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Influences of lignin from paper mill sludge on soil properties and metal accumulation in wheat

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Abstract The influences of lignin application on soil properties of three different soils, Jiangxi soil (Ultisol, Hapludult), Heilongjiang soil (Alfisol, Entioboralf) and Beijing soil (Alfisol, Haplustalf), and metal accumulation in wheat (*Triticum aestivum* L.) were studied in a pot experiment. By lignin amendment, soil pH, organic matter (OM) and cation exchange capacity (CEC) increased, except for CEC in the Beijing soil. Analysis showed that available P and K in lignin-amended soils were also elevated, except for P in the Jiangxi soil. A three-step sequential extraction procedure proposed by the Standards, Measurements and Testing Programme (formerly BCR) of the European Commission was used to investigate the fraction redistribution of heavy metals in soils with lignin application. The fractions were specified as B1: water soluble, exchangeable and carbonate bound, and weakly adsorbed; B2: Fe-Mn oxide bound; and B3: organic matter and sulfide bound. Generally, the heavy metal content of the B2 fraction decreased whereas that of the B3 fraction increased. Lignin application to arable soils can not only improve plant growth in vitro, but also reduce the accumulation of the heavy metals Cu, Zn, Cd, Pb, Cr and Ni in wheat plants.

Keywords Lignin · Metal accumulation · Fractionation · Soil properties

Introduction

Pollution from pulp and paper industries is a major environmental challenge worldwide. Paper mill sludges

generally contain organics such as cellulose, micro-organisms, lignin and wood extracts, and inorganics such as lime, clay, calcium carbonate, and trace metals (Pepin and Coleman 1984). As amendments with peat moss, composts, and farm manures are diminishing, opportunities for the beneficial use of paper mill sludge on land have increased (O'Brien et al. 2002). Although paper mill by-products as soil amendments have been used recently, they do not seem beneficial agricultural by-products due to their complex compositions (Xiao et al. 1999), and potential for environmental pollution when added to agricultural fields (Chirenje and Ma 2002; Chirenje et al. 2002; Xiao et al. 1999).

Lignin is a polymeric natural product originally present in large quantities in the cell walls of terrestrial plants (Sarkanen and Ludwig 1971). As one of the major components, lignin can easily be obtained from by-products of the pulp and paper industry. It is a polymer containing a number of functional groups like phenolic, hydroxyl, carboxyl, benzyl alcohol, methoxyl, aldehyde, etc. and it can bind heavy metal ions such as iron, copper, and zinc (Varma et al. 1989; Volchek et al. 2000). As a natural polymer, it should be preferred as an organic soil amendment rather than other non-natural biosolids.

In spite of the fact that lignin has already been applied as a fertilizer (Mu et al. 2001), it is still questionable whether this application will increase the heavy metal concentrations in plants. Lignin can contain heavy metals, and it can affect heavy metal speciation in soils with a possible increase in the amount of bioavailable metal. An evaluation of the dynamics of heavy metals in the soil-plant system can be obtained by understanding heavy metal speciation and plant uptake (Soon and Bates 1982; Sauerbeck and Hein 1991). Sequential extraction techniques provide a useful tool for understanding the retention of trace metals in soil (Lake et al. 1984; Ma and Rao 1997; Wang et al. 1997), and the water soluble and exchangeable fractions are normally considered to be the form most readily available to plants (Shuman 1985; Petruzzelli et al. 1989).

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After incubation, soils were air-dried and subjected to sequential extraction by the three-step sequential extraction procedure proposed by the Standards, Measurements and Testing Programme (Quevauviller et al. 1993) to give the following fractions: B1, water soluble, exchangeable, carbonate bound, and weakly adsorbed; B2, Fe-Mn oxide bound; B3, organic matter and sulfide bound. The extraction was performed on dried samples (0.50 g) in 50-ml polypropylene centrifuge tubes horizontally shaken with 20 ml 0.11 M acetic acid for 16 h at ambient temperature. The mixture was centrifuged at 1,500g for 20 min and the supernatant (B1 fraction) was separated from the sediment which was then shaken with 40 ml 0.1 M $\text{NH}_2\text{OH HCl}$ (acidified to pH 2 with HNO_3) for 16 h at ambient temperature. This mixture was then centrifuged at 1,500g for 20 min and the supernatant (B2 fraction) separated from the solid residue. The sediment of the second extraction was shaken with 10 ml H_2O_2 (pH 2–3) at room temperature for 1 h, then the mixture was heated at 85°C for 1 h, diluted with 50 ml 1 M NH_4OAc (pH 2) and shaken for another 16 h at ambient temperature. Then the mixture was centrifuged at 1,500g for 20 min. The supernatant (B3 fraction) was also separated from the solid residue, and the sediment was digested with 3 ml $\text{HNO}_3\text{--HClO}_4\text{--HF}$ mixture (1:1:1, v/v) under high pressure (Zhang and Shan 1997) before determination of heavy metals.

The concentrations of Cu, Zn, Cd, Ni, Cr, Pb, Mn and Mo in soil and plant tissue were determined by ICP-MS (VG PlasmaQuad3, Fisons Instruments, UK) after digestion of samples with 3 ml $\text{HNO}_3\text{--HClO}_4\text{--HF}$ mixture (1:1:1, v/v) under high pressure (Zhang and Shan 1997). The extractable concentrations of these metals in soil fractions were determined after dilution with 2% nitric acid. The ICP-MS operating conditions were optimized. An internal standard of ^{115}In at 20 $\mu\text{g l}^{-1}$ in 2% HNO_3 was used to compensate for the matrix suppression and the signal drifting during determination. All reagents used were of analytical reagent grade or better.

Statistic analysis

Data were analyzed by SPSS 11.5 for Windows (SPSS, Chicago, USA). All data reported are the mean values $\pm$ standard errors ($n=5$). Differences were judged to be significant at $P=0.05$ as determined by the least square means test.

Results and discussion

Changes in soil properties

Soil pH, CEC and organic matter content (OM) affect the availability of trace elements in soils (Alloway 1995; McBride et al. 1997). The application of lignin produced considerable changes in the chemical properties of the soils (Table 2). The pH values of the treated soils increased by 0.37, 0.22 and 0.08 units for the Jiangxi, Heilongjiang and Beijing soils, respectively. This pH increase was probably due to the addition of exogenous Na^+ , K^+ , Mg^+ and Ca^{2+} . These cations could displace H^+ from exchange sites in the soil and thus increase the soil base saturation. The OM content increased significantly ($P \leq 0.05$) by 3.95%, 4.46% and 4.1% due to lignin amendment of the Jiangxi, Heilongjiang and Beijing soils, respectively. Lignin amendment increased the concentrations of C and N in soils. Both C and N contents did not decrease after 8 weeks of incubation (Table 3). Both measurements are not sensitive enough to detect any degradation of organic matter in soil. Use of a ^{14}C -labeled substrate and determination of the $^{14}\text{C}\text{--CO}_2$ evolved is the best approach to measure any lignin degradation in soil. Owing to lignin amendment the CEC of the Heilongjiang soil showed the highest increase from 36.2 to 45.5 cmol kg^{-1} soil, the CEC of the Jiangxi soil increased from 11.2 to 17.5 cmol kg^{-1} soil, whereas that of the Beijing soil did not show any change in CEC. The differences in particle size distribution between the soils with and without lignin amendment were not obvious for all the soils.

Significant increases ($P \leq 0.05$) were observed in available K and P concentrations in the lignin-amended soils, with only the exception of available P in the Jiangxi soil (Table 2). Available P in Beijing and Heilongjiang soils increased by 43.4 and 40.0 mg kg^{-1} , respectively. Jiangxi soil is a red acidic soil with a relatively high concentration of crystalline and amorphous Fe-oxides and Al-oxides, which could react with phosphate, making it

Table 2 Soil properties in control and lignin-amended soils after 8 weeks of incubation under constant conditions

Soil	Jiangxi		Heilongjiang		Beijing	
	Control	Lignin application	Control	Lignin application	Control	Lignin application
pH (1:2)	5.88 $\pm$ 0.12 ^a	6.25 $\pm$ 0.10 ^a	7.12 $\pm$ 0.05 ^a	7.34 $\pm$ 0.06 ^a	7.34 $\pm$ 0.06	7.42 $\pm$ 0.08
Available K (mg kg^{-1})	490.3 $\pm$ 0.6 ^a	676.0 $\pm$ 0.6 ^a	392.6 $\pm$ 1.0 ^a	562.2 $\pm$ 0.7 ^a	97.0 $\pm$ 0.3 ^a	127.2 $\pm$ 0.4 ^a
Available P (mg kg^{-1})	119.6 $\pm$ 4.2	116.2 $\pm$ 5.7	192.0 $\pm$ 6.2 ^a	231.9 $\pm$ 2.6 ^a	182.3 $\pm$ 13.6 ^a	225.8 $\pm$ 14.9 ^a
CEC (cmol kg^{-1} soil)	11.2 $\pm$ 1.2 ^a	17.5 $\pm$ 0.8 ^a	36.2 $\pm$ 2.6 ^a	45.5 $\pm$ 3.8 ^a	57.0 $\pm$ 4.3	56.3 $\pm$ 3.2
Organic C (%)	0.51 $\pm$ 0.01 ^a	2.80 $\pm$ 0.03 ^a	1.15 $\pm$ 0.09 ^a	3.74 $\pm$ 0.08 ^a	0.77 $\pm$ 0.05 ^a	3.14 $\pm$ 0.06 ^a
Total N (%)	0.09 $\pm$ 0.00 ^a	0.15 $\pm$ 0.01 ^a	0.11 $\pm$ 0.01 ^a	0.16 $\pm$ 0.01 ^a	0.13 $\pm$ 0.01 ^a	0.18 $\pm$ 0.01 ^a
Organic matter (%)	0.88 $\pm$ 0.02 ^a	4.83 $\pm$ 0.06 ^a	1.99 $\pm$ 0.17 ^a	6.45 $\pm$ 0.17 ^a	1.32 $\pm$ 0.08 ^a	5.42 $\pm$ 0.09 ^a
C/N	5.44	19.1	10.8	24.1	5.89	17.1
Texture (% v/v)						
Clay (<2 μm)	10.6	12.3	53.4	50.5	38.6	35.6
Silt (2–63 μm)	72.9	73.1	44.1	45.8	57.1	59.3
Sand (>63 μm)	16.5	14.6	2.5	3.7	4.3	5.1

^a Significant difference between control and lignin application ($P \leq 0.05$, $n=5$)

Table 3 C and N contents and the ratio of C to N in soils with lignin amendment before and after 8 weeks of incubation

Soil	Before incubation			After incubation		
	% C	% N	C/N	% C	% N	C/N
Jiangxi	2.45±0.09	0.14±0.01	17.8	2.80±0.03	0.15±0.01	19.1
Heilongjiang	3.46±0.18	0.16±0.01	22.3	3.74±0.10	0.16±0.01	24.1
Beijing	3.34±0.09	0.18±0.01	18.8	3.14±0.05	0.18±0.01	17.1

unavailable to plants (Goldberg and Sposito 1985). The largest increase in available K was observed in the Jiangxi soil, followed by the Heilongjiang soil and the Beijing soil.

Wheat growth and uptake of elements

Lignin application showed a positive effect on winter wheat growth (Table 4), because it increased plant height, and shoot biomass by 12.3%, 39.0% and 127.2% ($P \leq 0.05$) in the Heilongjiang, Jiangxi and Beijing soils, respectively. The P and K contents of wheat shoots also increased (Table 4), which may add to the general elevation of available P and K in soils. The micro-elemental and trace-elemental concentrations of wheat shoots also changed with lignin application. Generally, Mn and Mo concentrations of shoots increased whereas the content of other elements decreased after lignin application. Similar results were observed by Walker et al. (2003) when the application of compost and manure in soil caused an increase of Mn in plants (*Brassica junce* and radish), whereas Zn, Pb and Cu decreased. The increase in the bioavailability of Mn and Mo due to lignin amendment could be a cause of the increase in the amount of bioavailable Mn and Mo in the soils. Physiological effects of lignin on plant uptake could be another factor. These results are very important for the future widespread application of lignin because it seems preferable to sewage sludge application, which causes enhanced heavy metal

accumulation in plants (Baldwin and Shelton 1999; Page et al. 1987).

Changes in fraction distribution of metals in lignin-amended soils

A comparison was made between the metal fraction distribution of soils incubated for 8 weeks with and without lignin (Table 5). Lignin amendment had a positive, negative or no effect on metal contents of the B1 fraction depending on soil type and metal properties. The contents of Zn, Ni, Mn and Mo of the B1 fraction increased ($P \leq 0.05$) in the Jiangxi soil, but the contents of Cu, Cd, Cr, and Pb decreased ($P \leq 0.05$) after lignin amendment. The contents of Cu, Cd, Ni, and Cr did not change in the Beijing soil, whereas the contents of Zn, Pb, Mn, and Mo increased by 16–150%. There was no change in the contents of Cu, Cd, Cr and Mn of the B1 fraction of the Heilongjiang soil whereas the contents of Zn, Pb and Mo were significantly increased, and the content of Ni was remarkably decreased ($P \leq 0.05$). A general trend was observed for the contents of Cu, Zn, Cr, Pb, Mn and Mo of the B2 fraction: they decreased after 8 weeks of incubation of the lignin-treated soil. The contents of both Cd and Ni of the B2 fraction were not affected by the lignin amendment. The contents of all metals, with the exclusion of Cd in the B3 fraction, were increased significantly ($P \leq 0.05$) by lignin amendment. The reason for this is that Cd is more labile and tends to distribute among the water soluble and exchangeable fractions (Lu et al. 2004).

Table 4 Length, biomass and elemental concentrations (mg kg^{-1}) of wheat shoot growth in control and lignin-treated soils over 8 weeks

	Jiangxi soil		Heilongjiang soil		Beijing soil	
	Control	Lignin-amended	Control	Lignin-amended	Control	Lignin-amended
Wheat shoot length (cm)	18.0±2.0 ^a	25.0±3.5 ^a	18.0±2.5 ^a	21.5±2.1 ^a	20.5±2.5 ^a	24.0±1.8 ^a
Biomass (g pot^{-1})	0.23±0.03 ^a	0.32±0.04 ^a	0.23±0.01 ^a	0.26±0.02 ^a	0.25±0.04 ^a	0.56±0.06 ^a
P	9,603.7±30.6 ^a	8,132.7±28.7 ^a	6,761.8±25.7 ^a	7,733.1±30.6 ^a	9,147.2±35.4 ^a	9,764.2±29.6 ^a
K	31,359.8±42.8 ^a	32,012.2±38.4 ^a	23,730.1±30.3 ^a	26,405.0±46.8 ^a	37,138.9±47.9 ^a	40,188.7±67.9 ^a
Cu	10.3±1.1 ^a	6.7±0.6 ^a	14.4±2.1 ^a	8.6±1.08 ^a	9.0±1.2	8.8±0.6
Zn	33.5±2.4 ^a	24.3±1.6 ^a	50.3±2.1 ^a	28.0±1.6 ^a	33.1±2.5 ^a	29.0±1.8 ^a
Mn	80.7±9.2	77.6±3.6	77.4±2.8 ^a	89.3±3.4 ^a	83.2±6.1 ^a	138.1±5.8 ^a
Mo	2.3±0.7 ^a	3.0±0.8 ^a	3.2±0.24 ^a	4.5±0.2 ^a	9.8±0.9 ^a	13.6±1.5 ^a
Cr	4.04±0.04 ^a	3.89±0.06 ^a	6.99±0.52 ^a	5.36±0.34 ^a	6.31±0.53 ^a	5.45±0.39 ^a
Ni	1.79±0.05 ^a	1.08±0.08 ^a	5.77±0.62 ^a	2.78±0.30 ^a	4.61±0.26 ^a	2.16±0.34 ^a
Cd	0.06±0.01	0.05±0.01	0.08±0.01 ^a	0.04±0.01 ^a	0.03±0.01	0.02±0.01
Pb	1.06±0.10 ^a	0.59±0.10 ^a	0.96±0.08 ^a	0.72±0.06 ^a	0.84±0.06 ^a	0.48±0.03 ^a

^a Significant difference between control and lignin application ($P \leq 0.05$, $n = 5$)

Table 5 Metal concentration (mg kg^{-1}) in each fraction of control and lignin-treated soil samples after 8 weeks of incubation under constant conditions

Fraction	Soil	B1 fraction			B2 fraction			B3 fraction		
		Jiangxi	Beijing	Heilongjiang	Jiangxi	Beijing	Heilongjiang	Jiangxi	Beijing	Heilongjiang
Cu	Control	0.25±0.01 ^a	0.37±0.02	0.49±0.02	1.66±0.08 ^a	4.48±0.22 ^a	2.07±0.10 ^a	2.14±0.11 ^a	7.18±0.36 ^a	6.94±0.35 ^a
	Lignin-amended	0.13±0.01 ^a	0.36±0.02	0.46±0.03	0.27±0.01 ^a	1.43±0.07 ^a	1.28±0.06 ^a	8.76±0.44 ^a	10.81±0.54 ^a	7.50±0.38 ^a
Zn	Control	0.60±0.03 ^a	1.89±0.09 ^a	0.87±0.04 ^a	1.16±0.06 ^a	15.88±0.58 ^a	6.10±0.26 ^a	4.09±0.20 ^a	12.04±0.60 ^a	7.41±0.38 ^a
	Lignin-amended	0.71±0.04 ^a	2.70±0.13 ^a	1.07±0.05 ^a	0.62±0.03 ^a	13.70±0.68 ^a	5.31±0.27 ^a	6.62±0.33 ^a	16.06±0.80 ^a	8.53±0.43 ^a
Cd	Control	0.26±0.01 ^a	0.65±0.03	0.46±0.02	0.97±0.05	1.11±0.06	1.02±0.04	1.41±0.07	1.55±0.08	1.02±0.06
	Lignin-amended	0.22±0.01 ^a	0.61±0.04	0.45±0.02	0.93±0.04	0.96±0.05	1.01±0.05	1.36±0.06	1.54±0.07	1.01±0.05
Ni	Control	0.44±0.02 ^a	2.20±0.11	1.58±0.08 ^a	0.31±0.02	3.93±0.20 ^a	1.39±0.07 ^a	1.65±0.08 ^a	5.17±0.26 ^a	1.39±0.08 ^a
	Lignin-amended	0.47±0.02 ^a	2.22±0.10	1.09±0.05 ^a	0.32±0.02	3.56±0.18 ^a	1.09±0.06 ^a	2.28±0.11 ^a	6.90±0.34 ^a	1.59±0.12 ^a
Cr	Control	0.90±0.04 ^a	0.69±0.03	0.71±0.04 ^a	0.63±0.03 ^a	0.61±0.03 ^a	0.40±0.01 ^a	17.81±0.89 ^a	16.14±0.81 ^a	14.82±0.74 ^a
	Lignin-amended	0.62±0.05 ^a	0.65±0.05	0.80±0.04 ^a	0.47±0.02 ^a	0.39±0.02 ^a	0.36±0.02 ^a	20.89±1.04 ^a	18.44±0.92 ^a	15.96±0.65 ^a
Pb	Control	0.67±0.03 ^a	0.13±0.01 ^a	0.43±0.02 ^a	6.22±0.31 ^a	2.42±0.12 ^a	6.92±0.35 ^a	3.15±0.16 ^a	5.68±0.28 ^a	7.25±0.26 ^a
	Lignin-amended	0.41±0.02 ^a	0.22±0.01 ^a	0.55±0.03 ^a	5.64±0.28 ^a	1.61±0.10 ^a	6.26±0.31 ^a	3.65±0.18 ^a	6.33±0.32 ^a	8.29±0.34 ^a
Mn	Control	27.79±1.39 ^a	41.53±2.08 ^a	40.65±2.03	22.83±1.14 ^a	82.64±4.13	79.28±3.96 ^a	10.14±0.51 ^a	64.84±3.24 ^a	33.76±1.69 ^a
	Lignin-amended	32.01±1.60 ^a	48.18±2.41 ^a	43.56±2.18	18.64±0.93 ^a	80.13±4.01	54.46±2.72 ^a	24.05±1.20 ^a	79.43±3.97 ^a	37.28±1.86 ^a
Mo	Control	0.13±0.01 ^a	0.02±0.00 ^a	0.04±0.00 ^a	0.03±0.00 ^a	0.07±0.00 ^a	0.02±0.00 ^a	0.28±0.01 ^a	2.02±0.10 ^a	0.24±0.01 ^a
	Lignin-amended	0.26±0.01 ^a	0.05±0.00 ^a	0.05±0.00 ^a	0.02±0.00 ^a	0.05±0.00 ^a	0.03±0.00 ^a	0.47±0.02 ^a	2.35±0.12 ^a	0.28±0.01 ^a

^a Significant difference between control and lignin-treated soils for individual metal ($P \leq 0.05$, $n = 5$)

With the present data it is not possible to explain why the influence of the lignin amendment on the contents of metals in the B1 fraction varied with soil and metal type. The decrease of metal content of the B2 fraction after lignin amendment probably depended on changes in the morphology of the Fe-oxides and Mn-oxides with a decreased affinity of these oxides for metals. The metal contents of the B3 fraction increased with lignin amendment, probably because the number of adsorption organic sites increased. The fact that such an increase was the lowest for the Heilongjiang soil, with the highest content of organic matter, and the highest for the Jiangxi soil, with the lowest organic matter content, support the above mentioned hypothesis.

Conclusions

Lignin, as a soil amendment, can improve soil properties such as CEC, OM and available P and K and affect the heavy metal speciation in soil as determined by the sequential extraction procedure. The change of water soluble, exchangeable and carbonate-bound fractions varied with soil and metal types. Metals of the Fe-Mn oxide bound fraction decreased whereas those of the organic and sulfide bound fraction increased for all the soils with lignin amendment. Pot experiments showed that application of lignin not only significantly increased the biomass and shoot height of winter wheat, but also decreased the accumulation of heavy metals in the wheat shoots.

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