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Vanadium in thirteen different soil profiles originating from Germany and Egypt: Geochemical fractionation and potential mobilization[☆]

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ABSTRACT

Knowledge about geochemical fractions of vanadium (V) in different soils is required to understand its potential mobilization which we assessed in thirteen soil profiles originating from Germany and Egypt using the sequential extraction technique of the Commission of the European Communities Bureau of Reference (BCR). The concentrations of total, AB-DTPA-extractable, and the geochemical fractions [acid soluble (F1), reducible (F2), oxidisable (F3), and residual (F4) fraction] of V in the soils were determined. The total V concentrations ranged from 20.7 to 133.1 mg kg⁻¹ and correlated positively with clay content and the total concentrations of iron (Fe_t), aluminum (Al_t), and manganese (Mn_t). The total V was stronger affected by free Fe and Mn oxides (Fe_d and Mn_d) in the Egyptian soils than in the German soils. The residual fraction of V was dominant in the soils followed by the reducible and the oxidisable fraction and showed a similar behavior to total V. The reducible V was higher in the Egyptian soils than in the German soils and was positively correlated with Fe_t, Al_t, Mn_t, Fe_d, and Mn_d. The impact of Fe_t, Al_t, and Mn_t on the reducible V was stronger in the Egyptian soils than in the German soils, while the impact of Fe_d and Mn_d on the reducible V was stronger in the German soils than Egyptian soils. The oxidisable V was affected by soil organic matter and total sulphur (S_t) in the German soils and by carbonates and S_t in the Egyptian soils. The acid soluble fraction of V was lower than the detection limits in all soils. The AB-DTPA-extractable V concentrations (potential available V) ranged between 0.04 and 4.04 mg kg⁻¹. The potential mobile fraction (PMF = ∑F1–F3) accounted 4.4–64.7% of the total V. The alkaline soils showed the highest potential mobility and availability of V compared to the acidic soils, and thus the AB-DTPA-extractable V correlated positively with soil pH as well as clay content, cation exchange capacity, and Fe_t. The reducible fraction contributed stronger to the potential mobility and availability of V than the oxidisable fraction. The canonical discrimination analysis explained 64% of the variability of the geochemical behavior of the different soil groups and showed that the different groups of soils could differentiate from each other. The German soil groups (Eutric Fluvisols, Calcic Luvisols, Tidalic Fluvisol and Haplic Gleysol (Marsh soils)), showed a different geochemical behavior; while the Egyptian Eutric Fluvisols and Sodic Fluvisols were relatively similar in their geochemical behavior and the Haplic Calcisols was relatively close to them. Our results demonstrate that the potential mobilization of V was high in the soils (except for Luvisols) - especially under alkaline conditions-which indicate a release of this toxic metal from the soils to soil solution. This release may cause potential environmental risks such as the transfer of V into the groundwater, the vegetation and food chain. Future studies should elucidate the temporal kinetics of V and the determining factors under different flooding conditions and remediation approaches are necessary to ameliorate V-contaminated soils.

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1. Introduction

Vanadium (V) is a trace element (TE) ranking as the 22nd most abundant element in the earth's crust (Kabata-Pendias, 2011; Imtiaz et al., 2015). Vanadium is an essential element to human

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beings and animals (Goldwasser et al., 2000). However, numerous reports have demonstrated the carcinogenicity and toxicity of V at higher concentrations (McCord et al., 2001; Antoniadis et al., 2017; Yang et al., 2017). Therefore, the environmental pollution by V could be a global environmental concern and a significant issue for both environmental protection and economic benefits (Wällstedt et al., 2010; Huang et al., 2015). The relevance of V in biological systems is known since many years and V-based catalysts have important industrial applications, however, until the beginning of the 80s research on V chemistry received less attention of the scientific community (Costa Pessoa, 2015) and research on V geochemistry has lagged behind that for other transition elements (Rehder, 2008).

Soil V is originating either from soil parent material or from anthropogenic sources. Vanadium naturally occurs in soils originating from weathering of bedrock. The relevance of anthropogenic V in the environment has increased significantly in the recent years due to an increased demand for V in high-temperature industrial activities (Nadal et al., 2004; Teng et al., 2011a). It was reported that approximately 2.30×10^8 kg of V was annually introduced to the environment through human activities, of which 1.32×10^8 kg was deposited on land and resulted in elevated V concentration in soil (Hope, 1997; Qian et al., 2014). Anthropogenic inputs from the burning of fossil fuels and mining activities may lead to an enrichment of V in soils (Teng et al., 2011a,b; Cappuyns and Slabbinck, 2012). This added V is usually associated with soil organic matter (SOM), clay, iron oxides, and compared to natural sources, is mobile and bioavailable in soils (Gäbler et al., 2009; Palmer et al., 2014). Total concentrations of TEs including V might be not able to provide sufficient information about the potential mobilization (Shaheen and Rinklebe, 2014; Rinklebe et al., 2017). The mobilization of V in soils depends on its total concentration, specific chemical form, binding state, environmental factors, and soil properties (Wright et al., 2014). Therefore, determination of the binding forms of V into different geochemical fractions is needed to evaluate its mobilization and pollution status in soils (Rinklebe and Shaheen, 2014). Soil TEs including V exists in various fractions such as soluble + exchangeable, carbonate-associated, Fe-Mn oxides associated, OM associated, and residual fractions. Among these fractions, the easily mobilizable fraction is considered to be bioavailable. The potential mobile fractions (PMF) of a metal, including the non-residual fractions (i.e., carbonate-, Fe-Mn oxides-associated, and OM-bound fractions), can also be bioavailable if the pH and redox potential of the soil change (Shaheen and Rinklebe, 2014; Rinklebe et al., 2017).

A proper understanding of geochemistry, fractionation, and mobilization of V in soils is limited, particularly under different soil conditions and types. Furthermore, knowledge about the geochemical fractions of V in different soils is required to understand its general mobilization processes and enable a more accurate prediction of V release into surface waters in response to soil types and properties. Such a geochemical approach is vital to link chemical behavior to the environmental risk of V. Soils are dynamic systems and their genesis depends on the climate and the position in the landscape which determines the hydrological regime, soil biota, parent material, and time. The progress of soil formation may, therefore, influence the geochemical distribution of V in soils. During soil development, the soil properties can dramatically change, impacting the fractions and mobility of V. The studied soils of Egypt and Germany differ widely in their origin, development, and properties and therefore it is expected that V content and its distribution among the different geochemical fractions also differ significantly.

Previous studies have determined the geochemical fractions of TEs in soil profiles representing Mollic Fluvisols and Eutric Gleysols

along the Elbe River in Germany (e.g., Rinklebe and Shaheen, 2014; Shaheen and Rinklebe, 2014). However, considerable knowledge gaps exist regarding the fractionation and depth distribution of V in soils; in particular, the geochemical fractionation of V in other soils such as Calcic Luvisols, Eutric Fluvisols, Haplic Gleysols, and Tidalic Fluvisols is still not studied. Tsadilas and Shaheen (2010) studied the distribution of total and available V in different soil profiles from Egypt and concluded that investigation of the distribution of V among the different geochemical fractions is recommended. Also, Shaheen et al. (2014a) presented the geochemical fractions of V in floodplain soils at the lower course of the Nile Delta; however, these were conducted in two top soils only, not in complete soil profiles and not in different soil types of Egypt.

Moreover, the geochemical fractions of V in different soil profiles originating from different regions under large variation of the soil forming factors and process is still limited. In addition, the relationships between soil properties and the vertical distribution of V fractions in various soil types have not been studied to our knowledge to date. Our hypothesis is that distribution of V among the geochemical fractions and its potential mobilization might be affected by the soil type, origin, and relevant soil properties. Moreover, investigation of the fractions and mobilization of V in different soils might be an aid to assess the environmental risk of this emerging contaminant in these ecosystems. Therefore, our objectives were 1) to quantify and compare the total and the geochemical fractions of V in thirteen selected soil profiles representing important soil types in Egypt and Germany, and 2) to assess the vertical profile distribution and potential mobilization of V as affected by relevant soil properties.

2. Materials and methods

2.1. Study areas, sites and soils

2.1.1. German soils

Six soil profiles representing different types of soil were sampled of three different study areas in Germany. Those are two Eutric Fluvisols, two Calcic Luvisols, one Haplic Gleysol, and one Tidalic Fluvisol. The two Eutric Fluvisols are floodplain soils along the Wupper River. The respective study area is located close to the confluence of the Wupper River into the Rhine River near Cologne in North Rhine-Westphalia, Germany. We selected two study sites within the study area and one soil profile was dug at each study site (Profile 1: $51^{\circ}4'0.48''N$, $6^{\circ}4'0.48''E$; Profile 2: $51^{\circ}7'49.86''N$, $7^{\circ}1'35.10''E$). More details about the first study site are given by (Frohne et al., 2011; Shaheen and Rinklebe, 2015) and the details about the second study site are given by (Mihajlovic et al., 2014a). The two study sites are used as grassland and are flooded seasonally by the Wupper River, usually in springtime. Both soil profiles are classified as Eutric Fluvisols (IUSS Working Group WRB (Eds.), 2014).

The two study sites of the Calcic Luvisols are located near Essfeld, a village 15 km south of Würzburg in Lower Franconia, Bavaria, Germany ($49^{\circ} 41'24.50''N$; $9^{\circ}56'49.00''E$). The sites are part of the "Main Frankish Loess Region." The bedrock consists of upper shell limestone (Rinklebe and Makeschin, 2003). A forest and an agricultural site that have been used as such for more than 190 years were selected for this study. The forest site (P3) consists of a deciduous forest (wild ginger-beech-oak-forest; *Galio-Carpinetum asaretosum*) in municipal ownership, where sustainable forestry with the use of single boles is practiced (Rinklebe and Makeschin, 2003). The forest is multilayer structured with deadwood. The plant population is considered as near-natural. On the agricultural site (P4), a conventional close crop rotation is practiced, which is interrupted through root and tuber crops. During soil sampling,

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