (2023)
	0.036**	_	_	_	_	_	China	Peng et al. (2022)
	0.12**	_	_	_	_	$0.80\pm0.07^{\star}$	China	Xue et al. (2021)
	$0.061 \pm 0.002 ^{**}$	_	_	_	< 1.0**	_	Spain	Arias et al. (2017)
	_	_	_	0.21 (0.03)	_	_	Canada	Kumaragamage et al. (2016)
	$n.d.^{a} - 0.31**$	_	_	_	_	_	China	Wang et al. (2013)
	< 0.01- 0.11**	_	_	_	_	_	Germany	Hölzel et al. (2012)
	0.4**	_	_	_	_	_	China	Ji et al. (2012)
	_	_	0.16	_	3.37**	_	Austria	Sager (2007)
	0.1-4.6**	_	_	_	_	_	Spain	Moreno-Caselles et al. (2002)
Cattle	$0.0084 \pm 0.0010 ^{\ast}$	_	_	_	_	_	Russia	Lukin (2024)
	0.03**	_	_	_	_	_	China	Zhang et al. (2022)
	0.044**	_	_	_	_	_	China	Peng et al. (2022)
	_	_	_	$\textbf{0.84} \pm \textbf{0.21}$	_	_	Botswana	Ultra et al. (2022)
	7.5**	_	_	_	_	_	Pakistan	Irshad et al. (2013)
	0.3213**	_	_	_	_	_	China	Ji et al. (2012)
	_	_	0.16	_	0.59**	_	Austria	Sager (2007)
	< 0.001	_	_	_	_	_	India	Tripathi et al. (2004)
	0.2 - 5.1**	_	_	_	_	_	Spain	Moreno-Caselles et al. (2002)
	0.02*	< 0.1	< 0.18	0.25	3**	< 0.1	USA	McBride and Spiers (2001)
Chicken	$0.156 \pm 0.04**$	_	_	_	_	_	China	Sha et al. (2023)
	0.04**	_	_	_	_	_	China	Zhang et al. (2022)
	0.035**	_	_	_	_	_	China	Peng et al. (2022)
	0.06**	_	_	_	_	1.40*	China	Xue et al. (2021)
	14.93**	_	_	_	_	_	China	Yu et al. (2021)
	< 0.05**	_	_	_	3.46**	_	Ecuador	Gavilanes-Terán et al. (2016)
	n.d 0.065**	_	_	_	_	_	China	Wang et al. (2013)
	9**	_	_	_	_	_	Pakistan	Irshad et al. (2013)
	0.02*	_	_	_	_	_	Turkey	Demirel et al. (2013)
	0.2727**	_	_	_	_	_	China	Ji et al. (2012)
	_	_	0.17	_	1.4**	_	Austria	Sager (2007)
	0.5-6.5**	_	_	_	_	_	Spain	Moreno-Caselles et al. (2002)
Sheep	0.84**	_	_	_	_	_	China	Li et al. (2024)
•	0.051**	_	_	_	_	_	China	(Peng et al., 2022)
	$0.33 \pm 0.01**$	_	_	_	_	_	China	Ma et al. (2020b)
	10**	_	_	_	_	_	Pakistan	Irshad et al. (2013)
	0.4-0.7**	_	_	_	_	_	Spain	(Moreno-Caselles et al., 2002)
Predicted no-effect concentration (PNEC) in Soil	0.022	_	_	37	0.044	1.41	EU	European Chemicals Agency ECHA (n.d.)

<sup>(</sup>a)n.d. (not detected).

has several research gaps, including its mobility from organic-amended crops and its potential toxicological effects (Padhye et al., 2023). However, in-vitro studies have demonstrated that Ag NPs can exert toxic effects on human hepatoma cell lines, leading to genotoxic effects such as DNA damage and chromosomal abnormalities (Wang et al., 2019a). In terms of livestock manure, Ag concentrations have been reported at  $0.80~\rm mg~kg^{-1}$  in pig manure from China. Cattle and chicken manure contained  $< 0.1~\rm mg~kg^{-1}$  in the USA and  $1.40~\rm mg~kg^{-1}$  in China, respectively (Table 3), while no data are available for sheep manure. Although these values are below the soil PNEC of  $1.41~\rm mg~kg^{-1}$  (ECHA, 2023d), the calculated RQ indicates a moderate risk, suggesting potential ecological impacts, particularly under repeated manure applications.

## 3.4.6. Thallium (Tl)

Thallium is a rare transition metal with high toxicity levels similar to those of Pb and Hg (Liu et al., 2024), and is known as emerging soil contaminant (Liu., et al. 2021). The natural occurrence of Tl in the environment is generally low; however, it can be introduced through various human activities such as cement production, coal combustion, and mining activities (Xiao et al., 2024). In soils, Tl is largely immobilized through binding to the soil matrix; however, soluble Tl salts can leach into groundwater or surface waters, increasing the risk of chronic exposure (Karbowska, 2016). Elevated concentrations of Tl from topsoil layers can be absorbed by plants and the exposure of Tl in plants can

inhibit growth, induce oxidative stress and cause chlorosis on leaves, thus entering into the food chain (Chang et al., 2024; Karbowska, 2016). Humans are primarily exposed to Tl through the consumption of crops grown on contaminated soils (Ma et al., 2020a). Thallium is a highly toxic element that predominantly targets the central nervous system, causing visual impairments (ranging from partial to complete blindness), hair loss, and, in severe cases, death (Xiao et al., 2004). Thallium is the least studied metal in livestock manure, with only a single report available: cattle manure from the USA contained < 0.1 mg kg<sup>-1</sup> of Tl (Table 3). Due to the extremely limited data and the absence of an established soil PNEC, RQ calculations could not be performed. Consequently, the toxicity and long-term ecological impact of Tl through manure application remain poorly understood. Given its high environmental toxicity and potential for bioaccumulation, this highlights an urgent need for further research to better assess Tl concentrations in manure, its fate in agricultural soils, and its possible entry into the food chain.

## 3.5. Mitigation strategies

The management and treatment of animal manure is necessary prior to its application as an organic fertilizer on agricultural land in order to mitigate the potential impact of metals in the environment (Kumar et al., 2013). Currently, three main techniques are commonly used for manure

<sup>\* = 1 &</sup>gt; RQ > 0.1 - moderate risk

<sup>\*\* =</sup>RQ > 1 - high risk; Blank cells indicate samples that were not analyzed or have a Risk Quotient (RQ) < 0.1.

treatment: pyrolysis, AD, and composting (Table 4).

## 3.5.1. Pyrolysis

The term "pyrolysis" refers to the thermal decomposition of organic materials at temperatures ranging from 250 to 1200°C, where the organic matter is converted into three main products: syngas, bio-oil, and biochar (Tayibi et al., 2021). The gas produced from pyrolysis can serve as an energy source due to its high calorific content, which can be converted into heat or electricity (Seyedi et al., 2019). Additionally, the liquid phase can be separated into the non-aqueous (bio-oil) and aqueous phases (APL). Bio-oil can replace diesel in internal combustion engines to generate power (Manara and Zabaniotou, 2012). Biochar derived from animal manure through pyrolysis is commonly used to improve soil fertility (Su et al., 2022). During the pyrolysis process, the total concentration of metals in the biochar increases compared to the raw manure due to the degradation of volatile materials and the breakdown of organic matter (Tian et al., 2019a). However, the bioavailability or mobilization of metals decreases in the biochar derived from the manure (Zeng et al., 2018; Zhang et al., 2020). The chemical fractionation of metals in biochar plays an important role in evaluating their toxicological impact on the environment. These fractions are available in the following order: exchangeable fraction (F1) > reducible fraction (F2) > oxidizable fraction (F3) > residual fraction (F4), with F1 and F2 considered bioavailable, as plants can absorb them (Li et al., 2021), whereas F3 and F4 are regarded as stable fractions (Tian et al., 2019a).

The temperature of pyrolysis is crucial as it can impact on the properties of the resulting biochar, and these chemical fractionations of metals are influenced by an increase in temperature (Dai et al., 2014; Zhang et al., 2020). A study by Zeng et al. (2018) found a reduction in the F1 +F2 fractions for Cd, Zn, Pb, Mn, Ni, Cu, and Cr at 800°C in both pig and goat manure, while the leachable concentrations of these metals significantly decreased. However, leachability of Mn increased by  $11\ \%$ in pig manure but decreased by 19 % in goat manure. Additionally, the F4 fraction increased due to the formation of stable minerals from metal ions and phosphate (Zeng et al., 2018). In addition to a reduction in the bioavailability of metals, Tian et al. (2019a) observed a decrease in the total concentration of Cd in pig and chicken manure during both lab and pilot-scale studies. Reduction was attributed to Cd existing as a carbonate, which likely volatilized at higher temperatures during the pyrolysis process. The physicochemical characteristics of biochar, such as its carbon content, pH, and mineral component, may be enhanced by copyrolysis of various biomass feedstocks and could enhance the effectiveness of the pyrolysis technique to mitigate metal pollution due to the dilution effect of the additive (Su et al., 2022). The pyrolysis technique for manure treatment offers both benefits and drawbacks. Its advantages include economic and environmental benefits, pathogen elimination and high efficiency. However, it also requires a substantial energy input, high capital and operational costs, and advanced training. Notably, pyrolysis is a relatively quick process (Su et al., 2022).

## 3.5.2. Anaerobic Digestion

Anaerobic digestion is widely used worldwide to reduce organic waste pollution, and it can also produce clean energy as a substitute for fossil fuels (Li et al., 2020). Anaerobic digestion uses microorganisms in anaerobic conditions to break down organic matter from manure, involving a series of sequential processes, including hydrolysis, acidogenesis, acetogenesis, and methanogenesis (Ma et al., 2019). Similar to pyrolysis, the total concentration of metals in the digestates increases compared to the initial concentration in the manure (Legros et al., 2017). However, the mobility and bioavailability of metals such as Zn and Cu decrease in the digestates compared to the raw manure (Legros et al., 2017). The presence of metals at higher concentrations in manure may negatively impact the AD process by inhibiting the activity of microorganisms (Tao et al., 2021b). Moreover, temperature plays a crucial role in the efficiency of the AD process for metal removal, with

thermophilic conditions proving more effective in mitigating the impact of metals (Tian et al., 2019b). Wang et al. (2021a) found that the addition of biochar in the AD of pig manure slightly increased the ecological risk of Cu, Zn, and Cd, with the digestate classified as moderate risk. Similarly, co-digestion of chicken manure and corn stover showed increased toxicity for most metals, but all digestates were classified as low ecological risk, posing minimal environmental threat (Yan et al., 2018). Zhu et al. (2015) applied an electrokinetic process to pig manure digestate, significantly reducing the total concentration and the toxicity of Zn and Cu in the digestate. In contrast to pyrolysis, anaerobic digestion is highly effective in mitigating GHG emissions and reducing odours. However, the process can also result in the emission of toxic gases, such as NH3 and H2S as well as the generation of wastewater, and it requires specialized training for plant operators and has a longer processing time, often taking several weeks to months (Su et al., 2022). The anaerobic digestion of animal manure is often less efficient than co-digestion due to the specific characteristics of manure. It typically contains a high proportion of large fibrous particles, which can potentially cause clogging in the system (Jasińska et al., 2023). Therefore, integrated treatment of several waste types will be more cost-effective and will improve the efficiency of the digestion process (Wang et al., 2012). The capital investment required for AD systems is significantly lower than that of thermal treatment plants, and statistical projections indicate that by 2050, costs will decrease by approximately 40 % compared to 2015 levels (Zheng et al., 2022).

## 3.5.3. Composting

The biological process of composting involves the use of microbes, fungi, and bacteria to facilitate the conversion of biodegradable organic matter into stable humus under specific controlled conditions (Dong et al., 2022). Composting has been demonstrated to be an efficient and cost-effective method for immobilizing metals in manure (Wang et al., 2019b). Composting transforms organic matter into stable humic substances through humification, where dissolved organic matter (DOM), rich in functional groups like carboxyl and hydroxyl binds metals via complexation, adsorption, and redox reactions, effectively reducing their mobility and bioavailability (Wu et al., 2023). Previous studies have found that composting can alter the speciation and concentration of metals in raw manure (Table 4), and the efficiency of composting can be influenced by factors such as duration, amendments, and temperature (Ejileugha et al., 2023). During composting, microbial activity and humus formation play a central role in reducing metal mobility and bioavailability (Guo et al., 2022). Metals can be directly immobilized through biosorption (Tang et al., 2019), while indirect immobilization occurs via humus formation, reducing their mobility and bioavailability (Wu et al., 2017). Moreover, the initial concentration of metals varies between different types of manure, which can significantly impact the efficiency of composting to remove metals (Gul et al., 2015). The biochemical processes during composting play a vital role in metal immobilization and can be influenced by moisture content, aeration rate, and the carbon-to-nitrogen (C/N) ratio (Shen et al., 2016; Wu et al., 2017). Due to the low C/N ratio, high moisture content, and high density of animal manure, various bulking agents, such as straw and cotton ball waste, are incorporated during the composting process to enhance physical and chemical properties (Chen et al., 2022; Petric et al., 2009). Composting swine manure with an initial C/N ratio of 20:1 or 25:1, combined with the addition of straw as a bulking agent, reduces the bioavailability of Cd, Cr, and As (Guo et al., 2020). Similarly, adding attapulgite-activated carbon composite (AACC) during the composting process enhances the immobilization of Cu, Zn, and As through metal precipitation and surface adsorption (Lin et al., 2021). In contrast, the addition of boron waste and phosphate rock as additives during the co-composting of pig manure and rice straw slightly increases the mobile fraction of Zn. However, it reduces the toxicity associated with Cu speciation (Wang et al., 2021b). Additionally, vermicomposting, the addition of earthworms in manure, significantly reduces the toxic

 Table 4

 Treatment techniques for metals from livestock manure.

Animal manure	Temperature	Additive	Time	Total co	oncentratio	on increase	e (+) /dec	ease (-) %	1			Toxicological information <sup>3</sup>	References
				Zn	Cu	Pb	Cd	Cr	Ni A	ıs	Hg		
Pyrolysis Pig	200 - 800 °C	NA <sup>2</sup>	1 h	+ 112	+ 117	+ 110	+ 111	+ 145	+ 117	-	-	The toxic fractions decreased approximately by 88 % for Cd, 74 % for Zn, 67 % for Pb, 65 % for Mn, 56 % for Ni,	Zeng et al. (2018)
Pig	300 −700 °C	NA	1 h	+ 129	+ 123	-	-	-	-	-	-	94 % for Cu, and 83 % for Cr.  The toxic fractions decreased by approximately 55 % for both Zn and Cu. Moreover, the leachable concentrations were also reduced by 98 % for Cu and 70 % for Zn.	Lee et al. (2024)
Pig	300 –700 °C Lab scale	NA	45 min	+ 71	+ 82	-	-32	+ 177	+ 173	+ 89	-	The leaching concentrations decreased by 36 % for Zn, 62 % for Cu, 71 % for Ni, and 88 % for As, along with a reduction in their toxic fractions.	Tian et al. (2019a)
Pig	$600 \pm 50~^{\circ}\text{C}$ Pilot scale	NA	45 min	+ 72	+ 94	-	-17	+ 179	+ 153	+ 95	-	The leaching concentrations were reduced by 38 % for Zn, 59 % for Cu, 71 % for Ni, and 88 % for As.	Tian et al. (2019a)
Chicken	300 −700 °C Lab scale	NA	45 min	+ 14	+ 113	+ 53	- 66	+ 174	+ 80	+ 57	-	The leaching concentrations decreased by 98 % for Zn, 97 % for Cu, 81 % for Ni, and 50 % for As.	Tian et al. (2019a)
Chicken	$600 \pm 50~^{\circ}\text{C}$ Pilot scale	NA	45 min	+ 29	+ 111	+ 62	-18	+ 133	+ 74	+ 67	-	The leaching concentrations were reduced by 97 % for Zn, 98 % for Cu, 81 % for Ni, and 50 % for As.	Tian et al. (2019a)
Sheep	200 –800 °C	NA	1 h	+ 132	+ 142	+ 94	+ 116	+ 148	+ 116	-	-	The toxic fractions decreased approximately by 99 % for Cd, 85 % for Zn, 82 % for Pb, 75 % for Mn, 63 % for Ni, 99 % for Cu, and 86 % for Cr. Leachability decreased for all elements	Zeng et al. (2018)
Anaerobic Digestion Pig	37 °C	NA	15d	+ 52	+ 19	-	_	-	_	-	-	Toxic fractions were reduced by 68 % for Zn and 8 % for Cu, while increasing the stable fraction.	Legros et al (2017)
Pig digested	NA	Ricestraw+Electrokinetic	NA	-81	-68	-	-	-	-	-	-	The stable fraction increased significantly, while the toxic fractions decreased by 93 % for Zn and 92 % for Cu.	Zhu et al. (2015)
Pig	$25\pm1~^{\circ}\text{C}$	Biochar	90d	+ 10	+ 12	+ 12	+ 22	+ 23	+ 4	+ 12	-	5 % biochar was most effective for passivating As and Ni, while 7 % biochar was most effective for Cd, Cr, and Zn. Despite a slight increase in ecological risk, the digestates remained at moderate risk.	Wang et al. (2021a)
Cattle	37 °C	NA	28d	+ 30	+ 41	-	-	-	+ 53	-	-	NA	Qi et al. (2018)
Cattle	55 °C	NA	18d	+ 16	+ 38	-	-	-	+ 35	-	-	NA	Qi et al. (2018)
Chicken	$37\pm0.2^{\circ}\text{C}$	Corn stover ratio (3:1)	NA	+ 13	+ 42	+ 31	+ 36	+ 27	+ 19	+ 20	-	Toxic fractions increased by 99 % for Cr, 114 % for Pb, 50 % for Cd, 150 % for As, 87 % for Ni, 150 % for Cu, and 68 % for Zn. However, Cu, As, and Cr were mostly found in their stable fractions and the digestate was classified as low ecological risk.	Yan et al. (2018)
Chicken	$55\pm0.4^{\circ}\text{C}$	Corn stover ratio (3:1)	NA	+ 33	+ 48	+ 34	+ 45	+ 23	+ 14	+ 15	-	Toxic fractions increased by 50 % for Cr, 242 % for Pb, 55 % for Cd, 99 % for As, 82 % for Ni, 125 % for Cu, and 60 % for Zn. However, Cu, As, and Cr were mostly found in their stable fractions and the digestate was classified as low ecological risk.	Yan et al. (2018)
Chicken	$37 \pm 0.2^{\circ}\text{C}$	Corn stover ratio (1:1)	NA	+ 57	+ 55	+ 42	+ 43	+ 29	+ 23	+ 21	-	Toxic fractions increased by 39 % for Cr, 185 % for Pb, 58 % for Cd, 99 % for As, 67 % for Ni, 50 % for Cu, and 85 % for Zn. However, Cu, As, and Cr were primarily present in their stable fractions, and the digestate was classified as posing low ecological risk.	Yan et al. (2018)
Chicken	55 $\pm$ 0.4 °C	Corn stover ratio (1:1)	NA	+ 35	+ 40	+ 32	+ 35	+ 21	+ 15	+ 17	-	Toxic fractions increased by 28 % for Cr, 257 % for Pb, 42 % for Cd, 99 % for As, 55 % for Ni, 41 % for Cu, and 45 % for Zn. However, Cu, As, and Cr were mostly found in	Yan et al. (2018)

(continued on next page)

Table 4 (continued)													
Animal manure	Temperature Additive	Additive	Time	Total cor	ncentratior	ı increase	(+) /decre	Total concentration increase (+) /decrease (-) $\%^1$				Toxicological information <sup>3</sup>	References
				Zn	Cu	Pb	po	Cr	Ni As		Hg		
												their stable fractions and the digestate was classified as low ecological risk.	
Composting Pig	$23\pm1~^{\circ}C$	Earthworms (E. fetida)	P06	+ 16	+ 25	+ 12	ı	+ 51	1	1	ı	The F1 fraction increased by 38 % for Zn, while the stable fractions increased for Zn, Cu, Pb, and Cr. Moreover, their	Lv et al. (2016)
Pig	NA	Rice straw, Boron waste	49d	+ 105	+ 57	ı	I	ı	I	ı	ı	mobility fractions were also reduced.  The bioavailable fractions decreased by approximately 42 % for Cu and 2 % for Zu	Wang et al. (2021b)
Pig	NA	${\bf Rice\ straw+Phosphate} \\ {\bf rock} \\$	49d	<b>88</b> +	99 +	I	ı	ı	1	ı	ı	The bioavailable fractions decreased by 48 % for Cu and 0.7 % for Zn with 7.5 % phosphate rock, while BF	Wang et al. (2021b)
Chicken	NA	Rice husk powder, 1 % calcium superphosphate,	21d	+ 17	+ 26	+ 25	+ 40	+ 80		+ 43 + 100	+ 100	increased for Zn with 2.5 % and 5 % phosphate rock. The exchangeable fractions of As, Cd and Hg reduced by 20 %, 89 % and 78 % respectively	Yu et al. (2021)
Cattle	$23\pm1~^{\circ}\text{C}$	termentation bacteria Earthworms ( <i>E. fetida</i> )	p06	+	+ 22	+ 21	ı	+ 48	1	1	1	The toxic fractions of Zn, Cu, Pb, and Cr have decreased, along with their mobility fractions	Lv et al. (2016)

are considered bioavailable or toxic fractions, while the oxidizable fraction (F3) and residual fraction (F4) are regarded as stable fractions. Toxicity information is calculated based on the concentrations or percentages of Percentages are calculated based on their mg/kg values 2NA means not available 3 The toxicity of metals depends on the proportions of different metal fractions. The exchangeable fraction (F1) and reducible fraction (F2) hese fractions present in the studies

fraction of metals while increasing their stable fraction, thereby reducing their overall availability and improving the quality of the compost (Lv et al., 2016). Composting is a simple and low-cost method for managing animal manure, requiring minimal technological input and operating expenses. In many developed countries (Awasthi et al., 2022), it is considered as sustainable solution to recycle nutrients and eliminate the negative impact of direct application of manure (Zheng et al., 2022). However, it is time-intensive, requires significant land, and can also result in nutrient loss and the release of toxic gases (Su et al., 2022). The application of these treatment techniques increases the overall concentration of metals in the final product; however, the toxicity of most major metals such as Zn, Cu and Ni decreases in the treated material. While pyrolysis offers potential for energy recovery, composting remains the most accessible and cost-effective option, and AD provides a balance between waste stabilization and energy production. The scalability of these technologies depends on various factors, including capital costs, energy requirements, and processing time. Nevertheless, the effectiveness of these techniques in mitigating the toxicity of lesser-studied metals, such as Hg, Se, Sb, and V, remains uncertain. Furthermore, integrated treatment approaches, such as combining AD with pyrolysis, should be further explored to evaluate their energy, economic, and environmental potential (Castells et al., 2024).

## 4. Conclusions

This review highlights under-investigated metals, including Hg, Se, Be, Sb, Ag and Tl, which are present in varying concentrations across different types of livestock manure. Mercury and Se present the highest ecological risks due to concentrations exceeding the PNECs, whereas other metals like Sb, Ag, and Tl show lower, but undefined, risks due to limited data. Moreover, RQ calculations indicate that not only these lesser-studied metals, but also commonly monitored metals such as Zn, Cu and As, exceed safe thresholds (RQ > 1), highlighting their potential for environmental harm. This indicates that both widely studied and emerging trace metals can accumulate in soils and enter the food chain, creating long-term ecological and human health concerns.

The current legislative framework governing raw manure is insufficient, with most regulations focusing on treated manure and routinely-monitored metals such as Zn, Cu, Pb and Cd. Raw manure, which constitutes the majority of land-applied manure, lacks specific regulations regarding metal content, which can create potential long-term environmental and human health hazards.

Manure management strategies such as pyrolysis, anaerobic digestion, and composting can reduce the bioavailability and toxicity of metal (Zn, Cu, As, etc.), though each approach has advantages and limitations in terms of efficiency, cost and scalability, and their effectiveness in mitigating lesser-studied metals remains largely unknown. This knowledge gap emphasizes the need for targeted research to understand and reduce the risks associated with these emerging contaminants. To mitigate environmental and health risks, regulatory frameworks should be expanded to explicitly address raw manure, including the establishment of maximum allowable concentrations for both well-studied and under-investigated metals. Development of evidence-based application guidelines that consider metal content, soil characteristics, and crop types is recommended to support sustainable manure applications. In addition, future studies should ensure quality assurance in analytical approaches for metal determination, using blanks and CRMs, to improve data reliability and comparability across studies, which will strengthen risk assessments and guide effective management strategies.

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#### CRediT authorship contribution statement

S. Farid: Writing - original draft, Methodology, Data extraction, Formal analysis. M. Healy: Writing - review and editing, Supervision, Project administration, Funding acquisition, Conceptualization. M. Danaher: Writing - review and editing, Funding acquisition. O.Fenton: Writing - review and editing, Funding acquisition. L. Morrison: Writing - review and editing, Supervision, Project administration, Funding acquisition, Conceptualization.

## **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.ecoenv.2025.119211.

## Data availability

Data will be made available on request.

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