Journal of Chemistry

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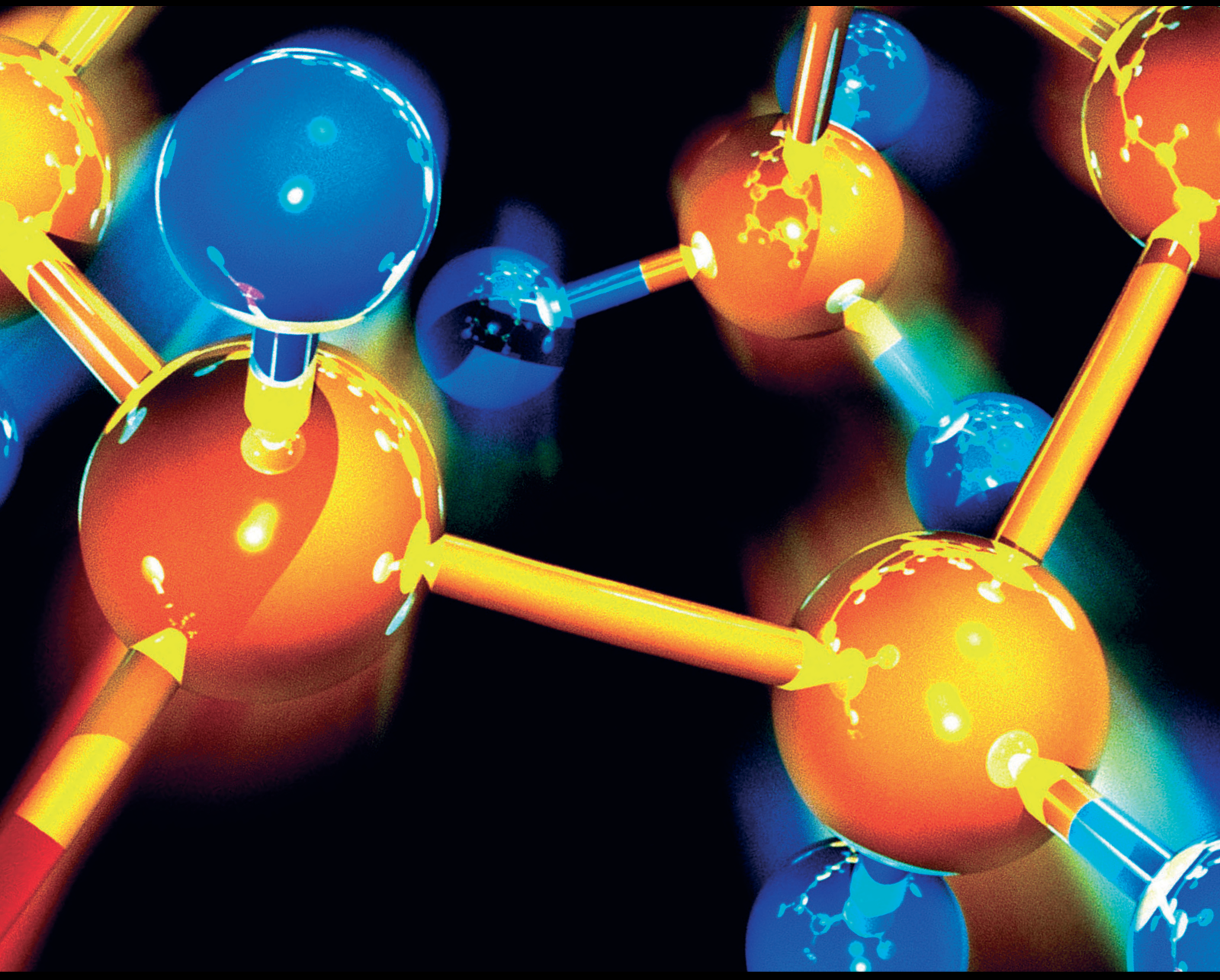

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Research Article

Migration and Transformation of Heavy Metals in the Soil of the Water-Level Fluctuation Zone in the Three Gorges Reservoir under Simulated Nitrogen Deposition

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The accumulation of heavy metals (HMs) in the water-level fluctuation zone (WLFZ) of the Three Gorges Reservoir (TGR) area is potentially harmful to the water environment. In order to reveal whether nitrogen (N) deposition is a potential driving factor for the migration and transformation of HMs (Cd, Cr, Cu, Ni, and Pb), a simulated N deposition experiment was performed on the soil in the WFLZ of the TGR. The results showed that the accumulative release amounts of HMs increased with the increase of N deposition. It was found that the Elovich equation, double-constant equation, and parabolic diffusion equation could well describe the release process of Cu, Cd, Cr, and Ni, while the double-constant equation, parabolic diffusion equation, and first-order equation could be applicable for Pb. The exchangeable fractions of HMs increased to varying degrees after the N deposition treatment, wherein Ni was most significant, indicating that N deposition could increase the ecological risk of HM pollution in the TGR area. The results provide insight into the major factors affecting the release of different HMs under N deposition in this vulnerable region ecologically.

1. Introduction

The Three Gorges Reservoir (TGR) area is located in the middle and upper reaches of the Yangtze River, southwestern China. The TGR stores water from October to April and discharges water from May to September, resulting in the water-level fluctuation between 135 m and 145 m, and the formation of a water-level fluctuation zone (WLFZ) with an area of 348.9 km^2. Affected by the periodic flooding, the ecological environment of the WLFZ is fragile, and the related environmental problems, e.g., accumulation of heavy metals (HMs), have raised the attention [1, 2]. Since the initial impoundment of the TGR, HMs in the WFLZ soil have shown an upward trend because of the external inputs from agricultural activities and domestic wastes [3]. Of note is that the cumulative HMs, in turn, can become the potential source of pollution and threaten the safety of the water environment.

Factors affecting the activity and mobility of HMs in the soil of WFLZ in the TGR are implicated in two aspects. Firstly, the local agricultural activities, such as plowing and fertilization in WFLZ during the period of exposure, can accelerate the migration of HMs from WFLZ to the water body of the TGR [4, 5]. However, with the government's prohibition of agricultural activities on WFLZ, this impact has been minimal. Secondly, the changes of physical,

chemical, and biological properties of soil under periodic recession (oxidation) and inundation (reduction) can cause the transformation and migration of HMs. Related research studies have made great progress [6].

Agricultural activities and periodic fading and flooding conditions are currently the two most concentrated researches on the migration and transformation of HMs in the WLFZ of the TGR area. To the best of our knowledge, however, the impact of precipitation on migration and transformation is rarely reported. Atmospheric precipitation, another important factor affecting the environmental behaviors of HMs in soil, involves not only physical migration but also involves chemical transformation depending on the chemical compositions of precipitation. Nitrogen (N) is the main chemical component in precipitation, mainly in the inorganic form (NO_3^--N and NH_4^+-N) and also includes a small amount of organic N. In recent years, not only the N flux of wet deposition has a great increase, but the N forms in a wet deposition have also been changed [7]. In this case, the response of the ecological environment to N deposition is particularly worthy of attention.

In the TGR area, a relatively higher level of N flux deposition (26.81 ± 13.83 kg N ha^{-1} yr^{-1}) is threatening the aquatic and forest ecosystems, even some farmland ecosystems [8, 9]. Excessive N deposition can cause soil acidification and further increase the solubility of potentially toxic metals in soil [10]. The exposure period of the WFLZ soil coincides with the rainy season (May to September), in which wet deposition N accounts for about 70% [9, 11]. Therefore, we collected undisturbed WFLZ soil columns and performed a simulated N deposition experiment to study the mobility characteristics of typical HMs, aiming to explore the relationship between N deposition and the migration and transformation of HMs in the WFLZ soil. This information has implications for better understanding the migration and transformation of HMs in the TGR area.

2. Materials and Methods

2.1. Sample Collection. A gentle WLFZ was selected at 154 m of water-level elevation in the Tanshao village, Wanzhou District (Figure 1); 12 undisturbed soil samples were collected with clean PVC pipes (15 cm in diameter and 20 cm in height). After collection, we covered both ends of the soil pillar samples with plastic wrap and brought them back to the laboratory for subsequent N addition experiment. The physicochemical properties of soil in WFLZ and concentrations of HMs are shown in Table 1. The single factor index method was applied to assess the pollution degree of HMs. The pollution index (P_i) for each HM was expressed by the ratio of the measured concentration (C_i, mg/kg) to the standard concentration (C_i, mg/kg) [12]. In this study, the background value of HMs in the WFLZ was used as the standard value [13]. Based on the results of single factor index method [12], Cd belonged to a high pollution degree ($P_i > 3$), while Cr, Cu, Ni, Pb, and Zn belonged to clean level ($P_i < 1$) in the original WFLZ soil in this study (Table 1).

2.2. Simulation of N Deposition. According to the N deposition flux (20.69 kgN/(ha·yr)) and the average annual rainfall (~1200 mm) in the TGR area [8], four N flux groups, including N-free group (N_0, 0 kgN/(ha·yr)), low N group (N_{20}, 20 kgN/(ha·yr)), middle N group (N_{40}, 40 kgN/(ha·yr)), and high N group (N_{60}, 60 kgN/(ha·yr)), were set, and each group was performed in triplicate. N_0, N_{20}, N_{40}, and N_{60} were about 0, 1, 2, and 3 times, respectively, of the actual N deposition fluxes in the TGR area. NH_4NO_3 was the only N source in this research, and the pH of each leaching solution was adjusted to 5.5, which was consistent with the local rainwater [11].

Siphon drip irrigation bags with adjustable flow rates were used to hold the leaching solution, and the flow rate was set to 0.8 mL/min to prevent water from accumulating in the soil column. Before leaching, two 0.45 μm microporous membranes at both ends of the soil column were fixed. The leaching volume was 0.5 L each day, and this process of leaching was continued for 40 days. 20 L of the total leaching volume (about 1162.6 mm rainfall amount) was consistent with the local multiyear average rainfall amount (about 1150 mm). The schematic diagram of the simulated N addition device was shown in Figure 2. After finishing the daily leaching, the volume of each leachate was recorded firstly and then filtered through 0.45 μm filter membrane and stored at 4°C for testing. Soil samples before and after eluviation were air-dried at room temperature, and then the plant roots and residues were removed. Hereafter, the soil samples were homogenized and grounded to pass through a 2-mesh sieve for determining the physicochemical properties and the metal fractions.

2.3. Sample Analysis. Soil pH (H_2O) was determined in 1 : 2.5 (w/v) soil water suspension using PHS-3C pH-meter (Shanghai Leici Instrument Co., Ltd, China). Organic matter was determined by a modified Walkley-Black method, and the detailed processes have been described elsewhere [14]. NH_4^+ and NO_3^- in the samples were analyzed by an ion chromatograph (Dionex-900, Diane, USA) with detection limits of 0.005 mg/L and 0.031 mg/L, respectively.

In order to determine the mobility and activity of HMs, the exchangeable fraction of typical HMs (Cd, Cr, Cu, Ni, and Pb) was extracted by the classical method [15]. In brief, 1 g of dried sample was extracted with 8 ml $MgCl_2$ (pH = 7.0) and continually shaken for 1 hour at 25°C, the extract was centrifuged at 4000 rpm, and the supernatant was made to volume in 25 mL volumetric flask. The residual soil was digested with a mixed acid (6 ml of HNO_3, 2 ml of HCl, and 2 ml of HF) by microwave digestion instrument (Mars5, CEM, USA). HMs were determined by inductively coupled plasma optical emission spectrometry (Optima 7000, PerkinElmer, USA). The detection limits were 0.006, 0.03, 0.008, 0.33, and 0.035 g/L, respectively. The recovery rates of samples were between 95% and 120%.

2.4. Statistical Processing of Data. In this study, the double-constant equation (1), Elovich equation (2), first-order equation (3), and parabolic diffusion equation (4) were used

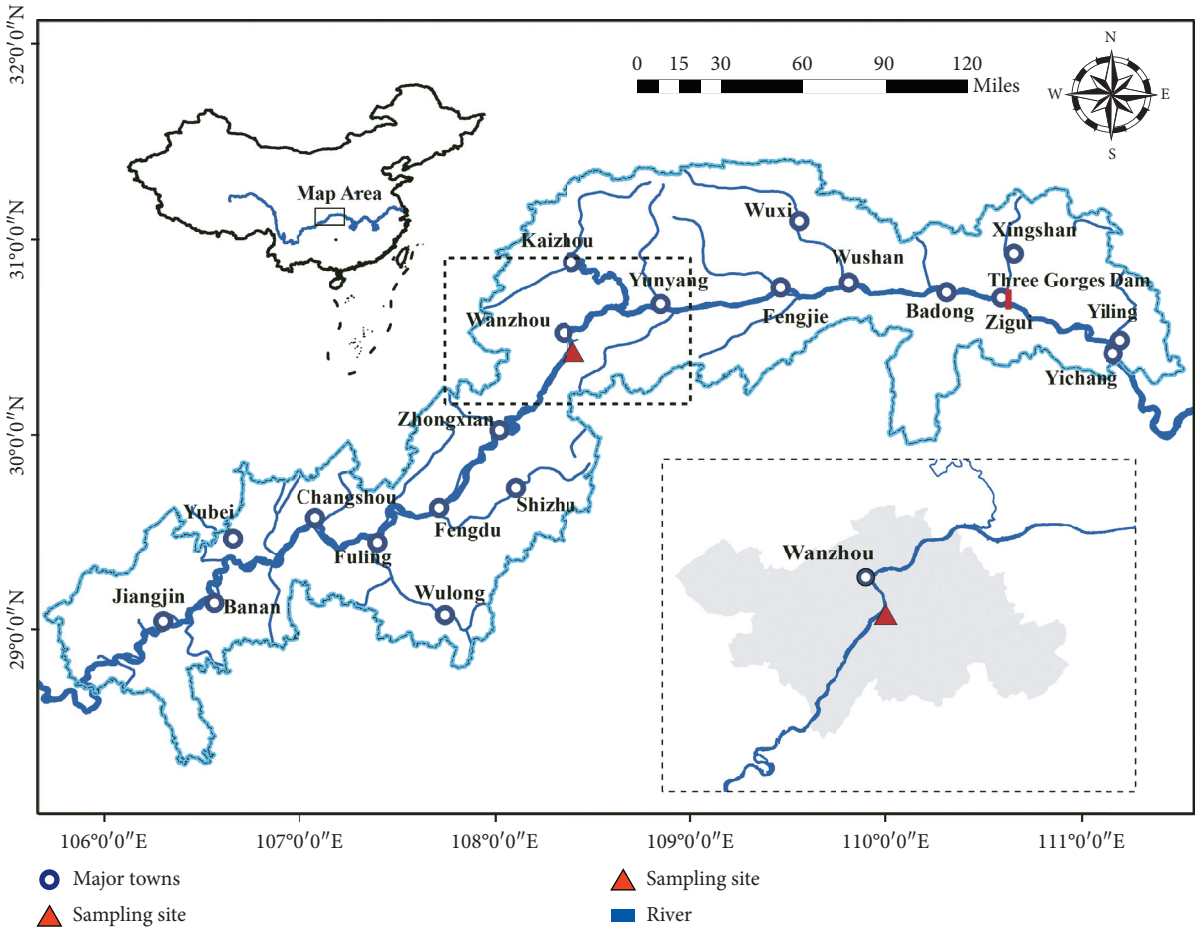

Figure 1: Location of the sampling site.

Table 1: Physicochemical properties of the original WFLZ soil in the TGR area.

Soil indexes	Content	Background values of WFLZ in the TGR[a]	Pollution degree[b]
pH	8.16 ± 0.13	7.84	n.d
OM (g/kg)	13.92 ± 0.47	n.d	n.d
Bulk density (g/cm^3)	1.4 ± 0.14	n.d	n.d
NO_3^--N (mg/kg)	2.13 ± 0.007	n.d	n.d
NH_4^+-N (mg/kg)	179.49 ± 6.47	n.d	n.d
Al (%)	3.98 ± 0.38	n.d	n.d
Fe (%)	4.88 ± 0.49	n.d	n.d
Mn (mg/kg)	1018.66 ± 149.05	n.d	n.d
Cd (mg/kg)	2.63 ± 0.67	0.321	High
Cr (mg/kg)	76.82 ± 5.89	55.5	Clean
Cu (mg/kg)	37.17 ± 5.13	37	Clean
Ni (mg/kg)	48.46 ± 0.95	29.5	Clean
Pb (mg/kg)	65.80 ± 7.64	29.3	Clean
Zn (mg/kg)	166.82 ± 21.89	72.7	Clean

[a]Background values of WFLZ in the TGR [13]. [b]Evaluation by single factor index method [12]. n.d. means no data.

to describe the release kinetics of HMs under N deposition [16].

$$\ln S = a \ln t + b, \quad (1)$$

$$S = a \ln t + b, \quad (2)$$

$$\mathrm{Ln}\left(\frac{S}{S_m}\right) = at + b, \quad (3)$$

$$\frac{S}{S_m} = at^{1/2} + b, \quad (4)$$

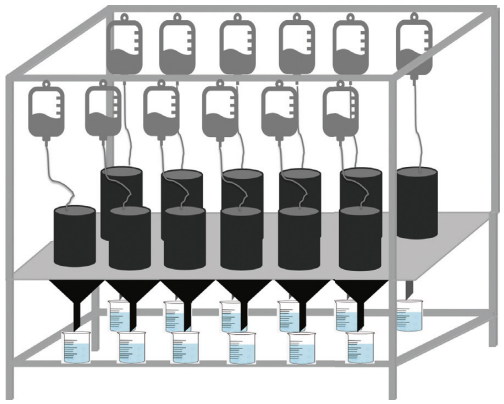

Figure 2: Leaching device of simulating N deposition.

where S (μg/kg) is the release amount of metals at a certain time, S_m (μg/kg) is the maximum release amount, t (d) is the leaching time, a and b are the constants with different meanings for each model.

One-way analysis of variance (ANOVA) was used to test for differences between groups of N deposition if the data conform to the normal distribution. Otherwise, Kruskal–Wallis rank sum test was applied to test the differences. In addition, Person's correlation coefficient was used to describe the relationships between variables. These analyses were performed using IMB SPSS version 22.0 statistical software.

3. Results and Discussion

3.1. Cumulative Release Amount. The cumulative release amounts of HMs were different under various treatments of N deposition (Table 2). Both Cr and Cu were leached out more than 30 μg, and the amounts under N_{60} treatment were significantly higher ($p < 0.05$) than those under N_0, N_{20}, and N_{40} treatments. In contrast, the release amounts of Ni and Cd were lower than 10 μg, and there were no significant differences ($p > 0.05$) between each N deposition treatment. In addition, the amount of leached-out Pb showed a significant difference between each N treatment. The results indicated that Pb was the most sensitive to the N deposition, and even a low N deposition load (20 kgN/(ha yr)) could stimulate the release of Pb from WFLZ soil. This could be ascribed to the relatively lower binding energy of Pb with Fe/Al hydro(oxide) in the WFLZ soil, which was more susceptible to the destruction of N deposition [17, 18]. However, a high N deposition load (60 kgN/(ha yr)) was required to promote the release of Cr and Cu significantly. Besides, there was no significant influence on the release of Cd and Ni under the treatments of N deposition in this study.

3.2. Release Rate. Under the simulated precipitation leaching, HMs presented three different release stages except that Cr showed two stages (Figure 3). Every release stage of HMs showed a good linear relationship (r^2 >0.85), and the slopes of the linear equations can be used to represent the release rate of HMs at each stage. The linear equations and coefficients (r^2) were shown in Table 3. The release rates of Cr, Cu and Cd exhibited a similar variation trend, showing the fastest release rate in the first stage, and gradually decreasing in the following stages. This may be related to the contents of water-soluble ions in the soil. In the beginning stage, the metal ions in the soil water were quickly released with the wet deposition. As the leaching continued in the second stage, the adsorbed HMs were gradually leached out. In the third stage, the release rate became slower as the active ions of HMs decreased, and this stage may involve chemical transformation and desorption. Since Cr usually presents in the soil in the form of negative valent acid radical ($Cr_2O_7^{2-}$ and CrO_4^{2-}), which were hardly adsorbed by soil colloid and easily mobilized in soil [19], only a two-stage leaching process was exhibited. The cumulative release rate of Ni increased instead after 32 days (the third stage), probably caused by some chemically bound forms leaching out. For Pb, the cumulative release curve fluctuated greatly, and there existed large differences in its release amount with different N deposition levels, pointing to more intricate physicochemical processes of soil Pb due to N deposition.

Table 2: Cumulative release amounts of HMs in the soil of WFLZ in the TGR area (unit: μg).

Treatment	Cr	Cu	Cd	Ni	Pb
N_0	32.44a	30.45a	1.61a	7.29a	6.76a
N_{20}	34.21a	30.83a	1.69a	7.98a	14.27b
N_{40}	35.08a	32.18a	1.67a	8.52a	22.74c
N_{60}	38.82b	36.08b	1.87a	7.90a	31.15d

Note. The same letters mean no significant difference (p>0.05) and different letters mean significant difference ($p < 0.05$) tested by one-way ANOVA.

3.3. Kinetics of Cumulative Release. The first-order kinetic equation, double-constant rate equation, parabolic equation, and modified Elovich equation are the common mathematical models to describe the characteristics of dynamics of soil HMs [20, 21]. The first-order kinetic equation is good at describing the simpler surface process of the diffusion mechanism [22]. The double-constant rate equation (also known as Freundlich's correction) is an empirical formula, which is suitable for more complex kinetic reaction processes and can better describe the uneven energy distribution process and the different affinity of adsorption sites to HMs on the surface of soil particles [16]. The parabolic equation is suitable to describe the process controlled by multiple diffusers [23]. The Elovich equation is also an empirical formula, which describes a process that includes a series of reaction mechanisms, such as the diffusion of solutes at the solution phase or interface, surface activation, and deactivation [24]. The equation is suitable for the reactions with large changes in activation energy processes (such as those on sediments and soils), which are less suitable for processes with a single surface diffusion mechanism [25]. The above four equations were used to fit the leaching data obtained in this research. The fitting results are shown in Table 3.

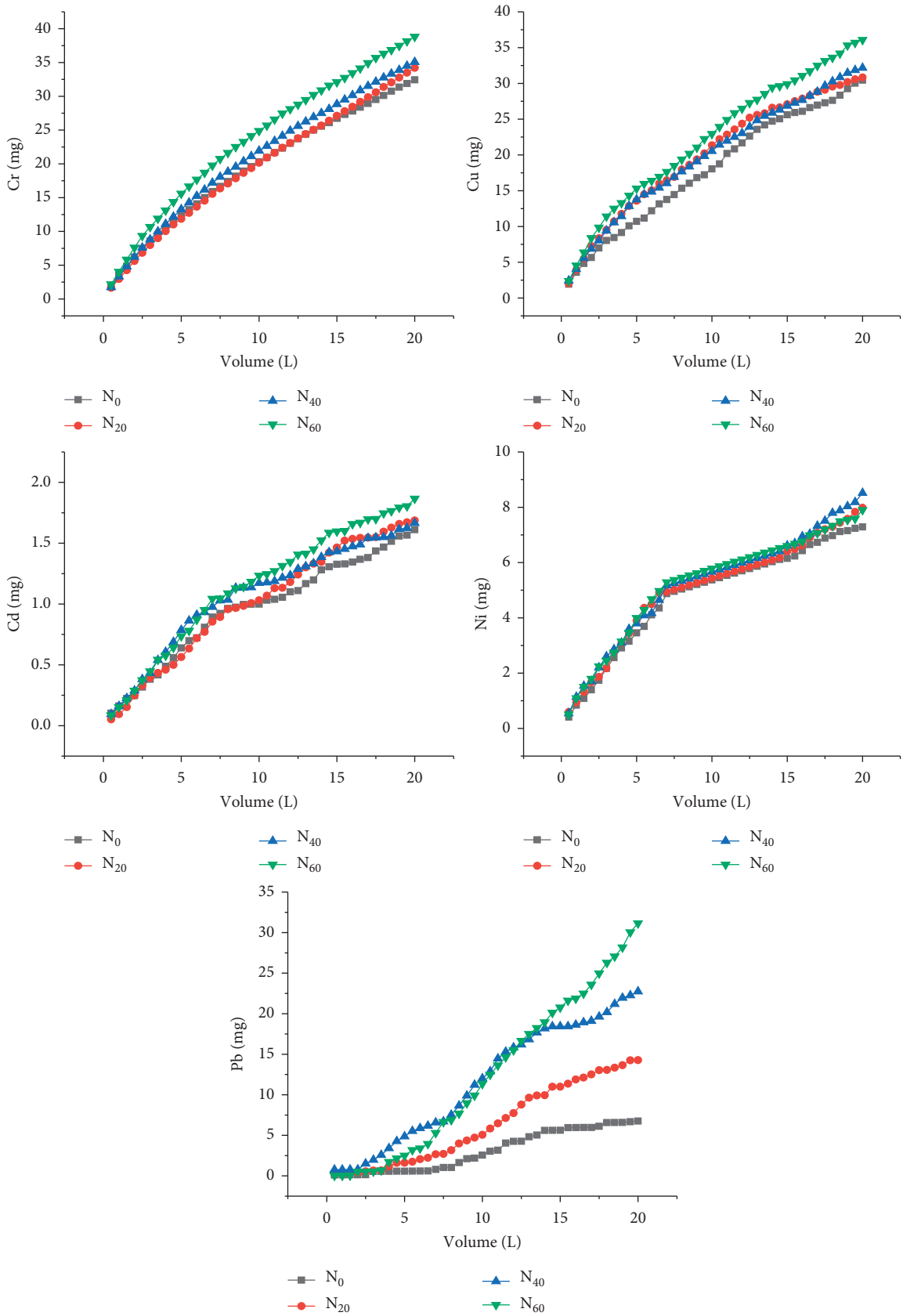

Figure 3: Cumulative release amounts of HMs in the soil of the WFLZ in the TGR area.

Table 3: Fitting functions of cumulative release amounts and the release rates of HMs.

N deposition	Release process	Fitting equation	Correlation coefficient (r^2)	Release rate (μg/d)
Cr				
N_0	First stage	$y = 1.14x + 1.38$	0.992	1.14
	Second stage	$y = 0.65x + 7.03$	0.996	0.65
N_{20}	First stage	$y = 1.14x + 0.84$	0.995	1.14
	Second stage	$y = 0.72x + 5.49$	0.999	0.72
N_{40}	First stage	$y = 1.27x + 0.92$	0.995	1.27
	Second stage	$y = 0.71x + 7.50$	0.996	0.71
N_{60}	First stage	$y = 1.48x + 1.34$	0.991	1.48
	Second stage	$y = 0.76x + 9.63$	0.995	0.76
Cu				
N_0	First stage	$y = 1.09x + 1.28$	0.982	1.09
	Second stage	$y = 0.78x + 2.86$	0.997	0.78
	Third stage	$y = 0.46x + 11.63$	0.989	0.46
N_{20}	First stage	$y = 1.43x + 1.04$	0.989	1.43
	Second stage	$y = 0.78x + 5.70$	0.998	0.78
	Third stage	$y = 0.38x + 15.66$	0.998	0.38
N_{40}	First stage	$y = 1.34x + 1.33$	0.997	1.34
	Second stage	$y = 0.70x + 6.39$	0.997	0.70
	Third stage	$y = 0.54x + 10.62$	0.997	0.54
N_{60}	First stage	$y = 1.70x + 1.13$	0.991	1.70
	Second stage	$y = 0.82x + 6.57$	0.995	0.82
	Third stage	$y = 0.60x + 12.23$	0.996	0.60
Cd				
N_0	First stage	$y = 0.06x + 0.03$	0.995	0.06
	Second stage	$y = 0.03x + 0.51$	0.927	0.03
	Third stage	$y = 0.03x + 0.28$	0.982	0.03
N_{20}	First stage	$y = 0.06x$-0.005	0.991	0.06
	Second stage	$y = 0.04x + 0.31$	0.980	0.04
	Third stage	$y = 0.02x + 0.88$	0.933	0.02
N_{40}	First stage	$y = 0.07x + 0.02$	0.991	0.07
	Second stage	$y = 0.03x + 0.64$	0.968	0.03
	Third stage	$y = 0.02x + 0.76$	0.961	0.02
N_{60}	First stage	$y = 0.07x + 0.005$	0.998	0.07
	Second stage	$y = 0.04x + 0.49$	0.989	0.04
	Third stage	$y = 0.03x + 0.81$	0.973	0.03
Ni				
N_0	First stage	$y = 0.33x + 0.12$	0.997	0.33
	Second stage	$y = 0.08x + 3.72$	0.997	0.08
	Third stage	$y = 0.09x + 3.55$	0.975	0.09
N_{20}	First stage	$y = 0.36x + 0.22$	0.993	0.36
	Second stage	$y = 0.09x + 3.63$	0.990	0.09
	Third stage	$y = 0.15x + 1.94$	0.986	0.15
N_{40}	First stage	$y = 0.33x + 0.47$	0.995	0.33
	Second stage	$y = 0.09x + 3.84$	0.985	0.09
	Third stage	$y = 0.19x + 0.70$	0.982	0.19
N_{60}	First stage	$y = 0.36x + 0.33$	0.998	0.36
	Second stage	$y = 0.08x + 4.14$	0.999	0.08
	Third stage	$y = 0.12x + 2.94$	0.965	0.12
Pb				
N_0	First stage	$y = 0.06x + 0.01$	0.850	0.06
	Second stage	$y = 0.36x$-4.53	0.984	0.36
	Third stage	$y = 0.11x + 2.54$	0.932	0.11
N_{20}	First stage	$y = 0.19x - 0.19$	0.937	0.19
	Second stage	$y = 0.62x - 6.97$	0.985	0.62
	Third stage	$y = 0.34x + 0.84$	0.979	0.34
N_{40}	First stage	$y = 0.51x - 0.59$	0.993	0.51
	Second stage	$y = 0.92x - 6.62$	0.979	0.92
	Third stage	$y = 0.40x + 6.29$	0.900	0.40
N_{60}	First stage	$y = 0.44x - 1.41$	0.895	0.44
	Second stage	$y = 1.07x - 10.21$	0.996	1.07
	Third stage	$y = 1.00x - 9.26$	0.977	1.00

Table 4: Fitting parameters of each kinetic model for HMs in the WFLZ soil in the TGR area under N deposition.

HMs	N load	Elovich equation $S = a\ln t + b$			Double-constant equation $\ln S = a\ln t + b$			First-order equation $\mathrm{Ln}(S/S_m) = at + b$			Parabolic diffusion equation $S/S_m = at^{1/2} + b$		
		A	B	R^2	a	b	R^2	a	b	R^2	a	b	R^2
Cr	N_0	22.71	−15.98	**0.912**	0.7375	1.6570	**0.998**	0.0495	−0.2814	0.805	0.7342	−0.7290	**0.996**
	N_{20}	24.03	−19.40	0.896	0.7999	1.4668	**0.998**	0.0537	−0.3862	0.806	0.7824	−0.9239	**0.992**
	N_{40}	24.98	−18.65	**0.915**	0.7807	1.5989	**0.995**	0.0517	−0.2670	0.783	0.8069	−0.8541	**0.997**
	N_{60}	27.22	−18.29	**0.926**	0.7433	1.8387	**0.993**	0.0490	−0.0745	0.774	0.8746	−0.8052	**0.999**
Cu	N_0	21.41	−15.98	0.888	0.7342	1.5831	**0.997**	0.0503	−3.5867	0.837	0.0283	−0.0308	**0.987**
	N_{20}	21.91	−12.55	**0.937**	0.6957	1.8161	**0.990**	0.0457	−3.3657	0.765	0.0283	−0.0208	**0.997**
	N_{40}	22.03	−13.22	**0.920**	0.6825	1.8470	**0.997**	0.0458	−3.3738	0.805	0.0288	−0.0234	**0.997**
	N_{60}	24.51	−14.23	**0.919**	0.6826	1.9633	**0.992**	0.0455	−3.2502	0.788	0.0320	−0.0249	**0.995**
Cd	N_0	1.1235	−0.7942	**0.920**	0.7580	−1.4149	**0.988**	0.0504	−6.0825	0.781	0.0023	−0.0022	**0.989**
	N_{20}	1.2880	−1.1353	**0.909**	0.9208	−1.8707	**0.985**	0.0599	−6.2842	0.745	0.0026	−0.0033	**0.993**
	N_{40}	1.1909	−0.7221	**0.954**	0.7594	−1.3068	**0.973**	0.0485	−5.9317	0.710	0.0024	−0.0017	**0.988**
	N_{60}	1.3679	−1.0362	**0.932**	0.8253	−1.4479	**0.986**	0.0536	−5.9971	0.745	0.0028	−0.0028	**0.995**
Ni	N_0	5.191	−2.730	**0.961**	0.7325	0.2866	**0.965**	0.0461	−3.7091	0.685	0.0196	−0.0113	**0.977**
	N_{20}	5.257	−2.398	**0.950**	0.6747	0.5061	**0.969**	0.0432	−3.5899	0.713	0.0199	−0.0095	**0.975**
	N_{40}	5.476	−2.533	**0.945**	0.6677	0.5663	**0.976**	0.0430	−3.5448	0.727	0.0209	−0.0107	**0.983**
	N_{60}	5.289	−2.055	**0.966**	0.6673	0.5661	**0.961**	0.0419	−3.5221	0.678	0.0199	−0.0064	**0.971**
Pb	N_0	5.730	−8.348	0.698	1.4801	−2.6781	**0.915**	0.1096	−5.4861	0.898	0.0367	−0.0859	0.873
	N_{20}	11.39	−16.09	0.717	1.3214	−1.4157	**0.924**	0.0986	−4.4358	**0.921**	0.0730	−0.1654	0.893
	N_{40}	18.21	−22.30	0.817	1.1846	−0.3050	**0.955**	0.0828	−3.3801	0.837	0.1128	−0.2150	**0.952**
	N_{60}	23.20	−34.11	0.729	2.1463	−3.3404	**0.975**	0.1416	−4.9676	0.760	0.1482	−0.3483	**0.904**

Note. Correlation coefficients (R^2) higher than 0.9 are in bold.

Based on the correlation coefficients (R^2) fitted by each equation (Table 4), it was found that the double-constant equation and parabolic equation can better describe the kinetic process of leaching of HMs in the WFLZ soil by simulated N deposition. At the same time, Cr, Cu, Cd, and Ni had a relatively high correlation coefficient of the Elovich equation, while Pb had a relatively higher correlation coefficient of the first-order equation. The results indicated that being controlled by the intricate reaction rate and the multidiffusion factors were the common kinetics' features of these HMs. In addition, the relatively good fitting of the Elovich equation for Cr, Cu, Cd, and Ni suggested that the mechanism of leaching and release of these elements in WFLZ soil was also influenced by the changes in activation energy, rather than a single surface diffusion process, while the release of Pb was also affected by single surface diffusion.

3.4. Activation of HMs. The exchangeable fraction of HMs was relatively low, but its mobility and activity were the highest in HM forms. In this study, exchangeable fractions of Cd, Cu, Ni, Pb, and Cr were 0.13, 0.20, 0.47, 0.60, and 0.81 mg/kg, accounting for 4.90%, 0.54%, 0.96%, 0.90%, and 1.05% of the total mass contents, respectively. Figure 4 presents the changes of an exchangeable fraction of HMs before (original) and after leaching (N_0, N_{20}, N_{40}, and N_{60}). It can be seen that the N deposition stimulated the increase of HMs' exchangeable fraction. For Cr, Cu, and Pb, the exchangeable fractions between each treatment of N deposition had no significant change ($p > 0.05$). For Cd, the exchangeable fractions after leaching (N_0, N_{20}, N_{40}, and N_{60}) were significantly higher than the original one, but there were no significant differences between the N-containing group (N_{20}, N_{40}, and N_{60}) and the N-free group (N_0). This may be affected by the pH (5.5) rather than the N of the leaching solution. For Ni, the exchangeable fraction after leaching by N_{40} was significantly higher than other groups. It was consistent with the aforementioned release amount of Ni. The results showed that N deposition was more conducive to promoting the activation of Ni compared with Cd, Cr, Cu, and Pb.

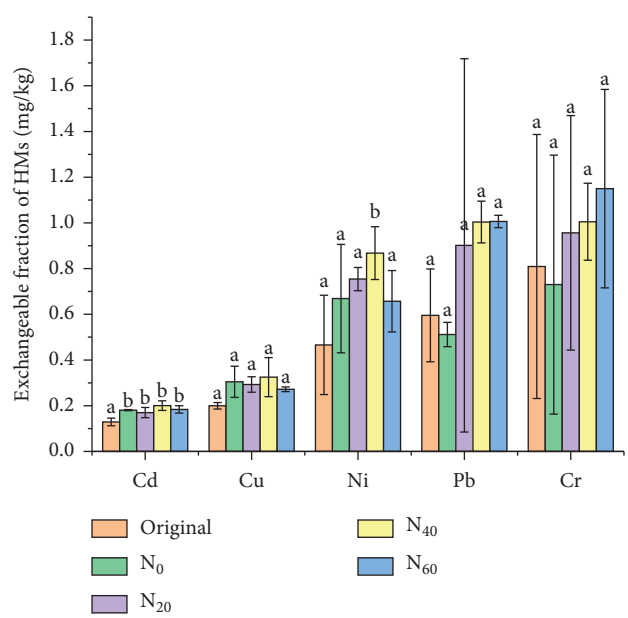

Figure 4: Changes of exchangeable fractions of HMs before (original) and after leaching (N_0, N_{20}, N_{40}, and N_{60}).

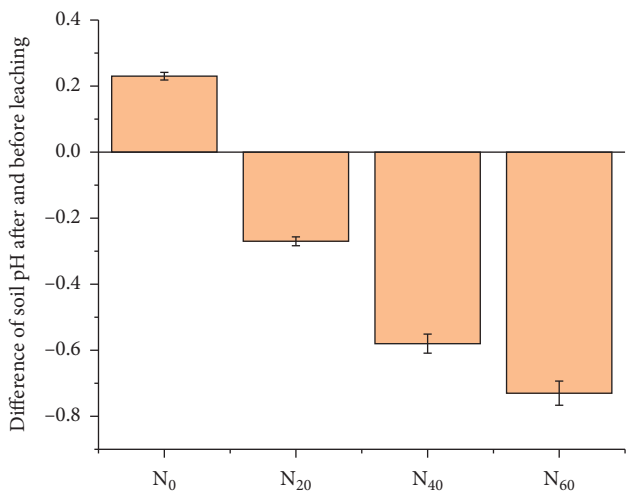

Figure 5: Changes of soil pH after and before leaching at different N deposition levels.

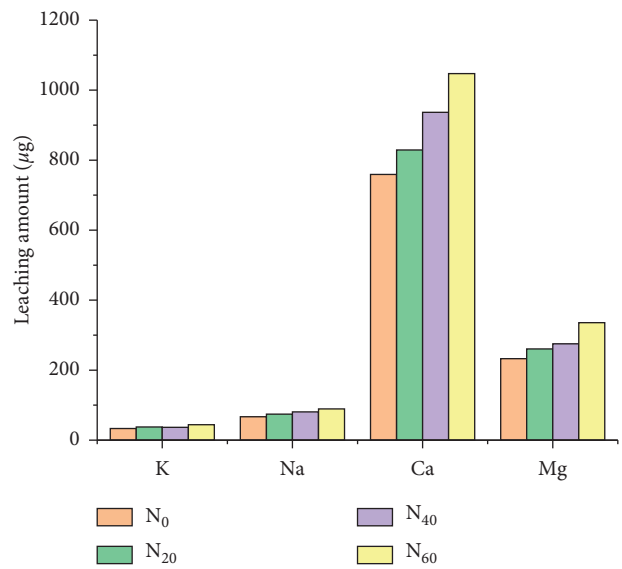

Figure 6: Leaching amounts of base cations under N deposition.

4. Discussion

The mechanism of N deposition-induced acidification of soil is different from acid deposition. Acidic deposition brings H^+ directly into the soil to activate trace metals, and the H^+ can displace the exchangeable fractions from their binding sites [26, 27]. Different HMs have different sensitivity to acid deposition. For purple soil in the Sichuan Basin, the transformability and mobility of Cu and Zn by acid deposition were higher than that of Pb and Cd [28]. However, the activation and migration of HMs induced by N deposition have latent characteristics. First, NH_4^+ displaces the base cations, resulting in the base cations being lost with NO_3^- and reducing the buffering capacity for soil acidity [29]. Additionally, plant-induced assimilation ($NH_4^+ + ROH \longrightarrow RNH_2 + H_2O + H^+$) and soil-induced nitrification would release H^+ to cause soil acidification [30], and the H^+ further promotes HMs' transformation and migration.

In this study, although this decrease was not significant ($p > 0.05$), the pH of WLFZ soil decreased with increasing N deposition (Figure 5), showing that N deposition has a potential acidification effect. Since this study did not involve plant ecosystems, this insignificant acidification may be attributed to the nitrification of soil NH_4^+ because NH_4NO_3 can promote the growth of soil nitrifying bacteria and accelerate the rate of soil nitrification, thereby accelerating soil acidification [31]. In addition, the leaching amounts of base cations (K^+, Na^+, Ca^{2+}, and Mg^{2+}) were increased as increasing N deposition (Figure 6), and the concentrations of base cations were all positively correlated with NO_3^- in leachate (r^2 ranged from 0.16~0.92, $p < 0.01$). Therefore, it was the NO_3^- that carried the base cations to loss with wet deposition. With the loss of base cations, the acid buffering of soil decreased, and toxic HMs began to active and migrate, resulting in ecological harm.

The WLFZ is a land-water interlaced zone. Thus there exist frequent material and energy exchanges between the WLFZ soil and the water body in the TGR area [32]. The high background content and the accumulating HMs in WLFZ soil as a result of external inputs (e.g., sewage discharge, agricultural nonpoint sources) have become the potential pollution sources of the TGR [1, 33, 34]. Under the influence of external environmental disturbance, these HMs will be activated and migrated, causing harm to the ecosystem. This study showed that N deposition was a non-negligible factor driving the transformation and migration of HMs. A moderate level of N deposition (40 kgN/(ha·yr)) could cause significant activation of Ni and cause migration of Cd, Cu, Pb, and Cr with wet deposition. According to our previous study, the N flux of wet deposition in the entire TGR area ranged from 12.17 to 51.93 kgN/(ha·yr), and it could exceed 40 kgN/(ha·yr) in the upstream area [8]. Therefore, the influence of N deposition on the migration and transformation of HMs in the soil of the WFLZ is worthy of in-depth exploration.

5. Conclusions

The effect of N deposition on the migration and transformation of HMs in the fluctuation zone of the TGR was investigated in this study. As the N deposition increased, the amounts of leached-out HMs increased. The cumulative release amounts of Cr and Cu were much higher than those of Pb, Ni, and Cd, whereas that of Pb showed significant differences between N deposition groups. Three-stage dissolution for Cu and Cd was observed. Their dissolution rates were gradually lower, and only physical elution was involved. In contrast, the dissolution rate of Ni increased at the third stage, likely caused by the activation effects. In comparison, Cr only experienced two stages of rapid and slow dissolution. The double-constant equation and the parabolic diffusion equation could well describe the leaching process of HMs, indicating that the release process of the HMs was a diffusion kinetic process with uneven energy distribution and controlled by multiple diffusion factors. After the N deposition treatment, the exchangeable fractions of HMs

increased to varying degrees, of which Ni was most significant, indicating that N deposition would enhance the ecological risk of HM pollution in the TGR area, a unique region with a vulnerable ecology environment.

Data Availability

The data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that there are no conflicts of interest regarding the publication of this paper.

Acknowledgments

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