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Ecological risk assessment of heavy metal contamination of six forest soils in China

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ABSTRACT: The toxic impact of heavy metals contamination on soil have been emphasized in the past year, however, the risk of soil contamination in forest areas cannot be neglected. The purpose of this study is to investigate the concentration and distribution of seven major elements (Na, Mg, Al, P, K, Ca and Fe) and the potential ecological risks of three metals (Mn, Cu, and Zn) induced by human activities after the conversion from natural forest (NF) to plantation forest (PF). The result showed that the average metal concentration followed the order: Fe>K>Al>Na>Ca>Mg>P>Mn>Cu>Zn. Mn and Cu were strongly influenced by soil disturbance. All sampling sites were considered as slight pollution (1≤PI<4) and as low potential ecological risk index for individual metals (<40), and the environment (RI<65). Contamination with Mn, Cu and Zn was uncontaminated to moderately contaminated (0<Igeo<1). It was concluded land use change did not alter the distribution of heavy metals concentrations.

KEYWORDS: Heavy metals; soil contamination; ecological risk; forest soil.

1 INTRODUCTION

During the last two decades the impacts of anthropogenic factors on activities have been increasing [1]. Forest land in many countries are being degraded at an alarming rate worldwide in order to gain higher economic benefits such as urbanization, industrialization, agricultural expansion, livestock, among other factors. Land use change (LUC) particularly the conversion from natural forest (NF) to plantation (PF) has impact not only on environment but also on soil quality particularly elements of soils [2]. Soil elements are necessary for maintaining the life processes in plants and/or animals including humans, and thus are essential micronutrients. Those elements can enter the soil via many pathways: natural and anthropogenic sources. In the context of LUC process, particularly the conversion from NF to PF, anthropogenic sources can occur through industrial wastes, automotive emissions, sewage sludge, soil erosion of metal, ions, and leaching of heavy metals, gasoline, lead-acid batteries; fertilizers, paints and treated woods [3, 4]. All these activities can affect both physical and chemical soil properties, consequently leading to changes in the behavior of trace elements in soils particularly heavy metals [5] that pollute soil.

Therefore, knowledge on the concentrations of heavy metals in forest soil is needed. Heavy metals even at low concentration can lead to poisoning because they can pollute groundwater, soil and air quality and consequently also affect human health [4, 6, 7] [8]. and Liu, Wen [9] and Jaradat, Masadeh [4] reported that soil quality is directly related to food safety, human health, and sustainable economic and social development. Therefore, it is crucial for environmental risk assessment of heavy metals in order to assess the impact of human activities in forest soil. In addition, inadequate supply of heavy metals result in a variety of deficiency diseases or syndromes and they are retained in soils indefinitely (not degradable) [10]. Previous studies on heavy metals concentrations of soils have been reported in China but most of them were related to mining activities [11, 12]; these studies have been done in urban area or agricultural land pollution [4, 13, 14].

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However, it is still unclear how LUC alters heavy metals concentration in forest soils. In spite of this, earth's crust is dominated (representing ≥99%) by total element concentration: Al (Aluminum), Fe (iron), Ca (Calcium), Na (Sodium), K (Potassium), Mg (magnesium), and P (Phosphorus) among others but the amounts of these elements are still not well known in Chinese forest. one of the major problems and difficulty facing researchers in reporting accurate assessment of soil pollution, is the reference values for uncontaminated soil conditions. In order to solve this problem, we considered in the present study NF soils as uncontaminated soil. Our purposes were: to compare soil heavy metals concentration between natural forests vs. plantation forests and assess the pollution and potential ecological risk levels of heavy metals.

2 MATERIALS AND METHODS

2.1 SAMPLING LOCATIONS

The experimental program was conducted in eastern China (18.44 to 52.92°N, 108.01-122.79°E) at 12 forest sites (which 01 natural and 01 plantation forest at each location): including Mohe (MH), Qingyuan (QY), Xinyang (XY), Huitong (HT), Dinghushan (DH), and Jianfengling (JF) (Figure 1).

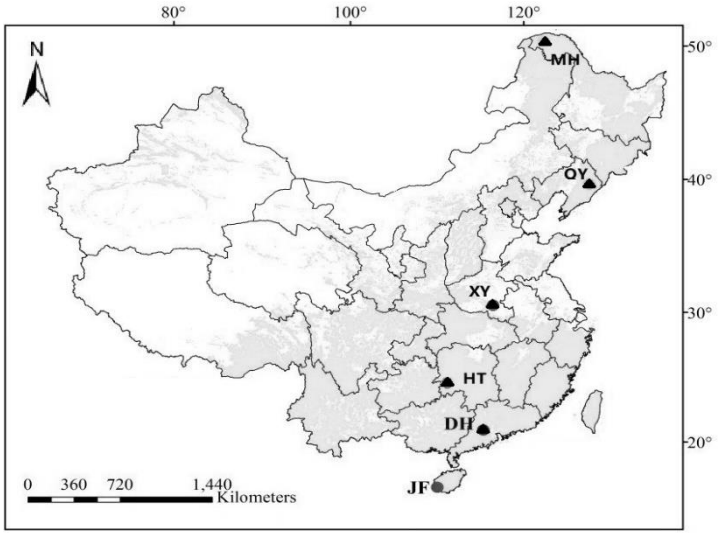

Fig. 1. The location of forest stands at six sites across eastern China.

MH (Mohe), QY (Qingyuan), XY (Xinyang), HT (Huitong), DH (Dinghushan), JF (Jianfengling)

2.2 SOIL SAMPLING AND STATISTICAL ANALYSIS

A total of 192 surface representative samples (0-10 cm) and subsoil (10-20 cm) were collected from each site with a distinct land use (natural forest and plantation) and were carried out in three plots with a size of 20 m x 20 m in each stand that were >100 m apart and randomly selected. The collected samples were air dried for 2 weeks, after plant residues, stone and debris were removed before passing through a 2 mm sieve. The samples were then stored in polythene bottles for analysis. The sample was then mixed with 3 g of dry soil and was sieve with 2 mm and after place into a 125 mL Erlenmeyer flask. 30 mL of the M3 extracting solution was added (soil: solution ratio 1: 10) and immediately placed on a reciprocating shaker for 5 min (120 oscillations min-1). After filter through M3-rinsed Whatman 42 filter paper into plastic vials and we stored at 48°C until further analysis. Determination of extractable P by manual colorimetric method; extractable Cu, Zn, Mn, K, Ca, Mg, and Na by atomic absorption (Ziadi & Tran 2007). Extractable Fe, and Al were determined by atomic absorption spectroscopy (Courchesne & Turmel 2007). Soil samples for elemental analysis were dried for 7 days at <40 ◦C.

Then, samples were ground with a diamonite mortar and then pestle to pass through a 125 µm sieve. A weight of 0.5 g aliquot was totally digested with trace metal grade perchloric ($HClO_4$), nitric (HNO_3) and hydrofluoric (HF) acids in order to dry overnight on a hot plate. The residue was solubilized with hydrochloric (HCl) acid and diluted to volume. One-gram sample was mixed with 10 mL of 0.5 M HCl at room temperature for 1 hour in order to release labile environmentally relevant fractions of

elements (Agemian & Chau 1976, Chester et al. 1985). Trace element concentrations were then determined using a Perkin-Elmer ELAN 6000 ICP-MS (inductively coupled plasma mass spectrometry). Two-way ANOVA method was used to test the significance differences in sites, depth under NF and PF at a significance level of α = 0.05. All statistical analyses were performed using the SPSS version 20.0 (Systat Statistical Software Package for Windows).

2.3 Evaluation Of The Contamination Degree Of Heavy Metals In Forest Soil

2.3.1 The Contamination Factors

The assessment of soil contamination was conducted using the contamination factor and degree suggested by Hakanson [15].

$$C_r^i = \frac{C_i}{C_n^i}$$

Where represent the single-element index. is mean concentration of an individual metal examined and C_r^i is the pre-industrial (natural forest) concentration of the individual metal. We considered the pre-industrial concentration of each element as the concentration found in natural forest. Four classes of were recognized by Hakanson [15]: (i) low contamination factor (if C_r^i < 1), (ii) moderate contamination factor (if 1 ≤ C_r^i < 3), (iii) considerable contamination factor (if 3 ≤ C_r^i < 6), and (iv) very high contamination factor (if C_r^i ≥ 6). The sum of contamination factors for all metals examined represents the contamination degree (C_d) of the environment. It is calculated as:

$$C_d = \sum_{i=1}^{n} C_r^i$$

The Cd was according to Hakanson [15] divided into four groups as follows: (i) low degree of contamination (if C_d < 5), (ii) moderate degree of contamination (if 5 ≤ C_d < 10), (iii) considerable degree of contamination (if 10 ≤ C_d < 20), and (iv) very high degree of contamination (if C_d ≥ 20).

2.3.2 Pollution Index (PI)

Pollution index is a measure of the level of heavy metal pollution for each sampling site. *PI* proposed by Tomlinson, Wilson [16] was calculated by the relation:

$$PI = (C_r^i 1 \times C_r^i 2 \times C_r^i 3 \times .....C_r^i n)^{1/n}$$

Where: n: number of assessed metals; C_r^i : contamination factor of individual pollutant. The value of *PI* was classified into seven groups: (i) Slight contamination (if *PI* < 0.25); (ii) moderate contamination (if 0.25 ≤ *PI* < 0.5); (iii) Severe contamination (if 0.5 ≤ *PI* < 1); (iv) Slight pollution (if 1 ≤ *PI* < 4); (v) moderate pollution (if 4 ≤ *PI* < 8); (vi) Severe pollution (if 8 ≤ *PI* < 16) and (vii) Excessive pollution (if *PI* > 16).

2.3.3 Ecological Risk Index ()

E_r^i is the ecological risk index of an individual metal. It can be calculated using:

$$E_r^i = T_r^i \times C_r^i$$

Where E_r^i is the toxic response factor provided by Hakanson [15] (Mn = Zn = 1, Cu = 5). T_r^i values were classified into five groups: (i) Low risk (if E_r^i < 40); (ii) moderate risk (if 40 ≤ E_r^i < 80), (iii) Considerable risk (if 80 ≤ E_r^i < 160), (iv) Great risk (if 160 ≤ E_r^i < 320) and (v) Very great risk (if E_r^i ≥ 320).

RI is the potential ecological risk index of the environment, which is the sum of:

$$RI = \sum_{i=1}^{n} E_r^i = \sum^{n} T_r^i \times C_r^i$$

Four classes of were recognized by Hakanson [15]: (i) low risk (if *RI* < 65), (ii) moderate contamination factor (if 65 ≤ *RI* < 130), (iii) considerable contamination factor (if 130 ≤ *RI* < 260), and (iv) very high contamination factor (if *RI* ≥ 260).

2.3.4 GEO-ACCUMULATION INDEX (IGEO)

The index of Geo-accumulation was used for evaluating the degree of metal contamination in soils. I_{geo} formula was proposed by Muller [17]:

$$I_{geo} = \log 2(\mathrm{Cn}/1.5\mathrm{Bn})$$

Where, Cn is the concentration of the element in the soil; Bn is the concentration of the metal of the geochemical background or in the unpolluted sample (natural forest). To classify the level of contamination of the soil, the pollution level of I_{geo} can be classified in seven classes as follows: (i) practically uncontaminated (if $I_{geo} \leq 0$); (ii) uncontaminated to moderately contaminated (if $0 < I_{geo} < 1$); (iii) moderately contaminated (if $1 < I_{geo} < 2$); (iv) moderately to heavily contaminated (if $2 < I_{geo} < 3$); (v) (if $3 < Ig_{eo} < 4$); (heavily contaminated); (vi) heavily to extremely contaminated (if $4 < I_{geo} < 5$) and (vi) extremely contaminated (if $5 < I_{geo} > 6$).

3 RESULTS AND DISCUSSION

3.1 HEAVY METALS CONCENTRATION IN NATURAL FOREST VS. PLANTATION FOREST

Land use change is one of the most important factors affecting the trace elements especially heavy metals [18]. Knowledge of behavior and mobility of heavy metals in forest soils are of great concern to environmental research. Trace metal concentrations in soil samples are provided in Mean trace elements concentrations in soil showed the following order: Fe>K>Al>Na>Ca>Mg>P>Mn>Cu>Zn in forest type. It is well known that trace elements originating from various sources especially anthropogenic are usually expected to accumulate in the surface soil [19]; the present study confirmed this trend. In the topsoil, total Mn concentrations were higher in NF than PF at DH, XY and QY while total Mn values were significantly higher in PF than NF at QY and MH in the topsoil (Table 1).

Extractable soil Mn concentrations were higher in NF than PF (at DH, XY and MH) but were higher at QY in the topsoil (Table 1). On the other hand, the level of total Cu concentrations increased after the conversion from NF to PF at DH, XY, QY and MH in both soil depth (Table 1). Similar results have been observed at XY and QY for extractable Cu concentrations. This finding was partially supported by Mäkelä-Kurtto [20] who reported a significant variation of Cu after land use change. This result could be explained by the canopy cover more closed in NF than PF. Our hypothesis was corroborated by other authors who reported that a closed canopy might reduce the deposition of atmospheric particulates and therefore reduce those elements deposition to the soil via litterfall and throughfall [21, 22]. Zhu, Wang [23] for example that human activities exert an apparent impact on the atmospheric heavy metal deposition.

Data regarding extractable and total concentrations of Zn in soils are presented in In general, extractable form of Zn decreased significantly ($p < 0.05$) with depth by 73%. This result reveal that total elements form of heavy metals was more responsive to external inputs than the exchangeable forms. Our results were opposite to those found by Bermudez, Moreno [24] probably due to the type of vegetation. Lee, Carter [25], for example suggested that the accumulation of heavy metals in surface soils may depend plant cycling.

Table 1. Total and extractable concentration of ten traces elements (K, Ca, Al, Fe, Na, P, Mg, Cu, Zn and Mn) in soils

Element	LU	Depth (cm)	MH		QY		XY		DH		HT		JF	
			Extrac	Total	Extrac	Total	Extrac	Total	Extrac	Total	Extrac	Total	Extrac	Total
Na	NF	0_10	107.70	5754.87	85.40	5332.36	54.73	2238.69	50.73	490.83	50.73	505.01	55.06	279.59
		10_20	122.45	4062.66	74.79	3295.24	55.52	2324.61	55.69	510.25	55.69	2053.50	63.64	300.26
	PF	0_10	76.48	4348.34	74.86	2388.95	49.25	1969.42	58.49	301.27	58.49	384.30	58.62	190.46
		10_20	97.93	5166.97	78.63	2355.77	49.78	1232.28	44.71	354.23	44.71	380.26	55.52	256.19
Mg	NF	0_10	258.36	837.62	397.65	3682.13	103.41	1277.14	49.58	708.77	82.90	951.58	38.59	109.33
		10_20	217.02	813.17	269.94	2270.23	91.99	1448.05	45.59	816.49	61.01	841.61	40.22	117.27
	PF	0_10	188.59	1057.87	222.43	2757.84	78.86	1532.37	35.53	421.60	52.68	823.37	43.41	139.42
		10_20	171.00	1310.88	192.20	3071.87	78.72	1176.69	38.60	474.31	38.53	837.89	36.83	167.40
Al	NF	0_10	1631.35	5734.17	1279.91	13249.64	1032.56	5236.49	1337.97	20543.20	2229.17	17983.10	1686.72	15702.02
		10_20	1696.71	7721.95	1428.98	11048.28	962.87	6031.68	1464.57	30349.64	1949.80	12819.85	1729.43	10502.65
	PF	0_10	1285.94	8994.32	1465.83	10271.66	814.72	10905.64	1503.07	11690.11	1557.21	20337.78	1570.75	24913.53
		10_20	1132.44	11012.42	1351.55	12687.89	884.62	7845.76	1231.39	13529.14	1455.94	21259.44	1615.68	26750.68
P	NF	0_10	26.10	176.20	16.95	255.61	61.56	199.89	3.07	31.90	2.41	98.90	3.72	19.82
		10_20	20.96	66.67	8.95	235.46	24.59	163.24	1.88	17.07	1.61	75.41	2.01	18.00
	PF	0_10	26.05	164.81	26.45	211.38	14.81	171.29	2.28	33.70	3.07	61.69	2.03	9.99
		10_20	12.83	177.03	18.30	318.41	10.18	124.13	1.42	21.34	1.77	52.28	1.43	19.62
K	NF	0_10	345.12	5286.64	145.97	6581.92	62.03	2361.15	42.36	14468.06	52.65	15237.00	88.77	1633.86
		10_20	305.00	4051.83	83.40	4540.45	56.05	2449.25	36.33	15570.49	41.31	11370.47	53.36	1650.46
	PF	0_10	177.89	5144.62	126.28	4754.57	67.25	2678.94	37.12	6371.42	73.49	10535.92	72.85	1118.38
		10_20	162.34	5511.62	82.21	4823.82	58.81	2254.32	34.94	7188.04	58.85	10785.00	53.75	1284.41
Ca	NF	0_10	1467.33	1348.96	1394.30	3773.54	634.15	1125.16	234.51	86.89	232.14	168.42	149.45	61.86
		10_20	1207.93	1041.80	2079.73	2076.00	500.24	912.53	224.95	58.24	199.88	545.33	192.99	102.02
	PF	0_10	947.09	1186.61	1973.06	1696.53	735.12	1075.90	186.50	80.60	254.62	131.86	182.39	94.47
		10_20	791.97	1257.30	1890.44	2057.22	637.79	748.08	203.24	63.33	177.16	109.87	166.33	65.32
Mn	NF	0_10	73.46	169.58	89.77	253.30	63.34	142.10	3.84	8.37	97.78	181.74	4.59	6.86
		10_20	48.83	71.85	52.76	230.63	47.61	127.39	3.91	8.74	62.42	145.36	4.06	4.18
	PF	0_10	66.82	216.56	114.55	225.65	20.76	86.79	4.09	8.55	51.42	94.44	4.71	9.75
		10_20	13.45	206.53	61.21	317.92	11.88	65.67	3.93	8.52	38.46	108.11	3.75	11.47
Fe	NF	0_10	386.36	2641.51	229.58	5716.27	246.87	2678.05	370.48	8365.16	277.65	6939.20	382.93	2335.10
		10_20	363.83	2590.59	200.61	5059.39	208.04	2931.14	273.35	10920.93	183.78	4935.91	360.64	1535.31
	PF	0_10	248.76	3492.92	295.09	4722.69	191.34	4470.62	261.63	3687.18	174.66	6464.08	282.04	3955.53
		10_20	170.36	4311.14	216.61	6042.89	205.56	3045.69	123.90	4389.62	137.27	7633.28	252.52	4418.37
Cu	NF	0_10	0.59	2.93	2.61	12.63	3.10	7.95	0.94	0.95	1.85	10.02	0.52	0.03
		10_20	0.60	1.20	1.33	8.70	2.24	7.88	0.60	0.27	1.97	8.65	0.40	0.29
	PF	0_10	0.75	3.14	5.82	12.74	2.91	7.52	1.29	0.41	1.61	7.91	1.85	0.07
		10_20	0.58	3.60	2.37	11.98	2.53	5.76	0.46	0.12	1.20	8.68	1.38	0.27
Zn	NF	0_10	1.77	0.43	3.79	16.09	3.45	12.03	1.29	35.61	2.24	26.77	0.61	11.23
		10_20	1.19	0.41	0.52	3.39	1.90	14.19	0.30	32.44	1.08	14.36	0.26	8.27
	PF	0_10	1.74	0.68	3.81	14.56	2.99	1.74	0.85	15.16	0.98	3.89	1.01	11.36
		10_20	0.35	0.54	0.72	9.88	1.33	3.63	0.18	13.78	0.59	7.69	0.54	10.35

Extrac (Extractable); NF (Natural forest); PF (Plantation forest); MH (Mohe); QY (Qingyuan); XY (Xinyang); HT (Huitong); DH (Dinghushan); JF (Jianfengling).

On the other hand, we observed a high deposition of total Zn in the subsoil after LUC at MH, QY, DH and JF (Table 2) probably because of the pesticides usage, especially fungicides used in those sites. Zn element is important for plant at different scale: production of proteins; plant growth hormones and involved in sugar consumption. Hence, it's used as a fertilizer in order to accelerate tree growth in those sites. Fertilizer use has been implicated in elevated zinc concentrations in soils [26-28]. This net accumulation could also be due to the influence of the filtering effect of vegetation which enhances scavenging of this element [29] or influence from pedogenic factors [30]. Our study also shows that Mn and Cu in both forms change significantly among sites (Table 2). This difference in total and extractable concentrations of deposited elements could reflect

the different sources of those elements within the sites. Xing and Dudas [31] also suggested that the pedogenesis process plays an important role in the distribution and partitioning of heavy metals. Additionally, it could be explained by the different components of various soil phases. Previous studies confirmed this trend. Kabata-Pendias [5] reported that behavior of heavy metals is governing by spatial and seasonal alteration of major soil variables which are one of the main features of the soil biogeochemical system.

Table 2. One-way ANOVA statistics of site, soil depth, and land use (forest type) on total and extractable concentrations of Mn Cu and Zn, in soils in 02 forest types in China

		Site		Depth		LU	
		F	***P***	***F***	***P***	***F***	***P***
Mn	Extractable	8.40	**	2.17	0.15	0.86	0.36
	Total	24.55	**	0.02	0.87	0.00	0.98
Cu	Extractable	5.14	**	1.91	0.18	1.04	0.31
	Total	80.63	**	0.15	0.69	0.003	0.98
Zn	Extractable	2.46	0.07	12.08	*	0.37	0.54
	Total Zn	1.90	0.14	0.001	0.98	1.01	0.32

*n=24, Land use (LU), Bold values were significant; *Significant at p<0.05; **Significant at p<0.01.*

3.2 ASSESSMENT OF SOIL CONTAMINATION BY HEAVY METALS

Soil pollution has become an important environmental issue in China due to changes in the land use over the last few decades. Although previous studies reported that the reserve of heavy metals can be significantly affected by anthropogenic disturbances [20, 32]. According to the categories defined by Hakanson [15] and based on the Table 3, the analyses of the contamination degree of individual metal (C_r^i) in the topsoil showed that MH, HT and JF were slightly contaminated by total Cu while QY and XY (C_r^i <1), and DH were moderately contaminated (1 ≤ C_r^i < 3). Whereas XY, HT, DH were moderately and JF considerable contaminated (3 ≤ C_r^i < 6) by Cu. The results showed a very high contamination (C_r^i ≥ 6) at MH, XY and DH by Zn because of heavy metal persistence and non-biodegradability. In addition, the analyses on the contamination degree of environment (C_d) showed that the environments around XY and HT were classified as moderately contaminated (5 ≤ C_d < 10) while forest soil at MH were considerably contaminated (10 ≤ C_d < 20). The degree of environmental contamination in the topsoil by heavy metals within sites was in the following order: MH> XY> DH> HT> QY> JF. Based on the PI (Table 3), analyzes all sampling sites were considered as slight pollution (1≤ PI <4). On the other hand, combined analyses of the potential ecological risk index of individual metals (E_r^i) and the potential ecological risk index of the environment (RI) showed that the soils among the study sites were classified as low risk (Table 3). The potential ecological risk of the sites was in the following order: JF > MH > HT > DH > XY > QY. [near here]

The statistical analysis in the present study showed that both total and extractable form of Mn, Cu, Zn were not significantly affected by LUC (Table 3). This result suggests also that LUC from NF to PF does not constitute a potential ecological risk in forest soil via contamination by these elements. Our findings are inconsistence with previous studies. Mahmoudabadi, Sarmadian [33] for example showed that Cu, Cd, Fe, Pb, Ni and Zn accumulation were not affected by land use. According to Pouyat, Yesilonis [34], this result suggests also that these elements are more related to other factors. In addition, E_r^i and RI were low because the human practice did not have a significant change on chemical, physical and biological processes in soils and consequently in the environment.

Table 3. Values of contamination factor (C_r^i), degree of contamination (Cd), pollution index (PI), ecological risk index (E_r^i), potential ecological risk index (RI) and Geo-accumulation index (Igeo) for each sampling site

	C_r^i			C_d	PI	E_r^i			RI	I_{geo}		
	Mn	**Cu**	**Zn**			**Mn**	**Cu**	**Zn**		**Mn**	**Cu**	**Zn**
0-10 cm												
MH	0.82	0.94	**11.01**	12.76**	2.02	0.82	4.68	11.00	16.50	0.24	0.21	0.02
QY	1.12*	0.99	1.79*	3.90	1.26	1.12	4.96	1.79	7.87	0.18	0.20	0.11
XY	1.64*	1.07*	**7.06**	9.76*	2.31	1.64	5.33	7.06	14.03	0.12	0.19	0.03
HT	0.98	2.25*	2.34*	5.57*	1.73	0.98	11.25	2.34	14.57	0.21	0.09	0.09
DH	1.92*	1.27*	**6.87**	10.06	2.56	1.92	6.33	6.87	15.13	0.10	0.16	0.03
JF	0.70	3.01**	0.98	4.69	1.28	0.70	15.00	0.98	16.69	0.29	0.07	0.20
10-20 cm												
MH	0.33	0.32	0.02	0.68	0.97	0.33	1.67	0.02	2.02	0.61	0.60	0.79
QY	0.73	0.73	0.34	1.79	1.21	0.73	3.63	0.34	4.69	0.28	0.28	0.58
XY	1.94*	1.36*	3.94**	7.25*	1.92	1.94	6.81	3.94	12.69	0.10	0.15	0.05
HT	1.02*	3.01**	2.35*	6.37*	1.84	1.02	15.00	2.35	18.37	0.20	0.07	0.09
DH	1.35*	1.01*	0.52	2.86	1.42	1.35	5.00	0.52	6.86	0.15	0.20	0.39
JF	0.37	1.02*	0.80	2.16	1.29	0.37	5.00	0.80	6.16	0.55	0.20	0.25

MH (Mohe), QY (Qingyuan), XY (Xinyang), HT (Huitong), DH (Dinghushan), JF (Jianfengling), LU (Land use), NF (Natural forest), PF (Plantation forest), (mean concentration of an individual metal index), Cd (contamination degree), (potential ecological risk index), RI (potential ecological risk index), index in italic represent site with low contamination, ∗ Moderate contamination, ∗∗ Considerable contamination, Index in bold very high contamination.

However, it was observed that total Zn and exchangeable Mn and Zn concentrations were significantly higher in NF than in PF (Table 1) due to geochemical weathering of rock fragments on which the soil has formed [27]. This finding suggests that they emanated from natural parent materials of soils. Moreover, this result could be also explained through the removal of these elements by timber harvest or by the enhanced leaching of heavy metals after timber harvest [35, 36]. Overall, the degree of contamination of element in the subsoil of MH, QY and JF where there was low contamination by Mn, Cu and Zn and moderate contamination at XY HT and DH by heavy metals. Moreover, the degree of environmental contamination was moderate at XY and HT while no risk was detected (RI < 40 and RI < 65; respectively) at all the study sites. However, XY and HT sites were most affected by anthropogenic inputs. Geo-accumulation index revealed that the status of heavy metal pollution in soil (0-20 cm) were uncontaminated to moderately contaminated ($0 < I_{geo} < 1$) for all the heavy metals (Mn, Cu and Zn) among the study sites (Table 3).

3.3 Relationship Between Heavy Metals And Properties

Correlation analysis was led to determine the relationships among heavy metals of different land use in soils. It has been suggested that the correlation analysis can provides little information about the sources of metals such as Mn, Cu or Zn [37-39]. Total and extractable soil Mn, Cu concentrations were positive significantly correlated to each other ($p < 0.05$; Table 4) and with the extractable form of Zn ($r = -0.013$) suggesting perhaps they have common origin. Total Zn was poorly correlated with other metals forms, which means that it has a different source. The increase of Mn concentration with the increasing Cu concentration in both forms observed in the present study is consistent with previously published data. The large amounts of pesticides and fertilizers used to control plant diseases and to promote plant growth in PF might have caused Cu and Zn accumulation in soil. Ma, Tan [30] reported that concentrations of Mn and Cu in 40 Florida soils positively correlated with each other. However, we observed negative correlation between total Zn and other forms of heavy metals indicating that Zn extracted decreases with the decrease in the total Zn concentration of soil contrary to previous studies. Behera, Shukla [13] for example found an increase in the average value of the total Zn concentrations of soils the extractable Zn concentrations increased due to dependence of Zn availability on Zn quantity present in the soil. The difference in our results could be due to the differences in land use type. In addition, the correlation analyses in the present study showed that total Zn were not significantly correlated with any other heavy metals in soils (Table 4), suggesting that perhaps its source is different from the other element forms. On the other hand, both total and extractable forms of Mn and Cu were closely related to each other

and with extractable form of Zn ($p < 0.05$, for all). This finding suggests that Mn and Cu elements may have a common origin. Moreover, this study reported also that Zn element in both forms was much less depleted than Cu due to the different concentrations of the parent rocks, a finding which is in agreement with other studies. Blaser, Zimmermann [29] for example, proposed that Zn is more intensively involved in nutrient cycling, by atmospheric deposition. In general, 2-0.05 mm and 0.05-0.002 mm particles were positively correlated with Mn, Cu and Zn in both forms while < 0.002 mm was negatively correlated (Table 4). The statistical analyses also report a significant ($p < 0.05$) correlation between pH and total Mn, extractable Cu and Zn. In addition, CEC concentrations were positively correlated with both total and extractable Mn concentrations ($p < 0.05$, for all). The heavy metals are closely related to the cation exchange capacity (CEC) of minerals [19]. In the present study, total and extractable Mn were significantly correlated with CEC ($r = 0.690$, $r = 0.600$ respectively; $p < 0.01$, for all). The CEC of the NF soil was relatively high compared to PF (Table 4) probably because of the high organic content. However, we also found a negative correlation between pH and total Zn ($r = -0.287$) but was positively correlated with both forms of Mn, Cu and extractable Zn (Table 4). This variation could probably be linked to processes such as leaching or weathering. Moreover, Goulding and Blake [37] and Menon, Hermle [39] suggested that this may not only lead to higher ecotoxicity and impairment of ecosystem functions but also to an increased risk of elements leaching into ground. The majority of pH values were lower than 7 indicating the acidic nature of the soil in the study sites. It was difficult to evaluate the impact of climate factor on heavy metals because of the lack of studies not only in China but also in the rest of the world.

Table 4. Pearson correlation coefficients (r values) between trace elements concentrations and soil properties in the studied soils among Chinese forest soils

	EMn	TMn	ECu	TCu	EZn	TZn	Particle composition (mm)			pH
							2-0.05	0.05-0.002	<0.002	
TMn	0.788**									
ECu	0.562**	0.414*								
TCu	0.785**	0.794**	0.712**							
EZn	0.677**	0.424*	0.751**	0.596**						
TZn	-0.068	-0.058	-0.052	0.041	-0.013					
2-0.05 mm	0.215	0.117	0.371	0.262	0.425*	-0.381				
0.05-0.002 mm	0.143	0.358	-0.098	0.107	-0.061	0.183	-0.761**			
<0.002 mm	-0.501*	-0.606**	-0.456*	-0.531**	-0.583**	0.370	-0.639**	-0.013		
pH	0.327	0.514*	0.440*	0.371	0.490*	-0.287	0.457*	0.110	-0.835**	
CEC cmol/kg	0.600**	0.690**	0.030	0.348	0.238	0.006	-0.352	0.612**	-0.183	0.198

4 CONCLUSIONS

Our results demonstrate that LUC does not constitute a potential ecological risk for forest soil suggesting, the conversion from NF to PF did not release large quantities of heavy metals into forest soils which can cause pollution. In addition, LUC did not have a significant impact on heavy metals concentrations of Cu and Zn because they are strongly recycled within the rooting zone. Although it is reasonable to assume that part of this enrichment at the surface horizon is due of anthropogenic activities, the assessment of soil contamination showed that MH was considerably contaminated by heavy metals followed by XY and HT which were moderately contaminated. On the other hand, total heavy metals of Mn, Cu and Zn was more responsive to external inputs than the exchangeable forms and more sensitive to LUC. Although the status of heavy metal pollution in soil were uncontaminated to moderately contaminated the assessment of heavy metals concentration requires further investigation because a long-term accumulation can represent serious environmental problem and cause variety of deficiency diseases or syndromes. This study will be more interesting if an analysis of pollution had been carried out at different scales (air and river).

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