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Application of cattle manure as fertilizer in pastureland: Estimating the incremental risk due to metal accumulation employing a multicompartment model

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Abstract

Specific-site data of metal concentration in cattle manure from NW Spain and a multicompartment fate and exposure model were used to evaluate metal fate and the main routes of exposure after a 100 year period of application of cattle manure as fertiliser in pastureland. Risk assessment was performed as a probabilistic analysis, and using a conservative worst-case exposure scenario. An accumulation model was used to predict the metal concentration in each environmental medium of concern. The incremental risk was estimated for the population inhabiting the surroundings of the area by a general multiexposure model. Monte Carlo simulations were performed to analyse uncertainty of the results. Furthermore, a sensitivity analysis was carried out to identify the contribution to variance by the different metals and exposure routes. Among the five pathways evaluated, the ingestion of meat and milk from cattle grazing in the area represents the main contribution to total exposure. The results indicate that the incremental risk to human health for people living in the surroundings of pasturelands due to continuous application of cattle manure after a 100 year period are not negligible for the metals considered (Cd, Cu, Ni, Pb and Zn), posing a total Reasonable Maximum Exposure (RME) of 0.75, being the ingestion of meat the main exposure pathway.

Keywords: Cattle manure; Pastureland; Metals; Accumulation; Exposure; Risk assessment

1. Introduction

Until the second half of the 20th century, the application of cattle droppings as fertiliser in pastureland has been a widespread practice in rural environments of the Northwest of Spain (Galicia). Currently, the method employed in all the intensive-farming installations is the storage of livestock droppings as manure in tanks, which leads to a more efficient and hygienic management of cattle, avoids the need of waste treatment in farms, and is easier to apply on fields. Manure can be defined as a heterogeneous material, product of a continuous fermentation process (mainly anaerobic) in the storage tank. Its main components are liquid and solid droppings of cattle together with cleaning waters employed to drag the excrements to the storage tank, and rainwater. Therefore, the two factors that more influence the composition of manure (or dilution degree) are the farm management and the climate, which may vary greatly between countries. In Galicia, the average characteristics of cattle manure expressed as percentage in dry matter are: 1.034 ±0.029 for density, 2.40±1.84 for ammonia N, 2.04± 0.86 for organic N, 41.51±5.53 for C and 11.74±4.73 for C/N ratio (Carballas and Díaz-Fierros, 1990). In the European context, data of manure characteristics and composition can be found in the ALFAM (2000) project, which tries to establish common rules for the addition rates of manure. The application of manure as fertiliser also presents several disadvantages concerning environment and to date, they have been mainly related with water contamination by nutrients (nitrates and phosphates) in rural zones, being fundamental the correct management and

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application rates of manure to avoid massive leaching of contaminants away from the plough layer of soil to groundwater (Calvo, 2003). In the case of Galicia (the region considered in this work), a study developed by Araujo et al. (1996) showed that more than a 70% of rural waters were not drinkable by N and P contamination. Another minor problem may be volatilization of certain organic compounds from manure which provoke bad odours. Intensive farming activities progressively increased the use of trace metals as feed supplements for improving animal health and productivity (Moore et al., 1995; Nicholson et al., 1999). An important percentage of these metals are excreted in faeces and urine, this resulting in metal-rich slurries, as in case of Cu (Kornegay et al., 1976).

Due to their slow accumulation (they don't degrade), and the contamination of soil by heavy metals can pose a serious problem in the near future, especially considering that some of them are strongly bound to organic matter (Bolan et al., 2004). In the United Kingdom, an important percentage of several metals contained in agricultural soils was due to manure application (Nicholson et al., 1999). However, little attention has been given to manure as a source of metal contamination, being most research in soil contamination and biotransfer to other media focused on municipal sewage sludge by both organic (Alcock et al., 1996; Duarte-Davidson and Jones, 1996; Smith et al., 2001) and inorganic (metals) compounds (Walter et al., 2006; Perez-Murcia et al., 2006; Page, 1974). Recently, a review by Bolan et al. (2004) showed the impacts of the increasing usage of certain metals present in manures in relation to their distribution in soils and their bioavailability to plants and subsequent phytotoxicity. These authors discussed the implications of manure-borne metals on environmental contamination and pointed out the necessity of applying specific management guidelines and best practices for the safe use of manure in agricultural activities. In fact, metal level increments in plants growing in manure-amended soil were reported (Zhou et al., 2005). The accumulation of metals in soil not only results in significant concentrations in plants, but also in cattle grazing in the fertilised pastureland (by ingestion of soil and pasture). Hence, the presence of metals in body tissues of cattle fed in slurry-amended pasturelands in Galicia has been reported (López-Alonso et al., 2000, 2002). Besides animal exposure and toxicity, human receptors may be exposed through different routes (ingestion, inhalation and/or dermal exposure). However, the impact of the continuous application of metal-rich manure in the pastureland over the environment and human health has not been evaluated under a probabilistic approach yet. The predicted concentrations of metals and the quantification of exposure can be assessed by employing a risk assessment process, which involves the application of fate and multi-exposure models. However, to perform a realistic modelling, the uncertainty of the model parameters and of the model itself has to be taking into account, especially when there are few data available. On the other hand, it is necessary to distinguish between uncertainty and variability. Uncertainty may be due to a lack of knowledge (incomplete data), to a lack of precision (measurement errors in the value of a parameter), or to the algorithms used for calculating model parameters, based on correlation of data collected in a wide range of field studies. Variability is due to the natural differences in the value of a parameter that affects risk between the members of a population (Cohen et al., 1996), and may be due to a range of human behaviours, e.g. breathing rates, or physiological characteristics (body weight). In addition, spatial and temporal variation inherent in natural processes (in this case the metal fate in soil), is also a cause of variability (Keller et al., 2002). Uncertainty can be reduced or even eliminated by collecting additional information and more-detailed data, while variability cannot and must not be eliminated, in order to obtain a realistic result.

In the present study, the quantification of the incremental risk of the population living near intensive-farming areas, due to a long-term application of cattle manure with relative high concentrations of heavy metals was estimated. The data employed in this work correspond to a field study carried out by the Edafology and Agricultural Chemistry Department of the University of Santiago de Compostela (Calvo, 2003) in pasturelands and surroundings of the basin of Magdalena river (Galicia, NW Spain) in year 2003. Cattle manure from 42 dairy farms were analysed for N, P, C, pH, density, phytoxicity and heavy metals among others. Application rates of manure per area and year were also measured. Evidence of metal accumulation in plants and animal growing and grazing in manure fertilised soils was found in several works on the literature. Based on these results, this study focused on the development of a preliminary evaluation of the impacts that this agricultural practice would have on human receptors in a long-term temporal horizon (100 years). For achieving this goal, the study was divided in the following subtasks: 1) Predicting the concentrations of heavy metals (Cd, Cu, Ni, Pb and Zn) in soil, pasture and leachate by means of an accumulation and fate model in a time period of 100 years. 2) Estimating the total exposure and the incremental health risk to population by considering five pathways of exposition to metals considering the concentrations determined in the previous objective. 3) Analysing the contribution of each exposure pathway and each metal to total health risk. 4) Carrying out an uncertainty and sensitivity analysis, to determine the main parameters which contribute to the uncertainty of the results. A propagation of uncertainty of the input parameters through the two main modules of the model (fate and exposure) was carried out by means of a Monte Carlo simulation, taking into account the inter- and cross-relations between them. As a result, the different risk ratios obtained in this screening evaluation would highlight the metals and their exposure pathways (in case that evidence of risk was obtained) that need a detailed assessment with more specific data and further research.

2. Methodology

The equations describing the accumulation and exposure models are summarised in the following. For predicting metal concentrations three equations were employed for each metal: a mass balance model for estimating the proper accumulation in soil, and two multi-correlation models for estimating the uptake from soil by plants and the free metal concentrations in soil solution. The exposure model was constituted by six equations, two of them being food-chain models for the estimation of metal concentration in the meat and milk of cattle. The remaining equations were employed to assess human exposure through the pathways considered: 1) ingestion of the meat and milk of cattle, 2) ingestion of the soil, 3) inhalation of the soil, and 4) dermal contact with the soil.

2.1. Accumulation

The accumulation of five heavy metals (Cd, Cu, Ni, Pb and Zn) in the soil was assessed by establishing a dynamic mass balance between input and output fluxes, according to the expression of Boekhold and van der Zee (1991) and Moolenaar et al. (1997):

$$d(C_s)/dt = R_i - R_l - R_p \tag{1}$$

where C_s is the concentration of the contaminant in soil, R_i is the input rate of contaminant, R_l is the leaching rate to groundwater, and R_p is the uptake rate by plants. The input rate of metals to the agricultural soil surface may be due to several contributions: total atmospheric deposition, addition of sewage sludge or manure, irrigation with wastewater and application of fertilizers. Taking into account that the output rates (leaching and plant uptake) are dependant on the concentration of metal in the soil, the integrated expression of Eq. (1) after some transformations for compatibility of units (de Meeûs et al., 2002), yields:

$$\begin{aligned} C_s(t) = {} & C_s(0)\exp[-(R_l + R_p)t] \\ & + \{R_i/[(10\rho d_p)(R_l + R_p)]\}\{1-\exp[-(R_l + R_p)t]\} \end{aligned} \tag{2}$$

where $C_s(0)$ is the background concentration in soil (mg kg^{-1}), $C_s(t)$ is the forecast concentration in soil at t years (mg kg^{-1}), d_p is depth of the plough layer (m) and ρ is the soil bulk density (kg m^{-3}). In Eq. (2), the units of the input rate R_i are g ha^{-1} y^{-1}, while the leaching R_l and the plant uptake R_p rates are in y^{-1}. As changes in the balance generally require long time scales, intraseasonal variations in plant (in this specific case pasture) uptake, leaching to groundwater and composition of the soil plough-layer are reduced by averaging of many growing seasons (Moolenaar et al., 1997).

In this study, application of cattle manure is considered the only input rate, since no other fertilizer was added. Aerial deposition was considered negligible because neither industrial plants nor important roads were present in the vicinity of the scenario. Meteorological conditions would favour metal deposition of emissions from a power plant, but this effect was considered almost null when compared with application of rich-metal manure. Therefore, Ri is the product of the application rate of cow manure (Ra) in m^3 ha^{-1} y^{-1} by the metal concentration in manure (Cm) in g/m^3.

The leaching behaviour of metals from soil plough layer mainly depends on the soil characteristics and the precipitation rate. The following equation describes the leaching rate (de Meeûs et al., 2002):

$$R_l = 1000F/(k_d \rho d_p) \tag{3}$$

where F is the precipitation excess (m y^{-1}), calculated as the product of the infiltration factor in soil (f) by the precipitation rate (P) in m y^{-1}, and k_d is the metal soil–liquid partitioning coefficient (l kg^{-1}).

Table 1
Algorithms for the estimation of soil–solution concentrations of metals

Metal	
Cd	$\log(C_l) = -0.47 \pm 0.02 \cdot \mathrm{pH} + 1.08 \pm 0.02 \cdot \log(\mathrm{Cs}) - 0.81 \pm 0.05 \cdot \log(\mathrm{OM}) + 3.42 \pm 0.11$
Cu	$\log(C_l) = -0.21 \pm 0.02 \cdot \mathrm{pH} + 0.93 \pm 0.05 \cdot \log(\mathrm{Cs}) - 0.21 \pm 0.02 \cdot \log(\mathrm{OM}) + 1.37 \pm 0.14$
Ni	$\log(C_l) = -1.05 \pm 0.09 \cdot \mathrm{pH} + 1.21 \pm 0.22 \cdot \log(\mathrm{Cs}) - 0.85 \pm 0.21 \cdot \log(\mathrm{OM}) + 7.02 \pm 0.62$
Pb	$\log(k_d) = 0.37 \pm 0.04 \cdot \mathrm{pH} + 0.44 \pm 0.07 \cdot \log(\mathrm{Cs}) + 1.19 \pm 0.22$
Zn	$\log(C_l) = -0.55 \pm 0.04 \cdot \mathrm{pH} + 0.94 \pm 0.08 \cdot \log(\mathrm{Cs}) - 0.34 \pm 0.12 \cdot \log(\mathrm{OM}) + 3.68 \pm 0.31$

C_l=metal in soil solution (μg l^{-1}); Cs=total metal in soil (mg kg^{-1}); OM=soil organic matter (% C)

Table 2
Algorithms for the estimation of metal concentration in plants

Metal	
Cd	$\ln(C_p) = 1.152 \pm 0.638 + 0.564 \pm 0.0047 \cdot \ln(\mathrm{Cs}) - 0.27 \pm 0.102 \cdot \mathrm{pH}$
Cu	$\ln(C_p) = 0.669 \pm 0.213 + 0.394 \pm 0.0044 \cdot \ln(\mathrm{Cs})$
Ni	$\ln(C_p) = -2.224 \pm 0.472 + 0.748 \pm 0.093 \cdot \ln(\mathrm{Cs})$
Pb	$\ln(C_p) = -1.328 \pm 0.350 + 0.561 \pm 0.072 \cdot \ln(\mathrm{Cs})$
Zn	$\ln(C_p) = 2.362 \pm 0.440 + 0.640 \pm 0.057 \cdot \ln(\mathrm{Cs}) - 0.214 \pm 0.077 \cdot \mathrm{pH}$

C_p=metal concentration in plant (mg kg^{-1}); Cs=total metal in soil (mg kg^{-1})

In Galicia, the leaching of contaminants to groundwater may be more important than in other parts of Spain, due to the higher precipitation rates. On-site values of k_d were not available, being necessary to estimate this coefficient for each metal. There are several studies in literature that present correlations between the metal in solution and different soil properties (pH, concentration of metal in soil, organic matter, cation exchange capacity,...) by applying multiple regression analysis. Nevertheless, most works refer to a single or at much to a couple of metals (Sauvé et al., 1997; Krishnamurti and Naidu, 2002; Weng et al., 2004; Carlon et al., 2004) or to specific soil conditions (Dijkstra et al., 2004). Few works consider data corresponding to a wide variety of soils and metals.

In this case-study, metal concentrations in soil solution are estimated from the algorithms developed by Sauvé et al. (2000), which involve soil pH and organic matter, except in case of Pb, being its soil–water partition coefficients only a function of pH and total Pb in soil. The equations employed for each metal are shown in Table 1. The algorithms proposed by Sauvé et al. (2000) only

Table 3
Value of parameters for metal accumulation and distribution

Parameter	Units	Type	Distribution
Cd in manure, (Calvo, 2003)	g m^{-3}	Log-normal	1.48±0.71
Cu in manure, (Calvo, 2003)	g m^{-3}	Log-normal	2.67±1.43
Ni in manure, (Calvo, 2003)	g m^{-3}	Log-normal	8.18±4.6
Pb in manure, (Calvo, 2003)	g m^{-3}	Log-normal	8.67±5.1
Zn in manure, (Calvo, 2003)	g m^{-3}	Log-normal	17.03±11.51
Application rate of manure, (Calvo, 2003)	m^3 ha^{-1} y^{-1}	Log-normal	88.93±45.33
Cd (initial) in soil	mg kg^{-1}	Log-normal	1.0±0.02
Cu (initial) in soil, (Fernández and Carballeira, 2001)	mg kg^{-1}	Log-normal	19.3±10.9
Ni (initial) in soil, (Fernández and Carballeira, 2001)	mg kg^{-1}	Log-normal	11.1±11.0
Pb (initial) in soil, (Fernández and Carballeira, 2001)	mg kg^{-1}	Log-normal	33.0±9.9
Zn (initial) in soil, (Fernández and Carballeira, 2001)	mg kg^{-1}	Log-normal	42.4±18.8
Average pasture production, (Calvo, 2003)	kg ha^{-1} y^{-1}	Point	12,000
Soil pH, (Fernández-Marcos, p. c., 2004)	Unitless	Log-normal	5.49±0.43
Soil organic matter, (Fernández-Marcos, p. c., 2004)	% C	Normal	11.69±2.82
Precipitation, (MeteoGalicia, 2003)	m y^{-1}	Log-normal	0.9±0.63
Infiltration factor (Fernández-Marcos, p. c., 2004)	Unitless	Point	0.44
ρ, soil bulk density	kg m^{-3}	Point	1300
dp, depth plough layer	m	Point	0.2
Time	y	Point	100

Table 4
Value of parameters for metal transfer to meat of cattle

Parameter	Units	Type	Distribution
Cd BTFmeat	day kg^{-1}	Point	4.0E−04
Cu BTFmeat	day kg^{-1}	Point	9.0E−03
Ni BTFmeat	day kg^{-1}	Point	5.0E−03
Pb BTFmeat	day kg^{-1}	Point	4.0E−04
Zn BTF meat	day kg^{-1}	Point	1.0E−01
PIRm	kg day^{-1}	Triangular	16.1(10–25)
SIRm	kg day^{-1}	Point	1.0
WIRm	l day^{-1}	Triangular	50(20–60)
fm, fraction of food from area	Unitless	Point	80

Data from ORNL (2004a).

attempts to distinguish the portion of a contaminant that is dissolved in the soil solution from that which is bound to soil solids. Bioavailability of the various chemical species present in solution are not considered in the models, or either the desorption potential of the fraction which is sorbed to the solid phase. However, the speciation of the metal is fundamental to estimate metal mobility and phytoavailability in soils. In fact, several reactions (adsorption, complexation, etc.) will control water runoff, leaching and plant uptake. Different studies (Pierzynski and Schwab, 1993; Canet et al., 1997; Walker et al., 2004) focused on metal fractionation have shown that metals in manure-amended soils are usually in organically complexed form, this being traduce in a reduction of its bioavailability, since only the soluble and exchangeable fractions are uptaked by plants. However, decomposition of organic matter with time will redistribute these metals in the different soil pools (Zheljazkov and Warman, 2004), being possible their availability for plant uptake. For that reason, bioavailability of metals in manure is expected to persist longer than in sewage sludge (Bolan et al., 2004). Metal speciation must be considered when assessing distribution of metals in soils. In this work, bioavailability was not taken into account, this may leading to an overestimation of plant uptake.

For the estimation of metal uptake rate by plants, a constant soil–plant uptake factor can be used (Baes et al., 1984), although uptake factors have been demonstrated to be dependant on the chemical concentration in soils (ORNL, 1998). Therefore, non-linear models could be more useful in risk assessment, however as in the estimation of metal in soil solution, the specific studies developed are focused on few metals and an unique plant type. For example, a large quantity of algorithms for the estimation of cadmium by plants as a function of soil properties and cadmium concentration is present in the literature, even for specific crop types (de Meeûs et al., 2002), but there are few models which consider a wide range of plant species, soil types and metals. In the present study, the selected algorithms for the estimation of Cd, Cu, Ni, Pb and Zn uptake were those developed by Efroymson et al. (2001). They are shown in Table 2. The measurements of plant concentration in this study corresponded to the growth form of above-ground tissue, predominantly herb and graminoid.

Once the concentration in plant is estimated, the uptake rate is calculated by multiplying the plant content and the production rate (in this case pasture), being the units of the result in g ha^{-1} y^{-1}. In order to transform these units to y^{-1}, it is necessary to refer plant uptake rate (R_p) to the initial concentrations of metal in soil. The values of the parameters employed for assessing metal accumulation and distribution are shown in Table 3. The background level in soil of cadmium was established taking into account those reported in the literature (de Meeûs et al., 2002).

2.2. Exposure

The identification of the main pathways through which people will be exposed to heavy metals is needed. The health risk of people living in the surrounding of the area of interest has been considered by the addition of five different exposure pathways: 1) ingestion of meat from cattle grazing in the zone, 2) ingestion of milk from cattle grazing in the zone, 3) dermal absorption by contact with soil, 4) ingestion of contaminated soil and 5) inhalation of resuspended soil particles. To calculate exposure through pathways 1 and 2, a previous assessment of the quantity of contaminants biotransfered to cattle is necessary. Animals are exposed to contaminants through the ingestion of contaminated food, soil or water, by inhalation of contaminants resuspended in air, and by dermal absorption. However, in this case, only ingestion has been considered, since dermal and inhalation exposures routes are generally not significant when compared with the ingestion route (ORNL, 2004a). Animal (cattle) and human exposures were calculated after application of cattle manure for a period of 100 years, based in the values predicted with Eq. (2) and the algorithms from Tables 1 and 2 for concentrations in soil, pasture and leachate of the five metals considered. In the scenario analysed in the present study, only the exposure of the adult population was considered.

2.2.1. Metal concentrations in cattle

The main factors affecting the accumulation of metals by grazing animals are the presence of the metal, its concentration in herbage and along the soil surface, and the duration of exposure to the contaminated pasture and soil (Wilkinson et al., 2004).The total concentration of contaminant in cattle tissue was estimated as a contribution of the three pathways: food (pasture), soil and water ingestion. Concentrations in each medium are multiplied by their relative ingestion rates and by the contaminant-specific biotransfer factor (food–meat) (U.S.EPA, 1989):

$$\mathrm{Cm} = (\mathrm{Cp\ PIRm\ fm} + \mathrm{Cs\ SIRm} + \mathrm{Cw\ WIRm})\ \mathrm{BTFm} \tag{4}$$

where Cm is metal concentration in meat (mg kg^{-1}), Cp is metal concentration in pasture (mg kg^{-1}), PIRm is pasture ingestion rate (kg day^{-1}), fm is the fraction of food that comes from the area (pasture), Cs is metal concentration in soil, SIRm is soil ingestion rate of cattle (kg day^{-1}), Cw is metal concentration in water (mg l^{-1}), WIRm is water ingestion of cattle (l day^{-1}) and BTFm is the biotransfer factor for meat (day kg^{-1}), which is specific for each metal (Table 4).

The concentration of metals in milk is estimated with a similar model (U.S. EPA, 1989):

$$\mathrm{Cmilk} = (\mathrm{Cp\ PIRmilk\ fm} + \mathrm{Cs\ SIRmilk} + \mathrm{Cw\ WIRmilk})\mathrm{BTFmilk} \tag{5}$$

where Cmilk is metal concentration in cattle milk, the ingestion rates (PIRmilk, SIRmilk and WIRmilk) are referred to cattle for milk production, and BTFmilk is the biotransfer factor for milk specific for each metal in day kg^{-1} (Table 5). The ingestion rates correspond to cattle for meat production, which in general eats more pasture and drinks a lower quantity of water than cattle for milk production. It is assumed that cattle are grazing in the area during the whole year, and that water provided to cattle comes from wells of the zone. No dilution factors were applied to concentrations in soil solution predicted with the algorithms of Table 1, which were employed in the Eqs. (4) and (5) as "Cw".

2.2.2. Human exposure pathways

The five exposure pathways were selected taking into account the main activities of the population (farming) inhabiting in the area of study. A high percentage of the people in this zone were in contact with soil because of these activities, and therefore it was decided to consider soil pathways as sources of exposure. Manure was applied for fertilising pastureland for cattle grazing and therefore, it was consider the ingestion of cattle products (meat and milk) as the main possible pathways of exposure. Otherwise, ingestion of local-grown products was not selected as exposure pathways since these products were not fertilised with manure in this area. Ingestion of eggs and poultry meat was also not evaluated because the poultry were mainly fed with animal food and herbage

Table 5
Value of parameters for metal transfer to milk of cattle

Parameter	Units	Type	Distribution
Cd BTFmilk	day kg^{-1}	Point	1.0E−03
Cu BTFmilk	day kg^{-1}	Point	1.5E−03
Ni BTFmilk	day kg^{-1}	Point	1.6E−02
Pb BTF milk	day kg^{-1}	Point	3.0E−04
Zn BTF milk	day kg^{-1}	Point	1.0E−02
PIRmilk	kg day^{-1}	Triangular	1.3(1–2.5)
SIRmilk	kg day^{-1}	Point	0.13
WIRmilk	kg day^{-1}	Triangular	75(50–100)
fm, fraction of food from area	Unitless	Point	80

Data from ORNL (2004a).

Table 6
Value of parameters for exposure to metals through the different pathways

Parameter	Units	Type	Distribution
MeatIR, (López Alonso et al., 2002)	g day^{-1}	Point	53.2
MilkIR, (ENNA, 1991)	g day^{-1}	Point	436
SoilIR, (LaGoy, 1987)	mg day^{-1}	Triangular	25(0.1–50)
fme	Unitless	Point	1
fmilk	Unitless	Point	1
BW, (Schuhmacher et al., 2001)	kg	Log-normal	67.52 ± 12.22
SABW, (Finley et al., 1994a)	cm^2 kg^{-1}	Log-normal	248 ± 28
CT, (U.S.EPA, 1989)	h day^{-1}	Uniform	1–2
AdhF, (Finley et al., 1994a)	mg cm^2	Log-normal	0.52 ± 0.09
DAF, (ORNL, 2004b)	Unitless	Point	0.001
fex	Unitless	Point	0.15
RES, (Hawley, 1985)	Unitless	Point	1.0E−02
InhR, (Finley et al., 1994b)	m^3 d^{-1}	Uniform	5.04–17.76
Pac, (MeteoGalicia, 2003)	mg m^{-3}	Point	0.1
fret	Unitless	Point	50
Cd AbF, (ORNL, 2004b)	Unitless	Point	0.01
Cu AbF, (ORNL, 2004b)	Unitless	Point	0.3
Ni AbF, (ORNL, 2004b)	Unitless	Point	1.6E−02
Pb AbF, (ORNL, 2004b)	Unitless	Point	0.15
Zn AbF, (ORNL, 2004b)	Unitless	Point	0.2

that grew in areas sited near the houses, where manure is not applied. Other type of artificial fertilisers could be employed (which also have high metal contents) for producing these local products, however no data are available in this sense.

Water was also not considered because the population drank water that comes from sanitary supplies which were not supposed to be contaminated, like the ponds where the cattle drank water. On the other hand, metal leaching to groundwater is not the only way of water contamination, since when manure is applied, superficial run-offs can also contaminate the river basin. However, as no fishfarms are placed in the area, the main river fishes consumed are some trout and salmon, but in a small part of the year (usually from March to June). It is clear that consumption of local fish would be a very small fraction of total fish ingestion, since Galicia has an important fish production due to its Atlantic Ocean shore. Besides, either dissolved or total metal content was expected to be dragged off by the river current, but specific analysis of the river freshwater would be needed.

The five exposure pathways were described by Eqs. (6), (7), (8), (9) and (10), adapted from Schuhmacher et al., 2001.

2.2.2.1. Ingestion of meat and milk. A 94% of the cattle grazing in the area is assigned to milk production, while the remaining is employed for meat production, which is usually consumed by people inhabiting the zone, and therefore, it was assumed that all the cattle meat comes from the contaminated area. Although most of the milk produced in the area goes to the dairy industry, a small percentage is destined for self-consumption. The average daily intake of metals from ingestion of meat and milk was estimated by multiplying the metal concentrations in cattle meat and milk by the daily amount of intake:

$$\mathrm{Ingm} = \mathrm{Cm\ MIR\ fme\,BW^{-1}10E{-}03} \tag{6}$$

$$\mathrm{Ingmi} = \mathrm{Cmilk\ MiIR\ fmilk\,BW^{-1}10E{-}03} \tag{7}$$

where Ingm is the estimated daily dose of each metal due to ingestion of meat (mg kg^{-1} day^{-1}), Ingmi is the estimated daily dose of each metal due to ingestion of milk (mg kg^{-1} day^{-1}), MIR is the ingestion rate of cattle meat (mg day^{-1}), MiIR is the milk ingestion rate (mg day^{-1}), fme and fmi are the fraction of meat and milk ingested that comes from the studied area, respectively (unitless) and BW is the body weight of each individual (kg) (Table 6).

2.2.2.2. Ingestion of soil. People may ingest contaminated soil from the surrounding area due mainly to hand-to-mouth transfer. The ingestion rate depends on many factors: age of the individual, time spent indoor/outdoor, profession, among others (U.S.EPA, 1989). The average daily dose corresponding to soil ingestion (Ings) in mg kg^{-1} day^{-1} is estimated by multiplying the predicted metal concentration in soil (Cs) in mg kg^{-1} by the soil ingestion rate (SIR) in mg day^{-1} (Table 6).

$$\mathrm{Ings} = \mathrm{Cs\ SIR\,BW^{-1}10E{-}06} \tag{8}$$

In the considered area, inhabitants are dedicated in a high percentage to farming, and a 95.5% of land is assigned to pasture. Thus, under a conservative approach, it is assumed that total soil ingested comes from the area.

2.2.2.3. Dermal absorption of soil. Daily dermal exposure from contact with soil was estimated with the model described in Eq. (9):

$$\mathrm{Derms} = \mathrm{Cs\ SABW\ CT\ AdhF\ DAF\ fexAbF^{-1}10E{-}06} \tag{9}$$

where Derms is the estimated daily dose of each metal due to dermal contact with soil (mg kg^{-1} day^{-1}), Cs is the predicted metal concentration in soil (mg kg^{-1}), SABW is the ratio of skin surface area/body weight of each individual (cm^2 kg^{-1}), CT is the contact time soil–skin (h day^{-1}), AdhF is the adherence factor soil–skin (mg cm^{-2}), DAF is the dermal absorption factor, specific for each metal (unitless), and fex is the fraction of skin exposed (unitless), which is assumed to be 0.15, considering a seasonal average (0.25 in spring and summer, and 0.10 in autumn and winter) (Table 6). AbF is an absorption factor necessary for route to route extrapolation (ORNL, 2004b). As in the previous exposure pathway, it is assumed that all the soil comes from the area.

2.2.2.4. Inhalation of resuspended particles of soil. Metals may enter in human organism by inhalation of the smallest fraction of soil particles. The metal daily dose by soil inhalation in mg kg^{-1} day^{-1} (Inhs) is:

$$\mathrm{Inhs} = \mathrm{Cs\ RES\ InhR\ Pac\ fret\ AbFi\,BW^{-1}10E{-}06} \tag{10}$$

where Cs is the predicted metal concentration in soil (mg kg^{-1}), RES is the fraction of resuspended particles from soil (unitless), InhR is the inhalation rate (m^3 day^{-1}), Pac is the particle concentration in air (mg m^{-3}), fret is the fraction of soil particles retained in the lungs (unitless) and AbFi is the contaminant specific absorption factor for the inhalation route, assumed to be 1 (Table 6). Although this last assumption is very conservative, the AbF was not a very sensitive parameter due to the low expected contribution of soil inhalation to total risk.

The total dose of Cd, Cu, Ni, Pb and Zn is calculated as the addition of the amount estimated by the different pathways of exposure.

2.3. Risk characterisation

For the estimation of health risk, total doses were compared to toxicological data obtained from the U.S.EPA Integrated Risk Information System (IRIS) (U.S.EPA, 2004) and from the WHO (Table 7). The quantification of potential non-carcinogenic risk was obtained by the determination of the Hazard Quotient (HQ), which was calculated by dividing the individual doses of each metal by its Reference Dose (RfD). Among the five metals studied, only Cd was considered to cause carcinogenic effects on human health by inhalation exposure, being the Individual Excess Lifetime Cancer Risk (IELCR) calculated by multiplying a Slope Factor by the estimated dose. In this study, the oral, inhalation and dermal routes were considered. However, studies involving different routes of exposure were not always available. Thus, route-to-route extrapolations were needed when no specific dose–response data were present. Oral RfDs have been used for dermal and inhaled exposures, especially for organic compounds. In case of

Table 7
Toxicity values: Reference Doses (RfDs) and Slope Factors (SF) for non-carcinogenic and carcinogenic effects, respectively

Metal	RfD (mg kg^{-1} day^{-1})	SF (kg day mg^{-1})	Source
Cadmium	1.00E−03	6.3E+00 (inhalation)	U.S.EPA (2004)
Copper	4.00E−02	–	U.S.EPA (2004)
Nickel	2.00E−02	–	U.S.EPA (2004)
Lead	3.60E−03	–	WHO (2003)
Zinc	3.00E−01	–	U.S.EPA (2004)

Table 8
Predicted accumulation of metals in soil, pasture and soil solution

		Mean	SD	Percentiles		
				10th	50th	90th
Cd soil	mg kg^{-1}	4.40	3.03	1.71	3.64	7.87
Cu soil	mg kg^{-1}	22.56	11.42	10.82	20.25	36.66
Ni soil	mg kg^{-1}	24.30	22.19	2.24	19.27	51.25
Pb soil	mg kg^{-1}	60.45	26.78	35.58	54.55	90.88
Zn soil	mg kg^{-1}	70.59	45.69	28.86	59.92	124.53
Cd pasture	mg kg^{-1}	2.08	1.71	0.55	1.59	4.20
Cu pasture	mg kg^{-1}	6.67	2.10	4.31	6.34	9.41
Ni pasture	mg kg^{-1}	1.29	1.37	0.18	0.91	2.72
Pb pasture	mg kg^{-1}	2.89	1.60	1.35	2.52	4.84
Zn pasture	mg kg^{-1}	40.24	28.94	13.96	32.69	74.41
Cd soil solution	mg l^{-1}	5.69E−03	6.04E−03	1.35E−03	3.88E−03	1.16E−02
Cu soil solution	mg l^{-1}	1.98E−02	1.36E−02	7.12E−03	1.64E−02	3.66E−02
Ni soil solution	mg l^{-1}	1.51E−01	3.35E−01	6.59E−03	6.64E−02	3.48E−01
Pb soil solution	mg l^{-1}	8.23E−03	8.00E−03	1.93E−03	5.78E−03	1.76E−02
Zn soil solution	mg l^{-1}	9.18E−02	1.32E−01	1.20E−02	5.37E−02	2.06E−01

inorganics, route extrapolations have to include a factor which accounts for the different absorption efficiencies for inhalation and dermal exposures. The Risk Assessment Information System (RAIS) of the ORNL provide the absorption factors necessary for dermal exposure extrapolation for the five metals studied (Table 6). No factors for the inhalation route were available, and a value of 1 was chosen. This assumption adds additional uncertainty to the risk characterisation process. Nonetheless, previous studies (Schuhmacher et al., 2004; Hough et al., 2004) showed the poor contribution of soil particles inhalation to total exposure, and therefore, a not significant effect on the results was expected. Another factor to take into consideration, is that the above toxicological values are referenced to individuals and do not consider variability and the ranges of exposure analysed in this study, and therefore, this fact will be another added source of uncertainty on the final results.

For the characterization of the uncertainty of risk, a probabilistic approach was applied. In this type of analysis, parameters are not taken as fixed point values, but a range of values, and the actual value may depend on both uncertainty (lack of knowledge), and variability (from person to person). The method employed in this study for the quantification of uncertainty was to assign to each parameter of the model a probability distribution. The distribution functions selected to describe the fate and exposure parameters are shown in Tables 3-6, and were collected from both site-specific data and the most current data available in literature. The form of the most appropriate distribution for each site-specific parameter was chosen by means of the commercial software package Crystal Ball (Version 5.2.2). For the estimation of risk uncertainty, a Monte Carlo simulation with a 10 000 iterations was applied, which propagates the uncertainty of the parameters throughout the model equations.

3. Results and discussion

The results obtained for predicted concentrations, doses of exposure and health risk were distributions of probability instead of single-point values. Therefore, for its analysis and discussion, the mean and standard deviation values, and the 10th, 50th and 90th percentiles were presented.

3.1. Predicted concentrations

For the estimation of the incremental health risk, predicted concentrations for each metal in a 100 year-period were estimated. In Table 8, the concentrations of Cd, Cu, Ni, Pb and Zn in soil (total), soil solution and pasture are shown. The higher concentrations in soil corresponded to Ni, Pb and Zn, especially the latter, with a 90th percentile close to 125 mg/kg soil. Cd and Cu concentrations were much lower, something expected if it is taking into account the lower content in manure of these metals. The range of predicted concentrations (90th/10th percentile ratio) in soil for Cd, Cu, Pb and Zn were around 4.5–2.5, however uncertainty for Ni concentration was quite high (23). The uncertainty was propagated through both the fate and exposure modules and therefore, it must be taken into consideration especially in the case of Ni forecasts. The higher concentrations in pasture were those corresponding to Zn, which presented a significant difference with the other metals. Although Cd concentrations in pasture seemed to be not very high, its highly toxic behaviour may pose a risk. Metal concentrations in soil solution have also been estimated, since they are necessary altogether with soil and pasture concentrations, to evaluate contamination of the food chain (cattle). Ni presented the higher concentration, according to the site-specific conditions (low soil pH and high organic matter content) although again, predicted concentrations of this metal present a high degree of uncertainty, being the 90th/10th percentile ratio equal to 53 (Table 8).

In Table 9, metal concentrations accumulated in meat and milk of cattle are shown. Regarding bioconcentration in meat, Zn contents are much higher than those obtained for the other metals, reaching average values of around 75 mg/kg. In milk, metal contents were lower than those in meat, except in case of Ni, which presented similar values. The highest concentrations corresponded to Ni and Zn. Uncertainty in Zn concentrations was acceptable for the objective of this study (a screening-level assessment), however the values for Ni showed a very wide range of variation for establishing a trustable result in the final estimation of risk. A survey was carried out in year 2000 by Alonso et al. with the goal of determining heavy metal (As, Cd, Cu, Pb and Zn) contents in liver, kidney and muscle (meat) of cattle slaughtered in Galicia. The study revealed concentrations broadly similar to those in the rest of Europe, Australia and Canada, except in case of Copper and Zinc. These last metal concentrations exceeded acceptable maximum values, however this occurred as a frequency which depends upon which limit was used. A comparison between the measures of Alonso et al. (2000) with the results of this study, shows that the predicted Cu and Zn concentration will be 80% and 60% higher than those measured, respectively. This increase is not significant considering the large temporal horizon established in this study. In case of Pb, concentrations almost 5 times higher would be obtained. Finally, Cd

Table 9
Biotransfer of metals to cattle meat and milk

		Mean	SD	Percentiles		
				10th	50th	90th
Cd meat	mg kg^{-1}	1.60E−02	1.22E−02	5.15E−03	1.25E−02	3.09E−02
Cu meat	mg kg^{-1}	1.23	0.44	0.75	1.16	1.81
Ni meat	mg kg^{-1}	0.26	0.23	0.05	0.21	0.52
Pb meat	mg kg^{-1}	4.40E−02	1.86E−02	2.59E−02	4.00E−02	6.65E−02
Zn meat	mg kg^{-1}	76.05	52.77	28.29	62.27	138.46
Cd milk	mg kg^{-1}	4.31E−03	3.04E−03	1.57E−03	3.5E−03	8.00E−03
Cu milk	mg kg^{-1}	2.26E−02	8.12E−03	1.35E−02	2.12E−02	3.31E−02
Ni milk	mg kg^{-1}	0.27	0.44	0.06	0.17	0.52
Pb milk	mg kg^{-1}	3.92E−03	1.61E−03	2.37E−03	3.58E−03	5.86E−03
Zn milk	mg kg^{-1}	0.80	0.53	0.33	0.66	1.43

Table 10
Summary of Monte Carlo estimates of Hazard Quotients by metal

	Mean	SD	Percentiles		
			10th	50th	90th
Cd risk	5.49E−02	3.51E−02	2.25E−02	4.58E−02	9.85E−02
Cd risk carcinogen	1.17E−07	9.64E−08	3.63E−08	9.08E−08	2.30E−07
Cu risk	2.90E−02	1.14E−02	1.65E−02	2.70E−02	4.39E−02
Ni risk	9.92E−02	1.52E−01	2.32E−02	6.50E−02	1.95E−01
Pb risk	2.25E−02	9.93E−03	1.28E−02	2.04E−02	3.43E−02
Zn risk	2.24E−01	1.61E−01	8.09E−02	1.80E−01	4.17E−01
Hazard Index	4.30E−01	2.55E−01	2.08E−01	3.70E−01	7.06E−01

concentrations in meat would experiment a 16 times increase, and even in the best case (comparing with the 10th percentile) the Cd content would be 5 times higher. Although uncertainty in the results for predicted metal concentrations in meat cannot be neglected, especially in the case of Cd, an increase was produced for all of them when considering the mean and the 90th percentile values.

3.2. *Exposure and risk assessment*

The Total Hazard Quotients for each metal were determined as the addition of the HQ of the five exposure pathways was considered. Table 10 shows a summary of the results (mean, standard deviation, 10th, 50th and 90th percentiles) of the predicted exposure to Cd, Cu, Ni, Pb and Zn in a 100-year period of the people leaving in the surrounding pastureland. It can be seen in Table 10 that Ni presented the highest uncertainty in the results of risk estimation, since the ratio between the 90th to the 10th percentile was equal to 8.4 for this metal. Otherwise, the results summarised in Table 11 correspond to the HQ of each exposure pathway, calculated as the addition of the five metals considered. A sensitivity analysis was carried out in the present study to evaluate the contribution of each metal and each pathway to the uncertainty in the estimation of risk. The sensitivity analysis for the total HQ from the different metal exposure doses indicated that Zn and Ni presented the highest contribution to the variance, with a 42.1% and a 22.2%, respectively, while Cd, Pb and Cu contributed in a lower percentage (15.0%, 10.8% and 9.9%, respectively). The sensitivity analysis of the total risk (total HQ) but from the different exposure pathways showed that the ingestion of meat and milk contributed 45.7% and 34.5% to the variance, respectively, while inhalation, dermal contact and ingestion of soil contributed to 9.3%, 7.1% and 3.4%, respectively.

An analysis of the contribution of each metal through each exposure pathway is shown in Fig. 1. Hazard Quotients of Zn through ingestion of meat and Ni through ingestion of milk were the highest, while the direct pathways of exposure (inhalation, ingestion and dermal contact with soil) resulted in very low HQ for each metal, except for Cd in the dermal pathway. However, as the background values used for Cd were quite high, not site-specific and thus could be not much realistic, the results of Cd exposure must be interpreted with caution. The high content of Zn in the cattle manure (which mainly came from nutrition complements in cattle feeding) employed in this study, together with its oligoelement character provoked high accumulation values in soil and pastureland, being biotransfered mainly to cattle meat, exceeding safe values. However, studies involving biotransfer of metals to cattle established that tissue Zn content between cattle grazing in Zn polluted and control regions was not significantly different (Koh and Judson, 1986; Spierenburg et al., 1988). In fact, a recent study (López-Alonso et al., 2000) carried out in Galicia points out that Zn concentrations in cattle did not significantly vary between animals from areas where pig slurry (with a very high Cu and Zn content) was added to pastures as fertiliser. The present screening work involves a temporal horizon of 100 years, this being traduced in a higher accumulation of metals in soil, and therefore, higher biotransfer to cattle meat is expected. Besides, it is necessary to determine specific BTF for meat in order to obtain more accurate results in further studies.

Table 11
Summary of Monte Carlo estimates of Hazard Quotients by route of exposure

	Mean	SD	Percentiles		
			10th	50th	90th
Meat ingestion	2.65E−01	1.59E−01	1.19E−01	2.25E−01	4.57E−01
Milk ingestion	1.46E−01	1.56E−01	5.78E−02	1.11E−01	2.54E−01
Dermal contact soil	1.62E−02	1.09E−02	6.62E−03	1.34E−02	2.90E−02
Soil ingestion	2.18E−03	1.72E−03	5.89E−04	1.76E−03	4.20E−03
Soil inhalation	4.07E−04	2.97E−04	1.47E−04	3.26E−04	7.55E−04

The total non-carcinogenic (Hazard Index) incremental risk from exposure to the five metals is shown in the last row of Table 10. The results corresponded to the 10th percentile, the average estimation of risk (50th percentile) and the reasonable maximum exposure (90th percentile). The uncertainty in the estimation of the total Hazard Index was equal to 3.4. It can be seen in Table 10 that the central tendency of the incremental risk is equal to 0.37, and the RME is equal to 0.75, these results show that the continuous application of cattle manure is not negligible and may contribute to the total risk due to exposure of heavy metals through another type of food from the diet (cereals, vegetables, fruit, another types of meat, fish, pulses) and from water. Nonetheless, the evaluation of risk in this study was developed under worst-case conditions: i) no dilution or attenuation factors were used in the exposure models, ii) the employed metal background values in the soil were high, since they corresponded to a survey in the year 2001 (Fernández and Carballeira, 2001) involving several and different areas of Galicia, including both rural and industrial soils, and from studies developed in Northern Europe for Cd levels (de Meeûs et al., 2002) which could not be rather adequate to this region, iii) speciation of metals in soil were not considered in this study, assuming a complete metal bioavailability. All of these factors contributed to the increment of the forecast risk.

The origin of Cu and especially of Zn may be traced to the nutrient supplements added to the cattle feed, which were usually provided in excess. Cattle excreted the excess of these oligoelements, which ended in the manure tank. The other metals can be accumulated in the manure by ingestion of artificial food, which may contain these metals (Cd, Pb and Ni) in trace quantities. Furthermore, analysis of the different

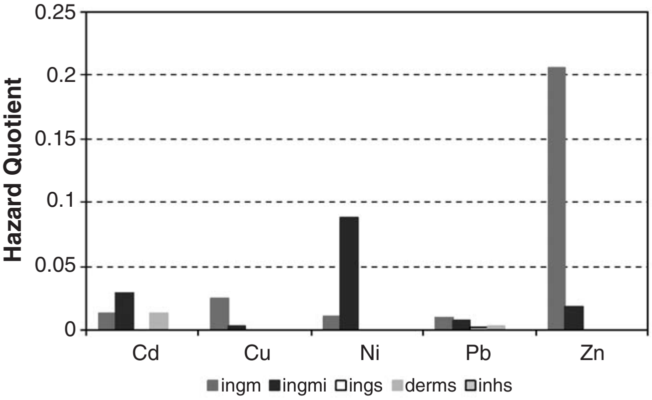

Fig. 1. Average Hazard Quotient of Cd, Cu, Ni, Pb and Zn by exposure pathway.

sources contributing to the metal accumulation in manure is needed to corroborate these assumptions.

4. Conclusions

The application of cattle manure as fertiliser in pastureland pose a good option for farming activities, since it avoids the waste treatment of manure and reduces the application of chemical fertilisers. However, metals present in manure can be released to the soil, water and plants and therefore, it can be biotransfered to cattle and subsequently to humans. In the present work, a conservative risk screening study was developed involving both direct and indirect exposure pathways, in order to estimate metal exposures of a population inhabiting the surrounding pasturelands in a 100-year period. The results of this study showed that a revision of management practices in intensive-farming installations would be needed, by establishing a specific legislation for manure application depending on its metal content, in the same way as the existing one for sludge application. Planning of fertiliser application in this area is developed considering the need for the soil's organic matter and nutrients depending on the culture to be carried out. The results of this work pointed out that these plans should also incorporate risk criteria which consider the contents in metals of the fertiliser applied. This could help prevent situations of diffused pollution from agricultural origin, by a more adequate management of soil and manure which could improve the protection barrier against water contamination and trophic chain.

Pathways of exposure ranked from the lowest to the highest contribution to incremental risk were: soil inhalation, soil ingestion, dermal contact with the soil, ingestion of milk and ingestion of meat, while metal contribution were higher following the order: lead, copper, cadmium, nickel and zinc. However, the results regarding Cd and Ni must be interpreted carefully, due to the high uncertainty of the results. Zinc via meat ingestion contributed importantly to the total risk. Thus, environmental and health policies should establish stricter threshold values which lead to a reduction in the use of metal-rich nutrition complements in cattle feeding. This control measure would pose an important improvement in managing the risk derived from fertilisation of soil by manure, especially taking into consideration that measured values of Cu and Zn in currently studies in Galicia showed similar results with respect to those predicted by this work. Therefore, in the present time the ingestion of meat may be an important source of Zn. Furthermore, although more specific background values would reduce the predicted RME, the optimisation of the manure application rate is needed as a crucial factor for avoiding metal accumulation in pasturelands.

The quantitative hazard index estimated using this conservative worst-case exposure scenario showed that a significant incremental risk can be obtained after 100 years of continuous application of metal-rich manure. In this work, fate and exposure models provided in the literature as well as risk assessment techniques have been successfully applied for evaluating the hazard and which metals and exposure pathways (by sensitivity analysis) will pose higher risk on human health and would have to be assessed in more detail. Site-specific data was employed in the present study, but more specific values for some parameters have to be obtained, especially those involving biotransfer factors of Cu and Zn for cattle meat and milk, in order to obtain more accurate estimations of metal exposure. Further research is needed for the determination of site-specific concentrations in different environmental media (background values in soil, pasture, feed, groundwater, and meat and milk of cattle) in order to develop specific fate models which accounted for a more detailed distribution of each metal in the soils of Galicia. Besides, the application of manure should be also evaluated in terms of fertilising land for crop growth.

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