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Organic Matter and Chromium Evolution in Herbage and Soil in a *Pinus radiata* Silvopastoral System in Northwest Spain after Sewage Sludge and Lime Application

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This article aims to compare the effects of applying three doses of sewage sludge, with or without liming, on organic matter, total and available chromium (Cr), and their concentration in plants. Unfertilized (NF) and mineral treatments were used as control. Soil organic-matter (SOM) modification depended on the interaction of liming and sewage sludge implementation. Liming, high sludge doses, and mineral treatment caused less SOM in the second year of study. However, after 3 years, SOM was increased by both mineral and sludge fertilizers compared to NF treatments as result of tree development and the reduction of organic-matter mineralization into the soil. These findings could have important implications for soil carbon storage capacity. Total Cr in soil and forage was increased by sewage sludge application compared to mineral or NF treatments. Liming increased Cr availability in the spring of 2000, where sewage sludge was applied, and reduced Fe availability.

Keywords Agroforestry system, heavy metal, plant

Introduction

Afforestation was an important issue for the European Union (EU) between 1994 and 1999, when more than 1 million hectares was afforested (European Commission 2005) as a result of Regulation No. 2082/92 implementation (EU 1992). The use of understory growth in afforested areas through the promotion of silvopastoral systems, as the last European Union Rural Development Council Regulation1698/2005 (EU 2005) recommends to produce outcomes (cattle and trees), will help to maintain an environmentally and economically sustainable system.

Adequate silvopasture management should increase synergies and reduce negative interactions among the components (soil, trees, grass, and cattle) to increase global system

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productivity. Therefore, farm income is produced on a continuous basis, unlike the exclusive use of land for forests (García-Barrios and Ong 2004; Jose, Gillespie, and Pallardy 2004). Fertilizer application is the simplest management practice for increasing production of pasture in a predictable way, and organic or mineral fertilizers can be used.

The organic fertilizer produced from municipal sewage sludge can be used to increase pasture production. The volume of municipal sludge generated has increased considerably in EU countries in the past decade because of the implementation of European Directive 91/271/CEE (European Directive 1991), the purpose of which is to preserve the quality of the continental waters. In various EU countries, the use of sewage sludge as a fertilizer (regulated by European Directive 86/278/CEE; European Directive 1986) is encouraged because of its organic-matter content and concentration of nutrients, especially nitrogen (N).

Agricultural systems and forestry plantations encounter problems of soil fertility caused by the substantial removal of soil organic matter (SOM) and nutrients, which occurs during harvest. Moreover, it has been recognized that a decline in SOM almost invariably accompanies land degradation (Young 1997), which encourages carbon dioxide (CO_2) released to the atmosphere. Sewage sludge inputs can increase the SOM concentration and thus soil fertility, while at the same time it applies nutrients (Smith 1996; Cameron, Di, and McLaren 1997). There are few studies dealing with SOM response in acidic soils, with high initial SOM, as result of the positive or negative soil organic impacts caused by liming or municipal sewage sludge applications. Municipal sewage sludge positive impacts are caused by the greater level of organic matter in the residue than in the soil. The reduction of SOM due to sewage sludge and lime application in acidic soils could come from the increment of the SOM mineralization rate as a result of soil pH improvement caused by both practices (liming and sewage sludge application) in acidic soils, which could therefore reduce the soil capacity to sequester carbon.

The use of municipal sewage sludge as a fertilizer may be limited by the heavy-metal concentrations, with zinc (Zn), copper (Cu), and chromium (Cr) levels in sludge often greater than is normally found in soils. Sewage sludge usually contains other heavy metals in lower concentrations, such as cadmium (Cd), lead (Pb), and mercury (Hg) (Smith 1996). All these elements can reach human beings through the food chain, potentially causing health problems (Wang et al. 2004), and for this reason sewage sludge use in agriculture is regulated (Spanish Royal Decree 1310/1990 1990, European Directive 86/278; European Directive 1986).

The role of SOM on heavy-metal adsorption in acidic soils has already been described (Kabata-Pendias and Pendias 1985; Alloway 1995). High levels of SOM reduce the negative effect of heavy metals, because SOM reduces metal availability (Kabata-Pendias and Pendias 1985). The effect of sewage sludge on heavy-metal availability will depend on the concentration of the heavy metals of the sludge but also on mineralization rate and the degree of incorporation of sewage sludge into the soil, which depends on sludge characteristics (Environmental Protection Agency 1994), the type of soil to which this residue is applied, as well as land use (forest or silvopastoral use). Acidic soils usually limit the mineralization rate because of greater soil pH requirements of the bacteria responsible for mineralization. An initial increase in pH, due to sewage sludge application, may occur and modify the mineralization rate and therefore SOM cycling and heavy-metal availability. Therefore, knowledge of the interaction of organic matter and heavy metals in both soil and plants after sewage sludge application is important to prevent detrimental effects on both the soil and human and animal health (Hillman et al. 2003) over the short and medium term.

There are some studies describing the effect of sewage sludge application on Zn and Cu solubility in very acidic soils (Mosquera-Losada, Rigueiro-Rodríguez, and López-Díaz 2001; Mosquera-Losada, López-Díaz, and Rigueiro-Rodríguez 2009). However, the modification of the solubility of Cr, the third main element limited by European policy, has not been studied in depth. The aim of this study was to investigate the effects of different doses of sewage sludge and no fertilization with or without liming and mineral fertilizer [%; 8 nitrogen (N)–24 phosphorus pentoxide (P_2O_5)–16 potassium oxide (K_2O)] on soil organic matter; total Pb, Cr, nickel (Ni), Hg, and Cd; Cr availability; and plant concentrations in a silvopastoral system located on an acidic soil (initial water pH below 5).

Materials and Methods

The experiment was carried out in Lugo (Galicia region, NW Spain) at 748 m above sea level during 3 years. Soil was sedimentary and classified as Umbrisol (FAO 1998) or Inceptisol (USDA 2006) with a depth of around 50 cm and very acidic [the initial soil pH in water (1:2.5) was 4.7], with a high initial concentration of SOM (12.32%) and N (0.52%). Nitrogen was mainly in organic form. Initial soil analyses detected 200.8 mg kg^{-1} ammonium (NH_4^+)-N and 4.4 mg kg^{-1} nitrate (NO_3^-)-N as inorganic soil N. The Olsen phosphorus (P) was very low (0.03%), as is usual in this area (Mombiela 1983). The initial heavy-metal concentration in soil (Table 1) was below the limits for using sewage sludge as a fertilizer in the European Union (Directive 86/278/CEE (European Directive 1986)) and Spain (Spanish Royal Decree 1310/1990 1990). The soil texture was a sandy clay loam (63% sand, 26% clay, and 11% silt).

The experiment consisted of a five-year-old *Pinus radiata* D. Don (Monterrey pine) plantation, with a density of 1667 trees ha^{-1}. The experimental design was of randomized blocks with three replicates. The plots each consisted of a square of 5 × 5 trees and occupied 96 m^2, which were sown in autumn 1997 with a mixture of 25 kg ha^{-1} of *Lolium perenne* var. Brigantia, 10 kg ha^{-1} of *Dactylis glomerata* var. Artabro, and 4 kg ha^{-1} *Trifolium repens* cv. Huia after plowing. The cell plots were initially fertilized with 120 kg P_2O_5 ha^{-1} and 200 kg K_2O ha^{-1}. Eight treatments were applied: no fertilizer (NF), three sewage sludge doses based on N application (S1, 160 kg total N ha^{-1}; S2, 320 kg total N ha^{-1}; S3, 480 kg total N ha^{-1}) with or without liming applied in 1998 before sowing [2.5 t calcium carbonate ($CaCO_3$) ha^{-1}]. A mineral fertilizer (MIN) treatment was also established as a control. The combination of lime and MIN treatment was not applied as a control because this treatment is not usually applied in the area. MIN treatment consisted of the application of 500 kg of 8% N–24% P_2O_5–16% K_2O ha^{-1}, following conventional practice for fertilizing pastures. All fertilizer treatments were applied at the start of the growing season in 1998, 1999, and 2000. Sewage sludge doses were based on total N concentration of sewage sludge (Table 2) following the U.S. Environment Protection Agency recommendation (Environment Protection Agency 1994), which establishes that around 25% of the total N applied is going to be mineralized during the first year when sewage sludge is anaerobically digested.

The sewage sludge came from the urban residues of the nonmanufacturing town of Lugo, which explains the low level of heavy-metal levels found in this residue (Table 1). Heavy-metal sewage sludge concentrations were below European and Spanish legislated limits for use in agriculture (Directive 86/278/CEE, European Directive 1986; Spanish Royal Decree 1310/1990).

Eight pasture samplings were made before harvesting in July and December 1998 and in May, July, and November of 1999 and 2000. At the same time, a composite soil sample

Table 1

Concentrations of Zn, Cu, Cr, Cd, Hg, Ni, and Pb in the sewage sludge (range in 1998, 1999, and 2000) and soil at the beginning of the experiment, their addition through each application of sewage sludge (range depending on the year), and legal limits established by EU European Directive 86/278 and Spain R.D. 1310/1990

	Zn	Cu	Cr	Cd	Hg	Ni	Pb
Sewage sludge							
mg kg^{-1}	746–821	154–244	39–141	1.0–5.0	1.5	21–49	94.7–203
Legal limits	2500–4000	1000–1750	1000–1500	20–40	16–25	300–400	750–1200
Elements inputs							
S1 kg ha^{-1} $year^{-1}$	3.71–4.99	0.77–1.21	0.19–0.28	0.005–0.02	0.006–0.007	0.10–0.18	0.47–1.01
S2 kg ha^{-1} $year^{-1}$	7.43–9.99	1.54–2.43	0.38–1.40	0.01–0.05	0.006–0.007	0.21–0.37	1.94–2.02
S3 kg ha^{-1} $year^{-1}$	11.14–14–99	2.30–3.64	0.58–2.10	0.01–0.07	0.018–0.022	0.31–0.56	1.41–3.03
Legal limits	30	12	3	0.15	0,1	3	15
Soil concentrations							
mg kg^{-1}	17.2	8.2	13.2	<1	0.13	<1	<1
Legal limits	150–300	50–140	100–150	1.0–3.0	1.0–1.5	30–75	50–300

Note. Limits depend on soil pH (minimum: soil pH < 7, maximum: soil pH > 7).

Table 2
Properties of the sewage sludge batches used in 1998, 1999, and 2000, showing dry-matter concentration (DM, g kg^{-1}), pH in water, organic-matter concentration (SOM, g kg^{-1}), the carbon/nitrogen (C/N) ratio, and the N, P, K, Ca, Mg, and Na concentrations (g kg^{-1})

Year	pH	C/N	DM (g kg^{-1})	SOM (g kg^{-1})	N (g kg^{-1})	P (g kg^{-1})	K (g kg^{-1})	Ca (g kg^{-1})	Mg (g kg^{-1})	Na (g kg^{-1})
1998	6.94	5.85	250.0	490.0	32.1	9.3	2.5	6.7	5.4	0.8
1999	6.94	7.09	250.0	392.5	32.1	5.2	2.5	6.9	4.3	0.2
2000	6.94	6.05	235.4	441.2	42.3	16.5	2.6	6.9	6.5	1.4

was taken from each plot to a depth of 5.5 cm to determine organic matter and available Cr concentration and to a depth of 25 cm to determine total heavy-metal concentration.

Soil samples were air dried, passed through a 2-mm sieve, and ground with an agate mortar. The SOM concentration was determined by using the Saverlandt method (Guitián and Carballás 1976). Total soil and plant (after drying in an oven 80 °C) heavy-metal concentrations were analyzed with the Varian 220FS spectrophotometer (Varian, Palo Alto, Calif.) using atomic absorption detection after a nitric acid digestion made in a CEM MDS-2000 microwave digestor (CEM 1994). Available Cr was measured with the spectrophotometer using atomic absorption detection, after extraction with Mehlich 3 extracting solution (Mehlich 1985), the effectiveness of which usefulness was evaluated by Monterroso, Álvarez, and Fernández-Marcos (1999) in acidic soils of NW Spain.

The results obtained were analyzed by analysis of variance (ANOVA), and means were separated using Duncan's multiple-range test (SAS 2001).

Results

The ANOVA results for SOM and total and available Cr in soil and in plants for 1998, 1999, and 2000 are presented in Table 3. The SOM was significantly affected by the interaction of lime × fertilizer in 1999 and by the fertilizer treatment in 2000. Total Cr was significantly modified by sampling date × fertilizer and sampling date × lime interactions in 2000. There was a significant effect of the sampling date × liming × fertilizer and sampling date × liming interactions on available Cr in 1999 and 2000, respectively. Finally, Cr in plant was significantly affected by the interaction sampling × lime interaction in 1999 and 2000. Levels of SOM were between 12.25 and 17.3 % (Figure 1). In 1998, there were no significant differences between fertilizer treatments, but in 1999, the response of SOM to the high dose of sewage sludge (S3) depended significantly on whether liming had been previously applied. In 1999, SOM was significantly reduced by liming from 16.1% (no liming) to 12.2% (liming) in the S3 treatment. In 2000, mineral (15.7%) and sludge (15.2–16.5%) fertilizer significantly increased the SOM concentration with respect to no fertilizer (13.7–14.2%), as shown in the equation in Figure 1 ($r^2 = 0.99$). However, no significant differences in the SOM between mineral and sludge application or among sludge doses were detected in the final year.

Total soil contents of Pb, Ni, and Cd were less than 0.01 mg kg^{-1} (below the limits for Pb, Ni, and Cd detection by atomic absorption spectrophotometry). Total Hg content in soil (0.08–0.17 μg Hg kg^{-1}) was similar to those detected in uncontaminated soils (0.01–2 μg kg^{-1}) (Kabata-Pendias and Pendias 1985; Fergusson 1990), and no significant

Table 3
ANOVA results for different variables (SOM, total and available Cr in soil and in plants) in 1998, 1999, and 2000

Variables	Year	S	Bl	L	F	L × F	S × L	S × F	S × L × F
SOM	1998	*	*	ns	ns	ns	ns	ns	ns
	1999	***	ns	**	ns	*	ns	ns	ns
	2000	***	**	ns	***	ns	ns	ns	ns
Total Cr	2000	***	*	ns	**	ns	*	**	ns
Available Cr	1999	***	***	***	***	ns	***	***	***
	2000	**	ns	**	ns	ns	**	ns	ns
Cr in plant	1999	*	*	***	ns	ns	***	ns	ns
	2000	***	ns	ns	ns	ns	*	ns	ns

Notes. S, sampling date; Bl, block or treatment replica; L, liming treatments; F, fertilizer treatments; L × F, interaction of liming × fertilizer; S × L, interaction of sampling date × liming; S × F, interaction of sampling date × fertilizer; S × L × F, interaction of sampling date × liming × fertilizer. Asterisks indicate significant interaction between factors; ns: not significant. Significance determined by Duncan's test.
*$P < 0.05$.
**$P < 0.01$.
***$P < 0.001$.

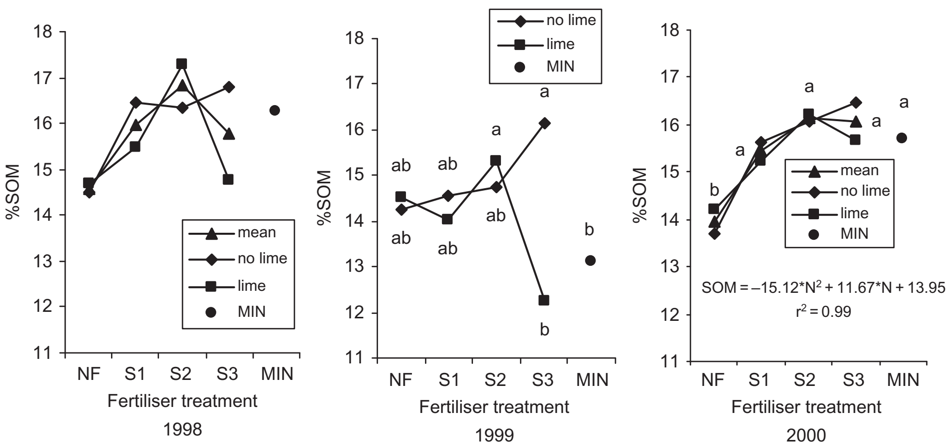

Figure 1. Mean organic-matter concentration (SOM, %) in soil under the different liming and fertilizer treatments in 1998, 1999, and 2000. Mean, mean values between no limed and limed treatments per each fertilizer dose (liming dose was 2.5 t CO_3Ca ha^{-1}); NF, no fertilizer; S1, low sewage sludge doses (160 kg total N ha^{-1}); S2, medium sewage sludge doses (320 kg total N ha^{-1}); S3, high sewage sludge doses (480 kg total N ha^{-1}); and MIN, mineral fertilizer. Different letters indicate significant differences between fertilizer treatments (♦, no lime; ■, lime) or the mean of both (▲) ($P < 0.05$). N in the equation means total added N ha^{-1}.

differences were detected between treatments, apparently due to the low concentration of heavy metals in the sewage sludge applied and in the tested soil.

In Figure 2, the mean total soil Cr concentration in autumn 2000 is shown. Results of the first 2 years (1998 and 1999) are not presented, because the effects of different treatments were minimal and increases were not observed. In general, in the final sampling

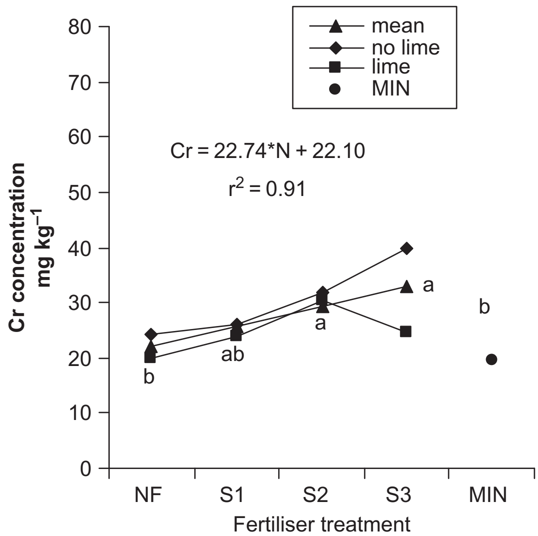

Figure 2. Mean total concentrations of Cr (mg Cr kg^{-1}) in soil under the different fertilizer treatments in November 2000. Mean, mean values between no limed and limed treatments per each fertilizer dose (liming dose was 2.5 t CO_3Ca ha^{-1}); NF, no fertilizer; S1, low sewage sludge doses (160 kg total N ha^{-1}); S2, medium sewage sludge doses (320 kg total N ha^{-1}); S3, high sewage sludge doses (480 kg total N ha^{-1}); and MIN, mineral fertilizer. Different letters indicate significant differences between fertilizer treatments (♦, no lime; ■, lime) or the mean of both (▲) ($P < 0.05$). N in the equation means total added N ha^{-1}.

(November 2000), soil Cr concentration was increased by sewage sludge application (from 19.8 to 24.4 mg kg^{-1} in unfertilized treatment and from 23.9 to 39.8 mg kg^{-1} in the high dose of sewage sludge treatment). Moreover, the increase of Cr with sewage fertilizer was proportional to the N applied with the sewage fertilizer, as the equation in Figure 2 indicates.

The values of available soil Cr were between 0.1 and 0.66 mg kg^{-1} (Figure 3). In 1998, the value range was between 0.10 and 0.25 mg Cr kg^{-1} (data not presented), and there were no significant differences in available soil Cr levels between treatments. In May and July 2000, the Cr percentage extracted by Mehlich 3 was greater when sewage sludge and liming were applied (0.35–0.68 mg kg^{-1} with lime application, compared to 0.1–0.46 mg kg^{-1} without lime) as shown by the significant differences between treatments found when May and July 2000 samplings were analyzed. Sewage fertilizer, without liming, increased available soil Cr in November 1999 (0.33–0.66 mg kg^{-1} compared to 0.1 mg kg^{-1} with no fertilizer). There were no significant differences in available soil Cr levels between treatments in November 2000 (data not presented), being values around 0.1 mg Cr kg^{-1}. Mineral and no-fertilizer treatments produced similar Cr values, and sometimes the Cr concentrations were lower than with sludge.

The obtained range of plant Cr concentration (Figure 4) was between <1 (below limit for Cr detection by atomic absorption spectrophotometry) and 2.7 mg kg^{-1}. In general, there were no significant responses of plant Cr to the treatments. Only in July 1999, there was a small reduction in the plant Cr concentration detected with sewage and mineral treatments. In July 2000, low and medium sewage sludge doses increased Cr plant percentages.

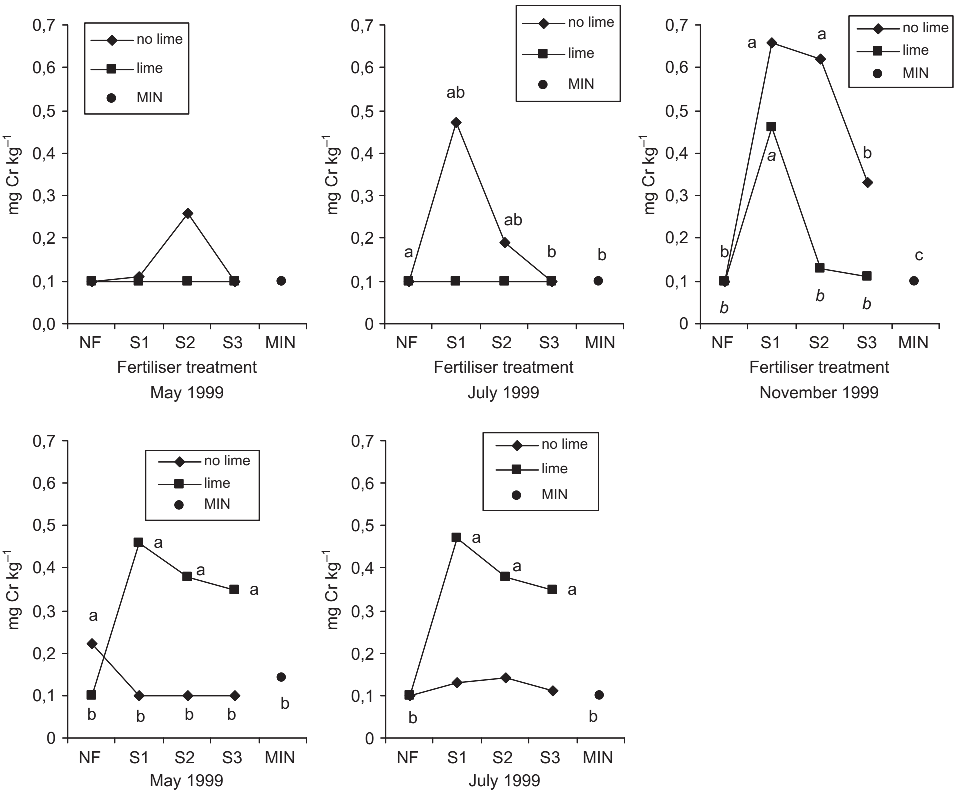

Figure 3. Mean available chromium concentrations (mg Cr kg^{-1}) in soil under the different liming and fertilizer treatments in 1999 and 2000. Mean, mean values between no limed and limed treatments per each fertilizer dose (liming dose was 2.5 t CO_3Ca ha^{-1}); NF, no fertilizer; S1, low sewage sludge doses (160 kg total N ha^{-1}); S2, medium sewage sludge doses (320 kg total N ha^{-1}); S3, high sewage sludge doses (480 kg total N ha^{-1}); and MIN, mineral fertilizer. Different letters indicate significant differences between fertilizer treatments (⧫, no lime; ■, lime) or the mean of both (▲) ($P < 0.05$). N in the equation means total added N ha^{-1}.

Discussion

Soil Organic Matter

The SOM levels were high compared to those on agronomic lands, which are considered to have high SOM levels when SOM is more than 3.5% (Porta, López, and Roquero 1999), but in grassland, the SOM mean is usually between 5 and 8% (Domínguez-Vivancos 1997). It is known that an adequate quantity of SOM is important for improving water retention, cationic exchangeable capacity, and nutrient availability (Porta, López, and Roquero 1999). However, the high SOM in woodlands of the Galician region is explained by the low pH, which limits soil microbial activity and therefore the rate of SOM mineralization.

Increased pH could result from the addition of lime or high-pH materials such as sewage sludge (pH 6.9). Thus, the initial application of a high dose of sewage sludge (S3 in 1999) and liming together produced a reduction in the SOM concentration caused by the activation of mineralization provoked by the higher Ca supplies of this treatment (sludge and lime) compared to other treatments (Wild 1992). The reduction in

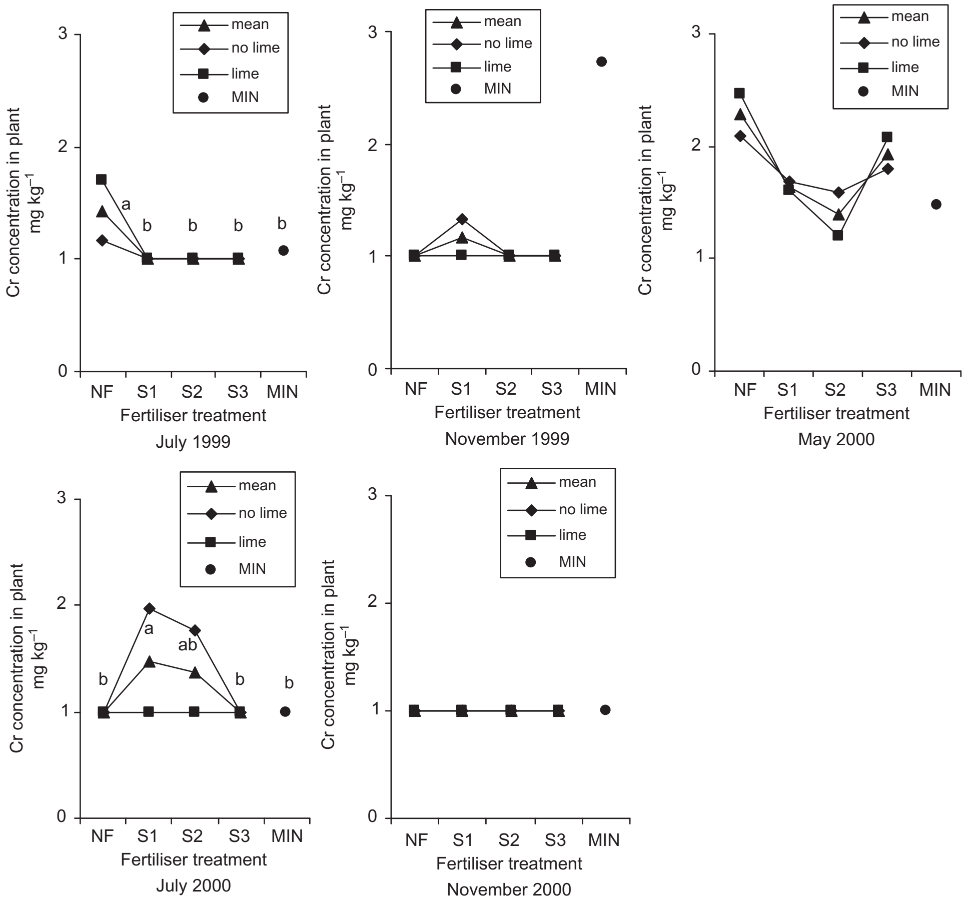

Figure 4. Mean chromium concentrations in forage (mg Cr kg^{-1}) under the different fertilizer treatments in 1999 and 2000. Mean, mean values between no limed and limed treatments per each fertilizer dose (liming dose was 2.5 t CO_3Ca ha^{-1}); NF, no fertilizer; S1, low sewage sludge doses (160 kg total N ha^{-1}); S2, medium sewage sludge doses (320 kg total N ha^{-1}); S3, high sewage sludge doses (480 kg total N ha^{-1}); and MIN, mineral fertilizer. Different letters indicate significant differences between fertilizer treatments (♦, no lime; ■, lime) or the mean of both (▲) ($P < 0.05$). N in the equation means total added N ha^{-1}.

SOM was faster with liming, as the rate of increase of pH with liming is higher than with sewage sludge alone (López-Díaz, Mosquera-Losada, and Rigueiro-Rodríguez 2007). The impact of sewage sludge on SOM depends on the initial soil pH and the type of sludge. When the soil pH was greater than 5.5, reduction of the SOM was not found in agronomic soils (with initial SOM around 2.94 g kg^{-1}) developed under pastures amended with municipal sewage sludge in Galicia (Rigueiro-Rodríguez et al. 2004), probably because of the greater mineralization rate of the organic matter added with the sludge at those pH values above 5.5 (Wild 1992), which also explains the initial lower SOM concentration (2.94%) of the soil when the sludge was added. On the other hand, there are many studies indicating that the use of sewage sludge favors the increase of SOM (Cameron, Di, and McLaren 1997; Lindsay and Logan 1998). The increment in SOM depends on the rate of mineralization of a particular soil, which depends on the

edapho-climatic conditions (pH, rain, and temperature). Under Galician conditions, there is a significant rate of soil mineralization if the pH is sufficient, because of adequate temperature and precipitation rate. For this reason, it is not easy to find an increase of SOM concentration unless the soil pH is reduced. This factor can have an important impact on C cycling in the soil. Soil C storage in the present experiment was high (200 and 280 t C per hectare) in the top 25 cm. These C levels are above the numbers given by Rigueiro-Rodríguez et al. (2007) for a 10-year-old *Pinus radiata* forest in agronomic land in the same area and by Dixon (1995) for silvopastoral systems (12–228 t C per ha).

In forest woodlands, trees can modify the soil microclimate. Soil shading caused by tree canopy growth was more important toward the end of the experiment, as described in the present experiment, because of the development of lower branches, which start to lose pine needles and so cause an increase of humidity and acidity in the soil (Mosquera-Losada, Fernández-Núñez, and Rigueiro-Rodríguez 2006). Microclimate modifications caused by *Pinus radiata* growth and the accumulation of three consecutive years of sludge application caused a significant increase in the SOM concentration in the final year (2000), as several authors have detected (Lindsay and Logan 1998; Pascual et al. 2004). The SOM increment correlates with the higher proportion of organic matter in sludge (between 39.3 and 49.0%) than in soil (12.3%).

The application of mineral fertilizer reduced initially SOM concentration, presumably because the N supplied reduced the C/N relationship and thus improved the mineralization rate. In the following years, the effect of mineral fertilizer on SOM changed and an increased SOM level was observed, probably because of the further reduction of pH to 4.4 (López-Díaz, Mosquera-Losada, and Rigueiro-Rodríguez 2007), which limited the development of mineralizer microorganisms (Wild 1992). Moreover, the increase in soil acidity reduces pasture growth and thus competition with the trees, and as a result, tree growth was improved (López-Díaz, Mosquera-Losada, and Rigueiro-Rodríguez 2007). The trees take greater advantage than pasture of the mineral nutrients added. The larger tree size increases the canopy cover, and thereafter the mineralization rate is slowed down. Therefore, it can be concluded that the modifications caused by the tree canopy developed on acidic soils reduce the mineralization rate and so become a main factor in the increase of the SOM, which explains significant differences in SOM between NF and MIN treatments as was found in an abandoned agricultural land in Galicia (Mosquera-Losada, Fernández-Núñez, and Rigueiro-Rodríguez 2006).

In this experiment, in a woodland rich in SOM and with a low pH (4.7 in H_2O), when mineralization conditions were improved (liming treatment, mineral fertilizer treatment), SOM concentration was reduced. However, in contrast, when sludge and mineral fertilizer improved tree growth, the decreased soil temperature associated with tree shading and resulting decrease in the mineralization rate increased SOM. The effect of liming on mineralization was reduced over time, possibly because of development of the tree canopy. Galicia has been heavily reforested in the past decade (close to 13%), and this could have had an important impact on regional soil C storage.

Soil Chromium

The total values of soil Cr are low when compared to the usual range for surface forest soils of various countries (1.4–1384 for Cr) detected by several authors, such as Kabata-Pendias and Pendias (1985). Moreover, all values (Cr: 4.31–67.6 mg kg^{-1} DM) were always low with respect to the legal limits (initial maximum levels in a soil with pH less than 7 for

sewage sludge application) in the Spanish (Spanish Royal Decree 1310/90 1990) and EU regulations (European directive 1986) for sludge application (Cr: 100 mg kg^{-1} soil). This could be explained by the fact that this experiment was located on a soil that was not fertilized or limed in the recent decades. The total soil Cr concentrations were only significantly increased in the final year (2000), after three consecutive annual sewage sludge applications. Chromium is one of the three main heavy metals of sewage sludge, and therefore the impact of sludge application is greater in those elements than with others such as Hg, Cd, Ni, and Pb.

The effect of treatments on soil extractable Cr depended on the influence of these treatments on other soil factors (SOM content, pH, Fe availability, total Cr inputs) that regulate heavy-metal availability for plants as was observed by Chaudri et al. (2000), Hillman et al. (2003), McBride, Richards, and Steenhuis (2003), and López-Mosquera et al. (2005).

The role of SOM on heavy-metal adsorption in acidic soils has already been described (Kabata-Pendias and Pendias 1985; Alloway 1995; Smith 1996; Pascual et al. 2004). High levels of SOM reduce the negative effect of heavy metals, because SOM reduces heavy-metal availability (Kabata-Pendias and Pendias 1985). However, under our conditions, and because of the Cr inputs made by the sludge after three consecutive years and rapid modifications of pH and Fe availability caused by liming and sludge application, the availability of Cr can be increased in spite of SOM increment caused by sludge application. This is due to the important effect of lime and sewage sludge application on mineralization, which mobilizes heavy metals from sludge and favors their incorporation into the soil as demonstrated by the greater total Cr levels in the last year of the study when sewage sludge was applied. Later, availability is regulated by the soil pH (Kabata-Pendias and Pendias 1985) but also by Fe availability (Bradl 2004). The soil pH increment caused by liming usually reduces Cr availability as happened in 1999 (Kabata-Pendias and Pendias 1985). The positive effect of lime on SOM mineralization at the end of 1999 caused an increment of soluble Cr in the soil and a reduction of iron (Fe) availability ($P < 0.001$) in limed (366.85 mg Fe kg^{-1} extracted by Mehlich 3, umpublished data) compared with unlimed (468.17 mg Fe kg^{-1} extracted by Mehlich 3, unpublished data) treatments in 2000. The adsorption of Cr by Fe oxides is reduced with increasing pH as a result of the reduction of Fe available in limed treatments (Bradl 2004; Covelo, Vega, and Andrade 2008). Kumpiene et al. (2009) also found a reduction of Cr soluble as result of Fe-amended soils.

The lack of response of Cr to mineral fertilizer could be because, despite the heavy-metal concentration of this fertilizer (Verloo and Willaert 1990), the total amount of fertilizer applied was much lower (500 kg ha^{-1} $year^{-1}$) than with the sewage sludge treatments (between 16 and 60 t ha^{-1} of fresh sludge). No differences in soil Cr total and available content were found as result of lime application in unfertilized treatments, which could be explained because Cr in lime is usually low and because of the reduced initial soil Cr content.

Pasture Chromium

Chromium is not considered an essential micronutrient for plants, but it has a relevant rule in the metabolism of animals, which explains the greater needs of animals than plants for Cr. Chromium pasture values found in this experiment were sometimes greater than those usually detected in plants (0.02–2 mg kg^{-1}), including in no-fertilizer treatments, because of their high availability in the soil. However, the Cr concentration in pasture was lower than those values considered toxic (5–30 mg kg^{-1}) (Kabata-Pendias and Pendias

1985) and were always much lower than the maximum levels recommended for livestock consumption (1000–3000 mg kg^{-1} in chloride or oxide, respectively) (NRC 1980).

In general, liming did not significantly modify the concentration of Cr in plants though Cr availability was varied by liming when sludge was applied. In July 1999, sewage sludge application produced a decrease in plant concentration of Cr, probably because of the high production of pasture with sludge treatments (López-Díaz, Mosquera-Losada, and Rigueiro-Rodríguez 2007). However, the increased concentration of Cr with S1 and S2 treatments in July 2000 could be explained by the residual effect of the previous applications. In July 2000, there was no response to the higher sewage sludge dose (S3), which contributed 3.53 kg total Cr ha^{-1} in the years 1998, 1999, and 2000, because of the imperfect incorporation of the sewage sludge into the soil. Patches were observed where the sludge remained on top of the soil, which physically limited pasture development, because of the microclimate caused by tree development.

The percentage of extracted heavy metals from pasture, compared to those heavy metals applied with sewage sludge, was low in Cr (0.49–1.41%). The lack of response of Cr in plant to the mineral fertilizer may be because the fertilizer applied had low amounts of heavy metals and the total dose (500 kg ha^{-1}) was much lower than with the sludge (between 16 and 60 t ha^{-1} of fresh sludge).

Conclusions

In this experiment, in a woodland rich in SOM and with a low pH (4.7 in H_2O), when mineralization conditions were improved (liming treatment, mineral fertilizer treatment), SOM concentration was reduced. However, when tree growth was improved by sludge and mineral fertilizer applications, the decreased soil temperature and resulting decrease in mineralization rate increased SOM. The effect of liming on mineralization was reduced over time, possibly because of the development of the tree canopy. Galicia has been heavily reforested in the past decade (close to 13%), and this could have had an important impact on regional soil C storage. Chromium availability was increased in the last year when liming and sewage sludge were applied, depending on the effect of these treatments on organic-matter mineralization, pH, and Fe availability. Liming had very little effect on the concentration of Cr in plants. The sludge fertilizer scarcely varied the concentration of Cr in plant. In all cases, the forage obtained was adequate for animal consumption.

References

Alloway, B. J. 1995. *Heavy metals in soils*. London: Blackie Academic and Professional.

Bradl, H. B. 2004. Adsoption of heavy metal ions on soils constituents. *Journal of Colloid Interface Science* 277:1–18.

Cameron, K. C., H. J. Di, and R. G. McLaren. 1997. Is soil an appropriate dumping ground for our wastes? *Australian Journal of Soil Research* 35:995–1035.

CEM. 1994. *Microwave digestion applications manual*. Matthews, North Carolina, USA: CEM.

Chaudri, A. M., C. M. G. Allain, V. L. Barbosa-Jefferson, F. A. Nicholson, B. J. Chambers, and S. P. McGrath. 2000. A study of the impacts of Zn and Cu on two rhizobial species in soils of a long-term field experiment. *Plant and Soil* 221:167–179.

Covelo, E. F., F. A. Vega, and M. L. Andrade. 2008. Sorption and desorption of Cd, Cr, Cu, Ni, Pb, and Zn by a Fibric Histosol and its organo-mineral fraction. *Journal of Hazardous Materials* 159:342–347.

Dixon, R. K. 1995. Agroforestry systems: Sources or sinks of greenhouse gases? *Agroforestry Systems* 31:99–116.

Domínguez-Vivancos, A. 1997. *Tratado de fertilización*. Madrid, Spain: Mundiprensa.

EC. 2005. *Communication on the implementation of the EU forestry strategy* (Commision Staff Working Document). Available at http://ec.europa.eu/agriculture/publi/reports/forestry/workdoc_en.pdf

Environment Protection Agency. 1994. *Land application of sewage sludge: A guide for land appliers on the requirements of the federal standards for the use of disposal of sewage sludge, 40 CFR part 503*. Washington, D.C.: U.S. Government Printing Office.

EU. 1992. *Council regulation (EEC) no. 2080/92 of 30 June 1992 instituting a community aid scheme for forestry measures in agriculture*. Available at http://www.legaltext.ee/text/en/T30207.htm

EU. 2005. *Council regulation (EC) no. 1698/2005 of September 2005 on support for rural development by the European Agricultural Fund for Rural Development (EAFRD)*. Available at http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2005:277:0001:0040:EN:PDF

European Directive. 1986. *Council directive 86/278/EEC of 12 June 1986 on the protection of the environment, and in a particular of the soil when sewage sludge is used in agriculture*. Available at http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=CELEX:31986L0278:EN:HTML

European Directive. 1991. *Council directive 91/271/EEC of 21 May 1991 concerning urban waste water treatment*. Available at http://faolex.fao.org/docs/texts/eur13224.doc

FAO. 1998. *World reference base for soil resources* (World Soil Resources Reports 84). Rome, Italy: FAO.

Fergusson, J. E. 1990. *The heavy elements: Chemistry environmental impact and health effects*. Oxford, UK: Pergamon.

García-Barrios, L., and C. K. Ong. 2004. Ecological interactions in simultaneous agroforestry systems in the tropics: Management lessons, design tools, and research needs. *Agroforestry Systems* 61:221–236.

Guitián, F., and T. Carballás. 1976. *Técnica de análisis de suelos*. Santiago de Compostela, Spain: Pico Sacro.

Hillman, J. P., J. Hill, J. E. Morgan, and J. M. Wilkinson. 2003. Recycling of sewage sludge to grassland: A review of the legislation to control of the localization and accumulation of potential toxic metals in grazing systems. *Grass and Forage Science* 58:101–111.

Jose, S., A. R. Gillespie, and S. G. Pallardy. 2004. Interspecific interactions in temperate agroforestry. *Agroforestry Systems* 61:237–255.

Kabata-Pendias, A., and H. Pendias. 1985. *Trace elements in soils and plants*. Boca Raton, Fl.: CRC Press.

Kumpiene, J., D. Ragnvaldsson, L. Lövgren, S. Tesfalidet, B. Gustavsson, A. Lättström, P. Leffler, and C. Maurice. 2009. Impact of water saturation level on arsenic and metal mobility in the Fe-amended soil. *Chemosphere* 74:206–215.

Lindsay, B. J., and T. J. Logan. 1998. Field response of soil physical properties to sewage sludge. *Journal of Environmental Quality* 21:410–419.

López-Díaz, M. L., M. R. Mosquera-Losada, and A. Rigueiro-Rodríguez. 2007. Lime, sewage sludge, and mineral fertilizer in a silvopastoral system developed in very acid soils. *Agroforestry Systems* 70:91–101.

López-Mosquera, M. E., R. Barros, M. J. Sainz, E. Carral, and S. Seoane. 2005. Metal concentrations in agricultural and forestry soils in northwest Spain: Implications for disposal of organic wastes on acid soils. *Soil Use and Management* 21:298–305.

McBride, M. B., B. K. Richards, and T. Steenhuis. 2003. Bioavailability and crop uptake of trace elements in soil columns amended with sewage sludge products. *Plant and Soil* 262: 71–84.

Mehlich, A. 1985. Mehlich 3 soil test extractant, a modification of Mehlich 2 extractant. *Communications in Soil Science and Plant Analysis* 1512:1409–1416.

Mombiela, F. A. 1983. El estudio de la fertilidad del suelo en Galicia. Apuntes históricos y problemática general de la investigación sobre la acidez y la falta de fósforo. *Xornadas de estudio sobor dos recursos da agricultura galega* 87–110.

Monterroso, C., E. Álvarez, and M. L. Fernández-Marcos. 1999. Evaluation of Mehlich 3 reagent as a multielement extractant in mine soils. *Land Degradation and Development* 10:35–47.

Mosquera-Losada, M. R., E. Fernández-Núñez, and A. Rigueiro-Rodríguez. 2006. Pasture, tree, and soil evolution in silvopastoral systems of Atlantic Europe. *Forest Ecology and Management* 232:135–145.

Mosquera-Losada, M. R., M. L. López-Díaz, and A. Rigueiro-Rodríguez. 2009. Zn and Cu evolution in herbage and soil in a *Pinus radiata* silvopastoral system in northwest Spain after sewage sludge and lime application. *Journal of Plant Nutrition and Soil Science* 172:843–850.

Mosquera-Losada, M. R., A. Rigueiro-Rodríguez, and M. L. López-Díaz. 2001. Sewage sludge fertilisation of a silvopastoral system with pines in northwestern Spain. *Agroforestry Systems* 53:1–10.

NRC. 1980. *Mineral tolerance of domestic animals*. San Diego, Calif.: Academic Press.

Pascual, I., M. C. Antolín, C. García, A. Polo, and M. Sánchez-Díaz. 2004. Plant availability of heavy metals in a soil amended with a high dose of sewage sludge under drought conditions. *Biology and Fertility of Soils* 40:291–299.

Porta, J., M. López, and C. Roquero. 1999. *Edafología para la agricultura y el medio ambiente*. Madrid, Spain: Mundi-Prensa.

Rigueiro-Rodríguez, A., M. R. Mosquera-Losada, and M. L. López-Díaz. 2004. Efecto de la fertilización con distintas dosis de lodos de depuradora urbana y complementación con potasio sobre la producción de la pradera mixta. *Pastos* 32 (2): 141–159.

Rigueiro-Rodríguez, A., M. R. Mosquera-Losada, and M. L. López-Díaz. 2007. Soil and forage N, P, K, Ca and Mg concentrations in a *Pinus radiata* silvopastoral system in northwest Spain after sewage sludge and lime application. *Grass and Forage* 62:208–224.

SAS 2001. *User´s guide, statistics*. Cary, N.C.: SAS Institute Inc.

Smith, S. R. 1996. *Agricultural recycling of sewage sludge and the environment*. Wallingford, UK: CAB International.

Spanish Royal Decree 1310/1990. 1990. *Regulación de la utilización de los lodos de depuración en el sector agrario* (BOE 262/1990 de 21-11-1990). Available at http://www.agroamb.com/spanish/pdf/LegislacionWeb/10_RD%201310-90.pdf

U.S. Department of Agriculature (USDA). 2006. *Keys to soil taxonomy*, 10th ed. Washington, D.C.: USDA Natural Resources Conservation Service.

Verloo, M., and G. Willaert. 1990. Direct and indirect effects of fertilizer practices on heavy metals in plants and soils. In *Fertilizer and the environment*, ed. R. Merckx, H. Verecken, and K. Vlassak. Leuven, Belgium: Leuven University Press.

Wang, H., N. M. Guija, M. O. Kimberley, R. W. Payn, P. J. Wilks, and C. R. Fisher. 2004. Environmental and nutritional responses of a *Pinus radiata* plantation to biosolids application. *Plant and Soil* 267:255–262.

Wild, A. 1992. *Condiciones del suelo y desarrollo de las plantas según Russell*. Madrid, Spain: Mundi-Prensa.

Young, A. 1997. *Agroforestry for soil management*. Wallingford, UK: CAB International.