

Heavy metals in pastureland soils situated in A Pastoriza (NW Spain) treated with cattle slurry and NPK fertilizers

Metales pesados en suelos de pradera de A Pastoriza (NO España) tratados con purín de vacuno y fertilizantes NPK

Metais pesados em solos de pastagem da A Pastoriza (NO Espanha) tratados com chorume de vaca e adubos NPK

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ABSTRACT

In Galicia (NW Spain), pasturelands cover a broad extension and are mainly used to feed cattle. Farms are managed in an intensive manner, using cattle slurry and inorganic fertilizers to increase pasture production, but also increasing risks of heavy metal pollution. In this work we studied the influence of fertilization practices on total concentrations and in-depth distribution of heavy metals and related elements (As, Cd, Cr, Cu, Mn, Ni, Pb and Zn) in two forest soils (SN1, SN2) and five pastureland soils (P1-P5) fertilized with cattle slurry and NPK, in a broadly explored farmland area (A Pastoriza, Lugo). Soils SN2 and P4 were developed over slate, whereas soils SN1, P1, P2, P3 and P5 evolved on Candana quartzite. Forest soils presented acid pH (4.58-4.68), high Al saturation (75-90%), and low available P concentration (4.78-11.96 mg kg⁻¹), whereas those parameters exhibited better scores in the pastureland soils, due to previous amendment and fertilization practices, thus giving pH 5.17-7.02, Al saturation 0.58-59.24%, and available P 5.24-42.07 mg kg⁻¹. Regarding heavy metals, soil depth did not affect significantly to total concentrations, contrary to that happening with parent material, with higher As, Cu, Fe, and Ni concentrations found in soils over slate (possibly due to the presence of pyritic materials). In most cases, heavy metal total concentrations were lower than that considered as reference background levels for soils developed over each of the parent materials, and were always lower than that considered phyto-toxic. In this study, natural soils usually presented heavy metal total contents similar or even higher than that of the fertilized soils (unless Zn in the P4 pastureland), thus indicating that the spread doses of fertilizers did not influence significantly their concentration levels.

RESUMEN

En Galicia las praderas ocupan una gran extensión, siendo utilizadas principalmente para la alimentación del ganado vacuno destinado tanto a la producción de leche como de carne. Las granjas se manejan de manera intensiva, utilizando fertilizantes inorgánicos y purín de vacuno para aumentar la producción de pastos. Esta práctica puede aumentar el contenido de metales pesados en el suelo. En este trabajo se estudian las concentraciones totales y la distribución en profundidad de metales pesados y elementos afines (As, Cd, Cr, Cu, Mn, Ni, Pb y Zn) en dos suelos forestales (SN1, SN2) y en cinco praderas (P1-P5) fertilizadas con purín de vacuno y NPK en una zona con una gran vocación ganadera (A Pastoriza, Lugo). Se pretende conocer el grado de influencia de la fertilización sobre los niveles de estos elementos. Los suelos elegidos se desarrollaron a partir de pizarras (SN2, P4) y de cuarcitas de la Serie de Cándana (SN1, P1, P2, P3, P5). Los suelos forestales presentaron pH ácido (4,58-4,68), elevada saturación del complejo de cambio por Al (75-90%) y baja concentración de P disponible (4,78-11,96 mg kg⁻¹); estos parámetros mejoran en los suelos de pradera como consecuencia de las enmiendas y fertilizantes aplicados, presentando un pH entre 5,17 y 7,02, una saturación de Al que varía entre 0,58-59,24% y P disponible entre 5,24 y 42,07 mg kg⁻¹. En relación con los metales pesados, la profundidad de la muestra no afecta de modo significativo a su concentración total, pero sí el material de partida, presentando concentraciones más elevadas de Fe, As, Cu y Ni

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los suelos desarrollados sobre pizarras, posiblemente debido a la presencia de materiales piriticos. En la mayoría de los casos, los metales pesados estudiados presentan concentraciones totales inferiores a las establecidas como genéricas para suelos desarrollados sobre los respectivos materiales geológicos, y siempre son menores que los límites considerados fitotóxicos. La fertilización aplicada no parece tener una influencia significativa sobre los contenidos totales de estos elementos, con la excepción del Zn en la pradera P4, ya que los suelos naturales en muchos casos presentan valores similares e incluso superiores a los obtenidos en las parcelas fertilizadas.

RESUMO

As pastagens ocupam uma grande área na região da Galicia (NO Espanha) destinando-se sobretudo à alimentação de bovinos para produção de leite e carne. As explorações são geridas de forma intensiva, aplicando-se adubos minerais e chorumes com o objetivo de aumentar a produção de pastos. Contudo, esta prática pode aumentar o teor de metais pesados no solo. Neste trabalho, a concentração total e a distribuição em profundidade de metais pesados e elementos associados (As, Cd, Cr, Cu, Mn, Ni, Pb e Zn) foram estudados em dois solos florestais (SN1, SN2) em cinco talhões (P1-P5) adubados com NPK e chorume de bovino, numa área com uma grande vocação para pecuária (A Pastoriza, Lugo). Teve-se por objetivo principal determinar o grau de influência da fertilização nos teores destes elementos. Os solos selecionados foram desenvolvidos a partir de ardósias (SN2, P4) e quartzitos da Série de Candana (SN1, P1, P2, P3, P5). Os solos florestais apresentavam pH ácido (4,58-4,68), alta saturação de Al (75-90%) no complexo de troca de e baixa concentração de P disponível (4,78-11,96 mg kg⁻¹); estes parâmetros melhoram em solos de pastagem, como resultado da calagem e fertilizantes aplicados, apresentando um pH entre 5,17 e 7,02; saturação por Al variando de 0,58 a 59,24% e P disponível entre 5,24 e 42,07 mg kg⁻¹. Em relação aos metais pesados, a profundidade da amostra não afetou significativamente a sua concentração total, contrariamente ao que se verificou com o material parental, que apresentou as concentrações mais elevadas de Fe, As, Cu e Ni nos solos desenvolvidos a partir de ardósias possivelmente devido à presença de materiais piriticos. Na maioria dos casos, os metais pesados estudados apresentaram concentrações totais inferiores aos valores geralmente considerados como referência para solos desenvolvidos a partir dos respetivos materiais parentais, sendo sempre inferiores aos valores limite considerados fitotóxicos. Neste estudo, os solos naturais apresentaram valores de metais pesados semelhantes ou mesmo superiores aos dos solos fertilizados (exceto para o Zn na pastagem P4), o que indica que as doses aplicadas de fertilizantes não influenciaram de forma significativa os seus níveis de concentração.

KEY WORDS
Trace elements,
organic
fertilization,
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fertilization, forest
soils

**PALABRAS
CLAVE**
Elementos traza,
fertilización
orgánica,
fertilización
inorgánica, suelos
forestales

**PALAVRAS-
CHAVE**
Elementos vestigiais,
fertilização orgânica,
adubação mineral,
solos florestais

1. Introduction

Heavy metals are elements with atomic number above 20 (excluding alkaline and alkaline-earth metals) with density $\geq 5 \text{ g cm}^{-3}$ when they are in elemental form (Oves et al. 2012). Some metalloids, such as As, are frequently included in this group due to having similar chemical characteristics and environmental behavior (Chen et al. 1999). Heavy metals entering and circulating into the biosphere constitute a matter of growing environmental concern (Facchinelli et al. 2001; Solgi et al. 2012). Some of them are essential for living organisms, but may cause severe problems when present in high concentrations (Khan et al. 2010; Sun et al. 2010). Prolonged exposition to high Cd levels may cause kidney failure, hypertension and cancer (Nordberg et al. 2002; Turkdogan et al. 2003). Cr is associated to thyroid, blood and coronary affectations, whereas Mn and Cu have been related with neurologic illness (Dieter et al. 2005). Ni may cause cardiac and breathing troubles, Zn can affect the immune system (Muhammad et al. 2011), As is related with skin cancer and neuropathies (Żukowska and Biziuk 2008), and Pb with nervous system, circulatory and enzymatic affectations (Zhang et al. 2012a).

Although natural geochemical processes can give high heavy metal concentration in soils, it may be caused by different anthropic activities (mining, industry, agriculture, waste management, etc.), resulting in soil degradation and productivity loss (Khan 2013). Among agricultural activities, slurry and inorganic fertilizers spreading may lead to increased heavy metal concentrations in soils (Sager 2007; Moral et al. 2008; Jia et al. 2010; Zhang et al. 2012b), then in plants, and subsequent transfer to the food chain (Sun et al. 2010).

An extension of 433,458 ha is devoted to pastureland in Galicia (IGE 2012), needing cattle slurry and inorganic fertilizers spreading to minimize nutrients deficit, thus implying risks of heavy metal accumulation and decrease of pasture quality (Dong et al. 2011).

In view of that, in this work we determine total content and distribution of As, Cr, Cu, Fe, Mn, Ni, Pb and Zn (depths 0-5, 5-10 and 10-20 cm) in pastureland soils from an intensive farming area (A Pastoriza, Lugo), where cattle slurry and inorganic fertilizer are spread, also comparing with the levels corresponding to forest soils from the same area, in order to distinguish between lithological and anthropogenic origin.

2. Material and Methods

The study area was placed in A Pastoriza (Lugo province, Galicia, NW Spain). Mean annual precipitation and temperature are between 950-1350 mm, and between 10-12 °C, respectively. Five pastureland plots (P1-P5) and two forest plots (SN1, on *Pinus insignis*, and SN2, on *Eucalyptus globulus*) were performed. Surface was around 500 m² for all plots. The pastureland plots were located in an area with almost no slope, whereas the forest plots had longitudinal slope equivalent to 30%. The forest soils were classified as Umbrisol (WRB 2006). The

pastureland plots were devoted to this soil use for more than 30 years. They included seeded species (*Lolium multiflorum* Lam. and *Trifolium pretense* L.) and spontaneous species, usually dominant in Galician meadows (Mosquera et al. 2000; Álvarez et al. 2010, 2012). These soils are usually spread with cattle slurry and NPK fertilizers, without systematic patter of application. Any case, usual yearly doses in the area are: 100 m³ ha⁻¹ for cattle slurry and 1000 kg ha⁻¹ for NPK 8:24:16. The dominant parent materials were Candana quartzite (SN1, P1, P2, P3 and P5 plots) and slate (SN2 and P4 plots).

Soils were sampled at three depths in each plot (0-5, 5-10 and 10-20 cm) to study total contents of heavy metals, whereas general characteristics were determined on 0-20 cm depth samples. Samples were taken in October 2013, when 5 transects were delimited in each plot and 5 sub-samples were taken at each depth (20 m longitudinal separation between subsequent points), in a zigzag manner. Subsamples were used to perform one composite sample for each depth and transect, giving a total number of 5 composite samples for each depth and plot. Subsamples were taken by using an open probe (20 cm depth), then differencing among three sections (0-5, 5-10, 10-20 cm) to study heavy metals, whereas undivided samples (20 cm) were used to study general parameters. Soil samples were oven dried (at 40 °C) and sieved through 2 mm mesh. The < 2 mm fraction was analyzed for pH (H₂O) and pH (KCl) (Gutián and Carballas 1976), total C and N total (LECO auto-analyzer CNS-2000), available P (Olsen and Sommers 1982), exchangeable cations and effective cation exchange capacity (eCEC) (Peech et al. 1946). Total P, Ca, Al, Fe, As, Cr, Cu, Mn, Ni, Pb, Cd and Zn were determined by X ray fluorescence (USC in-house dispersion spectrophotometer).

Data were statistically treated by using analysis of variance tests and Student's T test, determining the least significant differences, and linear regression, by means of the SPSS software, version 19.0 for Windows.

3. Results

Pastureland soils (P1-P5) showed higher pH values than that of forest soils in the area (SN1 and SN2), especially in the case of P5, and also usually higher available P concentrations (especially P4, although being lower in P3 and P5), as well as for eCEC, and for exchangeable Ca and Mg (especially in P5), and lower Al concentration and saturation in the cationic exchange complex (Table 1), this in relation with the previous application of amendments and fertilizers.

Both natural soils here studied (SN1 and SN2) showed Ca_t and a modifiers as per Buol et al. (1975), meaning that Ca concentration was $< 1.5 \text{ cmol}_{(+) } \text{ kg}^{-1}$ in the cationic exchange complex, and that Al saturation was $> 60\%$. Moreover, soil SN2 presented the Mg_t modifier, meaning that Mg cation exchange capacity was $< 0.4 \text{ cmol}_{(+) } \text{ kg}^{-1}$.

Among pastureland soils, P3 presented the lowest values for pH, eCEC, and exchangeable Ca and Mg, but the highest level for Al saturation (being near alic condition). In the opposite extreme was soil P5.

Table 1. General characteristics of the soils (0-20 cm depth). SN: forest soil; P: pastureland soil

	SN1	SN2	P1	P2	P3	P4	P5
pH_{H₂O}	4.58	4.68	5.3	5.74	5.19	5.54	7.02
pH_{KCl}	3.91	4.03	4.3	4.26	3.94	4.61	6.30
Available P (mg kg⁻¹)	4.78	11.96	18.99	37.94	5.24	42.07	8.91
C (%)	7.74	5.64	5.62	8.07	2.28	4.17	5.09
N (%)	0.58	0.41	0.50	0.75	0.19	0.41	0.42
Ca (cmol₍₊₎ kg⁻¹)	0.66	0.03	7.35	8.95	1.38	5.11	26.16
Mg (cmol₍₊₎ kg⁻¹)	0.71	0.20	1.00	1.18	0.38	0.84	2.35
Na (cmol₍₊₎ kg⁻¹)	0.18	0.11	0.26	0.20	0.18	0.15	0.39
K (cmol₍₊₎ kg⁻¹)	0.56	0.35	0.52	0.69	0.58	0.44	0.73
Al (cmol₍₊₎ kg⁻¹)	6.62	6.87	2.85	2.58	3.66	1.33	0.17
eCEC (cmol₍₊₎ kg⁻¹)	8.73	7.56	11.98	13.60	6.18	7.87	29.81
Al Saturation (%)	75.80	90.82	23.79	18.96	59.24	16.93	0.58

Regarding heavy metals, no significant differences were found as a function of depth, which allowed overall interpretation of data as a whole.

Total Fe was between 19000 and 35000 mg kg⁻¹ in pastureland soils, and between 28000 and 38000 mg kg⁻¹ in forest soils (Figure 1), thus within the range indicated by Fernández and Carballeira (2001) for the surface layer of soils in NW Galicia (5941-45858 mg kg⁻¹).

Total Mn was between 120-472 mg kg⁻¹ in pastureland soils, and between 337-516 mg kg⁻¹ in forest soils (Figure 1), with the highest levels corresponding to both natural soils and to the pasturelands P4 and P5; furthermore, SN1 and P5 are well above the reference Mn levels for soils over quartzite (197 mg kg⁻¹), and SN2 and P4 well above that corresponding to slate (346 mg kg⁻¹) (Macías and Calvo 2008); however all these were lower levels than that reported by

Franco-Uría et al. (2009) for pasturelands in A Pastoriza (average 659 mg kg^{-1}), and are well below the phytotoxic limit ($1500\text{-}3000 \text{ mg kg}^{-1}$) indicated by Kabata-Pendias and Pendias (1992).

Total Cu was between $0.1\text{-}24 \text{ mg kg}^{-1}$ in pastureland soils, and between $8\text{-}55 \text{ mg kg}^{-1}$ in forest soils (Figure 1). Soils over quartzite (SN1, P1, P2, P3 and P5) had Cu concentrations generally lower than the background reference (16.8 mg kg^{-1} , Macías and Calvo 2008), whereas soil SN2 (over slate) overpassed the reference background concentration (24.9 mg kg^{-1}), with higher levels at the highest depth. López-Mosquera et al. (2005) found 23 mg kg^{-1} as average total Cu concentration for Galician pasturelands, while Franco-Uría et al. (2009) detected 20.5 mg kg^{-1} as average total Cu levels in A Pastoriza pasturelands, near that corresponding to our P4 and P5 pastureland soils, but lower to that of our SN2 forest soil. Kabata-Pendias and Pendias (1992) considered as phytotoxic total Cu concentrations between $60\text{-}100 \text{ mg kg}^{-1}$, which were not reached by any of the soil samples analyzed in the present study. Hashim et al. (2011) indicate that total Cu concentrations between $30\text{-}100 \text{ mg kg}^{-1}$ can be considered phytotoxic, values that were not detected in our pastureland soils, but the lower limit was widely overpassed by our forest soil on slate.

Total Zn was between $18\text{-}73 \text{ mg kg}^{-1}$ in pastureland soils, and between $27\text{-}48 \text{ mg kg}^{-1}$ in forest soils (Figure 1), with the highest values corresponding to soil P4. These levels are similar to that signaled by Macías and Calvo (2008) as background reference for quartzite and slate (47 and 69 mg kg^{-1} , respectively), but lower than that found by Franco-Uría et al. (2009) in pastureland soils of the same geographic area (98.7 mg kg^{-1}), and to that signaled by López-Mosquera et al. (2005) for Galician pasturelands (66 mg kg^{-1}). Most samples were below the phytotoxic levels indicated by Kabata-Pendias and Pendias (1992) ($70\text{-}400 \text{ mg kg}^{-1}$), and by Hashim et al. (2011) (400 mg kg^{-1}).

Total As was between $4\text{-}19 \text{ mg kg}^{-1}$ in pastureland soils, and between $6\text{-}20 \text{ mg kg}^{-1}$ in forest soils (Figure 2), with the highest levels associated to

slate as parent material (concretely, soils SN2 and P4), but always lower than the background reference values indicated by Macías and Calvo (2008): 44.5 mg kg^{-1} on slate, and 25.1 mg kg^{-1} on quartzite.

Total Ni was between $2\text{-}23 \text{ mg kg}^{-1}$ in pastureland soils, and between $7\text{-}22 \text{ mg kg}^{-1}$ in forest soils (Figure 2), with the highest values corresponding to SN2 and P4 (soils over slate), although being lower than the background reference (43.2 and 34.9 mg kg^{-1} , on slate and quartzite, respectively) signaled by Macías and Calvo (2008), and clearly lower than the phytotoxic threshold levels indicated by Kabata-Pendias and Pendias (1992) (100 mg kg^{-1}). Franco-Uría et al. (2009) found average values of 23.5 mg kg^{-1} in pastureland soils of the same area, and López-Mosquera et al. (2005) detected 27 mg kg^{-1} as average values for Galician pastureland soils. All our soil samples were below these levels, although P4 was near them.

Total Cr was between $39\text{-}95 \text{ mg kg}^{-1}$ in pastureland soils, whereas it was $62\text{-}94 \text{ mg kg}^{-1}$ in forest soils, with increasing levels as a function of depth (Figure 2). Pastureland soils P1, P2, P3 and P5, as well as the forest soil SN1 had Cr concentrations above the background reference for soils over quartzite (28.3 mg kg^{-1} , Macías and Calvo 2008), with soils P4 and SN2 showing similar levels to the background for soils over slate (85 mg kg^{-1}). Our values were above those previously found by Franco-Uría et al. (2009) in the area (54.1 mg kg^{-1}), and the average for Galician pasturelands (44 mg kg^{-1} , López-Mosquera et al. 2005), although being lower than the phytotoxic levels ($75\text{-}100 \text{ mg kg}^{-1}$) indicated by Kabata-Pendias and Pendias (1992).

Total Pb was between $6\text{-}18 \text{ mg kg}^{-1}$ in pastureland soils, and between $13\text{-}18 \text{ mg kg}^{-1}$ in forest soils (Figure 2). Both natural soils and the pastureland soils P4 and P5 presented the highest levels, although being lower than the background for quartzite (19.2 mg kg^{-1}) and slate (26.1 mg kg^{-1}) soils (Macías and Calvo 2008). Soils P4 and P5, as well as our two forest soils exhibited higher Pb levels than that previously reported by Franco-Uría et al. (2009) (11.7 mg kg^{-1}) for pasturelands in the

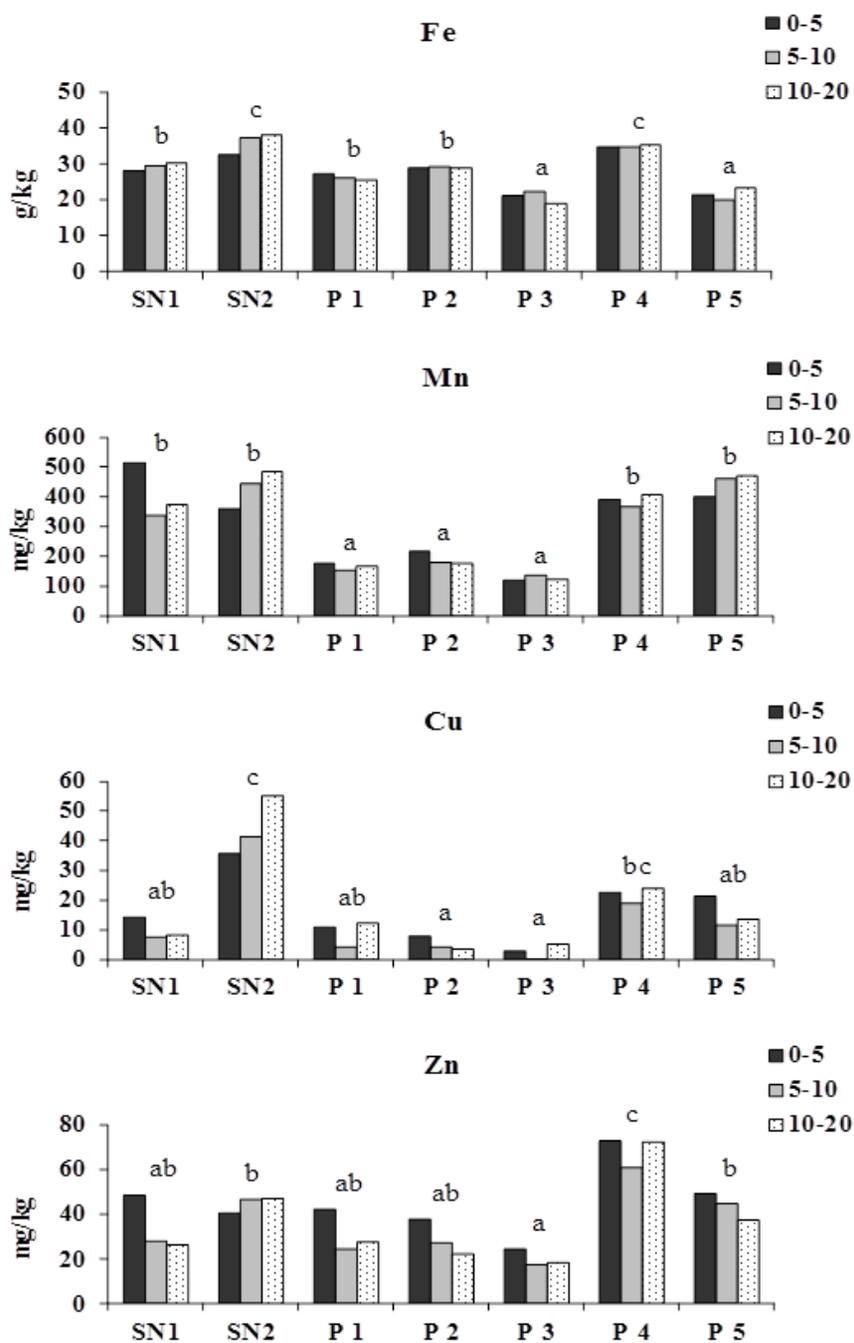


Figure 1. Total Cu, Fe, Mn and Zn concentrations in forest (SN) and pastureland (P) soils at various depths (0-5, 5-10, 10-20 cm). Different letters indicate significant differences between samples ($p < 0.05$), considering there is not soil depth influence.

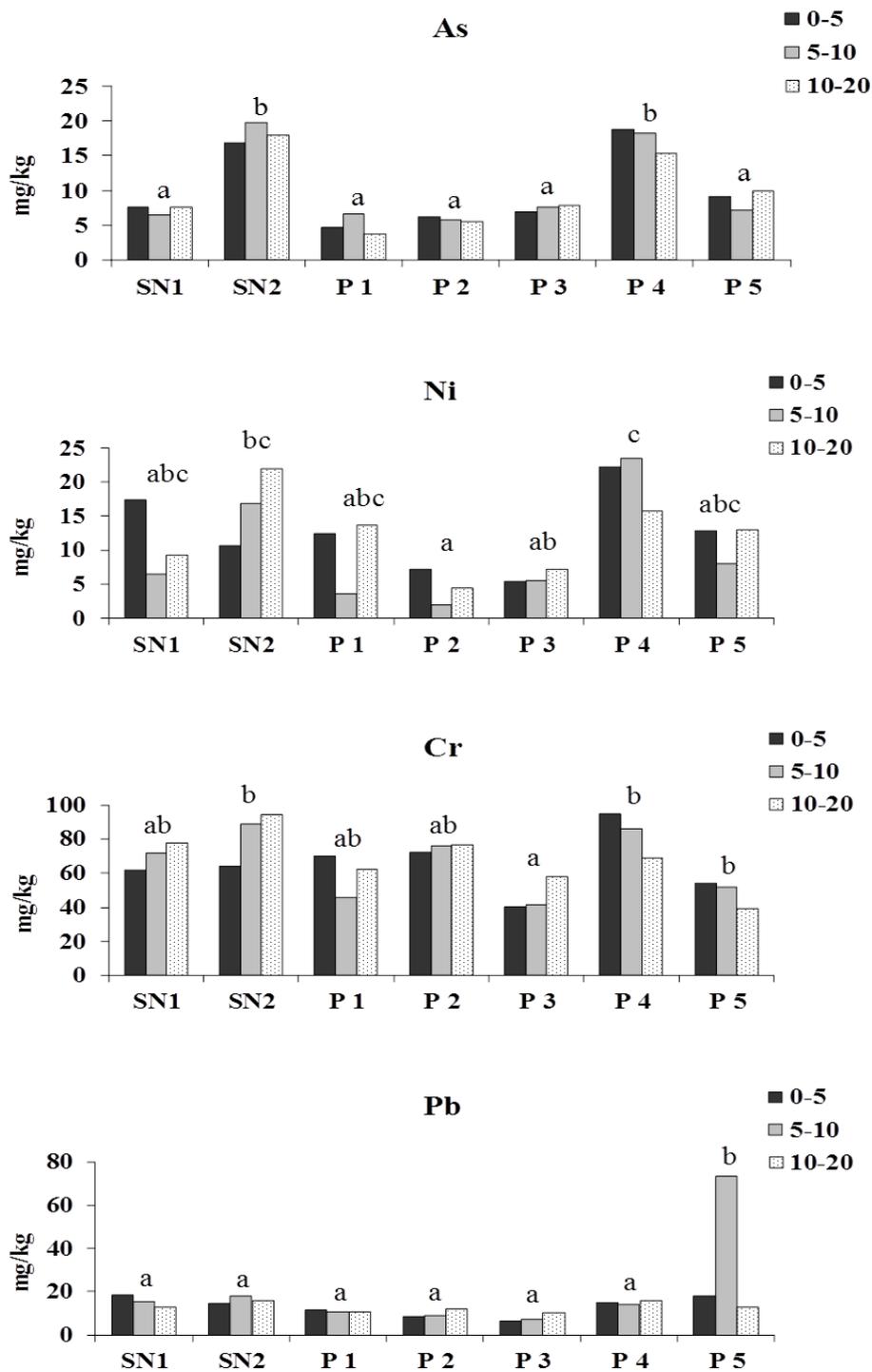


Figure 2. Total As, Cr, Ni, and Pb concentrations in forest (SN) and pastureland (P) soils at various depths (0-5, 5-10, 10-20 cm). Different letters indicate significant differences between samples ($p < 0.05$), considering there is not soil depth influence.

area, and by López-Mosquera et al. (2005) as average for Galician pastureland soils (12 mg kg⁻¹). Any case, all soil samples showed lower levels than the threshold for phyto-toxicity indicated by Kabata-Pendias and Pendias (1992) (100-400 mg kg⁻¹) and by Hashim et al. (2011) (30-100 mg kg⁻¹).

Cd was not detected in this study.

4. Discussion

Heavy metals concentration in soils, as well as its impact on ecosystems depends mainly on the parent material, climate conditions and anthropogenic activities (Khan et al. 2013). In addition, heavy metals can be incorporated to soils by means of pesticides, amendments, inorganic and organic fertilizers (Jia et al. 2010; Moral et al. 2008; Sager 2007; Zhang et al. 2012b). In A Pastoriza, high amounts of cattle slurry and inorganic fertilizers are spread to increase pasture production, which can increase heavy metals pollution (Carballas et al. 1990; Calvo-Rodríguez 2003).

The statistical study of the influence of soil depth (0-5, 5-10 and 10-20 cm), soil use (pastureland and forest), and parent material (quartzite and slate) on the parameters included in **Table 1**, gave as result that soil use was the only one affecting significantly to some of these parameters. Concretely, forest soils presented significantly lower levels for pH_{KCl}, total P and total Ca, in accordance with that expected as consequence of the spreading of amendments and fertilizers on pasturelands, and significantly higher levels for total Al.

Regarding heavy metals concentration, the order was as follows: Fe > Mn > Cr > Zn > Pb ≥ Ni ≥ Cu > As > Cd (**Figures 1 and 2**). Analysis of variance indicated that depth did not affect significantly heavy metals concentrations. The

Student's T test showed significantly higher As, Cr, Fe and Mn levels in forest soils than in pasturelands. Soils SN2 and P4 (over slate) presented significantly higher levels for Fe, Cr, Cu, Mn, Ni and Zn than soils over quartzite, which could be due to the frequent association of heavy metals to sulfides and arsenic compounds taking place in slates (Macías and Calvo 2008). Moreover, soil P4 presented significantly higher levels of Zn than soil SN2 (**Figure 1**), probably due to cattle slurry spreading (Carballas et al. 1990)

Table 2 shows that heavy metals concentrations correlated by pairs, unless with Pb. Correlations found between As and Fe suggest that As could derive from FeAsS or from FeAs₂, which are usually associated to slate. In the case of Cu, it could be associated to Fe in CuFeS₂, whereas Cr can adsorb on Fe oxy-hydroxides, and Ni can be in sulfides as (Ni, Fe)₉S₈, or substituting Fe(II) in pyrite or other sulfides (Macías and Calvo 2008). There was no significant correlation between heavy metals and P, which is an element incorporated to the studied pasturelands both with cattle slurry and with inorganic fertilizers.

Significant correlations between most heavy metals and Fe, as well as the absence of correlation with P (**Table 2**) and the fact of finding higher concentrations in soils over slate, and similar values for forest and pastureland soils, all direct towards the existence of a geological origin for most heavy metals in the soils of the area, as previously found by Jia et al. (2010) studying cultivated soils in China. Cr and Mn were the only two heavy metals showing higher levels than the background indicated by Macías and Calvo (2008) for Galician soils over the same parent materials, although the importance of fertilization at this regard can be discarded, with forest and pastureland soils presenting similar Cr and Mn concentrations. Zn levels in soil P4 could be in relation with cattle slurry and inorganic fertilizers spreading, being lower to those found by Franco-Uría et al. (2009) in A Pastoriza pasturelands, and similar to that found by López-Mosquera et al. (2005) in Galician pasturelands.

The pastureland soils studied presented lower levels of heavy metals than the threshold values indicated in the European Commission Directive 86/278/ECC (European Communities 1986, translated to the Galician legislation as Decreto 125/2012 (Anexo VII) de la Comunidad Autónoma de Galicia) referred to sewage sludge application on cultivated soils with pH < 7. However, taking into account the new limits proposed for 2015 (European Commission 2000) for soils with pH 5-6, 100% of our soil samples (including forest soils) are above the limit for Cr (30 mg kg⁻¹), while our two soils over slate (SN2 and P4) are above limits for Cu and Ni (20 and 15 mg kg⁻¹, respectively),

and the pastureland soil P4 is above the limit for Zn (60 mg kg⁻¹).

Although heavy metal levels in the area are related mainly to lithology, cattle slurry is spread every year without control, which could give progressive heavy metals accumulation and increasing risks of soil and water pollution, and eventual transfer to the food chain (Dong et al. 2011). In view of that, more careful regulations could be considered to diminish risks of soil and water pollution in such intensive farming areas with remarkable heavy metals lithological contribution.

Table 2. Matrix of correlations between pairs of elements (total concentrations, expressed in mg kg⁻¹, n = 525)

	P	Al	Fe	Mn	Cu	Zn	Ni	Cr	As	Pb
P	1									
Al	0.05	1								
Fe	0.27	-0.15	1							
Mn	0.04	-0.10	0.42*	1						
Cu	-0.04	-0.06	0.68***	0.65***	1					
Zn	0.29	-0.40	0.53**	0.67***	0.57**	1				
Ni	0.26	-0.21	0.61**	0.67**	0.73***	0.81***	1			
Cr	0.31	-0.13	0.84***	0.31	0.54**	0.46*	0.54**	1		
As	0.17	-0.14	0.72***	0.57**	0.81***	0.68***	0.74***	0.55**	1	
Pb	-0.11	0.10	-0.18	0.46*	0.11	0.25	0.06	-0.07	0.08	1

p: * < 0.05; ** < 0.01; *** < 0.001

5. Conclusions

In the pastureland soils here studied, most heavy metals (As, Cu, Fe and Ni) concentrations are in relation with the parent geological material, with higher levels in soils over slate and significant correlations with Fe, suggesting pyritic origin. Forest soils show similar or even higher heavy metal concentrations than pastureland soils,

although being always lower than the generic threshold levels considered for each parent material. Only Cr and Mn show some levels that can be higher than the generic for this kind of soils, although pastureland fertilization do not seem to be the cause, due to the fact that forest soils exhibit similar or even higher

concentrations. Zn levels in the P4 pastureland soil can be in relation with cattle slurry application, in view of being significantly higher than that found in the SN2 forest soil, developed over the same parent material. All samples show lower heavy metals levels than that established in current sewage sludge spreading regulations; however, taken into consideration the European Commission proposed levels for 2015, Cr would be limiting for slurry spreading in all the studied soils, whereas this would be the case for Cu and Ni in soils SN2 and P4, and for Zn in soil P4. Bearing in mind that the detected levels are in relation with natural lithological aspects, these results put in evidence the existence of clear repercussions on the management of the studied soils. To diminish risks of soil and water pollution, as well as transfer to the food chain, it would be necessary to carry out periodical determination of heavy metals concentrations in soils characterized by high natural heavy metal contents and intensive agriculture, which could even lead to improve cattle slurry and inorganic fertilizers spreading regulations.

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