Effects of exogenous salinity (NaCl) gradient on Cd release in acidified contaminated brown soil

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Abstract. Taking acidified Cd contaminated brown soil in Yantai as the research object, based on different exogenous salinity (NaCl) gradient (0%, 0.3%, 0.6%, 0.9%, 1.5%, 2% and 5%), indoor simulation experiments of Cd release were carried out after field investigation. Results showed that there was a significantly positive relation ($r>0.90$) between Cd release concentration/amount/ratio and exogenous salt (NaCl). Besides, the more exogenous salt (NaCl) was added; maximum release concentration/amount of Cd appeared the earlier. It was found that exogenous salt (NaCl) addition could obviously promote Cd release from acidified Cd contaminated brown soil. It was believed that this could be mainly due to the cation exchange between Cd$^{2+}$ and Na$^+$, together with the dissociation and/or complexation between Cl$^-$ and Cd$^{2+}$. In addition, available adsorption sites reduction by exchange base in soil causing Cd changed from solid state to soil solution was also a probable reason.

1. Introduction

Recently, with the rapid industrialization and urbanization, more and more heavy metals are being released into soil environment [1-2]. Investigation report on the ecological environment in the Middle East region carried out by State Environmental Protection Administration showed that more than 20000 thousand hectares of cultivated land was polluted by Cd, Cr, Pb, As, etc [3-4]. Meanwhile, results of a national soil survey jointly carried out by the Ministry of Land and Resources and the Ministry of Environmental protection showed that point ratios of Cd exceeding standard was 7%. In addition, research found that area of cultivated land polluted by Cd was 13 thousand hectares [5]. Thus, soil Cd pollution has been a hot issue at home and abroad [2].

Large amounts of studies on Cd release, migration and transformation in soil were carried out by researchers at home and abroad [2, 6-7]. Research results show that Cd release behavior is closely related to the salinity of environmental media. Under the same conditions, Cd release amount increases with the salinity of environmental media. There is a positive correlation between them [7, 8-9]. Researchers believed that soil salinity could enhance the activity of Cd [10]. It might be due to the content increasing of exchangeable and/or reductive Cd resulted by salinity [10]. In addition, earlier researches (unpublished) by authors and Shandong Geological Survey Institute showed that acidified brown soils around a copper mine were heavily contaminated by Cd in a coastal city (Yantai). There, soil salinity changes are greatly influenced by the ocean. However, whether or not these results are applicable for acidified Cd contaminated brown soil still need to be further confirmed. Besides, whether or not content changes of NaCl could enhance Cd release in acidified Cd contaminated brown soil are still needing to be further studied.
Considering those above, aiming to discuss effects of exogenous salt (NaCl) addition on Cd release in acidified Cd contaminated brown soil, indoor simulation experiments based on different addition concentration of NaCl were carried out after field investigation. And then Cd release laws were discussed. Besides, mechanisms of NaCl affecting on Cd release in acidified Cd contaminated brown soil were demonstrated.

2. Material and methods

Test soils were sampled after field investigation around a copper mine in March 2017 in Yantai. The sampling depth was 0-30cm. As a brown soil, it’s conductivity and pH Value were 140μs/cm and 5.6, respectively. Cd concentration was 1.98mg/kg.

Samples were air dried and sieved (2 mm), then were ground to fine particles (<0.25 mm) prior for simulation experiments [11]. The experiment had supposed seven salinity gradients (0%, 0.30%, 0.60%, 0.90%, 1.50%, 2.0% and 5.0%), 1 control group (CK), 3 repetitions, altogether 126 samples. Experimental water is ultra pure water produced by Ultra-pure water system (Milli-Q Reference). NaCl solutions and test soil were fully mixed in proportion to 1:10 [10], and then heated in a thermostat (HWS26). Supernate fluids were sampled at 2h, 4h, 6h, 8h, 12h and 24h, respectively. Test soil was dried in by drier at 105 ℃, and then digested using aqua regia with a full automatic microwave.

Cd contents (Table 1 and 2) were determined with an inductively coupled plasma mass spectrometer (ICP-MS, Thermo Electron Corporation, Element X Series). Quality assurance and quality control were estimated with the blank and duplicate samples and Certified Reference Materials (GBW07401, GBW07403) approved by the General Administration of Quality Supervision, Inspection and Quarantine of China. The accuracies met the qualification of China Geological Survey (China … 2005). Generally, the relative standard deviations (RSDs) for Certified Reference Materials were less than 4.0%.

| Table 1. Cd release contents under different exogenous salinity (NaCl) gradients (μg/L) |
|-----------------------------------------------|
| CK               | 0%   | 0.30% | 0.60% | 0.90% | 1.50% | 2%   | 5%   |
| 2h               | 0.08 | 0.09  | 0.99  | 1.21  | 1.51  | 1.76 | 1.82 | 4.63 |
| 4h               | 0.10 | 0.10  | 1.31  | 1.35  | 1.57  | 1.85 | 2.15 | 5.62 |
| 6h               | 0.12 | 0.11  | 1.24  | 1.53  | 1.84  | 2.06 | 2.22 | 6.47 |
| 8h               | 0.11 | 0.08  | 1.16  | 1.48  | 1.71  | 2.05 | 2.76 | 4.7  |
| 12h              | 0.15 | 0.17  | 1.26  | 1.44  | 1.52  | 1.98 | 2.24 | 4.64 |
| 24h              | 0.08 | 0.05  | 1.45  | 1.64  | 1.76  | 1.89 | 2.00 | 4.58 |

| Table 2. Cd contents of test soil after simulation experiments (μg/L) |
|-----------------------------------------------|
| Surplus Cd in soil (mg/kg)               | CK               | 0%   | 0.30% | 0.60% | 0.90% | 1.50% | 2%   | 5%   |
| Release amount (mg/kg)                   | 1.58 | 1.48  | 1.36  | 1.30  | 1.23  | 1.26  | 1.24  | 1.03 |
|                                                                 | 0.40 | 0.50  | 0.62  | 0.68  | 0.75  | 0.72  | 0.74  | 0.95 |

All the statistical analyses were performed by using STATISTICA 6.0 and Micro Excel 2003 for windows.

3. Results and discussion

3.1. Variation characteristics of Cd concentration released from soil under different salinity

Cd concentrations released from soil increased with the salinity (as shown in Fig. 1). The positive correlation was significant with the r value of 0.90. In detail, the lowest Cd concentration (0.05μg/L) was found at the salinity of 0%, and the highest (6.47μg/L) was found at 5%. Cd concentrations
ranged from 0.10μg/L to 5.11μg/L, with the mean value of 1.95μg/L. Results showed that the changes of Cd concentration could be divided into two stages. The faster growth was found at lower salinity (0%-0.3%), with the increasing speed of 2.3. And the slowly growth (mean increasing speed: 1.26) was seen at Medium (0.3%-1.5%) and higher salinity (2%-5%). All of these above indicate that salinity could obviously promote Cd content released from soils.

Figure 1. Characteristics of Cd release concentrations under different exogenous salinity (NaCl) gradients.

3.2. Variation characteristics of Cd release amount from soil under different salinity
Similar to concentration, Cd release amount from soil increased with the salinity (as shown in Fig. 2 and Table 3). The positive correlation was significant with the r value of 0.98. In detail, the lowest Cd release amount (0.04 mg/kg) was found at the salinity of 0%, and the highest (0.32 mg/kg) was found at 5%. Cd release amount ranged from 0.05 mg/kg to 0.26 mg/kg, with the mean value of 0.10 mg/kg. Results showed that the changes of Cd release amount could be divided into two stages. The faster growth was found at lower salinity (0%-0.3%), with the increasing speed of 1.9. And the slowly growth (mean increasing speed: 0.05) was seen at Medium (0.3%-1.5%) and higher salinity (2%-5%). All of these above reveal that salinity could obviously promote Cd release amount from soils.
3.3. Variation characteristics of Cd release ratio under different salinity
Based on total Cd concentrations in soil before and after the exogenous salt addition, Cd release ratios were calculated. According to Figure 3, Cd release ratios ranged from 25% to 48% under different salinity, with the mean release ratio of 35%. Meanwhile, it showed that Cd release ratios increased with exogenous salt addition. It also demonstrates that salinity could obviously promote Cd release from soils.

Figure 2. Characteristics of Cd release amounts under different exogenous salinity (NaCl) gradients.

3.4. Variation characteristics of Cd release concentration with extraction time
Results showed that maximum release content of Cd appeared earlier under higher exogenous salinity (Fig. 4). Specifically, all of the maximum Cd release contents appeared at 24h under the lower salinity (0%-0.6%). Meanwhile, it appeared at 12h when the exogenous salinity was 0.9%. And the maximum release contents of Cd appeared at 8h or so when the exogenous salinity was 1.5%-2%. What's more, the maximum Cd release concentration appeared at 6h when the exogenous salinity was 5%. All of these above can also show that the salinity obviously promote Cd release from soils.

In addition, it was interest that Cd release concentrations fallen down and gradually stabilized after the maximum release contents under the higher salinity (0.9%-5%). It was obvious under the salinity of 5%.

Figure 3. Characteristics of Cd release ratios under different exogenous salinity (NaCl) gradients.
Figure 4. Variation characteristics of Cd release concentrations with extraction time

3.5. Variation characteristics of Cd release amount with extraction time
Results showed that maximum release amount of Cd appeared earlier under higher exogenous salinity (Fig. 5). In detail, all of maximum Cd release amount appeared at 24h under the lower salinity (0%-0.6%). Meanwhile, it appeared before 12h when the exogenous salinity was 0.9%-2%. Especially, the maximum Cd release amount appeared at 6h when the exogenous salinity was 5%. All of these above also indicate that the salinity could obviously promote Cd release from soils.

In addition, it was interest that Cd release amount fallen down and gradually stabilized after the maximum release amount under the higher salinity (1.5%-5%).

Figure 5. Variation characteristics of Cd release amounts with extraction time

3.6. Possible causes of exogenous salinity influence on Cd release from soils
As mentioned above, Cd released from soils was affected by exogenous salinity. Both of Cd release concentration and amount, together with release ratio, increased with exogenous salinity. And there was an obvious positive correlation. These were generally consistent with previous studies [12-14]. For example, it was found that Cd release ratios ranged from 40% to 90% treated by natural seawater with different salinity [8]. And the release behavior was obvious. Besides, research carried out by Liu Yanan showed that exchangeable Cd ions content in beach soil decreased to 38.5% after leaching [15]. On one hand, Cd release from soil caused by cation exchange between Cd$^{2+}$ and Na$^+$, Mg$^{2+}$, Mn$^{2+}$ etc. On the other hand, this was mainly due to dissociation and/or complexation between Cl$^-$ and Cd$^{2+}$ [12]. In addition, authors believed that it resulted from available adsorption sites reduction by exchange base in soil. These all could promote migration of soil heavy metals from solid state to soil solution [8, 15-17].

4. Conclusion
Exogenous salt (NaCl) addition could obviously promote Cd release from soils. On one hand, there was a significantly positive relation ($r$>0.90) between Cd release concentration/amount/ratio and exogenous salt (NaCl). On the other hand, the more exogenous salt (NaCl) was added; maximum
release concentration/amount of Cd appeared the earlier. In addition, Cd release content/amount fallen down and gradually stabilized after the maximum release under the higher salinity (1.5%-5%).

This could be mainly due to the cation exchange between Cd\(^{2+}\) and Na\(^{+}\), together with the dissociation and/or complexation between Cl\(^{-}\) and Cd\(^{2+}\). Besides, available adsorption sites reduction by exchange base in soil causing Cd changed from solid state to soil solution was also a probable reason.

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