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Cumulative Health Effects of Metal(loids) through Aggregate Environmental Pathways

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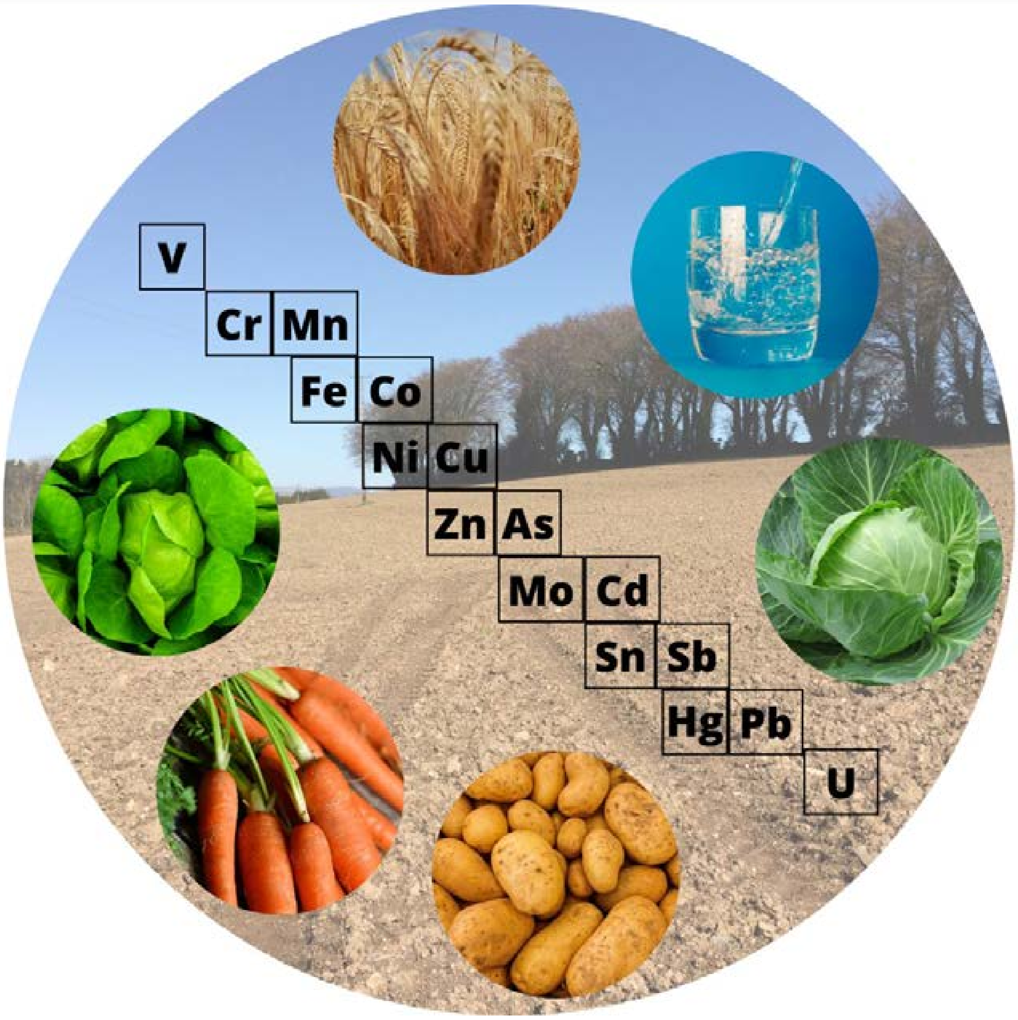

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Rialtas na hÉireann
Government of Ireland

ENVIRONMENTAL PROTECTION AGENCY

The Environmental Protection Agency (EPA) is responsible for protecting and improving the environment as a valuable asset for the people of Ireland. We are committed to protecting people and the environment from the harmful effects of radiation and pollution.

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- intensive agriculture *(e.g. pigs, poultry)*;
- the contained use and controlled release of Genetically Modified Organisms *(GMOs)*;
- sources of ionising radiation *(e.g. x-ray and radiotherapy equipment, industrial sources)*;
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- waste water discharges;
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- Promoting radon testing in homes and workplaces and encouraging remediation where necessary.

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- Office of Environmental Sustainability
- Office of Environmental Enforcement
- Office of Evidence and Assessment
- Office of Radiation Protection and Environmental Monitoring
- Office of Communications and Corporate Services

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EPA RESEARCH PROGRAMME 2021–2030

Cumulative Health Effects of Metal(loids) through Aggregate Environmental Pathways

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EPA Research Report

Prepared for the Environmental Protection Agency

by

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This report is based on research carried out/data from November 2019 to November 2020. More recent data may have become available since the research was completed.

The EPA Research Programme addresses the need for research in Ireland to inform policymakers and other stakeholders on a range of questions in relation to environmental protection. These reports are intended as contributions to the necessary debate on the protection of the environment.

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Executive Summary

Metal(loid)s are an essential requirement for plant and crop growth. Background levels coupled with anthropogenic sources (including the regional application of biosolids) may lead to increased levels of certain metals(loid)s in soil, leading to potential transfer to water sources and potential uptake by plants. The latter could result in transfer into the feed-to-food chain, namely via grazing animals, and also biotransfer to food products, resulting in human exposure.

This study undertook a review of the levels of metal(loid)s likely to be present in Irish soils and biosolids. The systematic review highlighted that the potential uptake of metal(loid)s by plants is a function of mobility/retainability of metal(loid)s in the soil, which is a complex phenomenon. This is highly influenced by soil pH, soil organic matter or soil organic carbon, soil texture class, topography and drainage properties of the soil.

The second part of this project focused on an assessment of the geographical distribution of 16 metal(loid)s (arsenic – As; cadmium – Cd; cobalt – Co; chromium – Cr; copper – Cu; iron – Fe; mercury – Hg; manganese – Mn; molybdenum – Mo; nickel – Ni; lead – Pb; antimony – Sb; tin – Sn; uranium – U; vanadium – V; and zinc – Zn) across Ireland using the Soil Geochemical Atlas of Ireland (SGAI). Based on the SGAI data, the baseline concentrations of Cd, Cu, Hg, Ni, Pb and Zn in the soil were found to be below the allowable limit (1–3, 50–140, 1–1.5, 30–75, 50–300 and 15–300 $mg\,kg^{-1}$, respectively) of Council Directive 1986/278/EEC. Based on *Codes of Good Practice for the Use of Biosolids in Agriculture*, in some regions, Cd and Zn exceeded the average threshold value of 1.25 $mg\,kg^{-1}$ and 125 $mg\,kg^{-1}$, respectively.

A risk quotient (RQ) methodology was used to compare reported levels of metal(loid)s and the maximum permissible values of metal(loid)s in various environmental media (soil, water, sediments) using the high-resolution Tellus database. The RQ ratio highlighted Cd, Zn, As and Pb as metals in soils as requiring vigilance, as they had an RQ greater than 1 in some locations. This research also developed a novel geographical information system (GIS) risk map combining the integrated RQ values with a number of other risk factors using a semi-quantitative probability–impact matrix. The east coast of Ireland was found to pose a higher relative risk when analysing the final risk score for arable lands. The east coast is a significant producer of vegetable crops, highlighting the need for further investigation.

A case study in County Louth using a human health risk assessment approach for exposure to metal(loid)s was conducted. The daily mean human exposure to Pb through selected food products was found to be 0.073 $mg\,day^{-1}$, and the mean weekly exposure was estimated to be 0.0065 $mg\,kg^{-1}\,bw\,week^{-1}$. Using a back-calculation procedure, the model can be used to evaluate the maximum level of metals in soil to ensure that mean levels of human exposure to Pb do not exceed the lowest observed effect level for Pb of 0.0012 $mg\,kg^{-1}\,bw\,day^{-1}$. For the scenarios considered in this model, this was found to be 51 $mg\,kg^{-1}$ Pb for agricultural soil media. This is in line with the lower threshold value of the permissible range for soils (range 50–300 $mg\,kg^{-1}$) as recommended by the European Commission. An analysis of the Tellus data revealed that Pb levels were below this limit (51 $mg\,kg^{-1}$) for ≈90% of arable land in the regions covered by the Tellus dataset. This study highlighted the need for selective growth of crops that are likely to accumulate metal(loid)s in soils of low metal(loid) content. In addition, the application of biosolids containing metal(loid)s needs to be viewed in the context of the background levels of those metal(loid)s in soil, thereby ensuring that resultant overall levels of metal(loid)s in the soil media remain within permitted threshold levels. This study also highlights the integration of an analysis of baseline concentrations of Pb through GIS with a probabilistic risk assessment approach to provide exposure estimates for metals of human health concern. The approach can be applied to a multitude of metals and other potential hazards and can help in the evaluation of potential environment–health interactions.

1 Introduction

1.1 Metal(loid)s

Several metals and metalloids (elements whose properties are intermediate between metals and non-metals) are essential for living organisms, with particular roles in cell division and metabolism, while also facilitating endocrine signals between organs (Collins *et al.*, 2010). On the one hand, deficiency of metals and/or metalloids (metal(loid)s) may inhibit the natural growth of organisms; on the other hand, excessive exposure to metal(loid)s may lead to serious health problems. The essential elements required for human growth are cobalt (Co), chromium (Cr), copper (Cu), iron (Fe), manganese (Mn), molybdenum (Mo), nickel (Ni), selenium (Se) and zinc (Zn) (Hejna *et al.*, 2018). Non-essential toxic metal(loid)s include arsenic (As), cadmium (Cd), mercury (Hg) and lead (Pb) (Hejna *et al.*, 2018). The European Chemicals Agency (ECHA, 2020) also classified Cd and Hg as a serious health hazard owing to acute toxicity, resulting in potential environmental risks. Gibb *et al.* (2019) indicated that, in 2015, ingestion of As, methylmercury (CH_3Hg), Pb and Cd resulted in more than one million illnesses, over 56,000 deaths and more than nine million disability-adjusted life-years (DALYs) worldwide.

Metal(loid)s are naturally present in the Earth's crust, and erosion effects can release the metal(loid)s from rocks, resulting in deposition in various environmental media (soil, water, sediments) while also making metal(loid)s available for plant uptake (Ling *et al.*, 2014). The continuous release of metal(loid)s from the geological bedrock is a natural process as a result of the weathering process. This results in a baseline (naturally occurring) concentration (Newman and Watling, 2007) of metal(loid)s in environmental media, including soil, sediments and water. However, there may also be many anthropogenic influences. Anthropogenic sources may include mining waste, agricultural activity (mainly biosolids and pesticide application) and proximity to smelters, big cities and roads (emissions from vehicles followed by atmospheric deposition), and these sources may elevate the baseline levels of metal(loid)s in environmental media (Beckers and Rinklebe, 2017; Arslan Topal and Elitok, 2018; Gupta *et al.*, 2019). Land-spreading of biosolids (domestic and urban sewage sludge) has been identified as a significant anthropogenic source of metal(loids)s (Fijalkowski *et al.*, 2017; Arslan Topal and Elitok, 2018). According to the Environmental Protection Agency (EPA) (2019a), in Ireland, approximately 79.6% (>44,000 tonnes dry solids) of biosolids is reused on agricultural land, with the remainder used for compost (19.2%) sent to landfill (0.16%), or used for other purposes (0.95%).

Biosolids can be applied to the soil before planting cereals, oilseed rape, grass (both permanent pasture and silage), fodder beet and forestry (DELG, 2009). However, there are regulatory restrictions in terms of composition and usage. There are three main European directives that have a significant impact on the management of biosolids: the Sewage Sludge Directive (Directive 86/278/EEC; European Union, 1986); the Nitrates Directive (Directive 91/676/EEC; European Union, 1991a) and the Waste Framework Directive (Directive 2008/98/EC; European Union, 2008). In Ireland, the use of a "Sludge Hub Centre and Satellite Dewatering Site" system for the management of wastewater sludge has been implemented in a number of counties (Irish Water, 2015). As a result of the increase in waste generation, the disposal of biosolids is a big challenge. The application of biosolids, being nutrient rich, to pasture land is in line with the circular economy (European Commission, 2014) and national policy (Healy *et al.*, 2017) to reduce and reuse waste streams where possible (DELG, 2009). However, health concerns persist regarding the application of biosolids, in particular the potential accumulation of metal(loids) in environmental media.

1.2 Health Concerns

Animal and human exposure to metal(loid)s can result from accidental ingestion or oral exposure through water or food/feed (WHO, 2017). Metal(loid)s such as Cd, Pb, As, Zn, Ni, Cu, and Cr affect metabolism by inactivating enzymes, can cause deoxyribonucleic acid (DNA) damage, can result in cardiovascular diseases, cancer, cognitive impairment and chronic anaemia, and can result in damage of kidneys, the nervous system, the brain, skin and bones (Das and Jayalekshmy, 2015; Khalid *et al.*, 2017). Hg, mainly as CH_3Hg, is a potent neurotoxin (at levels > 20 mg l^{-1} in the blood). Elemental Hg vapour is harmful to the central nervous system, and inorganic Hg affects the kidney (Beckers and Rinklebe, 2017). Pb may cause immunological, reproductive, cardiovascular, renal, neurological and developmental effects, pregnancy problems, chronic kidney disease, hypertension and cardiovascular disease (Entwistle *et al.*, 2019). Se and Sn are present in solid sludge in large concentrations and are potentially harmful to human health (Fijalkowski *et al.*, 2017). Cd is absorbed in the kidney, liver, lungs, testes, spleen, thymus, heart, epididymis, prostate and salivary glands and increases the mitotic index of skin cells, causing pneumonitis, renal dysfunction, bone demineralisation, endothelial cell injury and protein endocytosis (Huang *et al.*, 2017). Furthermore, As, Cd, Hg and Pb have been identified as the most toxic metal(loid)s to humans and the ecosystem (ECHA, 2020). A review of the scientific literature revealed that Cu, Zn, Pb, Cd, Ni, Cr, As, Hg, Mn and Fe are the top 10 most studied metal(loid)s in recent years.

1.3 The Fate of Metal(loid)s and Geochemistry

The transport of metal(loid)s from the environment to human exposure pathways can take place via the soil profile to surface water and groundwater aquifers (drinking water pathway) or via plant root uptake (food chain) (Shiva Kumar and Srikantaswamy, 2014). Atmospheric deposition and surface runoff can also occur (Hejna *et al.*, 2018). Once the metal(loid)s are introduced to the soil, they have several possible routes: (i) adsorption or desorption reactions, (ii) precipitation or dissolution reactions, (iii) plant uptake (bioavailability) and (iv) mobility through soil (Shiva Kumar and Srikantaswamy, 2014). The bioavailability of metal(loid)s depends on the mobility of metal(loid)s in the soil mass, and the soil adsorption effect reduces their mobility (Lo *et al.*, 1992). The availability of metal(loid)s for extraction by plants depends on the mobility of the metal(loid)s in the soil. Furthermore, the mobility of metal(loid)s is significantly influenced by soil geochemistry, including pH, organic matter/soil organic carbon (SOC), redox and cation potential, clay content (soil texture class), moisture content (Gupta *et al.*, 2019) and the topography (Sacristán *et al.*, 2015). Flat land and poorly drained soils prolong the retention of metal(loid)s in the soil, which increases the potential uptake of metal(loid)s by plants (Gall *et al.*, 2015). Field drainage is governed by the natural slope of the land and by micro- (capillary action) and macropores (gravity-driven preferential flow) (Shiota *et al.*, 2019).

1.4 Exposure Routes

Human exposure pathways to metal(loid)s are identified as mainly the ingestion of food and water that may have elevated metal(loid) levels. Dust inhalation of metal(loid)s (Mehta *et al.*, 2018) and absorption (by skin) of metal(loid)s such as Cd and Cr (Tchounwou *et al.*, 2012) are also reported. Ingestion of metal(loid)s through food and water has been identified as dominating exposure routes (Healy *et al.*, 2016a) in terms of the proportion of accumulated metal(loid)s people are exposed to; for example, vegetable consumption is estimated to contribute to 70–90% of Cd exposure in humans (Huang *et al.*, 2017). Consumption of plants is one of the main mechanisms by which Cd and Pb transfer from contaminated soils to humans (Chamannejadian *et al.*, 2013). The bioaccumulation of different metal(loid)s from soil to crops is not identical; in fact, there is great variation between crop species and crop components (leaves, stem, roots) and their potential to accumulate metal(loids) (Table 1.1). The bioaccumulation factor represents the transfer of metal(loid) from soil to the food material and is the ratio of the concentration of metal(loid) in the food products and the concentration in the soil. The bioaccumulation of metal(loid)s in the edible portion of a crop depends on the environmental growing conditions; for example, in situations where there is atmospheric deposition (volatile metals), leafy greens accumulate more metal(loid)s than root crops, as the leaves are exposed to polluted atmospheric sources. If the atmospheric deposition pathway is unlikely, root crops are likely to accumulate higher levels of metal(loid)s (Zhuang *et al.*, 2009). In addition, runoff from the soil surface may transport metal(loid)s to rivers/lakes, a source of drinking and irrigation water, thus potentially contributing to the accumulation of metal(loid)s in the environment and resulting in human exposure through water sources. Abstraction of groundwater for drinking water purposes is another exposure route, as pollutants may leach into the aquifer by infiltration through soil layers

Table 1.1. Calculated bioaccumulation factor of metal(loid)s from soil to edible portion of vegetables

Type of crop	Plant common name	Plant scientific name	Metal(loid)	Concentration in soil (mg kg^{-1})	Concentration in edible part/s (mg kg^{-1})	Bioaccumulation factor[a]	Concentration in edible part/s (mg kg^{-1}) based on other literature	Maximum accumulation capacity (mg kg^{-1})[b]	Reference[c]
Root crops	(Wild) carrot	*Daucus carota*	Cd	96	25	0.260	Cd (<0.06, 0.085, 1.2), Pb (0.72, 0.92, 1.42), Cu (3.60, 27.12), Zn (10.28), Mn (7.11)		2, 3
			Pb	0.01	390	***39000*** (exceptional case, contaminated soil), possible outlier			1
			Pb	847	24	0.028			2
			Zn	8635	950	0.110			2
			Cu	203	25	0.123			2
	Onion	*Allium cepa*	Mn	573	585	**1.021**	Cd (0.029), Pb (0.16), Cu (1.98), Zn (11.90)		1, 3
	Potato	*Solanum tuberosum*					Cd (0.08), Pb (0.47), Cu (7.76, 8.65), Zn (49.56), Mn (18.25)	Fe (111–122)	3
	Radish	*Raphanus sativus*					Cd (0.03, 0.99), Pb (0.012, 6.19), Cu (0.98, 6.08), Zn (8.90, 14.97), Mn (8.80)		3
Leafy vegetables	Lettuce	*Lactuca sativa*	Cd	1.3	130	***100***		Zn (9.97), Cu (1.97), Pb (1.162)	1, 3
			Cd	96	5	0.052			2
			Pb	–	28				1
			Pb	847	10	0.012			2
			As	5.83	14	**2.401**			1
			Zn	–	118				1
			Zn	8635	490	0.057			2
			Ni	1.11	48	***43.243***			1
			Cu	203	15	0.074			2
			Mn	619	512	0.827			1
	Chicory	*Cichorium intybus*	Cd	40	20	0.500			2
			Pb	847	20	0.024			2
			Zn	8635	950	0.110			2
			Cu	203	16	0.079			2

Table 1.1. Continued

Type of crop	Plant common name	Plant scientific name	Metal(loid)	Concentration in soil (mg kg^{-1})	Concentration in edible part/s (mg kg^{-1})	Bioaccumulation factor[a]	Concentration in edible part/s (mg kg^{-1}) based on other literature	Maximum accumulation capacity (mg kg^{-1})[b]	Reference[c]
	Spinach	*Spinacia oleracea*	Cd	40	10	0.250	Cd (0.3), Pb (5.5), Cu (0.03), Zn (2.5)	Zn (20.9–120.8), Fe (279–333)	2, 3
			Pb	66.78	20	0.299			1
			Pb	847	10	0.012			2
			Zn	124	84	0.677			1
			Zn	8635	490	0.057			2
			Cu	203	7	0.034			2
	Wild cabbage	*Brassica oleracea*	Pb	2.58	49	***18.992***	Cd (0.8, 0.12), Pb (1.66, 3.82), Cu (4.10, 12.08), Zn (0.75, 173.21), Mn (28.4, 29.43), Fe (0.54, 0.75)	Cu (35.72), Zn (63.63)	1, 3
			Cr	12.78	24	**1.878**			1
	Perennial wall-rocket	*Diplotaxis tenuifolia*	Ni	–	35				1
	Common purslane	*Portulaca oleracea*	Ni	–	36				1
	Coriander	*Coriandrum sativum*	Cu	–	48				1
			Cr	1.11	13	***11.712***	Cd (0.75, 3.8), Pb (1.80, 30), Cu (3.8, 71), Zn (121, 400), Mn (59), Fe (1618)	Zn (134.5), Fe (292–326)	1, 3
	Celery	*Apium graveolens*	Cu	46.85	11	0.235			1
Grains and pulses	Rice	*Oryza sativa*	As	–	1.3				1
	Maize (corn)	*Zea mays*	Zn	80	148	**1.850**			1
			Cu	41	47	**1.146**			1
	Broad bean	*Vicia faba* L.					Cd (0.06–0.09), Cu (0.3–0.6), Zn (0.47–1.23)		4
Fruit	Tomato	*Solanum lycopersicum*	Cd	11.24	13	**1.157**			1
			Ni	1.11	43	***38.739***	Cd (0.20, 0.41, 0.77, 0.90, 14.17), Pb (2.20, 2.59, 5.50, 9.70), Cu (0.04, 4.47, 8.20, 32.6, 54.56), Zn (3.56, 3.80, 14.40, 61.13), Mn (7.39), Fe (3.10, 14.64)		1, 3
			Cu	–	202				1

Table 1.1. Continued

Type of crop	Plant common name	Plant scientific name	Metal(loid)	Concentration in soil (mg kg^{-1})	Concentration in edible part/s (mg kg^{-1})	Bioaccumulation factor[a]	Concentration in edible part/s (mg kg^{-1}) based on other literature	Maximum accumulation capacity (mg kg^{-1})[b]	Reference[c]
	Bitter tomato	*Solanum aethiopicum*	Pb	452	144	0.319			1
			Cr	256	65	0.254			1
	Pepper	*Capsicum*	Cr	1.11	17	***15.315***			1
	Aubergine	*Solanum melongena*					Cd (0.16, 5.83), Pb (1.30, 4.93), Cu (11.8, 11.23), Zn (41.37, 46.53, 12.83), Mn (8.85), Fe (5.24)		3
	Okra	*Abelmoschus esculentus*					Cd (3.87), Pb (8.54), Cu (8.36), Zn (9.56), Fe (4.83)		3
	Squash (pumpkin, marrow)	*Cucurbita maxima*					Cd (0.01), Pb (0.25), Cu (11.44), Zn (46.10), Fe (5.82)		3
Oil crops	Rapeseed	*Brassica napus*	Cd	1	6	**6.000**			1
	Black mustard	*Brassica juncea*	Zn	190	201	**1.058**			1
	White mustard	*Sinapis alba*	Cr	1.11	13	***11.712***			1
Others	Mushroom	*Agaricus bisporus*	Cd	–	10				1
			Cu	–	36				1
	Perennial grass	*Cynosurus cristatus*	Cd	0.2	9	***45.000***			1
	Tobacco	*Nicotiana glauca*	As	14,660	92	0.006			1
			Zn	507	1985	3.915			1

[a]Bold indicates >1, but <10; bold and italic indicates >10. These may indicate short-term or permanent accumulation as grown on contaminated or polluted soil.

[b]Maximum accumulation capacity is the amount of accumulation possible in specified crops or vegetables.

[c]Reference 1, Khalid *et al.* (2017); reference 2, Roy and McDonald (2015); reference 3, Gupta *et al.* (2019); reference 4, Jin *et al.* (2017).

[d]Wild cabbage may be used as an indicator for cabbage, broccoli, cauliflower, kale, Brussels sprouts, collard greens, savoy, kohlrabi and gai lan.

(Punshon *et al.*, 2017). Animal products such as fish, milk and meat are a secondary route of metal(loid) transfer to humans (Mehta *et al.*, 2018). Biotransfer of metal(loid)s through the food chain occurs when herbivores are exposed to the contaminants when they eat phytoaccumulators such as grass and vegetables (Kuppusamy *et al.*, 2016). The maximum permissible limits of metal(loid)s in animal feed and animal food products to ensure limited biotransfer of metal(loid)s to humans are shown in Table 1.2. The accumulation of metal(loid)s in animals is also shown to vary greatly between different metal(loid)s (Bampidis *et al.*, 2019).

1.5 Guidelines and Legislation

The legislation that governs permissible levels of metal(loid)s in different environmental media varies from jurisdiction to jurisdiction. The threshold values or maximum allowable concentrations of metal(loid)s in soil, water and sediment for different jurisdictions are summarised in Table 1.3. This research identified significant variation between the maximum permissible level of metal(loid)s in the soil in the US and EU regulations, whereas the United Nations limits are similar to the EU regulations. Recent studies evaluating the levels of metal(loid)s in biosolids (in Ireland) are documented in Figure 1.1, including the allowable limits (Healy *et al.*, 2016b). Healy *et al.* (2016b) found that, under the conditions analysed, the observed levels of selected metal(loid)s in the biosolids did not exceed regulatory limits. At present, there is no regulatory limit for levels of Se, Sr, Mo, Ag, Sn, Sb, Cr and Fe in biosolids. The Sewage Sludge Directive (86/278/EEC; European Union, 1986) regulates the allowable limits of pathogens and metals (Cu, Ni, Pb, Cd and Hg) and allows the use of sludge on land under defined sanitary and environmentally sound conditions (Fijalkowski *et al.*, 2017). According to Council Directive 91/271/EEC (European Union, 1991b), urban wastewater requires treatment; in particular, higher levels of treatment are required in nutrient-sensitive areas. As the population is growing, the volume of waste is expected to grow; as a result, the volume of sludge arising from wastewater treatment in Ireland is set to grow substantially. Council Directive 91/271/EEC (European Union, 1991b) further encourages the use of wastewater sludge wherever appropriate (DELG, 2009). In *Codes of Good Practice for the Use of Biosolids in Agriculture* (DELG, 2009), the maximum permissible concentrations of certain heavy metals (Zn, Cd, Ni) in the soil prior to the application

Table 1.2. The maximum permissible limit of metal(loid)s in animal feed and animal food products ensuring limited potential biotransfer of metal(loid)s from animal feed to the animal food products

Metal(loid)	Species and maximum level per kg dry matter animal feed (mg kg^{-1})[a]	Species and maximum limit of metal(loid) in the animal product (mg kg^{-1})[b]	Reference
As	All (2)	Fish (5.0), meat (5.0), milk (1.0)	Government of Ireland (1972), Hejna *et al.* (2018)
Cd	Bovines, sheep, goats (1), others (0.5)	Meat (0.05), liver (0.5), kidney (1.0), fish (0.05), seafood (0.5)	European Union (2006); Hejna *et al.* (2018)
Co	Pigs (2), bovines (0.3–1)	–	Hejna *et al.* (2018)
Cu	Pigs (25–170), bovines (15–35)	–	Hejna *et al.* (2018)
Fe	Pigs (250–750), bovines 750	–	Hejna *et al.* (2018)
Hg	All (0.1)	Fish (0.5–1.0)	European Union (2006), Hejna *et al.* (2018)
Pb	All (5)	Milk (0.02), meat (0.1), fish (0.3), seafood (0.5)	European Union (2006), Hejna *et al.* (2018)
Mn	All (150)	–	Hejna *et al.* (2018)
Mo	All (2.5)	–	Hejna *et al.* (2018)
Sn	–	Milk and canned food (50)	European Union (2006), Hejna *et al.* (2018)
Zn	Pigs (150), bovines (100)	–	Hejna *et al.* (2018)

[a]Based on Directive 2002/32/EC (European Union, 2002) and Regulation (EC) No. 1831/2003 (European Union, 2003).
[b]Based on Regulation (EC) No. 1881/2006 (European Union, 2006).
–, not specified in Hejna *et al.* (2018).
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Table 1.3. Threshold levels of metal(loid)s in soil, water and sediments

Metal (loid)	Soil ($mg\,kg^{-1}$)							Biosolids ($mg\,kg^{-1}$)	Water ($\mu g\,l^{-1}$)				Sediments ($mg\,kg^{-1}$)[b]
									Surface water[a]	Drinking water			
	European Union	DELG		US ATSDR		UNEP		European Union	Government of Ireland	Government of Ireland	US Department of Health & Human Services	WHO	EPA and GSI
	Soil pH 6.0–7.0	pH 5.0–6.0 and/ or clay content 10–15%	Soil pH >6.0 and clay content >15%	Child	Adult	Threshold limit	Permissible limit						
As	–	–	–	20	200	5	50 (ER)	–	25[c]	10	10	10	300
Cd	1–3	1	1.5	10	100	1	10 (ER)	20–40	0.08–0.25	5	5	3	100
Co	–	–	–	–	–	20	100 (ER)	–	–	–	–	–	–
Cr	–	–	100[d]	200[b]	2000[b]	100	200 (ER)	–	3.4–4.7[c]	50	100	50	1000[e]
Cu	50–140	–	80	2000	20,000	100	50 (ER)	1000–1750	5–30[c,f]	2	1000	2000	100
Fe[g]	–	–	–	–	–	–	–	–	–	200	–	300[g]	10,000
Hg	1–1.5	–	1	–	–	–	–	16–25	–	1	2	6	5
Mn	–	–	–	3000	40,000	–	–	–	–	50	–	400[h]	5000
Mo	–	–	–	300	4000	–	–	–	–	–	–	10	–
Ni	30–75	50	80	1000	10,000	50	100 (ER)	300–400	4	20	100	70	1000
Pb	50–300	–	80	–	–	60	200 (HR)	750–1200	1.2	10	5	10	1000
Sb	–	–	–	20	300	2	10 (HR)	–	–	5	60	20	1000
Sn	–	–	–	–	–	–	–	–	–	–	–	1–2	1000
U	–	–	–	100[i]	1000[i]	–	–	–	–	–	–	30	–

Table 1.3. Continued

Metal (loid)	Soil (mg kg⁻¹)							Biosolids (mg kg⁻¹)	Water (µg l⁻¹)				Sediments (mg kg⁻¹)[b]
									Surface water[a]	Drinking water			
	European Union	DELG		US ATSDR		UNEP		European Union	Government of Ireland	Government of Ireland	US Department of Health & Human Services	WHO	EPA and GSI
	Soil pH 6.0–7.0	pH 5.0–6.0 and/ or clay content 10–15%	Soil pH >6.0 and clay content >15%	Child	Adult	Threshold limit	Permissible limit						
V	–	–	–	200	2000	100	150 (ER)	–	–	–	–	–	500
Zn	15–300	100	150	20,000	200,000	200	250 (ER)	–	5–100[c,j]	–	–	10	5000

Note: the limit of Cd, Cu, Ni, Pb, Zn and Hg that may be added annually to agricultural land, based on a 10-year average, is 0.15, 12, 3, 15, 30 and 0.1 kg ha⁻¹ year⁻¹, respectively (European Union, 1986). Highlighted values will be used in equation 2.3 (Chapter 2); where two values are indicated corresponding to different soil pH values, an average value can be used (Irish regulation is the priority; if a certain metal(loid) is not found in Irish legislation, the international standard was referred to).

The Water Framework Directive focuses on overall environmental aspects and is not limited to human health objectives. Water Framework Directive: Irish legislation S.I. No. 77 of 2019 (Government of Ireland, 2019) includes S.I. No. 272 of 2009 (Government of Ireland, 2009) and S.I. No. 386 of 2015 (Government of Ireland, 2015).

Data for soil from European Union (1986), DELG (2009), EPA and GSI (2009), UNEP (2013), Tóth *et al*. (2016) and Adagunodo *et al.* (2018). Data for biosolids from European Union (1986). Data for water from Government of Ireland (2014, 2019), WHP (2017) and US Department of Health & Human Services (2019). Data for sediment from EPA and GSI (2009).

[a]Soft water, 4.5 < pH < 9.0; hard water, 6.0 < pH < 9.0. This parameter is the Environmental Quality Standard expressed as an annual average value (EQS-AA). Unless otherwise specified, it applies to the total concentration of all isomers. Inland surface waters encompass rivers and lakes, and related artificial or heavily modified water bodies.

[b]Values assume sediment is 10% of the diet and that metals are bioavailable.

[c]Values for As, Cr(III) (oxidation state 3⁺), Cu and Zn are to be added to background (or baseline as interpreted) values.

[d]Soil pH > 5.0 and clay content ≥ 15%.

[e]Cr(III).

[f]Cu (hardness < 100 mg l⁻¹ calcium carbonate ($CaCO_3$)) 5; Cu (hardness > 100 mg l⁻¹ $CaCO_3$) 30.

[g]No health-based guideline found for Fe; values based on turbidity and colour.

[h]Derived value.

[i]U in soluble form.

[j]Zn (hardness < 10 mg l⁻¹ $CaCO_3$) 8; Zn (hardness 10–100 mg l⁻¹ $CaCO_3$) 50; Zn (hardness > 100 mg l⁻¹ $CaCO_3$) 100.

DELG, Department of the Environment and Local Government (Ireland); ER, ecological risk; GSI, Geological Survey Ireland; HR, health risk; UNEP, United Nations Environment Programme; US ASTDR, US Agency for Toxic Substances and Disease Registry.

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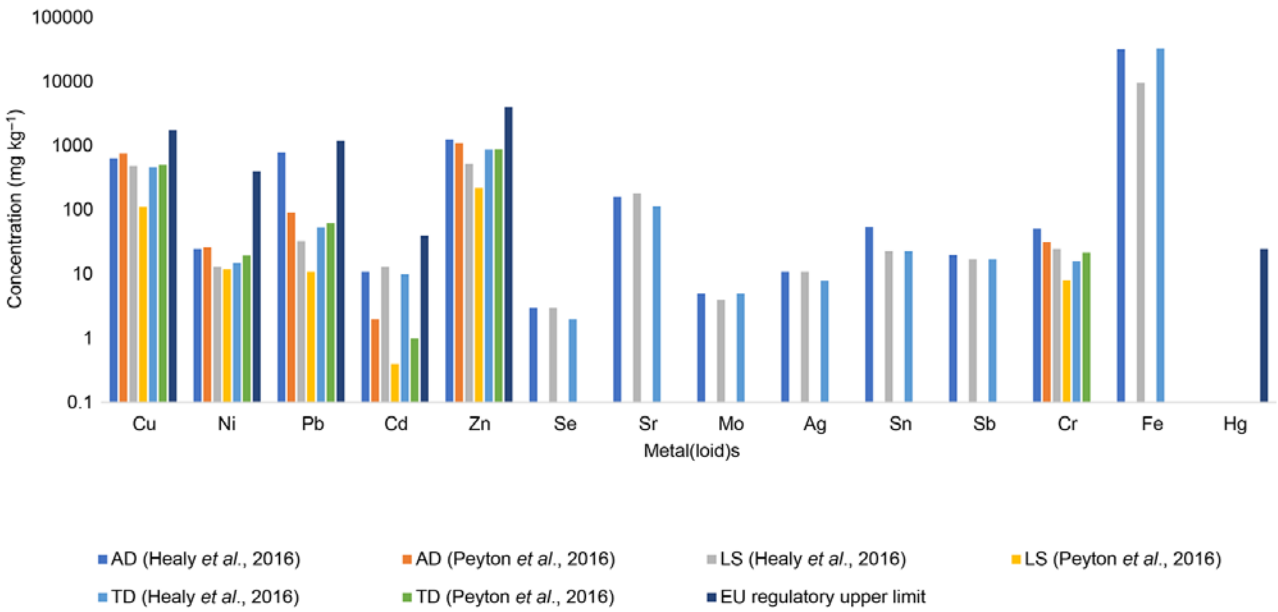

Figure 1.1. Mean concentration of metal(loid)s found in biosolids. AD, anaerobic digestate; LS, lime stabilised; TD, thermally dried. Data from Healy *et al.* (2016b) and Peyton *et al.* (2016). Source: Nag *et al.* (2022a); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

of biosolids are reported as 100, 1 and 50 mg kg^{-1}, respectively, for a soil pH of 5.0–6.0 and/or a clay content of 10–15%. When the soil pH and clay content increase (soil pH > 6.0 and clay content > 15%), these limits can be 150, 1.5 and 80 mg kg^{-1}, respectively. The limits of other metals such as Cu, Pb, Hg and Cr are reported as 80, 80, 1 and 100 mg kg^{-1}, respectively, for a pH of > 5.0 and a clay content of ≥ 15%.

1.6 Risk Assessment Methods

Given the range of metal(loid)s found in the environment and the myriad of environmental and toxicity behaviours, risk assessment methodologies are required to assess the potential human and environmental risk from exposure to metal(loid)s. This study found that an enrichment factor, geochemical mass balance, geoaccumulation index, contamination factor and pollution load index can all be used in initial hazard identification. In addition, the pollution index, integrated pollution index and potential ecological risk index are based on legal threshold values set by health authorities in different countries, therefore suggesting them as mid-point analysis methods. Hazard quotient (HQ), hazard index (HI), risk quotient (RQ), daily dietary index (DDI), daily intake of metals (DIM), health risk index (HRI), target hazard quotient (THQ), cancer risk (CR) and total cancer risk (CR_{total}) can be classified as end-point analysis methods, where exposure assessment and hazard characterisation concepts are combined to assess the overall potential human risk to pollutant metal(loid)s. However, it has been noted that RQ is applicable to most metal(loid)s. There are many mechanistic multimedia fate and transport models dealing with volatile, semi-volatile and involatile chemicals, such as the fugacity approach, concentration-based approach and activity approach models (Su *et al.*, 2019). Similarly, Clarke and Cummins (2014) highlighted the SimpleTreat 3.1, EUSES, QSAR, RADAR and P*h*ATE models, which are widely used as risk assessment model tools for human risk evaluation for chemicals and pharmaceuticals in the environment. A summary of different endpoint risk assessment methodologies reviewed in this project is collated in Table 1.4.

1.7 Aims and Objectives

Given the significant role that metal(loids) play in the health and wellbeing of living organisms and the need to balance potential detrimental health effects, the overall aim of this research was to (i) undertake a thorough review of the levels of metal(loid)s likely to be present in soil and potential anthropogenic sources, and (ii) analyse human exposure and adverse health impacts using source–pathway–receptor conceptual

Table 1.4. Methodologies for human health risk assessment of metal(loid)s

Method	Equation	Parameters and unit	Classification of risk	Reference
HQ	$HQ = DI \times \frac{C_{Mveg}}{RfD_o \times BW}$ (1.1)	DI = daily intake of vegetable (kg day^{-1}) C_{Mveg} = concentration of metal in vegetable (mg kg^{-1}); BW = the average body weight, adult (78.1 kg[a]); RfD_o = oral reference dose for the metal; varies (4×10^{-3} mg kg^{-1} day^{-1})	HQ > 1 risk (non-cancer) HQ < 1 no adverse health effects	Singh and Kumar (2020); RfD_o: US EPA (1987); Nguyen *et al.* (2019); Sarwar *et al.* (2019)
DDI	$DDI = A \times B \times \frac{C}{BW}$ (1.2)	A = metal content in vegetable (mg kg^{-1}); B = dry weight of the vegetable consumed (kg); C = approximate daily intake of vegetable (kg day^{-1}); BW = average human body weight (78.1 kg[a])	Can be compared with RDA	Gupta *et al.* (2019)
DIM	$DIM = A \times C \times \frac{D}{BW}$ (1.3)	A = metal(loid) concentration in plants (mg kg^{-1}); C = conversion factor (0.085 is to convert fresh vegetable weight to dry weight); D = daily intake of vegetables (kg day^{-1}); BW = average body weight, adult (78.1 kg[a])	Can be compared with RDA	Tsafe *et al.* (2012)
HRI	$HRI = \frac{DIM}{RfD}$ (1.4)	As above	HRI < 1 safe	Gupta *et al.* (2019)
THQ	$THQ = \frac{EF_r \times ED \times FI \times MC}{RfD_o \times BW \times AT} \times 10^{-3}$ (1.5)	EF_r = exposure frequency (365 days year^{-1}); ED = exposure duration (70 years); FI = food ingestion (g person^{-1} day^{-1}); MC = metal concentration in food (μg g^{-1}, on a fresh weight basis); RfD_o = oral reference dose for the metal; varies (4×10^{-3} mg kg^{-1} day^{-1}); BW = average body weight, adult (78.1 kg[a]); AT = averaging time for non-carcinogens (365 days year^{-1} × number of exposure years, assuming 70 years)	THQ < 1 unlikely to experience adverse effects	Zhuang *et al.* (2009); RfD_o: US EPA (1987)

Table 1.4. Continued

Method	Equation	Parameters and unit	Classification of risk	Reference
CR	$CR = ADD \times CSF$ (1.6) where $ADD = \frac{C \times IR \times EF \times ED}{BW \times AT}$ (1.7)	*ADD* = average daily dose (mg kg^{-1} bw day^{-1}); *CSF* = cancer slope factor (0.0085 mg kg^{-1} bw day^{-1})$^{-1}$; *ADD* can be computed from equation (1.7); *C* = concentration of pollutants (mg kg^{-1} or mg l^{-1}); *IR* = ingestion rate (kg day^{-1} or l day^{-1}); *EF* = exposure frequency (days year^{-1}); *ED* = exposure duration (years); *BW* = average body weight, adult (78.1 kg[a]); *AT* = average time (day)	CR (for a single contaminant) > 1×10^{-6} carcinogenic risk Adopted classification for the model based on Pipoyan *et al.* (2019) High risk ≥ 0.001; moderate risk ≥ 0.0001 but < 0.001; low risk ≥ 0.000001 but < 0.0001; very low risk < 0.000001	Mehta *et al.* (2018); Nain and Kumar (2019); CSF: Sarwar *et al.* (2019)

[a]The average weight of 78.1 kg was considered based on 86.9 kg for a man (18–64 years old) and 70.375 kg for a woman (18–64 years old). Beyond 65 years of age, the average weights are 82.4 kg and 68.1 kg for men and women, respectively.

RDA, reference daily allowance.

Source: Nag and Cummins (2022).

modelling and risk assessment approaches. The following set of objectives was identified to achieve the aims:

- quantify the level of metal(loids) arising from various sources (background levels and anthropogenic activities);
- develop an environmental exposure assessment for selected metal(loids);
- identify predominant exposure pathways and pollutant controls to reduce the risks of detrimental health effects from selected metal(loids).

2 A Geographical Information System Study to Rank Potential Human Hazards

2.1 Introduction

The systematic review (Chapter 1) identified metal(loid)s of human health concern (Cu, Zn, Pb, Cd, Ni, Cr, As, Hg, Mn and Fe) requiring further investigation. Elevated levels of these metal(loid)s in soil, coupled with varying bioavailability, can result in high concentrations in different food/feed crops and vegetables. The concentration of metal(loid)s in the soil is a key risk factor that can contribute to elevated levels in food and feed crops. The concentration of metal(loid)s in the soil is dependent on the background and anthropogenic sources of metal(loid)s, whereas the bioavailability is dependent on soil geochemistry, including pH, soil organic matter (SOM), cation exchange capacity, redox potential and ionic strength (Sheoran *et al.*, 2016). The background concentration reflects the type of natural bedrock and the weathering pattern in a location; weathering releases minerals from the rock mass and makes them mobile in the soil mass, and also makes them more bioavailable for plant uptake. Anthropogenic sources can also increase the levels of metal(loid)s in soil; such sources include mining activity, atmospheric deposition of exhaust fumes from vehicles and industries, and agriculture activity, including biosolids application.

The mobility of metal(loid)s influences the release of metal(loid)s in surface runoff and is inversely proportional to the retention ability of metal(loid)s in soil. The retainability of metal(loid)s is dependent on soil pH, SOC, soil texture class and field/soil drainage class. Favourable pH ranges for metal(loid) uptake by plants vary depending on the metal(loid)s; however, Pennisi *et al*. (2013) emphasised a general range of between pH 5.5 and 6.6. A higher SOC, which is an indicator of SOM, reflects higher retainability of metal(loid)s within the soil texture class; to be more specific, the clay content influences the retainability of metal ions, as they are charged particles. Furthermore, a field with well-drained soil may transport the metals away from the growing plants, resulting in a lower bioaccumulation risk in crops than a field with a poor drainage system, which will retain the liquid fraction of metals in the soil for a longer period.

On a global scale, mining activity, specifically bauxite residue and mine tailings disposal, has been identified as one of the major contributors to an increase in the concentration of metals in soil (Khairul *et al.*, 2019). This is followed by urban activities (smelting, e-waste, tannery effluent, wastewater, skeet shooting ranges), while industrial/municipal solid waste and proximity to highways may also result in a rise in the concentration of metal(loid)s in soil (Gerhardt *et al.*, 2017) by direct dumping or diffusion and atmospheric deposition (Beckers and Rinklebe, 2017; Arslan Topal and Elitok, 2018; Gupta *et al.*, 2019). Land-spreading of biosolids (domestic and urban sewage sludge) can also be an influential anthropogenic source of metal(loid)s (Fijalkowski *et al.*, 2017; Arslan Topal and Elitok, 2018).

As agricultural lands are not isolated, there is always a chance of potential secondary contamination (surface water runoff) from nearby areas where biosolids are applied on land at a higher elevation. Losses of metal(loid)s to the surface, or to subsurface water bodies, mainly originate in two ways: as chronic losses (long term, owing to the build-up of metal(loid)s in the soil) or as incidental losses (short term; within 48 h of application) (including Cu, Ni, Pb, Zn) following episodic rainfall events soon after land application of biofertiliser or biofertiliser amendment (Brennan *et al.*, 2012; Peyton *et al.*, 2016). These losses of metal(loid)s may also result in potential deposition and increase the levels of metal(loid)s in nearby lower elevation arable lands.

From the scientific literature consulted, it is clear that both background and anthropogenic sources of metal(loid)s can give rise to elevated metal concentrations in soil. These levels are, in turn, influenced by soil parameters that can affect metal(loid) retainability in soil, potentially resulting in higher bioaccumulation in food crops for human consumption. Therefore, the overall aim of this section was to identify and characterise critical risk factors and use a geographical information system (GIS) mapping approach to rank regions (mainly arable lands) in Ireland with respect to the potential for metal accumulation being transferred from the environment to food products.

2.2 Materials and Methods

This research uses GIS-based data mining followed by a reclassification using the ArcGIS tool (version ArcMap 10.7), which feeds into a semi-quantitative risk-ranking approach based on a probability–impact matrix. Nine risk criteria (baseline concentration (BC), pH, SOC, soil texture class, slope, field/soil drainage class, proximity to mines, urban activity and biosolids application) were identified as requiring evaluation and inclusion in the risk-ranking approach. The data sources of the model parameters are displayed in Table 2.1; shapefiles are available for soil texture class, slope, drainage, mine locations, population density and land use, while pH, SOC and BC are available in raster maps. A schematic diagram of the model is presented in Figure 2.1. A reclassification scoring system of all nine parameters is presented in Table 2.2.

The texture class of Irish soil is divided into six major categories (clayey, fine loamy, loamy, coarse loamy, sandy and peat). The clay, sand and silt content (Benham *et al.*, 2009) of each category are presented in Table 2.3. Based on the clay content, the soil texture classes were reclassified into the 1 to 5 scoring system (Tables 2.2 and 2.3). Peat soil has a high organic matter content (> 30%, ≈ 17% SOC) down to a depth of at least 30 cm (Fay *et al.*, 2007b). Higher organic content results in higher bioaccumulation. Therefore, in the absence of information about the percentage content of clay, sand and silt of peat (Table 2.3), the lowest score (5) is assigned to peat.

The RQ parameter looks at the environmental risk for each metal/chemical (Clarke and Cummins, 2014) and can be assessed using equation 2.1, by dividing the predicted environmental concentration (PEC) by the predicted no-effect (toxicity) concentration (PNEC). The PNEC is defined as the highest concentration below which no harmful effects are expected to occur; in this study, these are taken as the threshold values as given in Table 1.3. A high RQ reflects elevated levels of metal(loid)s, potentially also resulting in increased crop and vegetable uptake. This study proposes a novel approach to integrate the RQ of all 14 metal(loid)s in an integrated risk quotient (IRQ) (equation 2.2). PEC values (mg kg^{-1}) were obtained from Fay and Zhang (2020), while PNEC values (mg kg^{-1}) for this model are obtained from Table 1.3. It is noted that there is no PNEC value available for Fe and Sn levels in the soil. Substituting the PNEC values in equation 2.2 resulted in an IRQ presented in equation 2.3. PNEC values for Cd, Ni and Zn are considered as an average value of 1.25 (1, 1.5), 65 (50, 80) and 125 (100, 150) mg kg^{-1}, respectively (Table 1.3), considering the entire range of possible soil pH:

$$RQ = \frac{PEC}{PNEC} \tag{2.1}$$

Table 2.1. Risk factors influencing metal accumulation in soils

Parameter	Data source	Primary or raw data	Secondary or modified data
BC	Fay and Zhang (2020) – all 14 target metals	N/A	Raster maps
Soil pH	Fay and Zhang (2020)	N/A	Raster maps
SOC	Fay and Zhang (2020)	N/A	Raster maps
Soil texture	Fay *et al.* (2007a); EPA (2018)	✓	N/A
Slope	USGS (2013)	✓	N/A
Drainage	Fay *et al.* (2007a); EPA (2018)	✓	N/A
Proximity to mines	GSI (2014)	✓	N/A
Proximity to urban activity (population density used as an indicator)	CSO (2012)	✓	N/A
Proximity to potential biosolids application areas	EPA (2012)	✓	N/A

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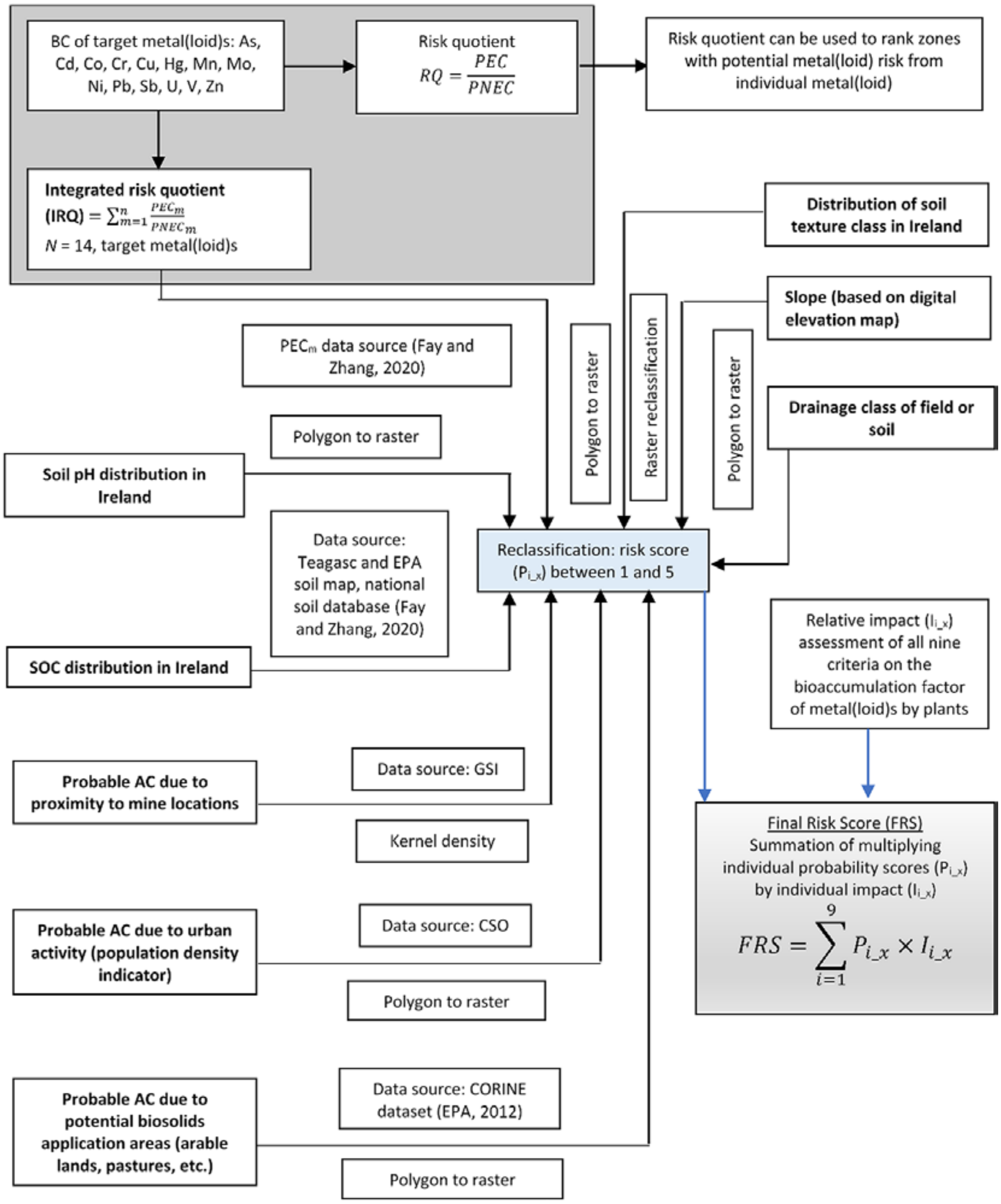

Figure 2.1. Schematic diagram of the GIS risk-ranking methodology. AC, anthropogenic concentration; PEC, predicted environmental concentration; PNEC, predicted no-effect concentration. Source: Nag *et al.* (2022b); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

$$\text{IRQ} = \sum_{m=1}^{n} \frac{PEC_m}{PNEC_m} \tag{2.2}$$

$$IRQ = \frac{PEC_{As}}{20} + \frac{PEC_{Cd}}{1.25} + \frac{PEC_{Co}}{20} + \frac{PEC_{Cr}}{100} + \frac{PEC_{Cu}}{80} + \frac{PEC_{Hg}}{1} + \frac{PEC_{Mn}}{3000} + \frac{PEC_{Mo}}{300} + \frac{PEC_{Ni}}{65} + \frac{PEC_{Pb}}{80} + \frac{PEC_{Sb}}{20} + \frac{PEC_{V}}{200} + \frac{PEC_{U}}{100} + \frac{PEC_{Zn}}{125} \tag{2.3}$$

2.2.1 Scenarios

Baseline scenario

The baseline scenario (BS) looked at the importance of forming a probability–impact matrix. Some risk factors may have a stronger influence than others on metal retainability within the soil. Therefore, the sum of the products of individual probability scores (P_{i_x}) multiplied by individual impact scores (I_{i_x}) results in a final risk score (FRS) (equation 2.4). The relative

Table 2.2. Reclassification criteria of nine parameters

Parameters	Range in Ireland or description	Reclassification of risk scores (P_{i_x}) (1 to 5)
Soil pH (for bio-availability)	3.99–4.50	2
	4.51–5.00	3
	5.01–5.50	4
	5.51–6.50[a]	5
	6.51–6.90	4
SOC (more organic, more release of metal, unit: %)	3.42–4.00	1
	4.01–6.00	2
	6.01–8.00	3
	8.01–12.00	4
	12.01–60.37	5
Soil texture (high clay content results in high retainability of water in the soil, including soluble metal(loid) salts; the retainability of water/soluble salts is inverse to the mobility)	Clayey	5
	Fine loamy	4
	Loamy	3
	Coarse loamy	2
	Sandy	1
	Peat	5
Slope (degree)	0–5.46	5
	5.47–10.91	4
	10.92–17.65	3
	17.66–28.25	2
	28.26–81.85	1
Drainage	Excessively	1
	Well	2
	Moderately	3
	Imperfectly	4
	Poor	5
IRQ (calculated)	0.81–1.69	1
	1.70–2.40	2
	2.41–3.11	3
	3.12–3.90	4
	3.91–5.43	5
Mine locations (kernel density)	0–0.03	1
	0.04–0.11	2
	0.12–0.22	3
	0.23–0.42	4
	0.43–0.81	5
Urban activity (indicator: population density, unit: number of people km^{-2})	2–255	1
	256–1326	2
	1327–5840	3
	5841–24,878	4
	24,878–105,157	5

Table 2.2. Continued

Parameters	Range in Ireland or description	Reclassification of risk scores (P_{i_x}) (1 to 5)
Potential biosolids application locations based on agricultural land use (probability of biosolid application; the focus was on agricultural land (arable land to be specific), and therefore other land use such as forestry was not considered)	Complex cultivation patterns	4
	Dumpsites	5
	Fruit trees and berry plantations	2
	Land principally occupied by agriculture, with significant areas of natural vegetation	5
	Natural grasslands	3
	Non-irrigated arable land	5
	Pastures	5
	All others	1

[a]Mostly all metals are absorbed by the plants in this range.
IRQ, integrated risk quotient.
Source: Nag *et al.* (2022b); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

Table 2.3. Soil texture class corresponding to clay, sand and silt percentage range; derived from soil textural triangle after Benham *et al.* (2009)

Soil texture	Clay (%)	Sand (%)	Silt (%)	Reclassified score
Clayey	Lower value 40–55; upper value 100	Lower value 30–42; upper value 66–75	Lower value 0; upper value 40–60	5
Fine loamy	27–40	Lower value 35–40; upper value 60–65	60–73	4
Loamy	8–28	Lower value 38–48; upper value 58–62	72–92	3
Coarse loamy	10–15	Lower value 70–86; upper value 90–95	Lower value 85–90; upper value 100	2
Sandy	0–10	87–100	88–100	1
Peat	–	–	–	5

Source: Nag *et al.* (2022b); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

impact scores (I_{i_x}) are based on a literature-based weight of evidence to indicate the relative importance of each input on potential plant uptake of metal(loid)s (Table 2.4).

$$FRS = \sum_{i=1}^{9} P_{i\_x} \times I_{i\_x} \quad (2.4)$$

Probability sum scenario or equal impact scenario

The probability sum scenario (S_p), which can be considered as an equal impact scenario, looked at the direct summation of probability values (each ranging from 1 to 5) for all nine criteria (Table 2.5), which are each multiplied by 1 (i.e. equal weighting of all risk factors). All nine criteria were treated equally for this scoring system.

2.2.2 *Clipping arable lands from the final risk score map*

The final step includes a clipping feature in ArcGIS using the "Data Management Tools > Raster > Raster Processing > Clip" command to show the FRS, which can be assigned to arable land use only, as these lands are responsible for the primary food production in Ireland.

2.3 Results

The spatial distribution of the baseline level of 16 metal(loid)s in the soil based on data of the Soil Geochemical Atlas of Ireland (SGAI) (Fay *et al.*, 2007b) was investigated. The areas where the PEC values were higher than threshold values were highlighted,

Table 2.4. Relative individual impact (I_{i_x}) of inputs on potential metal(loid) plant uptake

Parameters	I_{i_x}	Justification for the scoring based on literature
Soil pH	5	Appeared as the most critical parameter based on a literature search
SOC	3	Have a moderate effect on retainability of metal(loid)s in soil and potential plant uptake
Soil texture	3	
Slope	3	
Drainage	3	
IRQ	5	Origin of the hazard, reflection of cumulative effect of metal(loid)s
Proximity to mines	4	Biggest anthropogenic concern
Proximity to urban activities	3	Second most important anthropogenic source
Proximity to potential biosolids application areas	2	Secondary route of potential contamination

Source: Nag *et al.* (2022b); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

Table 2.5. Scoring criteria for scenarios that were used to generate final risk scores

Scenarios	Scoring criteria used for FRS
BS	"pH_Reclas" × 5 + "SOC_Reclass" × 3 + "Texture_reclass" × 3 + "Slope_Reclass" × 3 + "Drainage_Reclass" × 3 + "IRQ_Reclass" × 5 + "Mine_location_Reclass" × 4 + "Population density_Reclass" × 3 + "Potential_biosolid_application_Reclass" × 2
S_p	"pH_Reclas" × 1 + "SOC_Reclass" × 1 + "Texture_reclass" × 1 + Slope_Reclass × 1 + Drainage_Reclass × 1 + "IRQ_Reclass" × 1 + "Mine_location_Reclass" × 1 + "Population density_Reclass" × 1 + "Potential_biosolid_application_Reclass" × 1

Source: Nag *et al.* (2022b); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

which includes levels of As, Cd and Zn in certain regions (Figure 2.2). The results indicate that As (maximum value 31 mg kg^{-1}), Cd (maximum value 2.2 mg kg^{-1}) and Zn (maximum value 267 mg kg^{-1}) in soil exceeded the threshold values for the application of biosolids to agricultural land (DELG, 2009) of 20, 1.25 and 125 mg kg^{-1}, respectively. An IRQ map based on SGAI data (Fay *et al.*, 2007a) is also presented in Figure 2.3a. A closer analysis is possible for certain regions of the country through high-resolution Tellus data (GSI, 2020). The Tellus dataset presents levels of several metal(loid)s in soil (A and S as shallow and deeper soil, respectively), water (W) and sediment (C) samples. However, these data are available only for certain regions of the country to date. A similar approach based on higher resolution Tellus data (shallow soil sample A) suggests the existence of a higher cluster (Figure 2.3b) of areas exceeding the threshold values in the eastern part of the country. The classification of IRQ scores is based on a similar approach adopted for the IPI classification after Chen *et al.* (2005). The east coast is a significant producer of vegetable crops, highlighting the need for further investigation, such as conducting a quantitative farm-to-fork human health risk assessment of target metal(loid)s specific to crops grown on case study areas, as different crops have unique affinities towards the selective higher accumulation of metal(loid)s. The RQ based on higher resolution Tellus data (samples A and S) indicates that Cd, Zn, As and Pb require vigilance (Figures A1.1 and A1.2); however, very few locations exceeded the threshold values specified in the *Codes of Good Practice for the Use of Biosolids in Agriculture* (DELG, 2009) for the application of biosolids to agricultural land. The significance of individual RQ values to the overall IRQ and the order of influence, based on 5656 Tellus data points, is Pb > Cd > Zn > As > Co > Cu > Ni > Hg > Cr > Mn > V > Sb > U > Mo. The order of individual RQ exceedance (more than 1) is found as Cd > Zn > As > Pb > Mn > Co > Cu > Ni > Cr > Hg > U (Figure 2.4). The RQ was also calculated for the levels of a number of metal(loid)s in water (As, Cd, Cu, Ni, Pb, Zn) and sediments (Cu, Pb, As, Cd, Cr, Zn) based on the Tellus dataset, and the overall RQ result suggests minimal exceedance of threshold values for the metal(loid)s (Figures A1.3 and A1.4).

2.3.1 *Final risk score and a comparison between the baseline scenario and probability sum scenario*

The FRS is an integration of the risk factors identified (Figure 2.5) and indicates that the east coast of

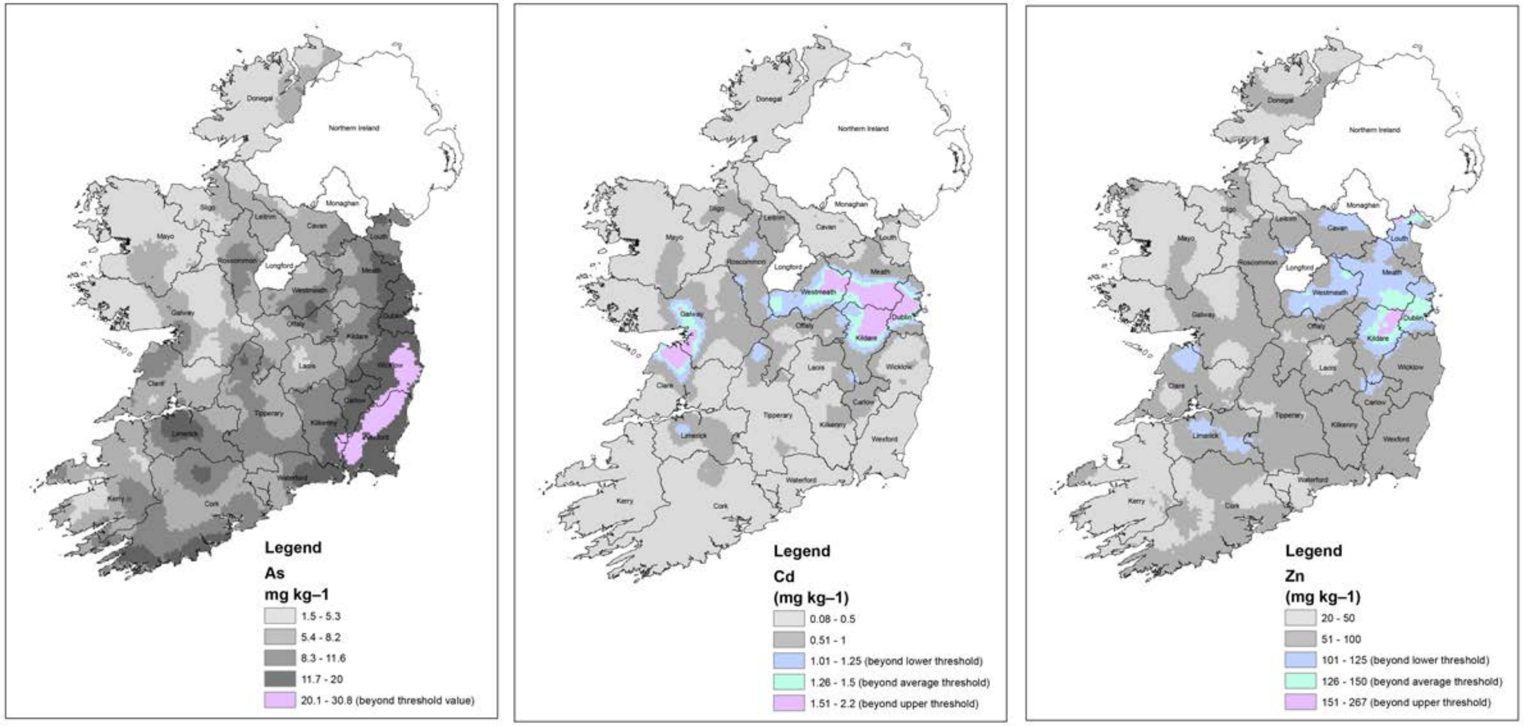

Figure 2.2. Spatial distribution of the baseline concentration of selected metal(loid)s (As, Cd and Zn) that partly exceeded the threshold value. Data: SGAI (Fay *et al.*, 2007a). Source: Nag and Cummins (2021); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

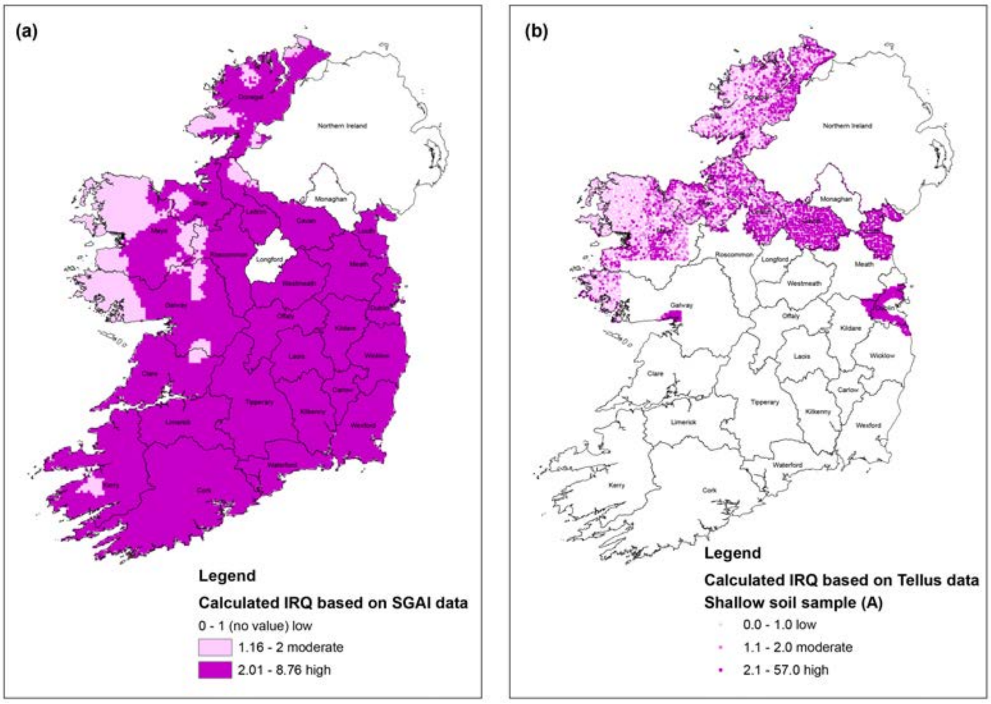

Figure 2.3. Spatial distribution of IRQ based on the concentration of 14 metal(loid)s in the soil. (a) Data source SGAI (Fay *et al*., 2007a), applicable for topsoil; (b) data source Tellus (GSI, 2020), shallow soil sample (A). IRQ with classification IRQ≤1 low; 1<IRQ≤2 moderate; IRQ>2 high; similar to the integrated pollution index (Chen *et al*., 2005). Source: Nag and Cummins (2021); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

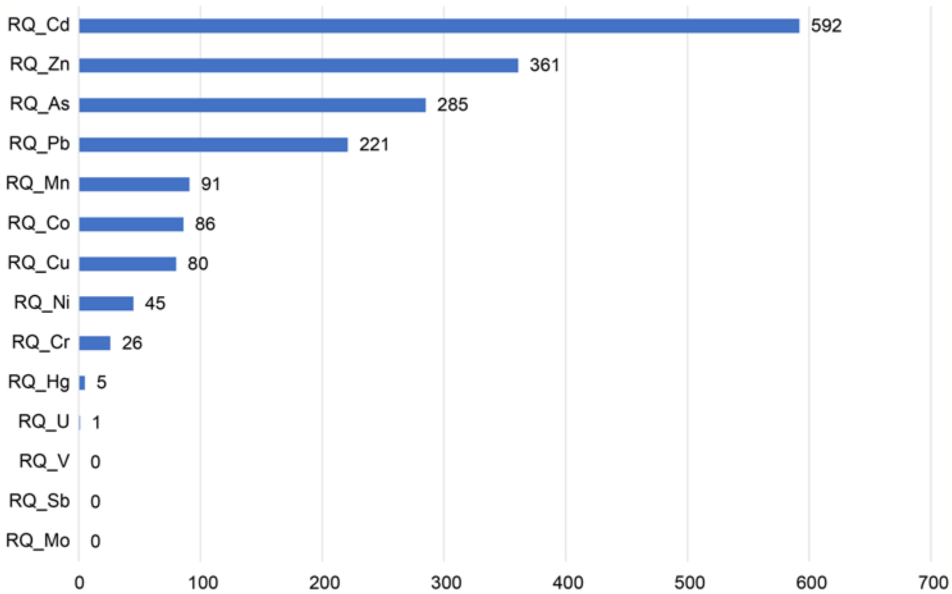

Figure 2.4. RQ number of exceedance (>1) out of 5656 data points. Source: Nag and Cummins (2021); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

Ireland poses a higher FRS; this gradually drops moving to the west coast. Figure 2.5a and b shows the FRS for BS and S_p scenarios, respectively. Random sampling points were introduced (Figure 2.5c) by the "Data Management Tools > Sampling > Create Random Points" command. A data probe was made for FRS for BS and S_p scenarios using the "Spatial Analyst Tools > Extractions > Extract multi values to points" command. A high positive correlation of 0.98 was found between FRS_{BS} and FRS_{S_p} (Figure 2.5c). Therefore, for the stated impact scores, there is no

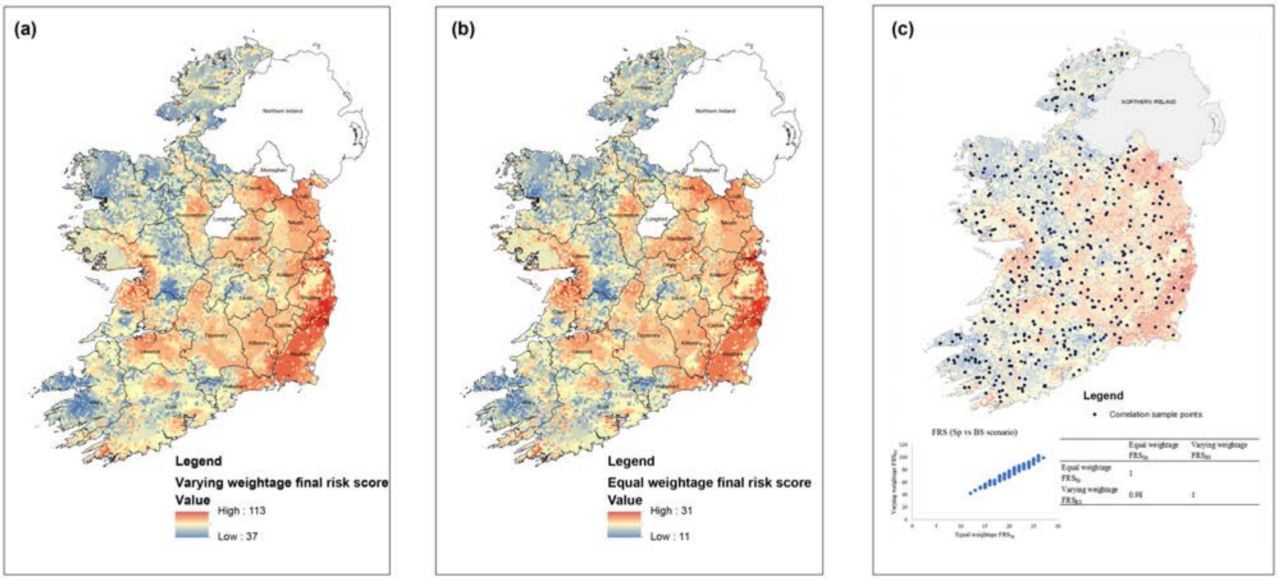

Figure 2.5. Final risk map after addition of reclassified scores of nine risk factor criteria (equal weightage). (a) BS; (b) probability sum scenario; (c) Pearson's correlation coefficient of 0.98. Source: Nag *et al*. (2022b); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

significant difference observed between BS and S_p scenarios.

2.3.2 *Clipped arable lands with the final risk score*

As crops and vegetables are not grown across the entire country, the arable lands (source CORINE (Coordination of Information on the Environment) land use map; EPA, 2012) are extracted from Figure 2.5. Using the "Data management Tools > Raster > Raster processing > Clip" function, the FRS_{BS} was clipped for arable lands (Figure 2.6). A visual assessment suggests that arable lands on the east coast could represent a higher relative risk.

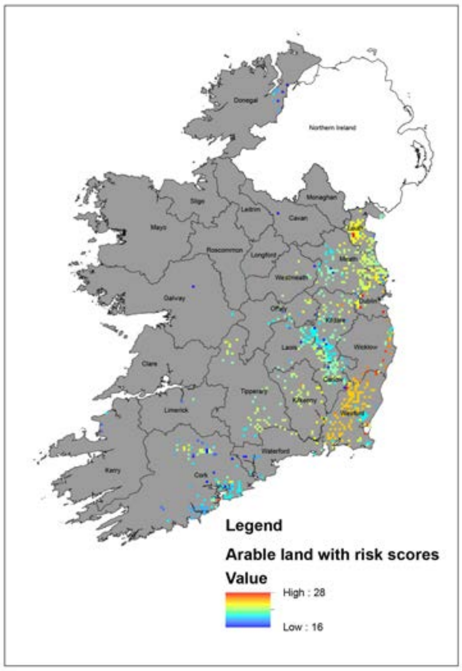

Figure 2.6. The final risk score associated with arable lands. Source: Nag *et al*. (2022b); licensed under CC BY 4.0 (https://creativecommons.org/licenses/by/4.0/).

2.3.3 *Limitations of the study*

- All mining locations were treated equally in the ranking process; however, due consideration should be given to the size and stewardship of the mine and the type of the main mineral extraction.
- The Tellus project of the Geological Survey of Ireland is ongoing for other counties in Ireland. Once complete data are released, an update on this study can be made.
- For some metal(loid)s, the no observed adverse effect level (NOAEL) or lowest observed adverse effect level (LOAEL) values and permissible limits in water/soil/food are not established. These fields can be updated in the future.

2.4 Discussion

This work reveals the usefulness of the GIS mapping techniques in collating multiple datasets to develop a risk map of the regional distribution of metal(loids). The results can inform policymakers regarding prioritisation of remediation/mitigation measures (e.g. limitations on the application of biosolids), and the methodology can also be applied to other areas with similar environmental conditions and potential pollution sources. In addition to the above study, the high-resolution monitoring data for levels of metal(loid)s in soil, water and sediment were used to create a revised RQ for designated areas using Tellus data (GSI, 2020). These data are currently available for only a small number of counties, hence limiting its nationwide application. It is noted that, out of 5656 Tellus sampling points, the RQ exceedances for As, Cd, Pb and Zn based on Tellus data were 5.0%, 10.5%, 3.9% and 21.2%, respectively, whereas lower resolution SGAI data showed RQ exceedances for As, Cd, Pb and Zn as 0%, 8.0%, 0% and 29.1%, respectively. This highlights the importance of the high-resolution Tellus data so that more accurate risk estimates can be made and risk regions identified.

Drinking water treatment plants can remove the metal(loid)s with chemical and mechanical treatments (Shen *et al.*, 2019). In Ireland, public water supply (PWS) provides approximately 81.8% of water, with only 9.2% and 0.3% coming from group water schemes and private wells, respectively (Cummins *et al.*, 2010). Currently, approximately 11% of people in Ireland get their water from private water supplies (Department of Housing, Local Government and Heritage, 2020). Cummins *et al.* (2010) also mentioned that the drinking water treatment plants in Ireland generally use primary treatment (pumping, screening, storage and preconditioning) followed by secondary treatment (coagulation and flocculation, sedimentation and filtration) and tertiary treatment (chlorination/fluoridation, ultraviolet treatment and ozone addition). However, these treatments cannot remove metal(loid)s from surface water. Membrane filtration can be broken down into four filtration types, namely reverse osmosis, nanofiltration, ultrafiltration and microfiltration (in order of the removing potential from smallest particle size to larger particle size). Of these, only reverse osmosis can remove mineral ions (Treacy, 2016). Therefore, at present, complete removal of metal(loid)s in Irish drinking water treatment plants is unlikely. According to the EPA (2019b), the major source of public drinking water supply in Ireland is surface water (rivers, lakes or streams) (80%), followed by groundwater (13%) and springwater (7%). In addition, the EPA (2019b) reported that, out of 804 PWSs, only in one, six, two and one PWSs could the drinking water standard not be met owing to high levels of As, Cu, Ni and Se, respectively. Therefore, a close monitoring system on the levels of As, Cu, Ni and Se of those locations is required.

As there is a positive correlation between high background levels of certain metal(loid)s in soil and higher bioaccumulation by plants (Sarwar *et al.*, 2019), close monitoring of the locations where the BC of metal(loid)s is high (Figure 2.3) is recommended if there are agricultural activities in those locations. However, it is recognised that this relationship can be specific to metal–plant combinations (de Vries *et al.*, 2007). The accumulation of metal(loid)s in the edible portion of a crop depends on the nature of the plants; for example, leafy greens accumulate more metal(loid)s than root crops, as the leaves are exposed to polluted atmospheric depositions (volatile metals), which adds to the uptake by their roots (Zhuang *et al.*, 2009). The bioaccumulation also depends on the mobility of the metal(loid)s in the soil. Furthermore, the mobility of metal(loid)s is hugely influenced by soil geochemistry, including soil pH, SOM/SOC, redox and cation potential, clay content (soil texture class) and moisture content (Gupta *et al.*, 2019).

A semi-quantitative risk-ranking approach was adopted to identify potential metal(loid)s of concern and to identify priority locations where elevated levels may occur. The integration of data capturing the influence of pH, SOC, soil texture class, slope, field/soil drainage class, BC, proximity to mines, urban activity and biosolids application on the potential uptake of metal(loid)s by crops was carried out as part of this study. GIS mapping techniques were found to be effective in interpreting large datasets. The results indicated that the east coast of Ireland poses a higher relative risk comparing FRS_{BS} density (km^{-2}) per county. In addition, the east coast is also a significant producer of vegetable crops, highlighting the need for further investigation. For example, periodic soil testing is recommended for the highlighted zones in this study to check the levels of metal(loid)s before growing crops and/or the application of biosolids. Through the SGAI and Tellus datasets, a baseline level of different metal(loid)s was established that fulfils objective 1 of this study, to "Quantify the level of metal(loid)s arising from various sources (background levels and anthropogenic activities)."

3 Quantitative Risk Assessment of Lead along the Environment, Food and Human Health Chain

3.1 Introduction

3.1.1 Global burden of lead exposure

Pb has been identified as a toxic metal at elevated concentrations, and extensive use of Pb is reported to result in widespread environmental contamination and health problems globally (Li *et al.*, 2019). Pb, being a cumulative toxicant, can influence the neurologicical system, kidneys and blood circulation, especially in children, infants and fetuses (Guo *et al.*, 2018). Pb is distributed in the brain, liver, kidney and bones (Zwolak *et al.*, 2019) and accumulates over time in teeth and bones, reflecting cumulative human exposure. Pb may also have an effect on the brain and intellectual development in young children, inducing apoptosis in organ tissues (FSAI, 2009; Mani *et al.*, 2019); in some cases, irreversible neurological damage occurs. Pb was considered to be responsible for 540,000 deaths worldwide in 2016 (Li *et al.*, 2019), and Pb exposure is estimated to account for 0.6% of the global burden of disease (expressed in DALYs) with the highest burden in developing regions (WHO, 2010). Recent reductions in the use of Pb in petrol (gasoline), paint, plumbing and solder are reported to have resulted in substantial reductions in Pb exposure levels.

3.1.2 Source

Pb is found at low levels in the Earth's crust, mainly as lead sulphide (PbS) (WHO, 2010). Hence, background levels of Pb may be present in the soil, depending on geological sources. Mining activity is reported as one of the most influential anthropogenic sources of heavy metal contamination and the cause of many health-related issues; for example, in Zamfara State, Nigeria, a Pb poisoning epidemic caused over 40 child deaths in 2010 (Lo *et al.*, 2012). Other anthropogenic activities and sources that can contribute to Pb levels in soils around industrial areas include emissions from vehicles (mainly use of leaded petrol/gasoline), smelting, electrical waste dismantling, paint, glass industries, agricultural practices and waste disposal (Zwolak *et al.*, 2019), with evidence reported in China, Sweden, France and Germany (Guo *et al.*, 2019). Furthermore, fixtures and plumbing work in drinking water distribution systems that are either made of Pb or use Pb solder potentially increase the burden of Pb (Li *et al.*, 2019). In addition, different biosolid production methods can result in high Pb levels in the biosolids (Figure 3.1).

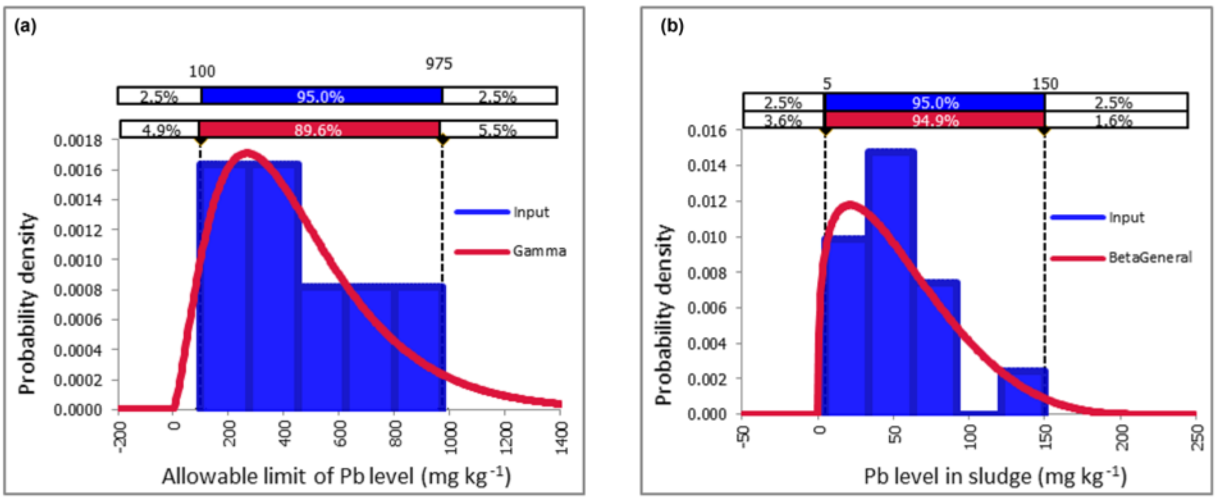

Figure 3.1. Distribution of Pb in biosolids as found in global studies, including allowable limit in sludge used as biofertiliser in agriculture. (a) The global range of allowable Pb level in sludge; (b) the global level of Pb found in sludge. Data sources: European Union (1986), US EPA (1993), LeBlanc *et al.* (2008) and Healy *et al.* (2016b). Source: Nag and Cummins (2022).

3.1.3 Pathways

For the non-smoking general population, the largest contributor to the daily intake of Pb is ingestion of food, including cereals and vegetables; the effect of packaging (use of Pb-soldered food and beverage cans, which is now diminishing); use of Pb-glazed ceramic or pottery dinnerware; household plumbing systems containing Pb pipes, solders and fittings; and dirt and dust (WHO, 2010). Smoking tobacco increases Pb intake. Consumption of a minimum of 400 g of fruit and vegetables per day (excluding potatoes and other starchy tubers) is recommended for the prevention of heart disease, cancer, diabetes, obesity and several micronutrient deficiencies, especially in less developed countries. However, it has been shown that leafy vegetables and rootstalk vegetables have the greatest ability to accumulate heavy metals. Hence, measures must be taken to minimise heavy metal accumulation through such foodstuffs, for example by restricting the growth of certain crops on soils with elevated metal levels (Zwolak *et al.*, 2019). Wheat (*Triticum aestivum* L.) is the third most important cereal worldwide after rice and maize, and the concentration of heavy metals, including Pb, is reported to decrease in the order of root > leaf > stem > grain in a wheat plant (Guo *et al.*, 2018). Principal crops of interest produced in Ireland include barley, wheat, potatoes and oats (CSO, 2020). The main vegetables include carrots, cabbages, broccoli, cauliflowers, swedes and parsnips, lettuce, onions, scallions and leeks (Bord Bia and DAFM, 2015).

The permissible concentration of Pb in soil, biosolids, surface water and sediments were summarised previously in Table 1.3. The global threshold range for Pb in sludge is also shown in Figure 3.1a (European Union, 1986; US EPA, 1993; LeBlanc *et al.*, 2008; Healy *et al.*, 2016b). It has been observed that the limit of Pb in the soil varies hugely (50–300 mg kg^{-1}) in Europe (European Union, 1986), whereas the limit in biosolids is comparatively high (750–1200 mg kg^{-1}). The recommended limit of Pb in drinking water is 10 µg l^{-1} (WHO, 2010). The US Code of Federal Regulations (US Department of Health & Human Services, 2019) recommended a limit of Pb in drinking water of 5 µg l^{-1}. The range of Pb concentration in Irish pastures (herbage concentration) is typically 0.5–20 mg kg^{-1} dry matter (Healy *et al.*, 2016a). Metal(loid)s are important for the growth of the plant as a nutrient; however, there is no requirement of Pb for animals. According to Directive 2002/32/EC on desirable substances in animal feed (European Union, 2002), the maximum permissible concentration of Pb in animal feed is 30 mg kg^{-1}.

Healy *et al.* (2016b) reported the limit values for metal concentrations in sludge for use in agriculture as 300 (Brazil), 300–1000 (China), 750–1200 (EU), 100 (Japan), 300 (Jordan), 250 (Russia) and 300–840 (USA) mg kg^{-1} dry weight (= parts per million). Anaerobic digestion-treated sludge shows very high (mean 791, ± standard deviation (SD) 1625 mg kg^{-1}) concentrations of Pb compared with sludge treated with thermal drying (mean 54, ± SD 30 mg kg^{-1}) and lime stabilisation (33, ± SD 25 mg kg^{-1}) (Healy *et al.*, 2016b). Pinto *et al.* (2018) indicated that the use of alkaline material such as lime reduces the heavy metal availability. A summary of the worldwide distribution (mean 54 mg kg^{-1}) of the variability of Pb in biosolids used in agriculture is captured in Figure 3.1b. The measured mean concentration of Pb in all types of treated sludge indicated in Healy *et al.* (2016b) was 252 mg kg^{-1}. Out of 16 wastewater treatment plants (WWTPs) in Ireland studied by Healy *et al.* (2016b), one WWTP was found to have a higher concentration of Pb (3696 mg kg^{-1}) in biosolids, which exceeded the EU limit of 1200 mg kg^{-1}. It must also be noted that organic Pb is more toxic than inorganic Pb owing to its lipid solubility; however, inorganic Pb is associated with an increased risk of cancer (Mani *et al.*, 2019).

3.1.4 Tolerable intake level

The tolerable level of metal intake is determined by dose–response relationships (Astolfi *et al.*, 2019). The LOAEL of Pb is 0.0012 mg kg^{-1} bw day^{-1} (US EPA, 1987). Considering this limit, the daily tolerable limit of Pb can be calculated as 93 µg day^{-1} for adults (for an average bodyweight of 78.1 kg in Ireland) and 30 µg day^{-1} for children (for a body weight of 25 kg). The drinking water and air (inhalation) limits are 10 µg l^{-1} and 0.5 µg m^{-3} (annual average), respectively (WHO, 2010). There is a recommendation to initiate public health actions if the blood Pb level (BLL) in children is ≥ 5 µg dl^{-1} (micrograms per decilitre) (previously 10 µg dl^{-1}) and in adults > 25 µg dl^{-1}. Intensive medical management and chelation therapy are recommended if the BLL exceeds 45 µg dl^{-1}. The permissible concentration of Pb in foodstuffs as a preventative measure (European Union, 2006), is documented in Table 3.1.

Table 3.1. Permissible Pb levels in foodstuffs (European Union, 2006)

Foodstuffs	Maximum levels of Pb (mg kg^{-1} wet weight)
Raw milk and milk-based products	0.02
Meat (excluding offal) from bovine animals, sheep, pig and poultry	0.1
Offal of bovine animals, sheep, pig and poultry	0.5
Muscle meat of fish	0.3
Cereals, legumes and pulses	0.2
Vegetables (excluding brassica vegetables): leaf vegetables, fresh herbs and fungi	0.1
Peeled potatoes	0.1
Brassica vegetables, leafy vegetables and cultivated fungi (mushrooms)	0.3
Fruit (excluding berries and small fruit)	0.1
Berries and small fruit	0.2
Fats and oils, including milk fat	0.1
Fruit juices, concentrated fruit juices as reconstituted and fruit nectars	0.05

Source: Nag and Cummins (2022).

3.1.5 Overall aim

A critical pathway of Pb exposure is ingestion of food grown on sites with elevated levels. The initial level of Pb in soil and bioaccumulation of Pb (from the soil to the edible part of the plant) are important parameters for the quantitative risk assessment of Pb. Therefore, the overall aims of the section are to:

- quantify the level of Pb arising from various sources (background levels and anthropogenic activities);
- develop an environmental exposure assessment for Pb contamination;
- identify predominant human exposure (HE) pathways and pollutant controls to reduce the risks of detrimental health effects from selected metal(loid)s.

3.2 Materials and Methods

The development of a quantitative risk assessment framework model is presented in Figure 3.2; the schematic presents the steps required to build a risk assessment model. The background concentrations of Pb in shallow (A) and deep (S) soil, water (W) and sediment (C) samples were collected from open source spatial data provided by the Tellus project (GSI, 2019) for a case study site (Hill of Rath, Co. Louth). The raw data were treated and analysed using ArcGIS (ArcMap version 10.7). The anthropogenic concentration of Pb (i.e. in biosolids) was collated from Louth County Council. The classification of land use, such as arable lands and pastures, was determined using the CORINE land use map (EPA, 2012).

These inputs were used to predict the maximum metal(loid)s concentration in soil and surface water, including surface water near drinking water treatment plant locations. Based on the Tellus shallow soil sample (A) and water (W) sample database, the variability of baseline levels of Pb in soil and water was captured using a probabilistic approach based on Monte Carlo simulation (10,000 iterations) with @RISK 7.5 software (Palisade Inc.), which is an add-in to Microsoft Excel version 2016. The BC of Pb in the soil [Tellus shallow soil sample (A)] in the study area was estimated as lognormally distributed, with a mean of 41.1 mg kg^{-1} and an SD of 21.5 mg kg^{-1} (range 14–188 mg kg^{-1}). This step was followed by an evaluation of the bioaccumulation potential of Pb (from soil to vegetables) and, finally, potential uptake by humans through crops and/or water. The consumption of different categories of food, water and beverages can be found using the Irish Universities Nutrition Alliance Survey (IUNA, 2011) for consumers and the entire population. Finally, the daily human exposure (HE_{daily}) of Pb was calculated by the product of the concentration of Pb in food/water and the daily ingestion of specified foodstuffs. The HE_{daily} was used further to evaluate risk using established risk assessment measures such as HQ, DDI, DIM, HRI, THQ and CR (Table 1.4), which are most relevant for a Pb risk assessment.

3.2.1 Anthropogenic source: biosolids

Agricultural practices were evaluated in the study area, with the rate of biosolids applied in the area noted.

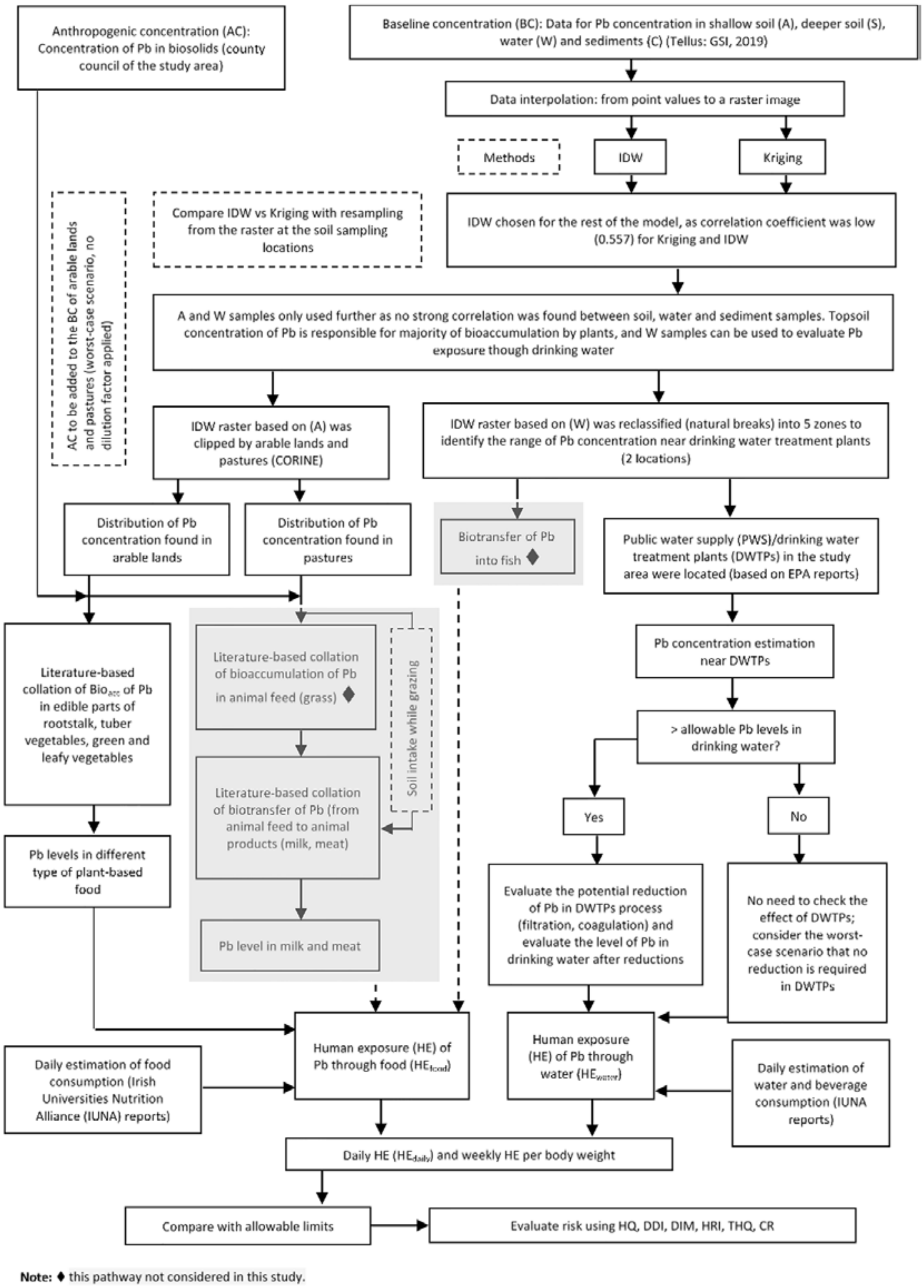

Figure 3.2. A schematic diagram of risk assessment methodology. Source: Nag and Cummins (2022). IDW, inverse distance weighting.

Over seven observations, the application rate of biosolids on arable land in the area varied between 26.8 and 34.8 tonne ha^{-1}. The density of biosolids was 4 tonne m^{-3} (dry solid) with organic matter content of 3% (of dry solid). The level of Pb in biosolids was found as 7.9 mg kg^{-1} for all study sites.

3.2.2 Bioaccumulation of Pb

The bioaccumulation factor (Bio_{acc}) is a ratio (equation 3.1) of the concentration of pollutant found in the plant tissue (C_{Pb_plant}) and the concentration of pollutants in the soil (C_{Pb_soil}) (Guo *et al.*, 2019). Bio_{acc} has been reported to significantly differ among wheat species tested for As, Cd and Pb. Cultivars reportedly accumulate Cd more readily than As and Pb in wheat (Guo *et al.*, 2018). The Bio_{acc} of metals in a wheat plant body was found to be in the order $Bio_{acc\_root} > Bio_{acc\_leaf} > Bio_{acc\_stem} > Bio_{acc\_grain}$. The typical order of bioaccumulation of metals in plants is found to be $Bio_{acc\_root} > Bio_{acc\_stem} > Bio_{acc\ leaf} > Bio_{acc\_fruit} > Bio_{acc\_seed}$, unless there is an abnormally high concentration of volatile metals (e.g. volatile Hg) in the air, which may increase the concentration of metals in leaves owing to the presence of volatile metal pollutants during stomatal gas exchange (Beckers and Rinklebe, 2017). A review of the studies reporting metal bioaccumulation in crops and their components (rootstalk, tuber vegetable, leafy vegetables, grain crops, fruit crops, oil crops) is presented in Table 3.2.

$$Bio_{acc} = \frac{C_{Pb\_plant}}{C_{Pb\_soil}} \qquad (3.1)$$

A positive correlation (steep linear slope, initially) between the concentration of metal(loid)s in soil and bioaccumulation has been observed (Dudka *et al.*, 1996). Although intact potato tubers showed a similar relationship for Pb, there is a non-linear relationship between the concentration of Pb in soil and bioaccumulation of Pb in peeled potato tubers; this means that Bio_{acc} is dependent on the initial level in the soil (C_{Pb_soil}) and the portion of the plant that is eaten. Guo *et al.* (2019) discovered that the Bio_{acc} of As and Cd was in the order of leafy, rootstalk, fruit and legume vegetables, and the Bio_{acc} of Cu, Pb and Zn was in the order of leafy, rootstalk, legume and fruit vegetables. Furthermore, Zhuang *et al.* (2009) discovered that the average Bio_{acc} values (Cu, Zn, Pb, Cd) of leaf vegetables were significantly higher than those of non-leafy vegetables. For grain crops such as rice, the average concentration of Cu, Zn, Pb, and Cd decreases in the order of stalk, husk and grain, with the exception of concentrations of Cu and Cd in grain, which were higher than those in husk. The range of Bio_{acc} of heavy metals in vegetables was reported to decrease in the order of Cd (0.02–0.08, mean 0.055), Zn (0.018–0.035, mean 0.024), Cu (0.015–0.022, mean 0.018), As (0.0025–0.012, mean 0.007) and Pb (0.001–0.004, mean 0.002), and the daily ingestion rate of vegetables was reported as the most sensitive parameter of the model, followed by the concentration of Pb in vegetables (Guo *et al.*, 2019). Furthermore, Zhuang *et al.* (2009) found that the Bio_{acc} of heavy metals in different vegetables was in descending order of Cd, Zn, Cu and Pb, with Pb Bio_{acc} ranging from 0.007 to 0.016 (leafy vegetables), from 0.0035 to 0.0085 (fruit vegetables), from 0.002 to 0.009 (root vegetables) and from 0.003 to 0.01 (rice), and having a C_{Pb_soil} range of between 6.8 and 127 mg kg^{-1} (mean 8.4–75 mg kg^{-1}) (Table 3.2). The Pb Bio_{acc_root}, Bio_{acc_leaf}, Bio_{acc_stem} and Bio_{acc_grain} values ranged from 0.23 to 0.89, from 0.021 to 0.044, from 0.0038 to 0.016 and from 0.0007 to 0.0024, respectively, for 16 wheat cultivars (Guo *et al.*, 2019). In the experiment, the C_{Pb_soil} ranged from 23.24 to 609.49 mg kg^{-1} (median 122.2, mean 196.96, SD 165.11 mg kg^{-1}), which is slightly higher than the C_{Pb_soil} in the study area, stretching from 7 to 264 mg kg^{-1} (mean 43 mg kg^{-1}). Therefore, C_{Pb_soil} reported in these studies (Zhuang *et al.*, 2009; Guo *et al.*, 2019) is close to the C_{Pb_soil} in the current study area; hence, it can be used as the most appropriate Pb Bio_{acc} for the probabilistic model.

3.2.3 Daily estimation of daily dietary intake: food and water consumption

An estimate of DDI of food products was considered from the Irish Universities Nutrition Alliance Survey (IUNA, 2011). Water consumption is considered as

Table 3.2. Estimated bioaccumulation factors (Bio_{acc}) of Pb for different types of crops

Plant	Scientific name	Type of crop	Concentration in soil (mg kg^{-1})	Pb Bio_{acc}	Pb Bio_{acc} adopted	Reference
Carrots	*Daucus carota* subsp. *sativus*	Root/rootstalk vegetables	6.8–127 (mean 8.4–75)	0.002–0.009	Uniform (0.002, 0.009)	Zhuang *et al.* (2009)
Potatoes	*Solanum tuberosum*	Tuber vegetables	18.03–24.90	0.005–0.034	Uniform (0.005, 0.034)	Musilova *et al.* (2016)
Green vegetables		Green vegetables	6.8–127 (mean 8.4–75)	0.007–0.016	Uniform (0.007, 0.016)	Zhuang *et al.* (2009)
Leafy vegetables		Leafy vegetables	6.8–127 (mean 8.4–75)	0.007–0.016	Uniform (0.007, 0.016)	Zhuang *et al.* (2009)

Source: Nag and Cummins (2022).

lognormally distributed (Clarke *et al.*, 2017), with a daily mean consumption of 564 g (SD 617 g) (IUNA, 2011). The selected food products used for this study are presented in Table 3.3. All mean and SD values were used to generate lognormal distributions for all food products.

3.2.4 HQ, DDI, DIM, HRI, THQ and CR for Pb risk assessment

The reference dose (RfD) is a benchmark dose derived from the NOAEL divided by an uncertainty factor (UF) and a modifying factor (MF) (equation 3.2) (US EPA, 2020). RfD as a result of ingestion is referred to as 4×10^{-3} mg kg^{-1} bw day^{-1} (Zhuang *et al.*, 2009; Guo *et al.*, 2018; Aendo *et al.*, 2019; Pipoyan *et al.*, 2019). Furthermore, the RfD and cancer slope factor (CSF) for Pb were found to be 0.004 mg kg^{-1} bw day^{-1} and 0.0085 (mg kg^{-1} bw day^{-1})$^{-1}$, respectively, in another study (Sarwar *et al.*, 2019).

$$RfD = \frac{NOAEL}{UF \times MF} \quad (3.2)$$

Six risk measures (HQ, DDI, DIM, HRI, THQ, CR) were adopted for this study, as each of these methods includes endpoint analysis (allowable value for human ingestion); the methods are documented in Table 1.4. The DDI and DIM can be compared with the recommended daily allowance (RDA), which is the average daily dietary intake level required to meet the nutrient requirements of the majority (97–98%) of healthy people of a specific sex, age, life stage and physiological condition (such as pregnancy or lactation) (Zohoori and Duckworth, 2019). There is no requirement for Pb (RDA_{Pb}), as it does not contribute to such body functions (Luis *et al.*, 2014). The allowable limits collated in Jin *et al.* (2014) suggest that the allowable limit of Pb intake varies globally, for example France 0.20 µg kg^{-1} bw day^{-1}; Canada 0.13 µg kg^{-1} bw day^{-1}; Australia 0.12–0.13 µg kg^{-1} bw day^{-1}; Lebanon 0.14 µg kg^{-1} bw day^{-1}; Germany 0.26 µg kg^{-1} bw day^{-1}; South Korea 0.41 µg kg^{-1} bw day^{-1}; Spain 1.21 µg kg^{-1} bw day^{-1}; and Italy 0.92 µg kg^{-1} bw day^{-1}. A distribution was fitted to the weekly equivalent (above) limits to capture the variability around the allowable limit (Figure 3.3). The mean allowable weekly intake (AWI) limit was calculated as 2.7 µg kg^{-1} bw week^{-1}. In the absence of a recommended limit, this AWI limit can be used to compare the simulated human exposure to Pb. Hence, an assumption can be made for RDA based on an AWI of 0.0004 mg kg^{-1} bw day^{-1} (= 0.0027/7). However, it must be noted that AWI is introduced for comparative purposes, as this is an average of the global limit, and multiple regions and final risk can be evaluated by widely accepted risk measures such as HQ, DDI, DIM, HRI, THQ and CR. According to Qu *et al.* (2018), cited in Nguyen *et al.* (2019), CR acceptance by the US EPA ranged from 1×10^{-6} to 1×10^{-4}, with risks exceeding 1×10^{-4} being considered unacceptable, whereas risks below 1×10^{-6} are not likely to pose significant health risks. A moderate CR value of 1×10^{-3} was proposed by Pipoyan *et al.* (2019), and the threshold level $CR > 10^{-4}$ was also suggested. The adopted risk classification for CR was documented in Table 1.4.

Table 3.3. Food intakes (g day^{-1}) in the population (18- to 64-year-olds) (IUNA, 2011)

	Population	
Food product	**Mean**	**SD**
Potatoes (boiled, mashed, baked)	71	74
Green vegetables	13	23
Carrots	13	19
Salad vegetables (e.g. lettuce)	21	28

Source: Nag and Cummins (2022).

3.2.5 Scenario analysis

Along with the baseline scenario, three other scenarios were performed (Table 3.4). Scenario S1 looked at the influence of Pb levels and the addition

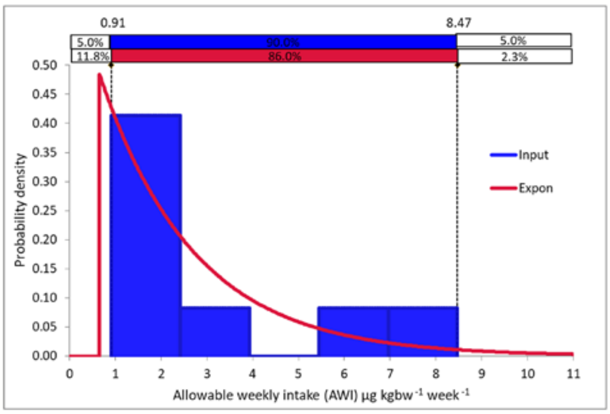

Figure 3.3. Fitted distribution on available AWI of Pb, a global comparison based on Jin *et al.* (2014): mean AWI 2.7 µg kg^{-1} bw week^{-1} or 0.0027 mg kg^{-1} bw week^{-1}. Source: Nag and Cummins (2022).

Table 3.4. Scenario analysis: deviation from the baseline scenario

Abbreviation	Scenario name	Deviation from the baseline scenario
BS	Baseline scenario	N/A: note – lognorm(41.1, 21.5) used for background concentration; range 14–188 mg kg^{-1}
S1	With biosolids: Pb level received from Louth County Council (7.9 mg kg^{-1})	BS: no anthropogenic concentration of Pb is added to Pb levels in background soil S1: concentration of Pb in soil = background concentration of Pb + monitored level of Pb in biosolids
S2	With biosolids: fitted distribution	S2: concentration of Pb in soil = background concentration of Pb + uniform (0, monitored level of Pb in biosolids with fitted distribution on published literature values documented in Figure 1.1)
S3	No potato consumed	A hypothetical scenario where it is assumed that no potato is ingested

N/A, not applicable.
Source: Nag and Cummins (2022).

of anthropogenic Pb to the BC Pb in soil. This anthropogenic level of Pb was received from the study area. Scenario S2 was set to look at the influence of the variability of the level of Pb in biosolids, as a distribution was fitted to the data presented in Figure 1.1. S3 represents a hypothetical scenario in which it is assumed that no one consumes potato; the objective of this scenario was to determine the influence of potato consumption, which was the most commonly eaten solid food product (Table 3.3) recorded in the survey.

3.3 Results

3.3.1 Data analysis on Tellus data

The distribution of Pb concentration in shallow and deeper soil (A and S samples, respectively) ranged from 7 to 264 mg kg^{-1} and from 4 to 258 mg kg^{-1}, respectively, while Pb concentration in surface water (W samples) ranged from 0.01 to 0.564 μg l^{-1}, which is less than the lowest limit of Pb (5 μg l^{-1}) as set by the US Code of Federal Regulations (2019) described in Table 1.3. The level in sediment was found to be between 13 and 108 mg kg^{-1}. A histogram of A soil samples (Figure 3.4) suggests that in 94% of observations, the Pb concentration in topsoil was below the allowable limit of 80 mg kg^{-1} set by the *Codes of Good Practice for the Use of Biosolids in Agriculture* (DELG, 2009) (Table 1.3). The maximum permissible limit of Pb in agricultural soil and biosolids is 50–300 mg kg^{-1} and 750–1200 mg kg^{-1}, respectively (European Union, 1986). Furthermore, based on a 10-year average application, the maximum amount of Pb in the biosolids to be added to agricultural land is

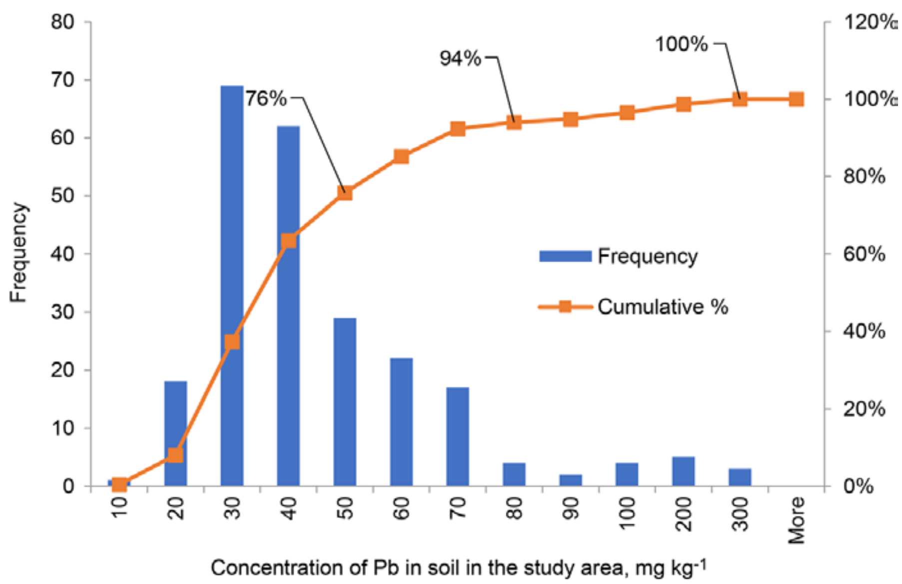

Figure 3.4. Histogram of topsoil samples (A), irrespective of land use, where 94% fall within the predicted no-effect Pb concentration level in the soil (PNEC$_{Pb_soil}$) of 80 mg kg^{-1}. Source: Nag and Cummins (2022).

15 kg ha^{-1} year^{-1}. Therefore, 76% of the observations were below 50 mg kg^{-1}, and under no conditions was the Pb concentration of soil observed to be beyond the permissible upper limit of 300 mg kg^{-1}.

3.3.2 Estimation of Pb concentration in topsoil and surface water

The Pb concentration in topsoil in the case study site ranged from 14 to 188 mg kg^{-1} (mean 39.7, mode 30.2 mg kg^{-1}) and from 7.0 to 248.4 mg kg^{-1} (mean 41.1, mode 28.3 mg kg^{-1}) in arable lands and pastures, respectively. The overall concentration of Pb in surface water was 0.01–0.563 μg l^{-1}; however, the range of Pb levels within the region of drinking water treatment plant locations was found to be 0.01–0.034 μg l^{-1}.

3.3.3 Exposure assessment: daily and weekly human exposure and sensitivity analysis

The HE, calculated weekly intake per body weight (WIPBW), probability of calculated WIPBW in comparison with AWI, and sensitivity analysis are presented in Figure 3.5. The HE ranged from 0.013 mg day^{-1} (5th percentile) to 0.199 mg day^{-1} (95th percentile), with a mean of 0.073 mg day^{-1} (Figure 3.5a), while a mean WIPBW was calculated as 0.0065 mg kg^{-1} bw week^{-1} (5th percentile 0.001 and 95th percentile 0.017, Figure 3.5b), which is greater than the AWI of 0.0027 mg kg^{-1} bw week^{-1}. A sensitivity analysis was performed, and the result (Figure 3.5c) revealed that the consumption of potato is the most sensitive parameter of the model, which is positively correlated (coefficient +0.75) with the HE. This is followed by the concentration of Pb in the arable soil (+0.44), bioaccumulation through tuber vegetables (+0.29), consumption of carrots (+0.22), and salad and vegetable consumption (+0.1), which are among the most sensitive parameters. The simulated mean WIPBW of 0.0065 mg kg^{-1} bw week^{-1} is equivalent to 0.9 μg kg^{-1} bw day^{-1}. A goal-seek function was used in @RISK software (Advance Analyses) to estimate the maximum level in soil media that could result in an exceedance of the LOAEL of 0.0012 mg kg^{-1} bw day^{-1}. This was found to be 51 mg kg^{-1}, which would result in a mean daily HE to Pb of below 0.0012 mg kg^{-1} bw day^{-1}.

3.3.4 Scenario analysis and goal-seek function

Figure 3.6 demonstrates that the contribution of drinking water to the overall HE is negligible when compared with crops and vegetables. It should be noted that this study focused on geological sources for surface water contamination and does not consider potential contamination in the distribution network (namely lead pipes) (EPA, 2019b). The scenario analysis (Figure 3.6) indicates that the variability in the Pb levels in biosolids can be a crucial parameter of the model, as the daily mean HE to Pb for S2 was the highest (0.121 mg day^{-1}), followed by baseline and scenario S1 (0.073 mg day^{-1}). The lowest HE value was observed to correspond to scenario S3 (0.022 mg day^{-1}).

3.3.5 Evaluated risk

The six methodologies for risk assessment of Pb result in an overall low risk as a result of Pb exposure (Table 3.5). HQ and THQ indicated "no adverse health effects" and "no risk", respectively, for RfD_o 4×10^{-3} mg kg^{-1} bw day^{-1} in all scenarios. This RfD_o value was also considered in recent studies (Zhuang *et al.*, 2009; Guo *et al.*, 2018; Aendo *et al.*, 2019; Pipoyan *et al.*, 2019). If the HQ is greater than 1, the pollution might result in a potential risk (non-carcinogenic) to human health (Qu *et al.*, 2018; Nguyen *et al.*, 2019). However, Sarwar *et al.* (2019) raised the important point that it may be an overestimate if only the HQ is checked; instead, the HI must be evaluated considering other metals.

3.3.6 Assumption, limitations and recommendation for future work

- This study assumed that the population consumes the specified food products grown in the designated case study site.
- This study focused only on foods that are not mixed with other ingredients; however, secondary food products, for example processed and homemade potato products and chipped, fried and roasted potatoes, which are not considered, may give rise to further Pb exposure. Given this, cumulative exposure routes should be investigated.

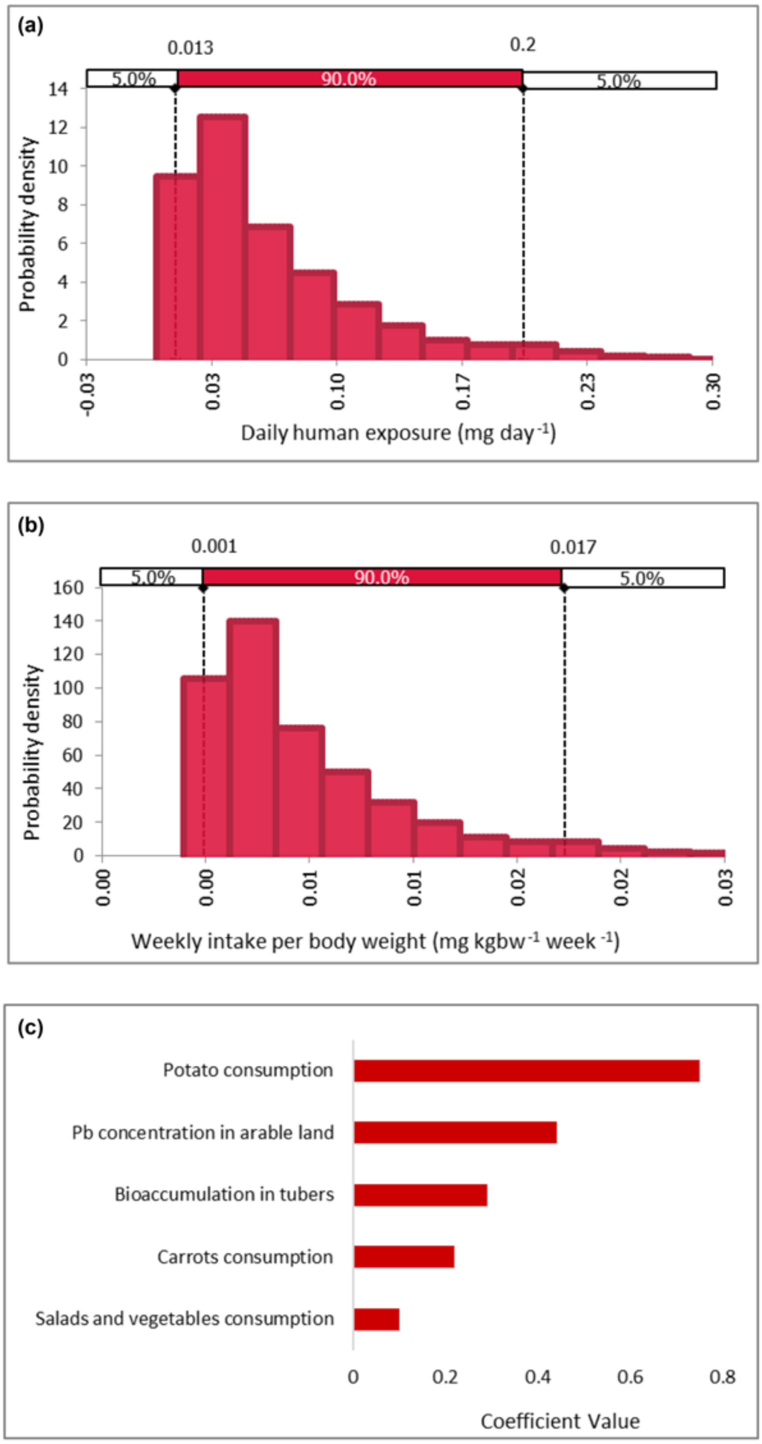

Figure 3.5. Daily (a) and weekly (b) exposure of Pb, followed by a sensitivity analysis (c). Source: Nag and Cummins (2022).

- Potential bioaccumulation and bioaccumulation of metals to plant and animal tissues can vary greatly between animal and plant species; these data should be captured where possible. Experiment-based case studies for bioaccumulation specific to Irish conditions are recommended.
- Validation at the point of food consumption on Pb levels in food products may improve the confidence in predictive modelling.
- This study proposes an expansion of the current study for future work looking at different toxic metal(loid)s, including the health impacts on adults, the elderly and children.

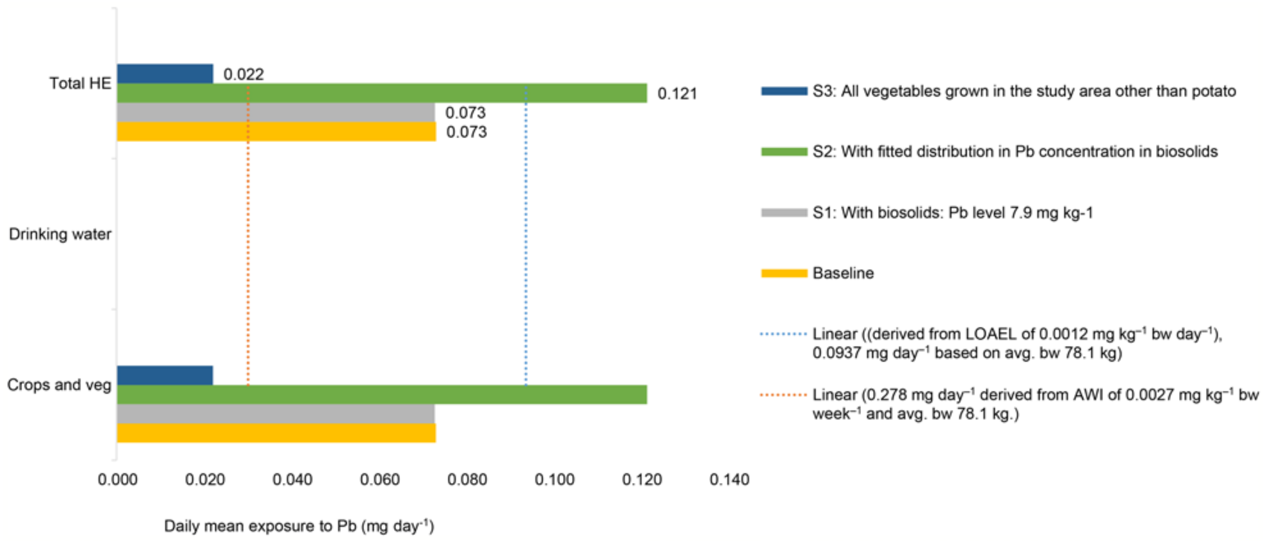

Figure 3.6. Scenario analysis for daily mean human exposure to Pb. Source: Nag and Cummins (2022).

Table 3.5. The evaluated risk for baseline and non-biosolid scenario using multiple risk evaluation methods

Methods[a]	Baseline score	Risk	S1	Risk	S2	Risk	S3	Risk
HQ	0.234	NoAHE	0.233	NoAHE	0.389	NoAHE	0.071	NoAHE
DDI	0.001	No risk	0.001	No risk	0.002	No risk	0.000	No risk
DIM	0.000	No risk	0.000	No risk	0.000	No risk	0.000	No risk
HRI	0.020	Safe	0.020	Safe	0.033	Safe	0.006	Safe
THQ	0.234	No risk	0.233	No risk	0.389	No risk	0.071	No risk
CR	0.00001	Low risk	0.00001	Low risk	0.000013	Low risk	0.00000	Low risk

[a]Units: HQ, unitless; DDI, mg day^{-1}; DIM, mg day^{-1} kg^{-1} bw; HRI, unitless; THQ, 10–3 kg^{-1} person^{-1}; CR, unitless.
NoAHE, no adverse health effects.
Source: Nag and Cummins (2022).

- The level of Pb in human blood is the ultimate criterion to evaluate exposure to Pb; therefore, a health survey would improve understanding in this area.

3.4 Discussion

This study highlighted the importance of GIS tools to collate data for Pb levels in soil and water. The concentration of Pb in topsoil varied from 14 to 188 mg kg^{-1} (mean 39.7) and from 7.0 to 248.4 mg kg^{-1} (mean 41.1) in arable lands and pastures, respectively. The highest potential bioaccumulation was observed in root and tuber crops, followed by leafy vegetables. The daily mean HE to Pb for the general population was found to be 0.073 mg day^{-1}, where the mean weekly exposure was calculated as 0.0065 mg kg^{-1} bw week^{-1}. The fitted distribution to the biosolids scenario (S2) increases the daily HE from 0.073 to 0.121 mg day^{-1} compared with the non-biosolids or BS. A sensitivity analysis highlighted that the intake of potatoes (as a highly consumed food product) is a critical input and is positively correlated (coefficient +0.75) with HE, followed by the concentration of Pb in arable soil (+0.44), bioaccumulation in tuber vegetables (+0.29), consumption of carrots (+0.22) and consumption of salad vegetables (+0.10). DDI, DIM, HRI and CR indicated “safe”, “no risk” or “low risk” owing to human exposure to Pb. Furthermore, HQ and THQ displayed no risk at higher RfD_o of Pb (4×10^{-3} mg kg^{-1} bw day^{-1}). This study estimates that, for the scenarios considered, the maximum level of Pb in the soil to ensure that mean HE to Pb does not exceed the LOAEL was 51 mg kg^{-1} in the soil media. This ensures limited uptake and bioaccumulation by plants, hence ensuring reduced HE to Pb through the

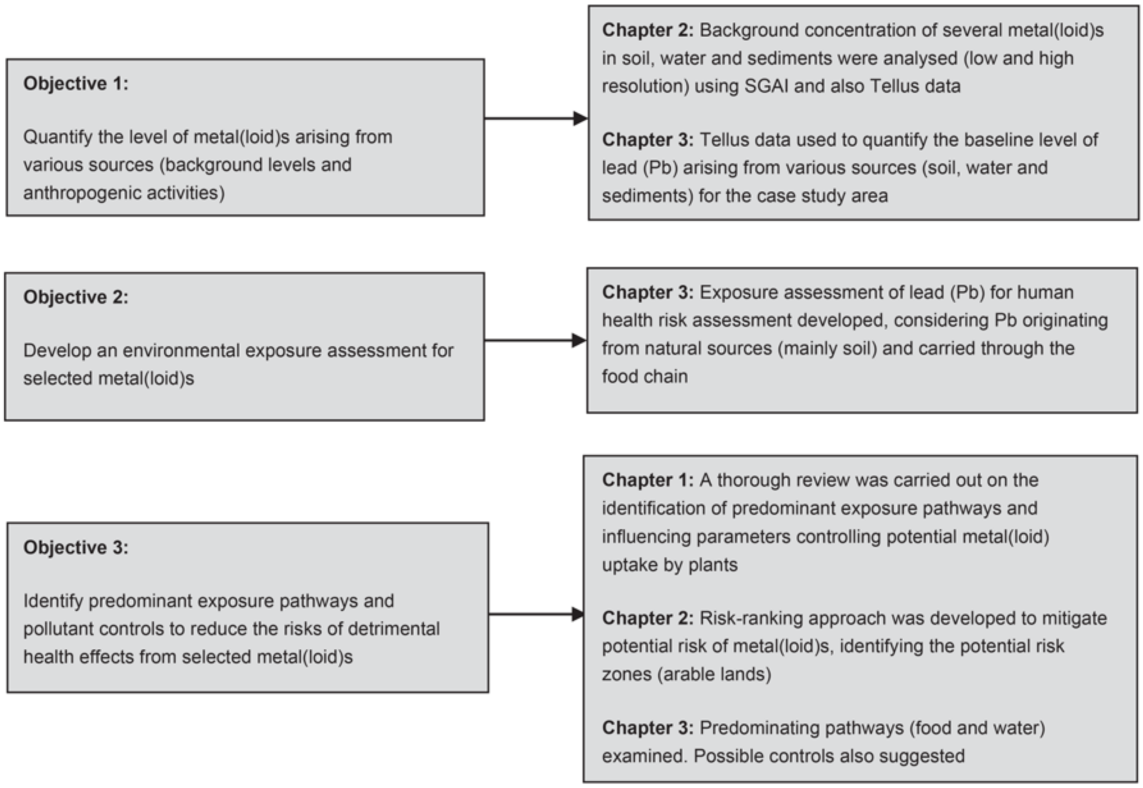

Figure 3.7. Fulfilment of the overall project objectives by results produced in the report chapters.

"environment–food" pathway. This is in line with the permissible range for soils (range 50–300 mg kg^{-1}) recommended by the European Commission (European Union, 1986), but below the limit of 80 mg kg^{-1} recommended by the *Codes of Good Practice for the Use of Biosolids in Agriculture* (DELG, 2009) prior to application of biosolids to agricultural land. The quantitative study on Pb exposure considers a worst-case scenario, as the overall concentration of Pb is treated as a summation of BC plus concentration in biosolids. It should be noted that this is a pessimistic approach, as the actual level is likely to be less than this owing to the loss of Pb following a combination of land application of biosolids and rainfall events.

3.4.1 Fulfilment of objectives

The fulfilment of the project objectives is presented in Figure 3.7, with the results indicated in Chapters 1, 2 and 3.

4 Conclusions

Based on the findings of this research, the following conclusions can be drawn.

- Metal(loid) uptake by plants is dependent on the retainability of metal(loid)s in the soil. The retainability of metal(loid)s in the soil is further influenced by pH, soil organic matter/carbon, existing ionic property of soil, soil texture class (mainly clay content), topography (slope) and drainage property of soil.
- The SGAI suggests that, mainly along the east coast of the country, the predicted environmental concentrations of As (31 mg kg^{-1}), Cd (2.2 mg kg^{-1}) and Zn (maximum of 267 mg kg^{-1}) were higher than the threshold values (*Codes of Good Practice for the Use of Biosolids in Agriculture*; DELG, 2009).
- The spatial analysis (using Tellus data) revealed that RQ values corresponding to Cd, Zn, As and Pb based on soil samples exceeded 1, which is the allowable upper limit of low-level classification of metal(loid)s in the environment. The RQs corresponding to As, Cd, Cu, Ni, Pb and Zn levels in water and Cu, Pb, As, Cd, Cr and Zn levels in sediments suggest minimal exceedance of threshold values for the metal(loid)s. Therefore, the RQ based on water and sediment samples shows that the BC of metal(loid)s in both media are below the allowable thresholds.
- The novel semi-quantitative screening analysis with the help of GIS maps suggests that the east coast of Ireland poses a higher relative risk when comparing the final risk score. In addition, the east coast is also a significant producer of vegetable crops, highlighting the need for further investigation. Furthermore, this research proposes that in-depth risk assessment studies on Cd, As and Pb are essential to realising the fate of metal(loid)s and their risk assessment for formulating and improving regulations around metal(loid)s.
- The quantitative analysis revealed that the highest value of the bioaccumulation factor was observed for root and tuber crops, followed by leafy vegetables. The daily mean HE to Pb for the general population was found to be 0.073 mg day^{-1}, and mean weekly exposure was calculated as 0.0065 mg kg^{-1} bw $week^{-1}$. The fitted distribution to the biosolids scenario (S2) increases the daily HE from 0.073 to 0.121 mg day^{-1}, compared with the no-biosolids or baseline scenario.
- A sensitivity analysis highlighted that the intake of potatoes (as a highly consumed food product) is a critical input and is positively correlated (coefficient +0.75) with HE, followed by the concentration of Pb in arable soil (+0.44), bioaccumulation in tuber vegetables (+0.29), consumption of carrots (+0.22) and consumption of salad vegetables (+0.10).
- HQ, DDI, DIM, HRI, THQ and CR indicated “no risk” “safe” or “low risk” owing to human exposure to Pb.
- The significance of limiting Pb concentrations in the soil is highlighted. This is in agreement with the lower permissible limit of Pb in the soil (range 50–300 mg kg^{-1}) recommended by the European Commission (European Union, 1986) and the more refined limit of 80 mg kg^{-1} recommended by the *Codes of Good Practice for the Use of Biosolids in Agriculture* (DELG, 2009).

5 Recommendations

The following recommendations are made as a result of the research findings.

- Field-based tests are necessary to estimate the actual bioaccumulation factor to predict the potential metal(loid) levels in the edible portion of the crops taken up from the soil. In particular, a periodic soil test is required where root and tubers crops are grown.
- This study highlights the significance of limiting the Pb concentration in agricultural soil media (51 mg kg^{-1} for the conditions studied in this report) to ensure limited uptake and bioaccumulation by plants, hence ensuring reduced Pb human exposure through the “food” pathway.
- Based on the data analysis on Tellus sampling points (GSI, 2020), ≈90% of the soil samples in the studied region had a soil concentration of Pb below 51 mg kg^{-1} (northern counties), highlighting production areas suitable for selected crops.
- Based on the findings of this study, it is recommended that a similar quantitative human health risk assessment on Cd and As exposure be conducted in future work. In addition, the concentration of As in both surface and groundwater needs to be evaluated, as international evidence suggests that groundwater abstraction for drinking water is one of the predominant pathways for As.
- It is important to identify the most suitable areas to grow certain crops, which could minimise the overall bioaccumulation of metal(loid)s in crops.
- Future studies should assess the biotransfer of metal(loid)s through animal products where Pb levels in pastures soil (through the grass to milk or meat products) and water (through fish products) can be included.

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Abbreviations

AWI	Allowable weekly intake
BC	Baseline concentration
Bio_{acc}	Bioaccumulation factor
BLL	Blood lead level
BS	Baseline scenario
CR	Cancer risk
DALY	Disability-adjusted life-year
DDI	Daily dietary index
DIM	Daily intake of metals
EPA	Environmental Protection Agency
FRS	Final risk score
GIS	Geographical information system
HE	Human exposure
HE_{daily}	Daily human exposure
HI	Hazard index
HQ	Hazard quotient
HRI	Health risk index
IPI	Integrated pollution index
IRQ	Integrated risk quotient
LOAEL	Lowest observed adverse effect level
NOAEL	No observed adverse effect level
PEC	Predicted environmental concentration
PNEC	Predicted no-effect concentration
PWS	Public water supply
RDA	Recommended daily allowance
RfD	Reference dose
RfD_O	Oral reference dose
RQ	Risk quotient
SD	Standard deviation
SGAI	Soil Geochemical Atlas of Ireland
SOC	Soil organic carbon
SOM	Soil organic matter
S_p	Probability sum scenario
THQ	Target hazard quotient
WIPBW	Weekly intake per body weight
WWTP	Wastewater treatment plant

Appendix 1 Additional Maps

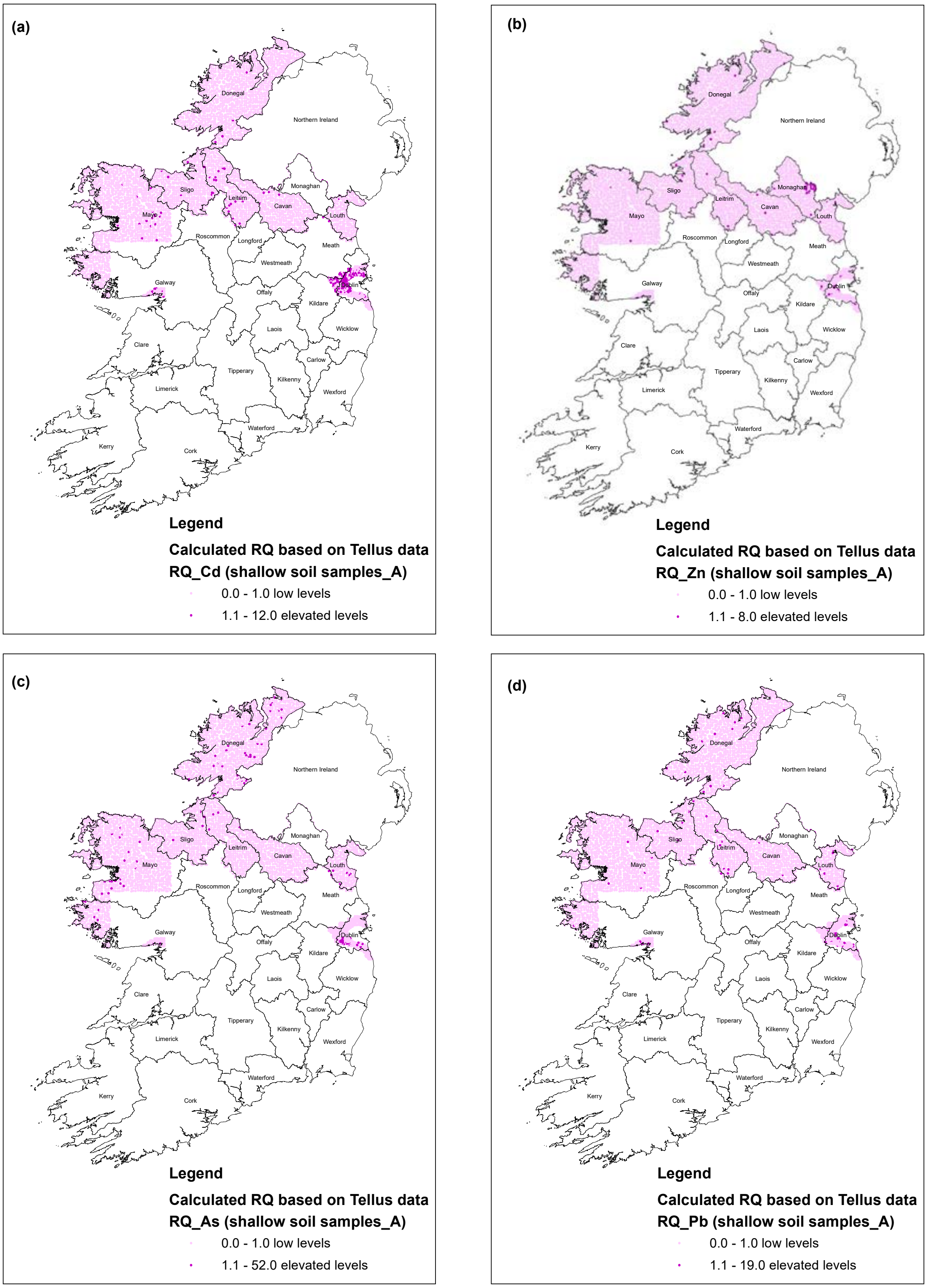

Figure A1.1. Spatial distribution of RQ for (a) Cd, (b) Zn, (c) As and (d) Pb in Tellus shallow soil (sample A). Publicly available data currently fully cover six northern counties (Donegal, Leitrim, Sligo, Cavan, Monaghan and Louth) and partly cover another three (Mayo, Galway and Dublin).

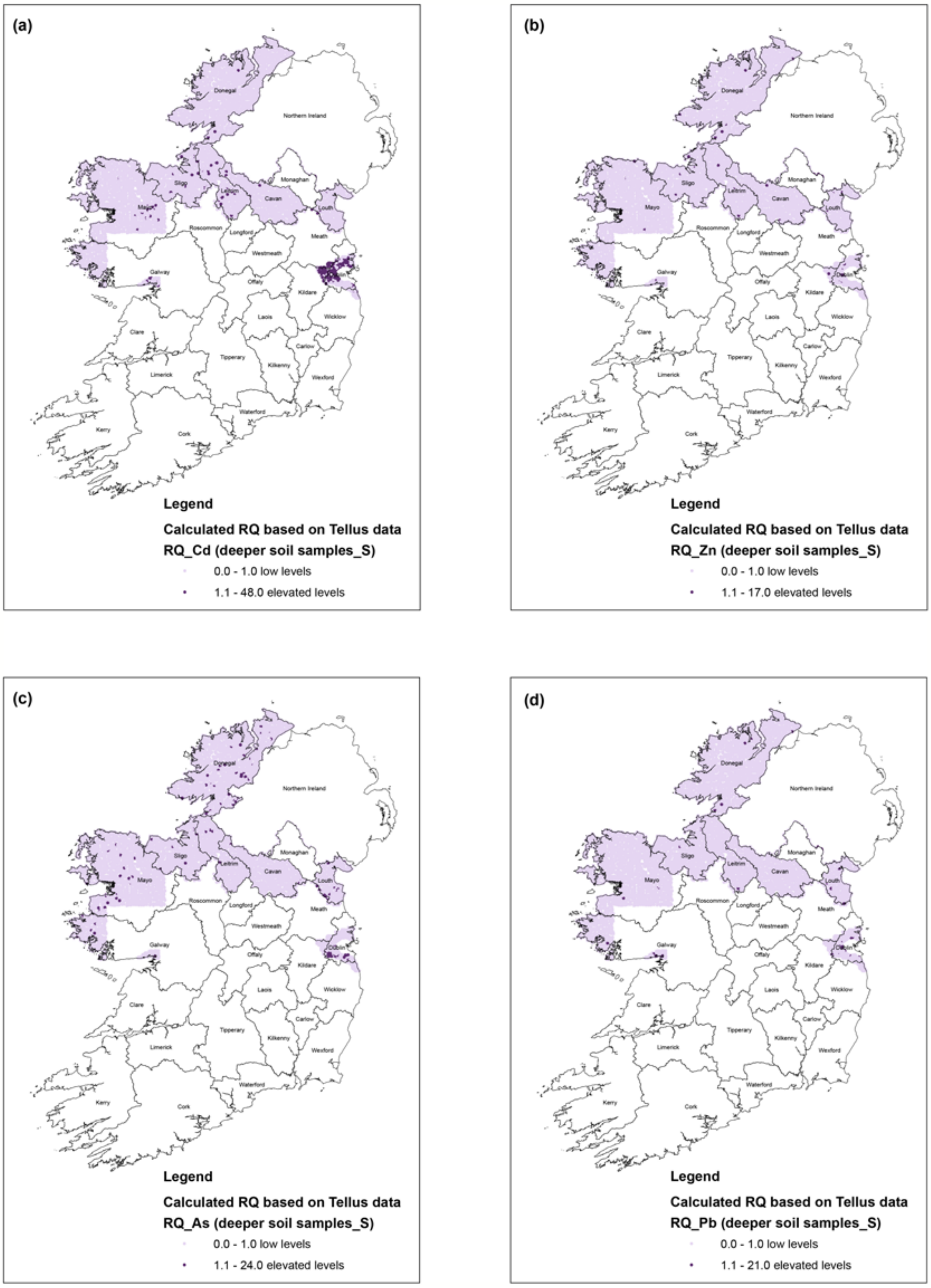

Figure A1.2. Spatial distribution of RQ for (a) Cd, (b) Zn, (c) As and (d) Pb in Tellus deeper soil (sample S). Publicly available data currently fully cover six northern counties (Donegal, Leitrim, Sligo, Cavan, Monaghan and Louth) and partly cover another three (Mayo, Galway and Dublin).

Figure A1.3. Spatial distribution of RQ for (a) As, (b) Cd, (c) Cu, (d) Ni, (e) Pb and (f) Zn in Tellus surface water (W). Publicly available data currently fully cover six northern counties (Donegal, Leitrim, Sligo, Cavan, Monaghan and Louth) and partly cover another three (Mayo, Galway and Roscommon).

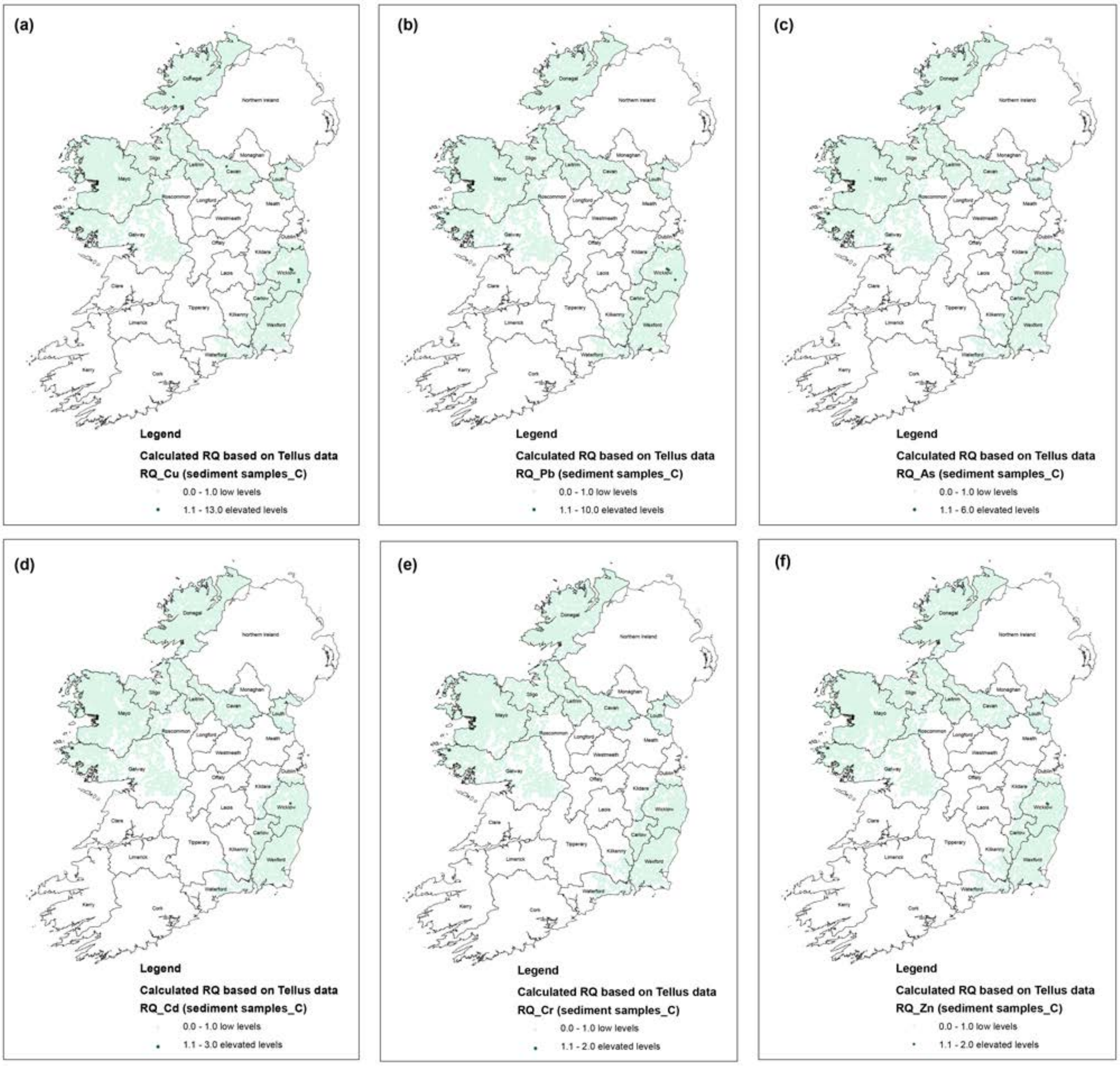

Figure A1.4. Spatial distribution of RQ for (a) Cu, (b) Pb, (c) As, (d) Cd, (e) Cr and (f) Zn in Tellus sediments (C). Publicly available data currently fully cover six northern counties (Donegal, Leitrim, Sligo, Cavan, Monaghan and Louth) and two south-eastern counties (Wicklow and Wexford) and partly cover Mayo, Galway, Roscommon, Dublin, Kildare, Carlow, Kilkenny and Waterford.

AN GHNÍOMHAIREACHT UM CHAOMHNÚ COMHSHAOIL
Tá an Ghníomhaireacht um Chaomhnú Comhshaoil (GCC) freagrach as an gcomhshaol a chaomhnú agus a fheabhsú mar shócmhainn luachmhar do mhuintir na hÉireann. Táimid tiomanta do dhaoine agus don chomhshaol a chosaint ó éifeachtaí díobhálacha na radaíochta agus an truaillithe.

Is féidir obair na Gníomhaireachta a roinnt ina trí phríomhréimse:

Rialú: *Déanaimid córais éifeachtacha rialaithe agus comhlíonta comhshaoil a chur i bhfeidhm chun torthaí maithe comhshaoil a sholáthar agus chun díriú orthu siúd nach gcloíonn leis na córais sin.*

Eolas: *Soláthraímid sonraí, faisnéis agus measúnú comhshaoil atá ar ardchaighdeán, spriocdhírithe agus tráthúil chun bonn eolais a chur faoin gcinnteoireacht ar gach leibhéal.*

Tacaíocht: *Bímid ag saothrú i gcomhar le grúpaí eile chun tacú le comhshaol atá glan, táirgiúil agus cosanta go maith, agus le hiompar a chuirfidh le comhshaol inbhuanaithe.*

Ár bhFreagrachtaí

Ceadúnú
Déanaimid na gníomhaíochtaí seo a leanas a rialú ionas nach ndéanann siad dochar do shláinte an phobail ná don chomhshaol:
- saoráidí dramhaíola *(m.sh. láithreáin líonta talún, loisceoirí, stáisiúin aistrithe dramhaíola)*;
- gníomhaíochtaí tionsclaíocha ar scála mór *(m.sh. déantúsaíocht cógaisíochta, déantúsaíocht stroighne, stáisiúin chumhachta)*;
- an diantalmhaíocht *(m.sh. muca, éanlaith)*;
- úsáid shrianta agus scaoileadh rialaithe Orgánach Géinmhodhnaithe *(OGM)*;
- foinsí radaíochta ianúcháin *(m.sh. trealamh x-gha agus radaiteiripe, foinsí tionsclaíocha)*;
- áiseanna móra stórála peitril;
- scardadh dramhuisce;
- gníomhaíochtaí dumpála ar farraige.

Forfheidhmiú Náisiúnta i leith Cúrsaí Comhshaoil
- Clár náisiúnta iniúchtaí agus cigireachtaí a dhéanamh gach bliain ar shaoráidí a bhfuil ceadúnas ón nGníomhaireacht acu.
- Maoirseacht a dhéanamh ar fhreagrachtaí cosanta comhshaoil na n-údarás áitiúil.
- Caighdeán an uisce óil, arna sholáthar ag soláthraithe uisce phoiblí, a mhaoirsiú.
- Obair le húdaráis áitiúla agus le gníomhaireachtaí eile chun dul i ngleic le coireanna comhshaoil trí chomhordú a dhéanamh ar líonra forfheidhmiúcháin náisiúnta, trí dhíriú ar chiontóirí, agus trí mhaoirsiú a dhéanamh ar leasúchán.
- Cur i bhfeidhm rialachán ar nós na Rialachán um Dhramhthrealamh Leictreach agus Leictreonach (DTLL), um Shrian ar Shubstaintí Guaiseacha agus na Rialachán um rialú ar shubstaintí a ídíonn an ciseal ózóin.
- An dlí a chur orthu siúd a bhriseann dlí an chomhshaoil agus a dhéanann dochar don chomhshaol.

Bainistíocht Uisce
- Monatóireacht agus tuairisciú a dhéanamh ar cháilíocht aibhneacha, lochanna, uiscí idirchriosacha agus cósta na hÉireann, agus screamhuiscí; leibhéil uisce agus sruthanna aibhneacha a thomhas.
- Comhordú náisiúnta agus maoirsiú a dhéanamh ar an gCreat-Treoir Uisce.
- Monatóireacht agus tuairisciú a dhéanamh ar Cháilíocht an Uisce Snámha.

Monatóireacht, Anailís agus Tuairisciú ar an gComhshaol
- Monatóireacht a dhéanamh ar cháilíocht an aeir agus Treoir an AE maidir le hAer Glan don Eoraip (CAFÉ) a chur chun feidhme.
- Tuairisciú neamhspleách le cabhrú le cinnteoireacht an rialtais náisiúnta agus na n-údarás áitiúil *(m.sh. tuairisciú tréimhsiúil ar staid Chomhshaol na hÉireann agus Tuarascálacha ar Tháscairí)*.

Rialú Astaíochtaí na nGás Ceaptha Teasa in Éirinn
- Fardail agus réamh-mheastacháin na hÉireann maidir le gáis cheaptha teasa a ullmhú.
- An Treoir maidir le Trádáil Astaíochtaí a chur chun feidhme i gcomhair breis agus 100 de na táirgeoirí dé-ocsaíde carbóin is mó in Éirinn.

Taighde agus Forbairt Comhshaoil
- Taighde comhshaoil a chistiú chun brúnna a shainaithint, bonn eolais a chur faoi bheartais, agus réitigh a sholáthar i réimsí na haeráide, an uisce agus na hinbhuanaitheachta.

Measúnacht Straitéiseach Timpeallachta
- Measúnacht a dhéanamh ar thionchar pleananna agus clár beartaithe ar an gcomhshaol in Éirinn *(m.sh. mórphleananna forbartha)*.

Cosaint Raideolaíoch
- Monatóireacht a dhéanamh ar leibhéil radaíochta, measúnacht a dhéanamh ar nochtadh mhuintir na hÉireann don radaíocht ianúcháin.
- Cabhrú le pleananna náisiúnta a fhorbairt le haghaidh éigeandálaí ag eascairt as taismí núicléacha.
- Monatóireacht a dhéanamh ar fhorbairtí thar lear a bhaineann le saoráidí núicléacha agus leis an tsábháilteacht raideolaíochta.
- Sainseirbhísí cosanta ar an radaíocht a sholáthar, nó maoirsiú a dhéanamh ar sholáthar na seirbhísí sin.

Treoir, Faisnéis Inrochtana agus Oideachas
- Comhairle agus treoir a chur ar fáil d'earnáil na tionsclaíochta agus don phobal maidir le hábhair a bhaineann le caomhnú an chomhshaoil agus leis an gcosaint raideolaíoch.
- Faisnéis thráthúil ar an gcomhshaol ar a bhfuil fáil éasca a chur ar fáil chun rannpháirtíocht an phobail a spreagadh sa chinnteoireacht i ndáil leis an gcomhshaol *(m.sh. Timpeall an Tí, léarscáileanna radóin)*.
- Comhairle a chur ar fáil don Rialtas maidir le hábhair a bhaineann leis an tsábháilteacht raideolaíoch agus le cúrsaí práinnfhreagartha.
- Plean Náisiúnta Bainistíochta Dramhaíola Guaisí a fhorbairt chun dramhaíl ghuaiseach a chosc agus a bhainistiú.

Múscailt Feasachta agus Athrú Iompraíochta
- Feasacht chomhshaoil níos fearr a ghiniúint agus dul i bhfeidhm ar athrú iompraíochta dearfach trí thacú le gnóthais, le pobail agus le teaghlaigh a bheith níos éifeachtúla ar acmhainní.
- Tástáil le haghaidh radóin a chur chun cinn i dtithe agus in ionaid oibre, agus gníomhartha leasúcháin a spreagadh nuair is gá.

Bainistíocht agus struchtúr na Gníomhaireachta um Chaomhnú Comhshaoil
Tá an ghníomhaíocht á bainistiú ag Bord lánaimseartha, ar a bhfuil Ard-Stiúrthóir agus cúigear Stiúrthóirí. Déantar an obair ar fud cúig cinn d'Oifigí:
- An Oifig um Inmharthanacht Comhshaoil
- An Oifig Forfheidhmithe i leith cúrsaí Comhshaoil
- An Oifig um Fianaise is Measúnú
- Oifig um Chosaint Radaíochta agus Monatóireachta Comhshaoil
- An Oifig Cumarsáide agus Seirbhísí Corparáideacha

Tá Coiste Comhairleach ag an nGníomhaireacht le cabhrú léi. Tá dáréag comhaltaí air agus tagann siad le chéile go rialta le plé a dhéanamh ar ábhair imní agus le comhairle a chur ar an mBord.

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Cumulative Health Effects of Metal(loids) through Aggregate Environmental Pathways

epaResearch

Authors: Rajat Nag and Enda Cummins

Background levels of metal(loid)s coupled with anthropogenic sources may lead to increased levels of certain metal(loid)s in soil, leading to potential uptake by plants. This study develops a source–pathway–receptor conceptual model for metal(loid)s in environmental media. An intergraded risk quotient (IRQ) highlighted certain metal(loid)s' in soils requiring vigilance, particularly in the east of Ireland. A case study in County Louth focused on the lead (Pb) exposure pathway and highlighted control measures, including the potential for selective growth of crops that are likely to accumulate metal(loid)s in soils of low metal(loid) content. The application of biosolids containing metal(loid)s needs to be viewed in the context of the background levels of those metal(loid)s in soil, thereby ensuring that overall levels of metal(loid)s in the soil remain within permitted threshold levels. The study presents an approach that can be extended to further evaluate pollutants and their environment–health interactions.

Identifying Pressures

Some metal(loid)s are an essential requirement for plant and crop growth. There are inherent background levels of many metal(loid)s' in regional soils depending on geological sources. In addition, anthropogenic sources of metal(loid)s may be derived from diffuse, regional land application of biosolid products. Background levels coupled with anthropogenic sources may lead to increased levels of certain metal(loid)s in soil, leading to potential transfer to water sources and potential uptake by plants. The latter could result in transfer into the feed-to-food chain, namely via grazing animals, and also biotransfer to food products, resulting in human exposure.

Informing Policy

The research shows the development of a risk quotient (RQ) methodology that is used to compare reported levels of metal(loid)s and the maximum permissible values of metal(loid)s in various environmental media (soil, water, sediments). The RQ can be used to inform policy with regard to metal(loid)s requiring vigilance and careful monitoring in environmental media. Further assessments should be undertaken on a national basis, when the Tellus database coverage is extended, which could help with human protection from metal(loid)s from environmental sources. The exposure assessment model can be used to assess likely exposure scenarios with a focus on environment–food interactions and to assess maximum permissible levels in soil in order to reduce the potential for bioaccumulation in plants that may be used for human consumption. Such techniques can inform national and international advisory bodies on the cumulative influence of risk factors on overall metal(loid) persistence in environmental media.

Developing Solutions

A semi-quantitative risk-ranking approach was adopted to identify potential metal(loid)s of concern and priority locations where elevated levels may occur. The integration of data capturing the influence of pH, soil organic carbon, soil texture class, slope, field/soil drainage class, baseline concentration, proximity to mines, urban activity and biosolids application on potential uptake of metal(loid)s by crops was carried out as part of this study. This study highlights the integration of an analysis of baseline concentrations of metal(loid)s through a geographical information system (GIS), with a probabilistic risk assessment approach to provide exposure estimates for metal(loid)s' of human health concern. The approach can be applied to a multitude of metal(loid)s and other potential hazards and can help in the evaluation of potential environment–health interactions.

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