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Research Article

Mobility of Iron-Cyanide Complexes in a Humic Topsoil under Varying Redox Conditions

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The potentially toxic Fe-CN complexes ferricyanide, $[\mathrm{Fe^{III}(CN)_6}]^{3-}$, and ferrocyanide, $[\mathrm{Fe^{II}(CN)_6}]^{4-}$, undergo a variety of redox processes in soil, which affect their mobility. We carried out microcosm experiments with suspensions of a humic topsoil (pH 5.3; C_{org} 107 g kg^{-1}) to which we added ferricyanide (20 mg l^{-1}). We varied the redox potential (E_H) from −280 to 580 mV by using O_2, N_2 and glucose. The decrease of E_H led to decreasing concentrations of Fe-CN complexes and partial reductive dissolution of (hydrous) Fe and Mn oxides. The dynamics of aqueous Fe-CN concentrations was characterized by decreasing concentrations when the pH rose and the E_H dropped. We attribute these dependencies to adsorption on organic surfaces, for which such a pH/E_H behavior has been shown previously. Adsorption was reversible, because when the pH and E_H changed into the opposite direction, desorption occurred. This study demonstrates the possible impact of soil organic matter on the fate of Fe-CN complexes in soil.

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1. Introduction

As a consequence of anthropogenic inputs, the Fe-CN complexes ferrocyanide, $[\mathrm{Fe^{II}(CN)_6}]^{4-}$, and ferricyanide, $[\mathrm{Fe^{III}(CN)_6}]^{3-}$, may be present in soil. Their occurrence is mainly due to the deposition of wastes originating from industrial processes such as coal gasification, pig Fe production, or paper recycling [1]. In these wastes, Fe-CN complexes are mainly present as sparingly soluble compounds, for example, $\mathrm{Fe_4[Fe^{II}(CN)_6]_3}$, $\mathrm{KFe[Fe^{II}(CN)_6]}$, or $\mathrm{K_2Zn_3[Fe^{II}(CN)_6]_2}$ [2]. A further source is road salt, to which $\mathrm{Na_4[Fe^{II}(CN)_6]}$ or $\mathrm{Fe_4[Fe^{II}(CN)_6]_3}$ are added as an anticaking agent [3]. The solubility of $\mathrm{Fe_4[Fe^{II}(CN)_6]_3}$, $\mathrm{KFe[Fe^{II}(CN)_6]}$, and $\mathrm{K_2Zn_3[Fe^{II}(CN)_6]_2}$ increases under neutral and alkaline conditions resulting in a release of Fe-CN complexes into the soil solution [4]. The presence of dissolved Fe-CN complexes is an environmental concern because they tend to decompose to extremely toxic-free CN ($\mathrm{HCN_{g,aq}}$ and $\mathrm{CN^-_{aq}}$) when irradiated by daylight [5].

Fe-CN complexes undergo a variety of processes in soil that affect their speciation and mobility. First, they form a redox couple [6]

$$[\mathrm{Fe^{II}(CN)_6}]^{4-} \longleftrightarrow [\mathrm{Fe^{III}(CN)_6}]^{3-} + e^-, \qquad E_H = 356\,\mathrm{mV}, \tag{1}$$

where E_H is the redox potential referred to the standard H_2 electrode. Birnessite, δ-$\mathrm{MnO_2}$, rapidly oxidizes $[\mathrm{Fe^{II}(CN)_6}]^{4-}$ to $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ [7], whereas the oxidation by O_2 is slow [8]. Second, dissolution and precipitation of compounds such as $\mathrm{Fe_4[Fe^{II}(CN)_6]_3}$ and Mn-containing hexacyanoferrates govern the concentrations of aqueous Fe-CN complexes, especially under reducing conditions [4, 9–11]. Third, Fe-CN complexes adsorb on soil minerals such as goethite [8] and amorphous Al hydroxides [12]. However, the mechanism, by which Fe-CN complexes are sorbed, differs between the type of the complex and that of the mineral. Ferrocyanide forms an $\mathrm{Fe_4[Fe^{II}(CN)_6]_3}$-like layer on the goethite surface, whereas $[\mathrm{Fe^{III}(CN)_6}]^{3-}$ forms monodentate inner-sphere complexes on it [8, 13]. Both complexes weakly adsorb on γ-$\mathrm{Al_2O_3}$ as outer-sphere complexes [12]. The pH affects adsorption and precipitation because both increase at decreasing pH.

In neutral and humic soils, additional processes may occur. Adsorption of both complexes in Fluvisols is enhanced by soil organic matter (SOM) because the soils did not adsorb the complexes after destruction of SOM [14]. Reduction of $[Fe^{III}(CN)_6]^{3-}$ by SOM and subsequent precipitation of $Fe_4[Fe^{II}(CN)_6]_3$ occurred during the transport in a humic topsoil [15]. Ferricyanide is reduced by humic acids, and afterwards $[Fe^{II}(CN)_6]^{4-}$ is associated with them [16]. Additionally, $[Fe^{III}(CN)_6]^{3-}$ oxidizes simple organic compounds such as phenols, alcohols, aldehydes, and ketones [17]. In neutral and slightly acidic soils, precipitation of Mn hexacyanoferrates dominates the mobility of Fe-CN complexes [9, 11]. Small amounts of Fe-CN complexes are adsorbed by SOM in the form of reduced $[Fe^{II}(CN)_6]^{4-}$; pyrogenic organic matter such as charred straw also adsorbs $[Fe^{II}(CN)_6]^{4-}$ [11].

These studies suggest an important influence of SOM on the mobility and speciation of Fe-CN complexes. Apparently, redox reactions are involved in interactions between the soil mineral phase, SOM, and Fe-CN complexes. However, these interactions have not been studied yet under varying redox conditions. Therefore, we investigated the fate of Fe-CN complexes in suspensions of an uncontaminated humic topsoil to which $[Fe^{III}(CN)_6]^{3-}$ was added and varied the redox potential. Information on previously unknown processes occurring in humic topsoils under varying redox conditions improves the overall knowledge on the fate of Fe-CN complexes in soil.

2. Materials and Methods

2.1. Soils and Soil Characterization. The soil sample under study is the A horizon of an arable Stagnic Fluvisol located in the floodplain of the river Oder in Germany (52° 43′N, 14° 13′E). The sample was dried at 333 K, sieved to <2 mm, and homogenized. We determined the soil texture by sieving and the pipette method [18]. Soil pH was measured potentiometrically in 0.01 M $CaCl_2$ with a soil:solution ratio of 1:2.5. The contents of crystalline Fe oxides as well as of amorphous Fe and Mn oxides were determined by extraction with dithionite-citrate and oxalate solutions, respectively [19, 20]. We analyzed total C by oxidation at 1223 K and heat conductivity detection with a Vario EL elemental analyzer (Elementar Analysensysteme, Hanau, Germany). We checked the presence of carbonate, but none was detected. Black carbon (BC) is one of the major aromatic compounds present in soil and is a product of incomplete combustion of biomass [21]. The BC contents were determined as described in detail by Brodowski et al. [22]. Briefly, BC is oxidized to benzene polycarboxylic acids (BPCAs) by concentrated HNO_3, cleaned, derivatized to trimethylsilyl derivatives, and subsequently analyzed by gas chromatography (Hewlett Packard 6890; Hewlett Packard, Waldbronn, Germany) with flame-ionization detection. The BPCA carbon yields were multiplied with a correction factor of 2.27 to obtain BC contents [23]. This factor provides a conservative minimum estimate of BC contents in soil [22].

2.2. Microcosm Experiments. The microcosms (Figure 1) were made of glass with the dimensions 28 cm inner diameter at the top and 21 cm inner height. In two experiments (no. 1 and no. 2), we suspended 1.2 kg soil in 6 L demineralized H_2O. The suspensions were stirred to prevent sedimentation. The microcosms were wrapped with Al foil to exclude daylight. Six days after suspending the soil (no. 1) and one day after suspending the soil (no. 2), a $K_3[Fe^{III}(CN)_6]$ solution was added to obtain an initial concentration of 20 mg $[Fe^{III}(CN)_6]^{3-} l^{-1}$. Redox potentials and pH were continuously measured in the suspensions with Pt electrodes and an Ag/AgCl reference system (EMC 33, Meinsberg, Ziegra-Knobelsdorf, Germany) and EGA 153 pH electrodes (Meinsberg, Ziegra-Knobelsdorf, Germany), respectively. The measured redox potentials were related to the potential of the standard H_2 electrode, for example, at 293 K, 207 mV were added. Temperature was continuously recorded. In the following, redox potentials are given as the potential of the standard H_2 electrode, E_H. We aimed to decrease the redox potential in the experiments by flushing the suspensions with N_2 at a flow rate of 80 ml min^{-1} and additions of 2 (no. 1) and 5 g (no. 2) glucose to stimulate microbial activity and to induce reducing conditions. The two experiments also differed in the numbers and the moments of the glucose additions. At the end of the experiments, O_2 was flushed through the suspensions to reaerate. In intervals of 24 or 48 hours, about 20 ml were taken from the suspensions with a syringe and a tube through the sampling port. These samples were filtered (0.45 μm cellulose-nitrate filter) and analyzed for Fe, Mn, and total CN. We did not add acid or base to vary the pH. The experiments lasted 56 (no. 2) and 103 (no. 1) days. In experiment (no. 2), we accelerated the establishment of reducing conditions, whereas we retarded it with (no. 1). After the microcosm experiments, aliquots of the suspensions were filtered, the filters were air dried and total CN was extracted from soil.

2.3. Analyses and Interpretation. Fe and Mn concentrations in the filtrates as well as in the dithionite-citrate and oxalate extracts were determined by induced coupled plasma atomic emission spectrometry using a CIROS^{CCD} instrument (Spectro Analytical Instruments, Kleve, Germany). Additionally, the concentrations of other major cations in the filtrates were measured with the same instrument and concentrations of major inorganic anions by ion chromatography with conductivity detection (Dionex DX 500, Idstein, Germany). Total CN in the filtrates was analyzed by acid distillation (Micro-Distiller, Eppendorf-Netheler-Hinz, Hamburg, Germany) and subsequent spectrophotometrical detection at 600 nm (detection limit 1 μg l^{-1}; Lambda 2, Perkin Elmer, Überlingen, Germany) [24]. We checked the presence of free CN, but none was detected. Total CN present in soil after the experiments was extracted using 1 M NaOH in duplicate [24] and subsequently determined as in the filtrate in duplicate.

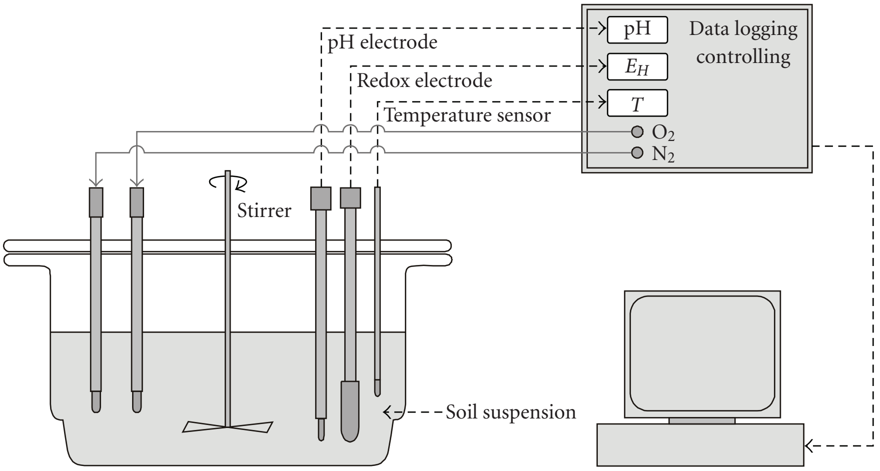


Figure 1: Scheme of a microcosm and control device.

Partially, we interpreted the data with the geochemical speciation program ECOSAT 4.7 [25] using E_H, pH and the concentrations of all cations and anions analyzed to check possible precipitation of $Fe_4[Fe^{II}(CN)_6]_3$, $Mn_2[Fe^{II}(CN)_6]$, and $Mn_3[Fe^{III}(CN)_6]$. The solubility constants of the compounds are as follows: $\lg K_{sol} = -84.5$ ($Fe_4[Fe^{II}(CN)_6]_3$; [4]), $\lg K_{sol} = -25$ ($Mn_2[Fe^{II}(CN)_6]$), and $\lg K_{sol} = -27$ ($Mn_3[Fe^{III}(CN)_6]_2$; [9]).

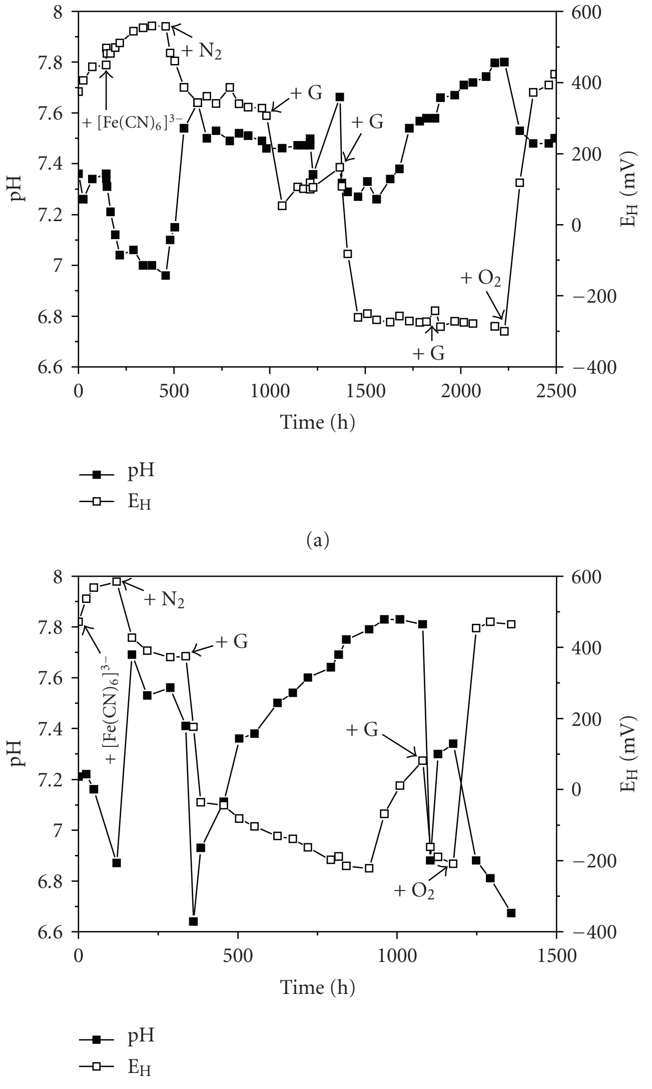
3. Results and Discussion

3.1. Soil Characteristics. The soil has a sandy-clayey texture ($563\,g\,kg^{-1}$ sand, $124\,g\,kg^{-1}$ silt, $313\,g\,kg^{-1}$ clay) and is moderately acidic (pH 5.3 in $CaCl_2$). It contains $107\,g\,kg^{-1}$ organic C of which 10.3% is BC that has the potential to interact with $[Fe^{III}(CN)_6]^{3-}$ [11]. Another important feature of the soil is that it contains Fe and Mn oxides, which may dissolve under reducing conditions (dithionite-extractable Fe $9870\,mg\,kg^{-1}$, oxalate-extractable Fe and Mn 7800 and $1650\,mg\,kg^{-1}$, resp.).

3.2. Microcosm Experiments. At the beginning of the experiments, the redox conditions were oxidizing (Figures 2(a) and 2(b)), and flushing the soil suspensions with N_2 led to a decrease of E_H. Under the N_2 atmosphere, an almost constant E_H in the range of 340 to 370 mV was achieved in both experiments. The first addition of glucose induced a strong decrease of E_H to approximately 100 mV (no. 1) and even negative potentials (no. 2). The difference between the experiments is caused by the varying amount of glucose added. Negative redox potentials with (no. 1) were achieved later, after a further addition of glucose. The decrease in E_H is connected with an increase in pH revealing their well-known reciprocal relation when the E_H varies. The initial pH measured in both experiments is higher than the soil pH determined in $CaCl_2$. This is caused by the stronger release of Al^{3+} from soil in the presence of $CaCl_2$ compared to the release from soil suspended in water as in the microcosm experiments. The establishment of reducing conditions was accompanied with the disappearance of NO_3^- ($c < 0.1\,mg\,l^{-1}$) in both experiments after the E_H had dropped to <350 mV. Previously, $40 \pm 5\,mg\,NO_3^-\,l^{-1}$ were present in each experiment. The main inorganic cations were Ca^{2+}($150–270\,mg\,l^{-1}$) and Mg^{2+} ($4–10\,mg\,l^{-1}$), the main anion was SO_4^{2-} ($100–140\,mg\,l^{-1}$). The concentrations of dissolved Mn accompanied with additions of glucose that induced a drop in E_H (Figures 3(a), 3(b)) leading to reductive dissolution of (hydrous) Mn oxides in soil. Reductive dissolution of (hydrous) Fe oxides occurred at very low redox potentials only (after 1860 hours with no. 1) as shown by the increase of the aqueous Fe concentration to $3.5\,mg\,l^{-1}$. The release of Fe and Mn ions induced by dissolution of oxides governed the mobility and solubility of Fe-cyanide complexes in a subsoil low in organic C by precipitation of sparingly soluble phases such as $Fe_4[Fe^{II}(CN)_6]_3$ and $Mn_2[Fe^{II}(CN)_6]$ [10]. Similarly, precipitation of $Mn_2[Fe^{II}(CN)_6]$ was the main process of $[Fe^{III}(CN)_6]^{3-}$ added to humic and neutral soils [11].

After decreasing E_H due to the N_2 atmosphere and subsequent additions of glucose, the concentrations of Fe-CN complexes decreased in both experiments (Figures 4(a), 4(b)). The decrease in experiment no. 1 was retarded compared to (no. 2), similar to the less pronounced decrease in E_H. Qualitatively, the $[Fe^{III}(CN)_6]^{3-}$ added is reduced to $[Fe^{II}(CN)_6]^{4-}$ during the establishment of reducing conditions as shown by direct measurements and geochemical calculations [10]. The $[Fe^{II}(CN)_6]^{4-}$ formed is completely dissociated because all pK_a values are <4.19 [26], which is at least 2 pH units lower than the pH during the experiments (Figures 2(a), 2(b)).

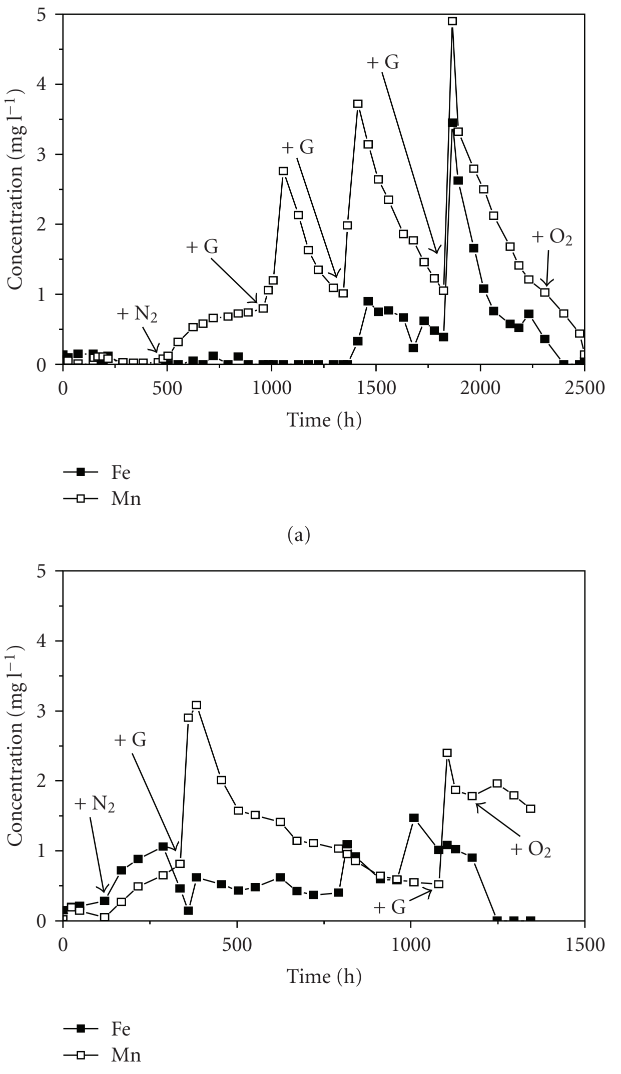
After 1200 hours, the Fe-CN concentration in experiment (no. 1) increased from 14.7 to $16.7\,mg\,l^{-1}$, while the pH slightly decreased and the E_H increased (Figures 2(a), 4(a)). Subsequently, under more reduced conditions, the Fe-CN concentrations continuously decreased to approximately $2.5\,mg\,l^{-1}$. The course of Fe-CN concentrations in experiment (no. 2) revealed similar features: after a steep decrease



(a)

(b)

FIGURE 2: Redox potentials and pH during the microcosm experiments (a) no. 1 and (b) no. 2. “+$[Fe(CN)_6]^{3-}$” denotes addition of ferricyanide, “+ G” denotes additions of glucose, “+ N_2” and “+ O_2” denote the gas purged through the suspensions.



(a)

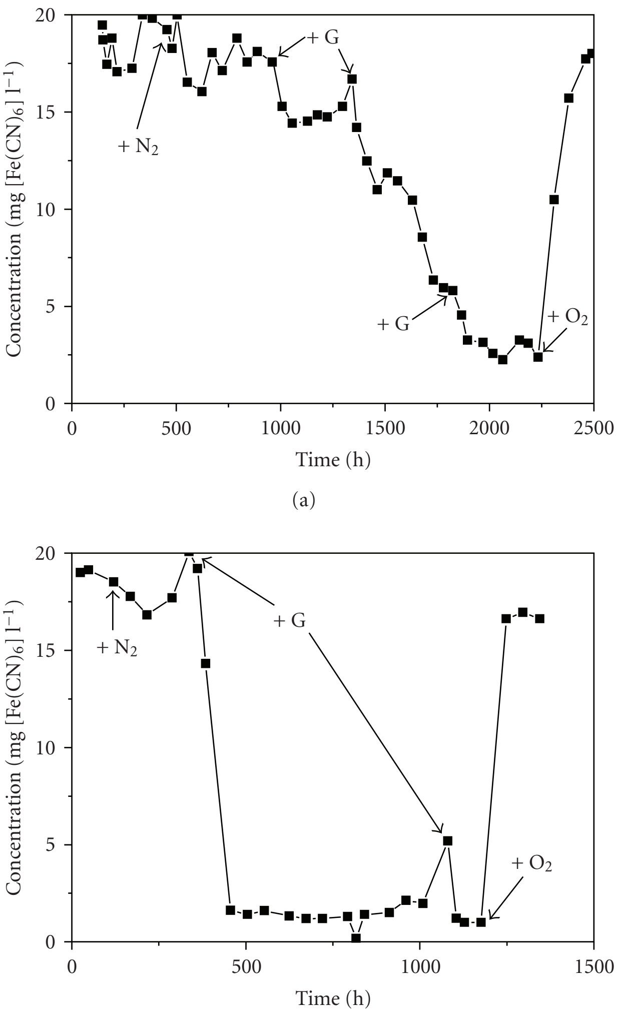
(b)

FIGURE 3: Fe and Mn concentrations during the microcosm experiments (a) no. 1 and (b) no. 2. “+ G” denotes additions of glucose, “+ N_2” and “+ O_2” denote the gas purged through the suspensions.

to 1.5 ± 0.5 mg l^{-1}, the Fe-CN concentration increased to 5.2 mg l^{-1}. Simultaneously, theE_H increased to 80 mV and the pH decreased (Figure 2(b)). After reaeration (E_H > 400 mV), the level of the initial concentration was almost equalled with 18.1 (no. 1) and 17 mg l^{-1} (no. 2) while the pH dropped to 7.5 (no. 1) and 6.6 (no. 2). Conversely, decreasing concentrations were linked with increasing pH during the experiments. In both experiments, the sum of the amounts of CN extracted from soil after the experiments and of the aqueous species equalled the amount initially added. This indicates that microbial degradation of Fe-CN complexes has not occurred.

The course of Fe-CN concentrations with an increase under subsequent oxidizing conditions, the low Fe concentrations as well as geochemical calculations clearly indicated that precipitation of $Fe_4[Fe^{II}(CN)_6]_3$ cannot have occurred. Precipitation of Mn hexacyanoferrates as the main process removing Fe-CN complexes from solution is also very questionable because (i) the presence of Mn ions is necessary for precipitation, but their concentrations are rather low (Figures 3(a), 3(b)), (ii) Mn hexacyanoferrates once precipitated are stable under subsequent oxidizing conditions [9, 10], which contradicts the mobilization of Fe-CN complexes observed after reaeration, (iii) the pH dependency of the dissolution of $Mn_2[Fe^{II}(CN)_6]$ is weak in the range at the end of the experiments (6.9 to 7.8) as checked by geochemical calculations, and (iv) the pH during the experiments (up to 7.8) generally prevents precipitation.

Furthermore, Fe-CN complexes possibly adsorbed on mineral surfaces were not desorbed when the pH decreased



(a)

(b)

Figure 4: Total Fe-CN complex concentrations during the microcosm experiments (a) no. 1 and (b) no. 2. "+ G" denotes additions of glucose, "+ N_2" and "+ O_2" denote the gas purged through the suspensions.

from 7.8 to 7.5 and from 7.3 to 6.6 as found here after reaeration because desorption rises with growing pH. Therefore, we found the rather surprising situation that decreasing pH and increasing E_H enhanced the mobility of Fe-CN complexes in soil. Theoretically, a positive effect of increasing pH on adsorption on mineral surfaces is possible when the pH increases to the pK_a of the conjugate acid of an anion adsorbing on a mineral surface [27]. However, as pointed out before, the pK_a values of ferrocyanic acid are much lower than the pH during the experiments so that adsorption on the mineral soil phase cannot have determined the dynamics of Fe-CN complexes.

The previous discussion points up that any process that includes inorganic soil minerals cannot explain the dynamics of the Fe-CN complex concentrations observed. Therefore, interactions with organic surfaces must be considered for a comprehensive explanation. Adsorption of $[Fe^{III}(CN)_6]^{3-}$ on organic surfaces occurred by two different pathways [11]. First, it weakly adsorbed on oxidized functional groups such as carboxyls, carbonyls, and alcohols under neutral conditions by hydrogen bonds. Then, $[Fe^{III}(CN)_6]^{3-}$ underwent partial reduction to $[Fe^{II}(CN)_6]^{4-}$ as inferred from Fourier transform infrared (FTIR) spectroscopy and by voltammetry [11, 16]. However, this type of adsorption should be unimportant here because under oxidizing and neutral conditions at the beginning of experiment (no. 2), the Fe-CN concentrations did not decrease. Second, $[Fe^{III}(CN)_6]^{3-}$ was adsorbed by phenols and was reduced to $[Fe^{II}(CN)_6]^{4-}$ [11]. Phenolic species are present in SOM, especially in BC. Ferrocyanide formed inner-sphere complexes with the organic matrix as again inferred from FTIR spectroscopy. Alkaline and reducing conditions enhanced reduction and adsorption [11]. Thus, $[Fe^{II}(CN)_6]^{4-}$ previously adsorbed on phenolic species such as quinones is released into solution when the E_H rises or the pH drops, which accords with the dynamics of Fe-CN complexes found here in the experiments. At the beginning of experiment (no. 2), oxidizing conditions prevailed and the pH decreased. Consequently, the initial Fe-CN concentration remained almost unaffected. The same geochemical milieu applied to the end of both experiments, E_H increased, and the pH dropped. This was followed by remobilization of adsorbed Fe-CN complexes (Figures 4(a), 4(b)). The mobility of aqueous Fe-CN complexes depended on pH and E_H as we would expect when they interact with quinone species. Therefore, we assume that these aromatic species are the most important reactants in the soil matrix with regard to Fe-CN complexes and that the observed dynamics of Fe-CN complexes in this soil was most likely and to a large proportion governed by interactions with SOM. The soil contains large amounts of Fe oxides, but the effect of pH on the mobility of Fe-CN complexes in the microcosm experiments documents that adsorption on their surfaces seems to be marginal. The prevailing alkaline pH in this experiment limits adsorption on mineral surfaces and excludes precipitation. However, Fe-CN complexes are not entirely mobile under alkaline conditions as long as organic adsorbents are present, and reducing conditions are necessary to induce these adsorptive processes.

4. Conclusions and Outlook

The mobility of Fe-CN complexes may be decreased in soil even under alkaline conditions that minimize sorption processes such as precipitation of sparingly soluble Fe-CN compounds and adsorption on soil minerals. In this study, we attribute the reduced mobility to adsorption on organic surfaces such as quinone groups notably present in BC. However, Fe-CN adsorption on organic surfaces is rather weak and completely reversible. Further research is essential to study and to qualify further possible organic adsorbents and to quantify their bonding strength in order to implement interactions with organic matter in a comprehensive geochemical model on the fate of Fe-CN complexes in soil.

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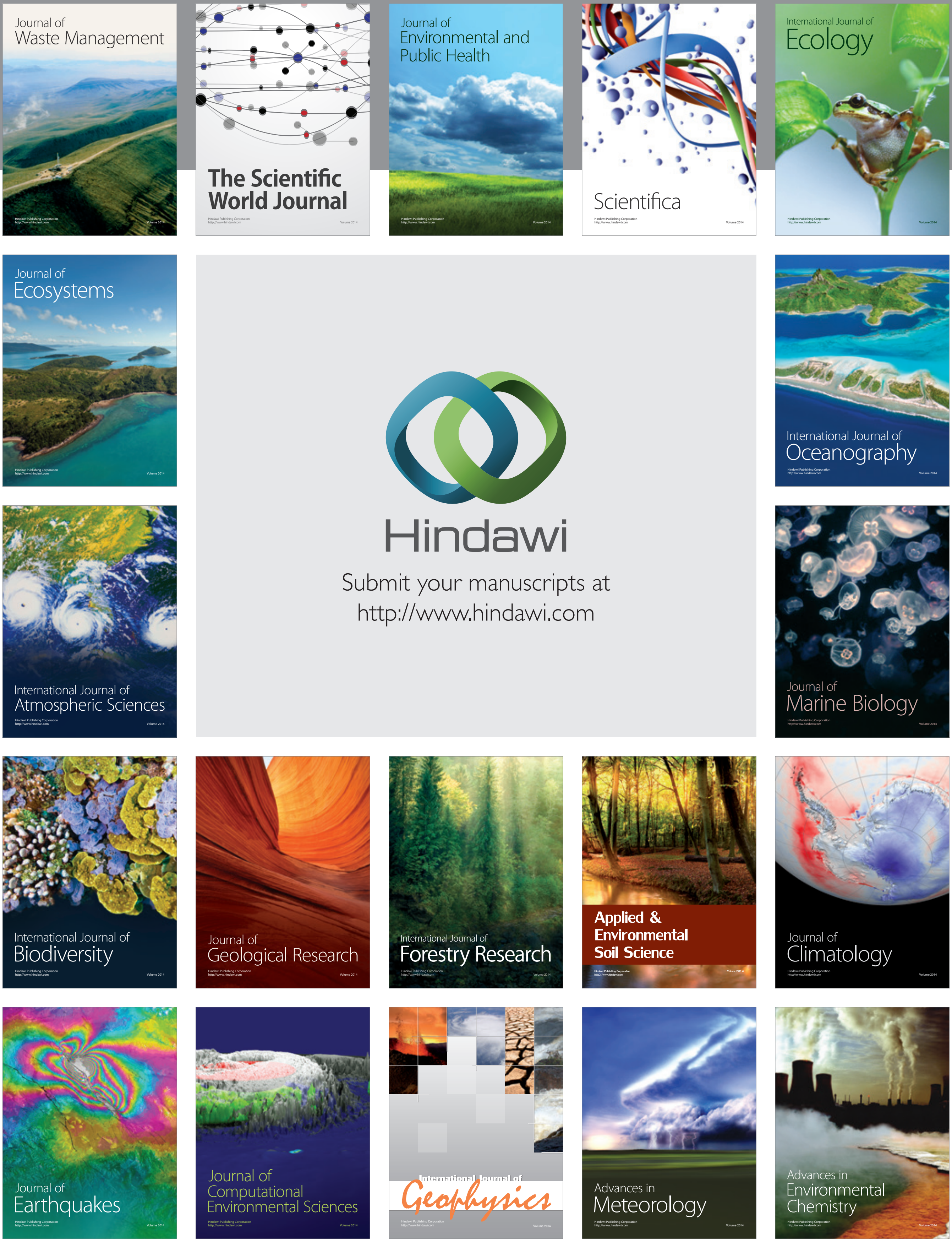
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