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Remediation of vanadium contaminated soil by nano-hydroxyapatite

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Abstract

Purpose Vanadium (V) contamination in soil can cause diverse damage to soil ecosystem and has attracted research interests in exploring soil V stabilization methods, but only a few materials were proposed and studied. Here, a pot experiment was firstly conducted to estimate the efficiency of nano-hydroxyapatite (n-HAP) in stabilizing V in soil. To verify the impact of n-HAP on soil V bioavailability and phytotoxicity, cabbages (*Brassica chinensis* L.) were grown in V-spiked soils after n-HAP amendment.

Materials and methods Soils were sampled from a farmland in China, and the n-HAP was prepared in the laboratory. In each pot of soil spiked with 0, 75, 150, 300, and 600 mg/kg V, 2% n-HAP was amended for 30 days, while soils without n-HAP amendment were set as controls. The stabilization effect of n-HAP on V in soil was estimated by the water-extractable and bioavailable V concentrations in soils. Cabbages were grown in pots subsequently. The V(V/IV) concentrations in cabbage leaves and roots, the organic bound V concentrations in cabbage roots, and the chlorophyll concentrations in leaves were determined. Bioconcentration factor and translocation factor were calculated. The composition of organic bound V in leaf was characterized by fluorescence excitation–emission matrix.

Results and discussion In soils spiked with 150 mg/kg V, n-HAP amendment yielded the highest stabilization rates of 51.0% and 42.4% for water-extractable and bioavailable V, respectively. In 75, 150, and 300 mg/kg V-spiked soil, the plant weight, plant height, and root length of cabbage after 60-day growing decreased 54.6%/89.6%, 30.9%/45.5%, and 41.5%/51.4% in groups with/without n-HAP, respectively. Cabbage leaf chlorophyll concentrations descend firstly then ascend with rising soil V concentration. Leaf V speciation analysis revealed that less leaf V was reduced to V(IV) in groups amended with n-HAP than groups without n-HAP amendment. In 150 and 300 mg/kg V-spiked soil, n-HAP effectively reduced the V content and the V bioconcentration factor of cabbage root. Tyrosine-like and humic acid-like analogues composed the principal part of V complex.

Conclusions In general, n-HAP amendments are potential to decrease the mobility of V in soils, as well as inhibit the bioavailability and phytotoxicity of V to cabbage. In V-spiked soils, n-HAP amendment can alleviate the toxicity of V to the cabbage. Overall, 2% n-HAP is efficient for the amendment of slight V-polluted (150–300 mg/kg) soils to alleviate the soil V stress to cabbage.

Keywords Nano-hydroxyapatite · Soil · Soil amendment · Plant growth · Stabilization · Vanadium

1 Introduction

Vanadium (V) is a widely distributed element in the Earth's lithosphere and soil (Pyrzyńska and Wierzbicki 2004). Human activities such as fossil fuel combustion, oil refinery, steel industry, mining industry, and fertilizing can cause soil V pollution (Nriagu 1998; Teng et al. 2011). Vanadium is classified as a dangerous pollutant which could cause potential toxicity at higher concentrations (Naeem et al. 2007). Pentavalent vanadium [V(V)], the predominant soil V species which mainly exists as vanadate ($H_2VO_4^-$), is suggested to be more mobile and toxic than tetravalent vanadium [V(IV)] in soil (Baken et al. 2012). Although the general mobility of V in soil is relatively lower than that of other heavy metals (Połedniok and Buhl 2003; Teng et al. 2009; Yang et al. 2014), V has already been proven to be toxic to plant growth and morphology (Kaplan et al. 1990; Hou et al. 2013). Excessive V can cause root damage and inhibit plant growth (Panichev et al. 2006; Larsson et al. 2013; Tian et al. 2014; Qian et al. 2014)

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and can lead to hazardous effects on animal and human health through the food chain (Fox 1988). The increasing pollution and potential biotoxicity of V in soil have attracted interest of researchers, and a number of studies aimed at remediating V-contaminated soil have been conducted (Jiang et al. 2017; Li et al. 2017).

Hydroxyapatite (HAP), a non-toxic material widely used in medical engineering, has been proposed to be an appropriate stabilizer for heavy metal in soil (Seaman et al. 2003; Kim and Day 2007). It is demonstrated that oxovanadium (VO^{2+}) can be adsorbed on the surface of HAP by coordination to OH groups without crystalline lattice change (Vega et al. 2003). The V(V) phase with an additional pyrovanadate phase was the dominant V species on the HAP surface, which was loaded with 15% V by the wet impregnation technique (Dasireddy et al. 2015). Vanadium loaded in HAP crystalline structure might be stable. The solid NMR (nuclear magnetic resonance) observation on V ion-exchanged HAP by Pizzala et al. (2009) revealed that the V substitution into HAP is less affected by phosphorus than lead. Moreover, the adsorption of VO^{2+} on commercial calcium hydroxyapatite in aqueous solution has been determined (Vega et al. 2003). However, although the interaction between V and HAP has already been studied, the application of this material for the remediation of V-polluted soil has not yet been reported.

A number of remediation strategies of V-polluted soil/water have been proposed, including adsorption, leaching, and electrothermal (Jiao and Teng 2008; Guan et al. 2014; Gao et al. 2017). Among suggested strategies to solve soil V pollution, stabilizer application is an efficient approach. Feng and Shi (2015) applied 3% commercial nano-HAP (n-HAP) into two agriculture soils, and the heavy metal (Cd, Pb, Zn, and Cu) adsorption abilities of the soils were significantly increased and the desorption amounts were significantly decreased. However, the stabilization ability of n-HAP on V in soil is unknown, and the subsequent plant culture as an assessment of soil V stabilization is not conducted yet. In the present study, based on the hypothesis that n-HAP amendment would reduce V bioavailability and activity in soil and improve the subsequent plant growth in V-contaminated soil, n-HAP synthesized in the laboratory was applied to V-spiked soil to study its stabilization effect on V. Vanadium concentrations (water-extractable, bioavailable, and total V) in soil were measured. In the subsequent pot culture experiment, cabbage (*Brassica chinensis* L.) growth, V bioconcentration factor (BCF), translocation factor (TF), V(V/IV) concentrations, and organic bound V concentrations in the cabbage leaf were estimated to determine the effects of V on cabbage and the effect of n-HAP application on soil V phytotoxicity. The aim of this study is to investigate the ability of n-HAP as a V stabilizer in soil and to explore the impact of n-HAP on the V phytotoxicity on cabbage (*B. chinensis* L.).

2 Methods

2.1 Preparation of n-HAP

To synthesis n-HAP, $Ca(NO_3)_2$ ethanol solution was preheated to 80 °C and stirred at 200 r/min on a magnetic stirrer, and following the reaction ratio of Ca/P (1.67), the $(NH_4)_2HPO_4$ aqueous solution was gently added at a speed no more than 100 mL/min. The pH of the mixture was monitored by a pH meter (Lei-ci PHS-3C, Shanghai, China) and maintained constant between 10.0 and 10.5 by $NH_3{\cdot}H_2O$. After that, the mixture was treated with ultrasonication for 30 min and then settled for 24 h. After removing the supernatant liquid of the stratified mixture, the substrate slurry was washed with ethanol until the strong odor of ammonia was removed. The substrate slurry was then vacuum filtrated and washed with deionized water. The washed slurry (n-HAP) was dried in a microwave oven, powdered in a ceramic mortar, and then roasted in a muffle furnace at 600 °C for 2 h. The n-HAP was ground thoroughly in an agate mortar and stored in polyethylene bags (Li et al. 2008; Pang et al. 2013).

2.2 Soil preparation and aging

The test purple soil was collected from a farmland in Longquanyi District, Chengdu, Sichuan province, China. The surface organic residues were removed before sampling. Four soil samples were collected at four sampling sites in the same area and then mixed up. The soil sample was stored in polyethylene plastic bags and transported to the laboratory immediately. The soil sample was ground after air drying and sieved through a 2-mm nylon sieve. The soil pH was 6.67 ± 0.24 determined by a pH meter (Lei-ci PHS-3C, Shanghai, China) at a water/soil ratio of 2.5:1. The soil organic matter content was $1.34 \pm 0.33\%$ determined following the Walkley and Black method (Walkley and Black 1934). The soil total V concentration was 69.97 ± 3.28 mg/kg according to potentiometric titration method (Tian et al. 2003; Bao et al. 2012), and was below the background value of soil total V in China (82.4 mg/kg) and close to the median value of total V concentration in European topsoil (60 mg/kg) (Larsson 2014). Different amount of V as $NaVO_3$ was dissolved into an appropriate volume of deionized water and mixed into 1.25 kg of soil in a pot (180 × 180 × 140 mm), corresponding to V spike level of 0, 75, 150, 300, and 600 mg/kg, with the soil water content of 60% field capacity. $NaVO_3$ was chosen to produce vanadate (the most soluble and toxic form of V) as the main spiked V species (Larsson 2014).

2.3 Pot experiment

To study the interrelation between n-HAP, soil V concentrations, and plant growth, a pot experiment was conducted from

10 July to 9 November 2017. After V spiking, soils were aged for 30 days to reach a balanced state in chemistry and reactivate the microflora before stabilization. After 30 days of aging, soils were amended with n-HAP. For each V spiked level, 25.0 g of n-HAP was mixed into the soils, corresponding to n-HAP concentration of 2%. The n-HAP treatment group was marked as 0N, 75N, 150N, 300N, and 600N, corresponding to n-HAP amended soils of 0, 75, 150, 300, and 600 mg/kg spiked V, respectively. The control group without n-HAP was marked as 0C, 75C, 150C, 300C, and 600C, respectively. Each treatment was conducted in triplicate. Soil water contents of each pot were maintained at 60% field capacity by watering the soils with deionized water every 2 days. The concentrations of water-extractable and bioavailable V in soil were determined at 1, 4, 7, 11, 15, and 30 days of stabilization process. After bioavailable V levels in all pots were stable, 15 selected and sterilized cabbage (*B. chinensis* L.) seeds were sown in each pot. Seedlings were watered every 2 days and incubated in an artificial climate chamber (PRX-350A, Shanxi, China). Plants were cultivated at 27 °C and 16-h photoperiod during the day and at 23 °C in the dark for 8 h during the night. The relative humidity was set at ~ 80%. After 20-day growing, redundant seedlings were thinned out and eight healthy seedlings were kept in each pot. Pots were moved out of the artificial climate chamber and grown at room temperature of 15–27 °C during the day and 10–20 °C at night, and the sunshine duration was 13–14 h and 10–11 h for light and dark, respectively. Pots were placed randomly and the positions were changed stochastically every time after watering.

Plants were harvested after 60-day growing and rinsed carefully with deionized water. The cabbage roots were rinsed with 0.02 M EDTA to remove surface-adsorbed heavy metals. After drying with absorbent paper, plant weight, plant height, and root length of cabbages were recorded immediately. The number of leaves was measured by counting and averaging the amount of leaves. Fresh leaves were collected for chlorophyll and V(IV/V) concentration analysis and were freeze-dried for organic bound V analysis. Roots and leaves were dried at 105 °C for 30 min and then at 70 °C until constant weight for total V concentration analysis. Unless otherwise noted, all parameters were calculated based on dry weight.

Acetone extraction was applied for the determination of chlorophyll content (Lichtenthaler 1987). Approximately 0.25 g (fresh weight) of fresh leaf fragment was cut off from the green leaves of the plant with a puncher to avoid the main veins. Leaves of the same position and age were selected from every plant. Leaf fragments were added into a mortar filled with 2.5 mL of 80% acetone, 1.0 g of $CaCO_3$, and 1.0 g of quartz sand, grounded into homogenate, and then 3 mL of 80% acetone was poured into the homogenate. The tissues were ground until they turned white. After filtration of the homogenate, the aliquot was diluted to 25 mL. Absorbance of aliquot at 663, 652, and 645 nm was measured by spectrometer (UV 1100; Mapada, Shanghai, China) to determine the chlorophyll concentration.

2.4 Chemical analysis

2.4.1 Vanadium in soils

To determine the soil total V concentration, 1.000 g air-dried soil sample was digested in a polytetrafluoroethylene (PTFE) crucible on an electric heating plate at 120–130 °C. HNO_3, $HClO_4$, and HF were successively added into the crucible at different digestion stages. The soil samples were digested until the digestion liquor was clear (Lu 1999). After cooling, the product was diluted to 25 mL for V determination. Standard soil sample GBS07428 (GSS-14, from Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences) was digested for quality control. The standard addition recovery of V was 98.13 ± 3.87%.

Considering the lack of standard method for determining bioavailable V in soil, the bioavailable V in soil was extracted by diethylenetriaminepentaacetic acid (DTPA), a wildly used extractor for bioavailable heavy metal in soils (Hodson et al. 2000; Keller et al. 2005). DPTA solution preparation and the extraction process were conducted according to the method in ISO 14870-2001 (ISO 2001).

To determine water-extractable V in soils, totally 40 mL of deionized water was added into a conical flask with 2.000 g of soil. The mixture was shaken for 16 h in a constant-temperature oscillator at 20 ± 2 °C and then filtrated. The supernatant was collected for V analysis (Mandiwana and Panichev 2004). Deionized water with no soil sample was used as control.

The stabilization rates (K) were calculated as the ratio of the soil V concentrations after stabilization process to the soil V concentrations before stabilization (Eq. (1)).

$$K = 1 - C_{\text{after}} / C_{\text{before}} \quad (1)$$

where C_{before} means the water-extractable or bioavailable V concentration in soil before stabilization, and C_{after} means the water-extractable or bioavailable V concentrations in soil after stabilization.

2.4.2 Vanadium in plants

To determine the plant total V content, 1.000 g fresh plant was digested in a PTFE crucible on an electric heating plate at 120–130 °C. HNO_3 and $HClO_4$ were successively added into the crucible in different digestion stages until the digestion liquor was clean. After cooling to room temperature, the liquor was diluted to 25 mL for V determination by potentiometric titration. Standard plant sample GBW 10021 (GSB-12,

from Institute of Geophysical and Geochemical Exploration, Chinese Academy of Geological Sciences) was digested, and the standard addition recovery was 105.41 ± 1.19%.

To extract V(V/IV) in cabbage leaves, 0.5000 g (fresh weight) of fresh leaves was fracted and steeped in 20 mL of 1% HNO_3, and then heated to 55 °C for 15 min, 75 °C for 15 min, and 95 °C for 35 min (Sun et al. 2008). The suspension was subsequently filtrated and diluted to 25 mL. Fresh cabbage leaves were collected for the extraction process to avoid the oxidation of leaf V. The V(V) and V(IV) concentrations were measured immediately.

To extract the organic bound V, 0.5000 g (fresh weight) fresh leaves was vacuum freeze-dried and ground in an agate mortar. The plant material was then steeped into 40 mL of 0.15 M Tris–HCl solution (pH = 8.6) for 24 h. After extraction, the suspension was filtrated and the filter liquor was dialyzed in a dialysate bag (3000 Da) for 48 h (Almeida et al. 2014; Amiard et al. 2008; Fukushima et al. 2009). The aliquot was then diluted to 40 mL for V concentration determination and excitation–emission–matrix spectra test on a F-7000 FL Spectrophotometer (Hitachi, Japan). All processes were conducted at 4 °C.

The root bioconcentration factor (BCF) was calculated as the ratio of the V concentration in cabbage root (C_{root}) to the concentration of total V in the soil (C_{soil}). The translocation factor (TF) of V from cabbage roots to leaves was calculated as the ratio of V concentration in leaf (C_{leaf}) to that in root (C_{root}) (Eqs. 2–3).

$$BCF = C_{root}/C_{soil} \quad (2)$$

$$TF = C_{leaf}/C_{root} \quad (3)$$

2.4.3 Determination of vanadium in samples

V(V/IV) and total V concentrations in all samples were detected using $FeSO_4$ and $KMnO_7$ potentiometric titration, based on the methods of Bao et al. (2012) and Tian et al. (2003), respectively. The detection limit of $FeSO_4$ and $KMnO_7$ potentiometric titration was 0.1 μg V(V)/mL, 0.1 μg V(IV)/mL, and 0.1 μg V/mL, respectively.

2.5 Statistical analysis

Excel 2013 was used to analyze the mean value and standard deviation of the triplicate results in each treatment. To examine the differences between treatments, a one-way analysis of variance (ANOVA) was performed, and the significance was evaluated at $p < 0.05$, carried out using SPSS 20.0 (IBM) program.

3 Results and discussion

3.1 Soil vanadium stabilization

To verify the stabilization effect of n-HAP on soil V, soil water-extractable and soil bioavailable V concentrations, representing the activity and bioavailability of soil V, were determined during the stabilization process, respectively (Fig. 1). The maximum stabilization rates for soil water-extractable V (51.0%, Fig. 1c) and soil bioavailable V (42.4%, Fig. 1h) were obtained in 150N. The water-extractable V concentrations in soils of all groups decreased with the sampling time. After 30 days, the K value of soil water-extractable V of 0N, 75N, 150N, 300N, and 600N reached 33.1%, 22.6%, 51.0%, 41.8%, and 31.6%, respectively. Meanwhile, n-HAP amendment brought forth a significant decrease of water-extractable V concentration in soil of higher V spiked levels (300 mg/kg and 600 mg/kg). The bioavailable V concentrations in soils showed a similar tendency as the water-extractable V concentrations, and the K value was 28.4%, 27.3%, 42.4%, 37.6%, and 39.8% for 0N, 75N, 150N, 300N, and 600N, respectively.

During 30 days of stabilization, the water-extractable V and bioavailable V concentrations in 0N group decreased 33.1% and 28.4%, respectively, indicating that V in uncontaminated soils were stabilized by n-HAP. Thus, the impact of soil background V on tested V mobility and bioavailability should be considered. At day 30, the water-extractable V and bioavailable V concentrations in n-HAP treated groups were significantly lower than those of the control groups, demonstrating that the amendment of n-HAP stabilized V in soil. Moreover, the soil water-extractable V and bioavailable V level turned into a stable stage at day 30, indicating that the spiked V in soils reached an equilibrium status and were ready for pot experiment.

The decrease of soil V activity and bioavailability by n-HAP is mainly caused by the adsorption of V on n-HAP and interaction with dissolved phosphate species from n-HAP (Wang et al. 2002; Corami et al. 2008; Wang et al. 2009). Vanadium is able to adsorb on HAP surface through coordination to –OH groups. On the other hand, the phosphate released into soil water can readily bind to V species and reduce its mobility. Deydier et al. (2003) proposed a simplistic equation of possible apatite dissolution in water:

$$Ca_{10}(PO_4)_6(OH)_2 + 14H^+ \rightarrow 10Ca^{2+} + 6H_2PO^4 + 2H_2O \quad (4)$$

This process may also undergo in the natural soil solution, and the occasions of n-HAP remediated heavy metal-polluted soils. Phosphate has a major impact on V transportation because of its high structural similarity with V species (Larsson

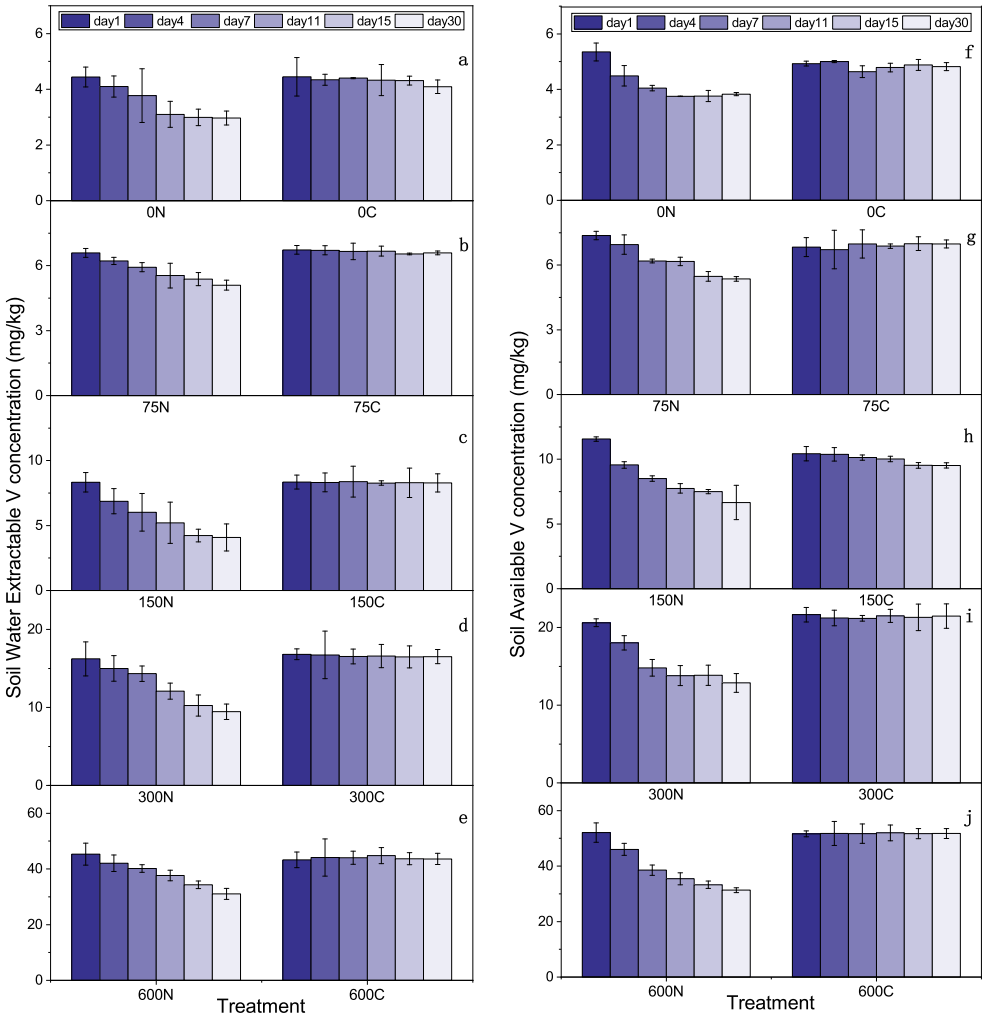

Fig. 1 Stabilization effect of n-HAP on vanadium activity and bioavailability in soils with different vanadium spike amount. (**a**)–(**e**) show soil water-extractable V concentrations in 0, 75, 150, 300, and 600 mg/kg V-spiked soils, respectively. (**f**)–(**j**) show soil bioavailable V in 0, 75, 150, 300, and 600 mg/kg V-spiked soils, respectively. Letter N in each *x*-axis label means 2% n-HAP application in soil, while letter C represents control group with no n-HAP application. Sampling date, 1, 4, 7, 11, 15, 30 days after stabilizer application

2014). In addition, vanadate can form lattice substitution phosphorus in HAP (Pizzala et al. 2009). The strong interaction of VO^{2+} with phosphate group in adenosine triphosphate (ATP) inhibited the oxidation of VO^{2+}. Phosphate is also likely to coordinate with VO^{2+} and $VO(OH)^{3-}$ to form thermodynamically stable complexes (Vega et al. 2003).

3.2 Plant growth and chlorophyll content

Growth of the cabbages varied significantly among different V level treatments (Fig. 2). Biomass, plant height, and root length of the cabbages of different treatments are shown in Table 1. All parameters except the number of leaves negatively correlated with V spike level. The number of leaves could reflect the growth period of plant, and the results show no correlation between soil V loading level and cabbage growth period. All cabbages in 600N and 600C stopped growing and gradually withered in the seedling stage, indicating that soil V could inhibit cabbage growth and even kill cabbage at a high concentration. In general, the inhibition of cabbage growth by V was not obvious at soils spiked no more than 150 mg/kg V. From 0 mg/kg to 300 mg/kg V spike, plant weight, plant height, and root length decreased 54.6%/89.6%, 30.9%/45.5%, and 41.5%/51.4% in soils with/without n-HAP

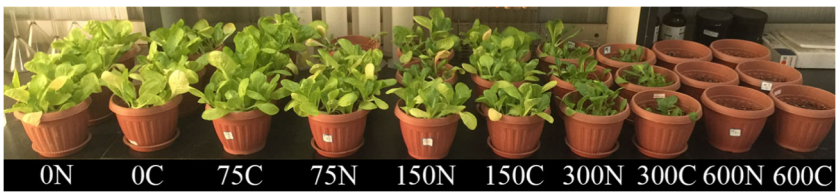

Fig. 2 Growth and leaf color of cabbages in different groups. Different numbers below each column of pots represent different V spike concentration from 0 mg/kg to 600 mg/kg, and letter N or C means 2% n-HAP application or no n-HAP application in soil

Table 1 Plant growth at different level of vanadium and n-HAP treatments

Treatment	Plant fresh weight (g)	Plant height (cm)	Root length (cm)	Number of leaves
0N[a]	5.15 ± 0.16A[b]	9.62 ± 0.20AB	12.42 ± 1.03A	5.69 ± 0.02AB
0C	4.13 ± 1.01A	9.99 ± 0.49A	12.58 ± 1.76A	5.72 ± 0.76A
75N	5.38 ± 0.77A	10.28 ± 0.53A	11.42 ± 1.35A	6.24 ± 0.31A
75C	3.05 ± 0.97A	8.77 ± 0.13A	11.10 ± 0.11A	5.73 ± 0.08A
150N	3.18 ± 0.61AB	8.90 ± 0.48B	11.23 ± 0.13A	5.54 ± 0.33B
150C	3.08 ± 0.21A	9.30 ± 0.34A	12.46 ± 0.75A	5.15 ± 0.22A
300N	2.34 ± 0.24B	6.65 ± 0.99B	7.27 ± 0.43B	4.37 ± 0.42C
300C	0.43 ± 0.23B	5.47 ± 1.60C	6.11 ± 0.64B	5.67 ± 0.76A
600N	–[c]	–	–	–
600C	–	–	–	–

[a] Different number of each treatment represents different V spike concentration from 0 mg/kg to 600 mg/kg, and letter N or C means 2% n-HAP application or no n-HAP application in soil

[b] Mean values and standard deviation of three replicates are shown. The different capital letter in each line represents a significant difference under the same n-HAP treatment but at different V level

[c] No data obtained because of plant death

application, respectively. The plant weight and plant height yielded a significant decrease between 150N/150C and between 300N/300C, respectively. Considering the results of soil bioavailable and water-extractable V in section 3.1, it can be inferred that n-HAP is able to reduce soil V phytotoxicity by lowering its bioavailability and activity. However, in soils of low V spike levels (0 mg/kg and 75 mg/kg), the amendment of n-HAP did not lead to any significant differences on the plant growth between n-HAP amended group and n-HAP absent group at the same V level. Besides, since the soil background V in this study (69.97 ± 3.28 mg/kg) was close to the V spike level (75 mg/kg), the potential impact of soil background V on cabbage growth should be considered. However, no significant effect on plant fresh weight, plant height, and root length was observed between 0C and 0N group ($p > 0.05$).

Chlorophyll *a*, chlorophyll *b*, and total chlorophyll content of the cabbages yielded a different variation tendency from the plant biomass (Table 2). No significant difference ($p > 0.05$) between chlorophyll concentrations and soil V concentration was noted (Fig. 2). Particularly, although biomass decreased to the lowest level, leaves in 300N and 300C were greener than in the other groups. Meanwhile, n-HAP amendment decreased chlorophyll content in the cabbage leaf compared with the corresponding control group, with an exception of 75N. These results may suggest a complex relationship between soil V stress and plant chlorophyll content (or stability). We infer that a possible combination of cabbage defense mechanism and the growth prohibition of V may jointly lead to such a result. Moreover, it has been evidenced that V is capable of stimulating chlorophyll formation and Fe metabolism (Basiouny 1984) and serving as an alternative element of Mg in the porphyrin structure (Hilliard 1992), and then form a stable V compound (Walker et al. 1975). Therefore, it is reasonable to infer that V could promote the formation and stability of chlorophyll during the cabbage growth and the chlorophyll extraction process, thus leading to a more complicated interaction.

The initial decrease of plant chlorophyll from 75N to 150N could be attributed to the V phytotoxicity and the inhibition of chlorophyll synthesis process by V, while the subsequent increase of plant chlorophyll from 150N to 300N might be a result of V–chlorophyll combination in plant leaves. The higher leaf V concentration in 300N supported this hypothesis, but a direct evidence should be obtained to confirm this conjecture in further research. Vanadyl-pheophorbide applied in anti-cancer therapy

Table 2 Chlorophyll content in cabbage leaves from different treatment

Treatment	Chlorophyll content (mg/g)[a]		
	Chlorophyll *a*	Chlorophyll *b*	Chlorophyll *a* + *b*
0N[b]	0.37 ± 0.15A[c]	0.14 ± 0.05A	0.42 ± 0.01B
0C	0.48 ± 0.06B	0.18 ± 0.02B	0.68 ± 0.09B
75N	0.44 ± 0.17A	0.17 ± 0.07A	0.77 ± 0.15A
75C	0.28 ± 0.02B	0.11 ± 0.01C	0.41 ± 0.03C
150N	0.34 ± 0.07A	0.15 ± 0.01A	0.51 ± 0.07B
150C	0.38 ± 0.20B	0.18 ± 0.05B	0.72 ± 0.19B
300N	0.61 ± 0.09A	0.22 ± 0.04A	0.78 ± 0.03A
300C	0.77 ± 0.06A	0.33 ± 0.03A	1.16 ± 0.10A
600N	–[d]	–	–
600C	–	–	–

[a] Calculated based on fresh leaf weight

[b] Different number of each treatment represents different V spike amount from 0 mg/kg to 600 mg/kg, and letter N or C means 2% n-HAP application or no n-HAP application in soil

[c] Mean values and standard deviation of three replicates are shown. The different capital letter in each line represents a significant difference under the same n-HAP treatment but at different V level

[d] No data obtained because of plant death

has shown its in vivo and in vitro stability (Iwai et al. 1989), indicating a potential link between V and chlorophyll and chlorophyll derivatives in green plants, and the generally found V–porphyrin complexes in crude oil could be structural evidences (Riley and Saxby 1982). In addition, the water content of plant could be decreased by V (Yang and Tang 2015), and the lower water content of cabbage leaf might lead to a rise of chlorophyll concentration, which is calculated based on the leaf fresh weight. However, the water content of cabbage leaves was not determined in this study, and further studies aiming on the impact of V on plant leaf chlorophyll concentration should consider the change of plant leaf water content.

3.3 Vanadium concentrations in cabbage

Vanadium concentrations in the cabbage tissues varied with different soil V stress and n-HAP application (Table 3). Leaf V concentrations of all samples were lower than 5 μg/g (fresh weight). There is no significant difference of leaf V concentrations caused by n-HAP application among the low-level V treatments ($p > 0.05$), but the leaf V concentrations rose significantly from 150N and 150C to 300N and 300C, respectively ($p < 0.05$). This is in accord with the trend of plant weight and plant height, which decreased gently at low V level (0–150 mg/kg) followed by a significant drop at high V spike amount (150–300 mg/kg). In addition, the root V concentrations also showed a significant rise at 150–300 mg/kg V level (17.81–29.31 μg/g and 27.31–39.75 μg/g corresponding to n-HAP treated groups and n-HAP absent groups, respectively).

Low V levels in the cabbage leaves and low TF values suggest an effective defense mechanism of the plant against soil V stress. The V concentrations in the roots were approximately 3–10-fold higher than those of the leaves, suggesting that the cabbage root is the major tissue of binding and fixing V. In groups of 0–300 mg/kg V spike, the root V concentrations increased while the TF values generally decreased, suggesting a possible inhibition of the upward V translocation from cabbage root to leaf.

The n-HAP amendment caused a significant decrease ($p < 0.05$) of BCF, from 11.4% (150N) to 8.1% (150C) and from 11.5% (300C) to 8.3% (300N), in groups of high soil V levels. In contrast, in 0 mg/kg and 75 mg/kg V spike treatments, n-HAP was less effective in reducing cabbage V BCF (no significant difference was noted between 0N/75N and 0C/75C, $p > 0.05$) than in higher V spike treatments, indicating the limited effect of n-HAP on V bioavailability in soil of low V spike. The amendment of n-HAP reduced cabbage root V concentrations from 27.3 μg/g (150C) to 17.8 μg/g (150N) and from 39.8 μg/g (300C) to 29.3 μg/g (300N), but did not make any significant difference between low V treatment groups, which is in accord with the change trend of BCF values. This also indicates that n-HAP can effectively reduce the bioavailability of V to cabbage in heavier V-contaminated (> 150 mg/kg) soil than that in slight V-polluted soils. Contrary to the effect on BCF and root V concentration, no significant difference of total leaf V concentrations was found between n-HAP treated and n-HAP absent groups, which suggests that n-HAP may have few impacts on leaf V concentration and V translocation.

Table 3 Concentrations of vanadium in the leaves and roots of cabbage (*Brassica chinensis* L.) and V enrichment factors of cabbage of different treatments

Treatment	Plant V concentration		BCF[b] (%)	TF[c] (%)
	Leaf[a] (μg/g)	Root (μg/g)		
0N[d]	2.81 ± 0.28B[e]	13.95 ± 2.30B	14.6	20.1
0C	2.68 ± 0.26B	14.26 ± 1.47B	13.3	18.8
75N	3.33 ± 0.30B	14.58 ± 0.81B	9.60	22.8
75C	3.05 ± 0.64B	18.29 ± 3.79B	9.90	16.7
150N	3.05 ± 0.32B	17.81 ± 6.00B	8.10	17.1
150C	3.00 ± 0.59B	27.31 ± 5.29B	11.4	11.0
300N	4.17 ± 0.37A	29.31 ± 1.98A	8.30	14.2
300C	4.92 ± 0.85A	39.75 ± 2.65A	11.5	12.3
600N	–[f]	–	–	–
600C	–	–	–	–

[a] Calculated based on fresh leaf weight

[b] BCF: bioconcentration factor

[c] TF: translocation factor

[d] Different number of each treatment represents different V spike amount from 0 mg/kg to 600 mg/kg, and letter N or C means 2% n-HAP application or no n-HAP application in soil

[e] Mean values and standard deviation of three replicates are shown. The different capital letter in each line represents a significant difference under the same n-HAP treatment but at different V level

[f] No data obtained because of plant death

3.4 Vanadium species and organic bound vanadium in cabbage leaves

Bio-reduction is believed to be an effective way of plant detoxification against heavy metal stress (Lytle et al. 1998); here, concentrations of V species in cabbage leaf were determined to reveal the bio-reduction on V in the cabbage, and the impact of n-HAP was considered. The V(V) and V(IV) concentrations of plant leaves increased with soil V levels (Table 4). The sum of V(V) and V(IV) contents was generally lower than the total leaf V content in all treatments. This might suggest the existence of lower V valence in cabbage leaf. Meanwhile, higher concentrations of V in leaf (75C/150C/300C) led to a decrease of V(IV)/V(V) proportion in cabbage leaves, indicating that a lower ratio of V was reduced from highly toxic V(V) to less toxic V(IV) when soil V stress increased. It can be inferred that a defense mechanism of V reduction might take

Table 4 Total V, pentavalent V, tetravalent V, and organic bound V concentrations in the leaves of cabbages in different treatments

Treatment	Leaf V concentration[a]			V(IV)/V(V) (%)	Organic bound V (μg/g)
	Total (μg/g)	V(V) (μg/g)	V(IV) (μg/g)		
0N[b]	2.81 ± 0.28B[c]	0.92 ± 0.12	0.62 ± 0.19	70.1	0.209 ± 0.009
0C	2.68 ± 0.26B	0.84 ± 0.04	0.59 ± 0.01	71.0	0.208 ± 0.009
75N	3.33 ± 0.30B	1.70 ± 0.21	1.06 ± 0.04	66.1	0.203 ± 0.003
75C	3.05 ± 0.64B	1.14 ± 0.25	1.34 ± 0.36	117.5	0.198 ± 0.003
150N	3.05 ± 0.32B	1.30[d]	1.19	91.3	0.195 ± 0.003
150C	3.00 ± 0.59B	1.24	1.36	109.8	0.191 ± 0.001
300N	4.17 ± 0.37A	1.65 ± 0.28	1.21 ± 0.36	73.4	0.192 ± 0.003
300C	4.92 ± 0.85A	2.03	1.87	92.3	0.191 ± 0.007
600N	–[e]	–	–	–	–
600C	–	–	–	–	–

[a] All parameters were calculated based on fresh leaf weight

[b] Different number of each treatment represents different V spike amount from 0 mg/kg to 600 mg/kg, and letter N or C means 2% n-HAP application or no n-HAP application in soil

[c] Mean values and standard deviation of three replicates are shown. The different capital letter in each line represents a significant difference under the same n-HAP treatment but in different V level

[d] No standard deviation is shown because the plant biomass was insufficient for replicate analysis

[e] No data obtained because of plant death

place in cabbage, and the reduction rates weaken with heavier V stress. This is in accord with the decreasing cabbage growth observed in groups with more V spiked. In addition, n-HAP amendment did not lead to a significant impact on the cabbage leaf total V concentrations. However, at the same V level, leaf V(IV) concentration in 75N, 150N, and 300N were lower than

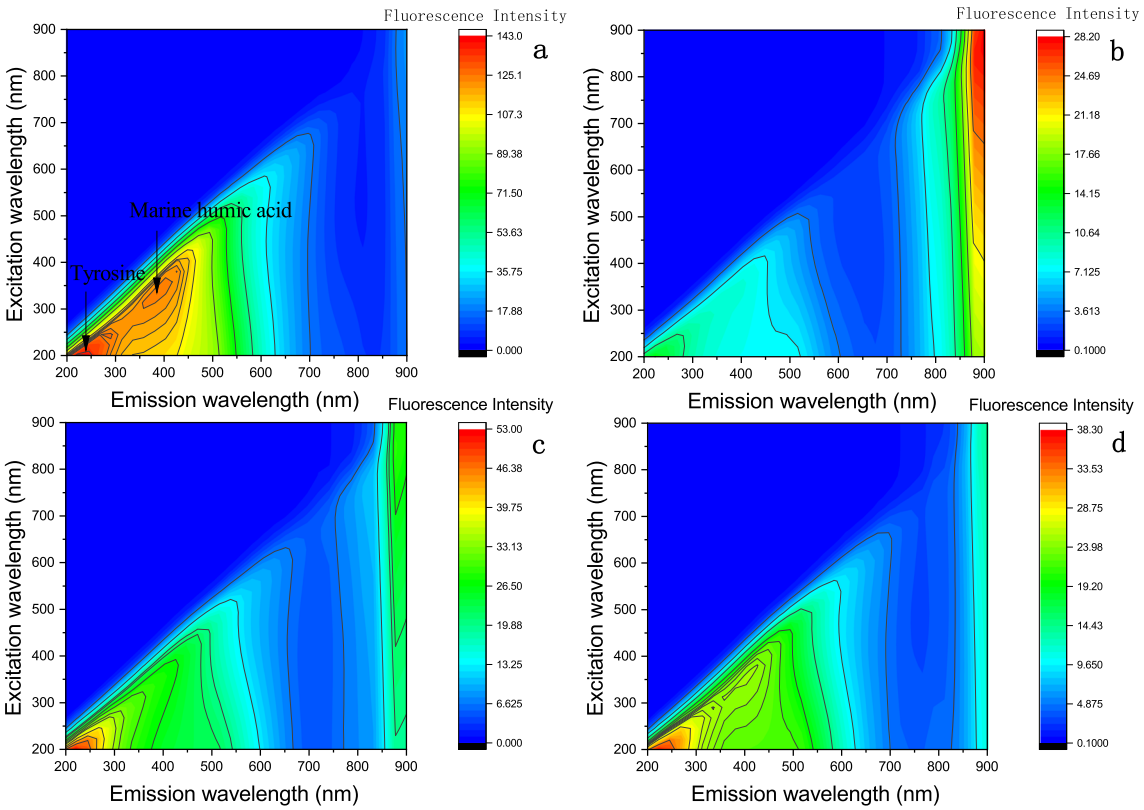

Fig. 3 Fluorescence excitation–emission matrix spectroscopy of the extract from cabbage leaf in V-spiked group of (**a**) 0 mg/kg, (**b**) 75 mg/kg, (**c**) 150 mg/kg, and (**d**) 300 mg/kg without n-HAP application. Extractor: 0.15 M Tris–HCl, pH = 8.6

that of 75C, 150C, and 300C, and it is the same with the ratio of V(IV) and V(V) concentrations. This might indicate that less V was reduced by cabbage, and can be attributed to the lower plant defense system response under the relatively slight V stress caused by n-HAP (compared with the control groups). However, further studies and plant physiological evidences are needed to confirm this hypothesis.

Heavy metal stress has been demonstrated to be capable of inducing the production of certain plant proteins, particularly metallothioneins (MTs) and phytochelatins (PCs), which act as two main functional compounds in plant detoxification strategy against the uptaken heavy metals (Cobbett 2000; Wang and Xing 2002). However, the stress of V showed a conflicting influence on different objects. Vanadium failed to induce the production of PCs in plant cell cultures (Schmöger et al. 2000), but soil V stress caused an increase of protein in the leaf and stem of *Lycium chinense* Mill. and *Brassica juncea* grown in V-spiked soil (Hou et al. 2016). Previous researches focused on the plant proteome change only (Shahbaz et al. 2010; D'Alessandro et al. 2013). Few attentions were paid to the protein bound V concentration. In the present study, results showed that only a small part of leaf V was bound to water-soluble proteins with a molecular weight over 3000 Da. The concentration of organic bound V in cabbage leaves was quite low (from 0.10 μg/g to 0.21 μg/g) compared with leaf total V concentration (from 2.68 μg/g to 4.92 μg/g) and has no significant difference among V loadings. Meanwhile, the n-HAP application had no impact on the organic bound V concentration in cabbage leaf. Moreover, considering no significant difference of organic bound V concentrations was found between different soil V levels, it is reasonable to infer that V stress has a weak impact on PCs or MTs production in cabbage.

The fluorescence excitation–emission matrix (EEM) results reflected the composition of the water-soluble organic compounds in cabbage leaf extractant at different V levels (Fig. 3). The low level of fluorescence intensity signal indicated that little soluble organisms existed in the extract and this was in accord with the low level of leaf organic bound V concentrations in this study. Based on the regional location of EEM peaks summarized by Chen et al. (2003), the EEM spectrum in Fig. 3 suggests the existence of tyrosine-like and humic acid-like analogues. Tyrosine-like material was the major component and existed in leaves of all V-stressed cabbages. In contrast, the peak of humic acid-like analogues disappeared in 75 mg/kg and 150 mg/kg V stressed leaves (Fig. 3b, c). Tyrosine-like analogues may be a potential functional compound of cabbage detoxification mechanism. Aromatic protein tyrosine was found in the complexation of extracellular polymeric substances produced by the alga–bacteria biofilm grown under Pb, Co, Ni, Zn, and Cd stress (Ma et al. 2018). Moreover, the decrease of tyrosine-like analogues indicated an efficiency loss of cabbage detoxification mechanism with increasing V stress.

4 Conclusions

In pot experiment, the amendment of 2% n-HAP led to an obvious reduction of soil V activity and bioavailability in all treatments. In 0–600 mg/kg V treatment, the maximum stabilization efficiency was recorded in soils spiked with 150 mg/kg and 300 mg/kg V. Within 30 days of stabilization by 2% n-HAP, the V activity and bioavailability in soil dropped and then tended to be stable; 2% of n-HAP might be efficient for slight V-contaminated (150–300 mg/kg) spots.

Biomasses of cabbages in n-HAP treated groups were significantly higher than that of the control groups in soils spiked with 150 mg/kg and 300 mg/kg V; this indicates that n-HAP is able to efficiently reduce the growth inhibition by V. The general phytotoxicity of V was not obvious until V spike concentration reached 300 mg/kg, and this could be due to the defense system of cabbage against soil V. Moreover, application of n-HAP can weaken the phytotoxicity of V by reducing soil V bioavailability, yielding a relatively lower V concentration and BCF in cabbage root. The special trend of cabbage chlorophyll contents at different V levels in soil is an interesting finding and might be caused by the interaction of V toxicity, cabbage defense, and V–porphyrin combination in plant leaves, but direct evidence need to be obtained to confirm this conjecture. The decrease of tyrosine-like analogues in V-bound organic matter suggests that the cabbage detoxification efficiency decreased with rising soil V stress. In general, 2% n-HAP amendment is able to alleviate the phytotoxicity of V in soil. Nano-HAP is a suitable material for V stabilization and has a positive impact on the cabbage cultivation in V-contaminated purple soil.

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Compliance with ethical standards

Disclaimer The authors confirm that there are no conflicts of interest.

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