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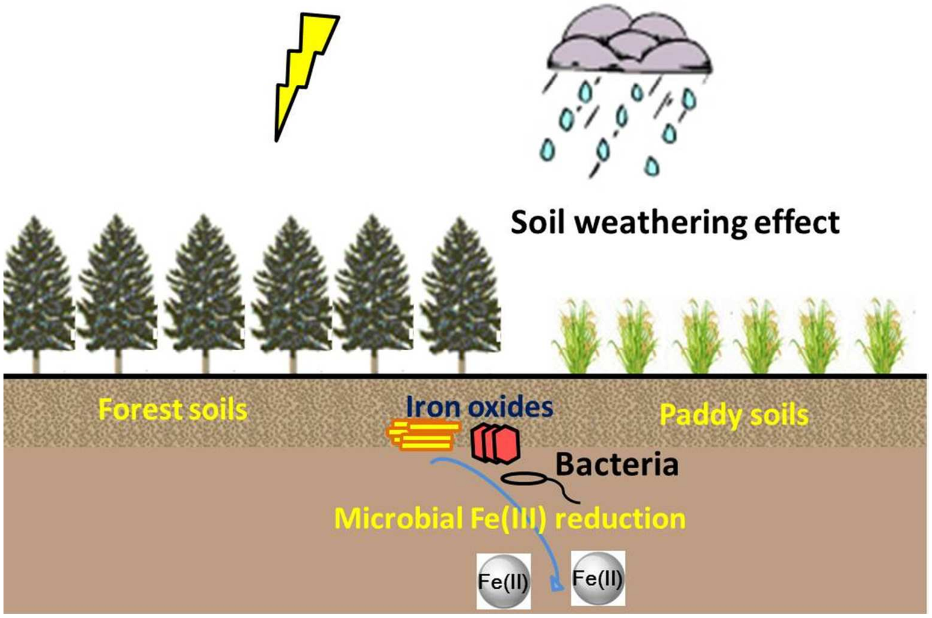

Geochemical and Anthropogenic Constraints on the Microbial Reduction of Fe(III) in Iron-rich Soils.

Environmental impact

Soil Fe(II) species produced from iron(III) reduction in soil geochemical processes are crucial to the behavior and fate of soil contaminants. This work studied the geochemical and anthropogenic constraints on the microbial reduction of Fe(III) by evaluating the possible Fe(II) production in soils. Here we found that human activities, such as the tillage of soils, can accelerate Fe(III) reduction processes, and more importantly, the Fe(III) reduction rates were highly negatively correlated with the soil weathering degree. The goal of this work was to provide the key factors of the soil Fe(III) reduction efficiency to scientists, site managers, and regulators for improved decision-making strategies regarding the soil oxidation-reduction potential with respect to the extent of Fe(III) reduction capacity.

Influence of geochemical properties and land-use types on the microbial reduction of Fe(III) in subtropical soils

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Abstract

Microbial Fe(III) reduction significantly impacts the geochemical processes and the composition of most subsurface soils. However, up to now, the factors influencing the efficiency of Fe(III) reduction in soils were not fully described. In this study, soil Fe(III) reduction processes related to geochemical properties and land use types were systematically investigated using iron-rich soils. The results showed that microbial Fe(III) reduction processes were efficient and their rates varied significantly in the different types of soils. Fe(III) reduction rates were 1.1-5.6 times in the soil with glucose as much as that without glucose. Furthermore, Fe(III) reduction rates were similar in the soils from the same parent materials, while they were highest in the soils developed from sediments with the mean rate of 1.87 mM d^{-1} when with glucose. In addition, the Fe(III) reduction rates, reaching 0.99 and 0.59 mM d^{-1} averagely when with and without glucose, were higher in the paddy soils affected heavily by human activities than those in the forest soils (average rates of 0.38 and 0.15 mM d^{-1} when with and without glucose). All the soil weathering indices were linearly correlated with Fe(III) reduction rates, even though the reduction of iron in soils with higher weathering degrees were partly inhibited by the higher soil protonation trend and less available iron reduction sites in the soils, so as to obtain lower reduction rates. These results clearly illustrated the soil Fe(III) reduction rates were greatly dependent on the soil geochemical properties and land use types and helped define what soil types exhibited similar degrees of Fe(III) reduction under field conditions.

Abbreviations: DCB, dithionite-citrate-bicarbonate; ST, soil taxonomy; CST, Chinese soil taxonomy; TOC, total organic carbon; HSD, honest significant difference; PCA, principle component analysis; CWI, chemical weathering indices; PA, potassium-sodium-calcium to aluminum; BA, base to alumina; V, Vogt's residual Index; CIA, chemical index of alteration; WIP, weathering index of Parker; CIW, chemical index of weathering; MWPI, modified weathering potential index.

1. Introduction

Iron cycling on the Earth's surface is one of the most important geochemical processes for enhancing the bioavailability of iron in soil biochemistry [1]. The reduction of Fe(III) to Fe(II) is a key step to influence the geochemical cycling of iron [2]. The reduction, which occurred under oxygen depleted environments and involved complex geochemical and microbial reactions, was environmentally significant on the micro-, macro-, and global scales [3, 4]. The conversion of Fe(III) to Fe(II) can change the mobility and bioaccessibility of soil nutrients, such as phosphate and nitrate, which can cause further impacts on both microbial activities and plant growth [5, 6]. Additionally, it was well known that the reductive transformation of Fe(III) decreased methanogenic processes and CH_4 emissions from soil, which in turn might reduce the pace of global warming [7]. Moreover, this reductive process may greatly impact the transport and the fate of both soil organic pollutants through reductive transformation [8-10], and soil heavy metal pollutants through stabilization during the formation of secondary iron minerals, which occurred as a result of the iron reduction products of Fe(II) species [11, 12].

The geochemical constraints for soil Fe(III) reduction have been paid significant attention [13]. The pool of different Fe(III) reducibilities in soils may highly determine the amount of reduced

Fe(II) in the soil [14]. Water soluble Fe(III) and exchangeable Fe(III), amorphous Fe(III) oxides, and crystalline Fe(III) oxides, in the same order, decreased Fe(III) reduction susceptibilities [15, 16]. In addition, the biological properties of soil, such as enzymes, soil respiration, soil biomass nitrogen and carbon, played crucial roles in the iron cycle [17]. Soil weathering from rocks and minerals were the key process to form the soil geochemical properties. Therefore, weathering degree of soils was considered to act as an integrated geochemical property and also as one of the most important of geochemical properties of soils [18]. Many basic soil properties, such as mineral composition, water content, and particle size distribution, were thought to be related to the weathering degree of soil [18]. However, until now, few studies of the correlation between soil geochemical properties and the anaerobic reduction of Fe(III) have been reported, and the key geochemical factors that affected the reduction of Fe(III) remained unknown [19, 20].

Soil is a complex system of minerals, organic material, water, gasses, and living organisms, and many factors can regulate the efficiency and extent of soil Fe(III) reduction [1, 14]. For example, in addition to the geochemical factors of soil [13], land use types of soils greatly affected the efficiency of Fe(III) reduction by altering the properties of soils [21] due to human activities on soils. Land-use processes of soils had the complex effects on soil properties [22, 23], including the changes of the physical, chemical, biological, and biochemical properties of soil [24]. Generally, among the different soil land-use types, forest soils were subject to fewer disturbances than agricultural soils [25] because agricultural soils, which had suffered intensive tillage, including plowing and/or harrowing, were considered to be the most degraded system of land use [26]. In tillage soils, plant residues were physically split and mixed with the soil, aggregates were disrupted, and the temperature, aeration, and biological activity of soil were increased [27]. Therefore, land use types apparently affected the Fe(III) reduction processes in the soil [28].

In this study, we aimed to fill the gap between geochemical index and Fe(III) reduction in soils by bridging key soil properties. To achieve this objective, we investigated the impact of soil geochemical and anthropogenic properties, including soil parent materials, soil land use types, and soil weathering degree, on the Fe(III) reduction efficiencies of a vast array of iron-rich soils throughout Guangdong province, China, located in a subtropical region. Our goal was to elucidate the key factors that determined soil Fe(III) reduction efficiency and then to provide this information to scientists, site managers, and regulators for improved decision-making strategies regarding the soil oxidation-reduction potential with respect to the extent of Fe(III) reduction capacity.

2. Materials and methods

2.1 Chemicals and Solutions

1,4-Piperizinebis (ethane-sulfonic) acid (PIPES) was purchased from Advanced Technology Industrial Co., Ltd., Hong Kong. Glucose was from Guangzhou Chemical Industry, Guangzhou, China. All commercial chemicals were of analytical grade and used as received. Deoxygenated deionized water (DDW) was prepared by deoxygenating ultra-pure water (18 MΩ cm, Easy Pure’II RF/UV, USA) with nitrogen for at least 2 h and then was stored in an anaerobic chamber before use in the preparation of aqueous solutions, which included acidified ammonium oxalate buffer, alkaline sodium pyrophosphate, and dithionite-citrate-bicarbonate (DCB).

2.2 Soil sampling and characterization

Twenty-one soil samples were collected from sites throughout Guangdong province, China (Fig. 1). Detailed information, including the parent materials, soil taxonomy (ST), Chinese soil taxonomy (CST), and land-use types, was summarized in Table 1. Each soil sample was taken from a soil profile at a depth of 5-15 cm and then was stored in plastic bags. After transportation to the lab, the samples were air dried, and then disaggregated by gentle grinding using a mortar and pestle, and sieved to provide the soil fraction with the diameter < 2 mm for use in the experiments.

[Fig. 1]

[Table 1]

Table 2 summarized the physicochemical properties of the soils. Amorphous Fe (A-Fe), complexed Fe (C-Fe), and DCB-Fe forms were extracted using three different extractions of acidified ammonium oxalate buffer solution at pH 3.0, alkaline sodium pyrophosphate at pH 8.5, and DCB, respectively [29]. The Fe concentrations were quantified using atomic absorption spectrometry (AAS).

The total Fe, Mg, K, Na and Ca contents of the soils were analyzed by AAS after the soils were digested with perchloric acid and hydrofluoric acid. The total Al content was measured using inductively coupled plasma atomic emission spectroscopy (ICP-AES) after digestion with perchloric acid and hydrofluoric acid. Detailed analysis procedures for the total metal contents were provided in Pansu and Gautheyrou [29]. The total Fe, Mg, Ca, Al, K and Na contents in the soils were presented in mol/kg soil as Fe_2O_3, MgO, CaO, Al_2O_3, K_2O, and Na_2O, respectively. The total organic carbon (TOC) contents in the soils were determined using a Leco C230 carbon analyzer (St. Joseph, MI, USA) after the soils were washed with 10% HCl to remove inorganic carbon and then were dried at 60 ^{o}C overnight. The SiO_2 contents in the soils were detected using the method of sodium carbonate fusion [30].

[Table 2]

2.3 Microcosm set-up for microbial iron(III) reduction in soils

The microcosm experiments were conducted in aluminum-sealed amber culture bottles under anaerobic conditions. Thirty mM PIPES solution buffered at pH 7.0 ± 0.5 was used as the reaction medium after sterilization by autoclaving and cooling under a constant stream of O_2-free N_2. Each microcosm was added 10 mL of reaction suspension and 0.5 g of soil with or without 10 mM of glucose. After capping the mixture with butyl rubber stoppers and mixing the solution to uniformity, the vials containing the reaction suspensions were incubated at 25 ± 1°C in the dark in a Bactron Anaerobic/Environment Chamber II (Shellab, Shedon Manufacturing, Inc., Cornelius, OR, USA).

At the specified intervals in 40 days, samples were taken from the vials. The HCl extractable Fe(II) was extracted with 0.5 M HCl for 1.5 h [16] and then was centrifuged at 1980 g for 10 min. The supernatant was collected through a 0.22-µm syringe filter and then Fe(II) was analyzed using the 1,10-phenanthroline colorimetric method by a UV-Vis spectrophotometer (UV-Vis TU-1800, Purkinje General, Beijing). The two different treatment methods without the addition of carbon source (μ_1) and with the addition of 10 mM glucose (μ_2) for Fe(III) reductions were studied. Each experiment was conducted in triplicate and included blanks, and analytical determinations were performed in duplicate.

2.4 Statistical analyses

All the soil properties were measured according to the dry soil samples. Multiple comparisons of the contents of TOC, complexed Fe, amorphous Fe, DCB Fe, Fe_2O_3, MgO, CaO, SiO_2, Al_2O_3, K_2O, and Na_2O were performed with Tukey's honest significant difference (HSD) test using SPSS 11.5 (SPSS, Inc., US). To determine how the weathering indices and the soil parameters could account for the variation in Fe(III) reduction rates in the soils, principle component analysis (PCA) was first conducted with ADE-4.0 to identify the possible co-factors and then a linear regression procedure was applied between the rates of the Fe(III) reduction and weathering indices. Final regressed correlations were developed using simple, straight-forward stepwise multiple regression analyses with SPSS.

3. Results

3.1 Anoxic Fe(III) reduction in the soils

Fe(III) reduction processes in the 21 soils with or without glucose as carbon source were shown in Fig. 2. The model derived from a microbial logistic growth equation can well fit the Fe(III) reduction processes in the soil systems [31, 32]. This model [33] was shown as the follows:

$$C_t = A/(1+Be^{-kt}) \qquad (1)$$

$$\mu = 0.25\,A \times k \qquad (2)$$

where t is the reaction time, C_t is the Fe(II) concentration at time t, A is the maximum fraction of biotransformable Fe(II), B is a constant, k is the constant of the rate of Fe(II) formation, and μ is the apparent reduction rate. The obtained values of μ and the coefficient constant R^2 from the modified microbial logistic growth equation were presented in Table 3.

[Fig. 2]

[Table 3]

The fractions of Fe(III) in all the soils underwent steady reduction to form HCl-extractable Fe(II). As shown in Fig. 2, the concentrations of HCl-extractable Fe(II) in the soils were initially formed quickly and then slowly. Glucose represented the possible carbon source and can be utilized as the biostimulation methods for the activation of soil microorganisms [9], which consequently accelerated the microbial reduction of Fe(III). The Fe(III) reduction rates in different soils also varied greatly. The apparent reduction rate (μ_1) for Fe(III) without glucose varied significantly among the 21 soils (Table 3), ranging from 0.09 mM• d^{-1} (in G-A) to 1.12 mM• d^{-1} (in S-A3) in the unamended treatments. With glucose in the incubation system, the reduction rate of Fe(III) was significantly increased in all the soils, reaching nearly twice as many as those without glucose (Fig. 3A).

[Fig. 3]

3.2 Effect of land-use types on the reduction rates of soil Fe(III)

The soils from two land use types (paddy field and forest) were studied in this work (Table 1). As shown in Fig. 3B, the average Fe(III) reduction rates in the paddy soils were much higher than those in the forest soils under both of the treatments, because the forest land received little tillage activity, while the paddy fields have suffered significant tillage activity, which strongly influenced soil properties [28]. Except for G-A and B-F, the rest of nineteen soils fell into three soil orders, i.e., Cambosols, Anthrosols, and Ferrosols (Table 1). Anthrosol is a type of soil formed or heavily modified by long-term human activity like irrigation, the addition of organic waste or wet-field cultivation, while cambosol and ferrosol are types of soil rarely affected by human activities, in which cambosol has undergone a low degree of soil development and ferrosol has undergone a high degree of development. Therefore, the reduction rates of Fe(III) in anthrosols were much higher than those of the other two soil orders, while the rates in soils from these two orders exhibited slight differences in the two treatments (Fig. 3C).

3.3 Effect of parent materials on the reduction rates of soil Fe(III)

The soils in this work were developed from six types of parent materials, including granite, alluvial deposit, basalt, quaternary period red earth, sediments, and limestone (Table 1). The average Fe(III) reduction rates in the soils with glucose were apparently greater than those without glucose in soils from all the six parent materials, suggesting the glucose as carbon source greatly improved the microbial activity (Fig. 4). Furthermore, the average Fe(III) reduction rates in the different soils with and without glucose have the similar patterns: the Fe(III) in the soils of sediments reached the highest average reduction rates (1.87 and 1.02 mM• d^{-1}), which were more than two times as many as those in other parent materials; and the Fe(III) in the soils of basalts with and without glucose obtained the lowest values among these 6 parent materials.

[Fig. 4]

3.4 Effect of soil weathering degree on the reduction rates of soil Fe(III)

The soil weathering degree as one of soil properties has an important impact on iron reduction susceptibility. Chemical weathering indices (CWI) were employed to indicate the weathering degree of the soils in this study, because they are widely used in the study of both modern and ancient *in situ* weathering degrees and are commonly applied in the characterization of soil weathering degrees by incorporating the bulk chemistry of major element oxides into a single parameter value for soils [34]. Weathering indices are conventionally calculated using the molecular ratios of major element oxides [35], especially for "mobile" oxides like Na_2O, K_2O, MgO, CaO, and SiO_2 and "immobile" oxides like Al_2O_3, Fe_2O_3 and TiO_2 [36]. The chemical weathering indices based on the ratios of "mobile" to "immobile" oxides can clearly describe the weathering degrees in the soils from the subtropical region of South China, where chemical weathering is the dominant process under high temperatures and humid conditions [35, 37].

Seven representative chemical weathering indices based on the ratios of "mobile" oxides to "immobile" oxides, including potassium-sodium-calcium to aluminum (PA, $(K_2O+Na_2O+CaO)/Al_2O_3$), Vogt's residual Index (V, $(Al_2O_3+K_2O)/(MgO+CaO+Na_2O)$), chemical index of alteration (CIA, $100\times Al_2O_3/(Al_2O_3+CaO+Na_2O+K_2O)$), weathering index of Parker (WIP, $100\times(2Na_2O/0.35+MgO/0.9+2K_2O/0.25+CaO/0.7)$), base to alumina (BA, $(K_2O+Na_2O+CaO+MgO)/Al_2O_3$), chemical index of weathering (CIW, $100\times Al_2O_3/(Al_2O_3+CaO+Na_2O)$), and modified weathering potential index (MWPI, $100\times(K_2O+Na_2O+CaO+MgO)/(SiO_2+Al_2O_3+Fe_2O_3+K_2O+Na_2O+CaO+MgO)$) [35, 36], were calculated from the obtained contents of metal oxides in the soils (Table 4) and were used to characterize the soil weathering degree of the present study. The equations and the values of the seven weathering indices were provided in Table 4.

[Table 4]

The linear correlations between weathering indices and the reduction rates of Fe(III) and the correlative parameters were listed in Table 5. The results showed that all the reduction rates of Fe(III) were linearly correlated with the majority of the studied weathering indices. The indices of BA, WIP, and MWPI were significantly correlated with both of the two series of Fe(III) reduction rates at the level of 0.01. The other four weathering indices were highly correlated with the Fe(III) reduction rates, either at the level of 0.01 or 0.05, except for three correlations with P values, which were slightly higher than 0.05. The four indices in "mobile" to "immobile" oxides, i.e., PA, BA, WIP, and MWPI, were positively correlated with the reduction rates of Fe(III), while the other three indices in "immobile" to "mobile" oxides, such as V, CIA, and CIW, were negatively correlated with the rates. These results strongly suggested that the reduction of Fe(III) in these soils was highly dependent on the degree of soil weathering and high weathering degrees would inhibit the reduction of Fe(III) [35].

[Table 5]

4. Discussion

4.1 Effects of soil land-use types on the reduction of Fe(III) in soils

The results in this work clearly indicated that land-use types exerted significant effects on soil Fe(III) reduction rates and the Fe(III) reduction rates were higher in soils from paddy fields suffered more intensive human activities than those in forest soil because the alternate drying-flooding farming method applied to paddy fields offered the soils alternating oxidizing and reducing conditions, which had important effects on soil mineral status, as well as soil iron [28, 38]. Paddy soils provided seasonal alterations of oxidation and reduction resulted in the build-up of a relatively large fraction of fine-grained, poorly crystalline or amorphous iron oxides, which were more reducible than the crystalline iron oxides [14]. Further, large quantities of organic fertilizers, including rice straw residue, synthetic fertilizer, and organic manure, were seasonally applied to the paddy soils, resulting in higher contents of organic ligands in the paddy soils than those in the forest soils [39]. With more organic ligands, the reductive dissolution of iron oxides occurred more easily and the reduced Fe(II) species were more readily detached from the surface of the soil iron minerals, leaving active sites for the further reduction of more Fe(III) [40-42]. Additionally, the organic ligands in soils can complex with reduced Fe(II) and act as sinks for Fe(II), both of which can increase the extent of Fe(III) reduction under chemical equilibrium theory [38] and retard the possible consequent oxidation of Fe(II) [43]. As a result, the Fe(III) reduction rates in paddy soils were higher than those in forest soils.

Another reason of the different Fe(III) reduction rates in soils from different land-use types was related to the activities of microorganisms in different land-use type soils. The tillage on agricultural soils made the cleavage of soil aggregates with more new surfaces can increase the biochemical activity [44]. Further, the input of organic fertilizer into paddy soils during tillage can increase soil microbial community diversity and enhance microbial activities [45, 46]. A wide range of microorganisms were found to function in terms of the dissimilatory iron reduction of microbes, for example, *Geobacter* spp., the *Anaeromyxobacter* spp., *Clostridium* spp., and *Bacillus*, and all of them have been confirmed to be enriched in paddy soils [10, 47, 48]. Therefore, the microorganisms in paddy soils to reduce Fe(III) may be activated and enriched during the tillage activities, leading to the higher Fe(III) reduction efficiencies.

4.2 Geochemical constraints on the reduction of Fe(III) in soils

Our results indicated different Fe(III) reduction rates in soils from different parent materials, because of their constraints of soil geochemical properties in the iron reduction processes. The parent materials were essential for forming the soil minerals, and to some extent, decided the mineral composition and geochemical properties of the soils [49], consequently affecting the iron reduction reactions of the soil. Sediments and alluvial deposits experienced mild conditions during soil formation processes, and the soils from these two parent materials may contain high contents of water soluble Fe(III), exchangeable Fe(III), and amorphous Fe(III) oxides, which were readily reducible [16]. While the soils from the other four parent materials underwent extreme conditions, such as high temperature and pressure, during the formation processes so that they contained high contents of crystalline iron oxides in lowly reducible forms [19]. Therefore, their Fe(III) reduction rates were lower in the soils from granite, basalt, quaternary period red earth and limestone than those of the soils from the sediments and alluvial deposits.

To differentiate the relative importance of the various geochemical properties on Fe(III) reduction, stepwise linear regression analyses were conducted using Fe(III) reduction rates with the soil properties data given in Table 2. The results indicated that a combination of amorphous Fe (A-Fe) content in mol/kg and soil pH (2:1 DI water:soil) was suitable to predict the Fe(III) reduction rates of the various soils (Table 6). The relationships of Fe(III) reduction rates under the two different conditions were

$$u_1 = 0.46 + 13.84 \times \text{A-Fe} - 0.09 \times \text{pH} \qquad (3)$$

$$u_2 = 1.35 + 21.02 \times \text{A-Fe} - 0.24 \times \text{pH} \qquad (4)$$

Whether additional carbon sources were added to the soils or not, the independent variable in both of the two models had P values of <0.001 for A-Fe and <0.05 for soil pH, indicating that this was a significant (>95%) contributor to Fe(III) reduction rates (Table 6). The models suggested that Fe(III) reduction rates increased with the decrease of soil pH and the increase of soil fractions of amorphous Fe. The independent variables (soil pH and content of amorphous Fe) had an highly actual significance in their contribution to predicting the reduction of Fe(III) by the soils. Amorphous Fe was considered to be the most active iron species in soil environmental processes [38, 50]; additionally, although this species was partly reducible, it was also presumed to be the dominant component of reducible Fe(III) in soil [16]. Conditions of lower soil pH were more favorable for the activities of iron-reducing bacteria, which resulted in higher Fe(III) reduction rates [51].

[Table 6]

4.3 The constraints of weathering processes on the reduction of soil Fe(III)

Weathering refers to processes that physically break down and chemically alter earth material, as well as soils, in which the driving force comes from both natural geochemical reactions and anthropogenic actions [52, 53]. Thus, the soil weathering degree is a combined factor of both geochemical and land-use activities. Our results showed the significant negative correlation of chemical weathering degree with Fe(III) reduction rates. In addition, PCA of all the geochemical properties with the two series of Fe(III) reduction rates, including μ1 and μ2, was calculated and the interrelationships between multiple variables were shown in Fig. 5. A single two dimensional model on loading plot of PCA was exhibited and most of the information (62.48% of variance) was explained by the first and second principal components (PC1 and PC2). PC1 is predominated by Fe_2O_3, DCB-Fe, SiO_2, and Al_2O_3, whereas PC2 is dominated by weathering indices and Fe(III) reduction rates. Small angle vectors in Fig. 5 indicated significant correlation and similarity between the Fe(III) reduction rates and the soil wreathing indices. The physicochemical properties of soils were formed during soil weathering processes. To some extent, the weathering degree of soils can be regarded as a combination of multiple soil physicochemical properties and acted as an indirect combined parameter of soil properties [18].

[Fig. 5]

The inhibition effect of higher weathering degrees on the reduction of soil Fe(III) can be explained by several factors. Firstly, weathering processes can result in different reducible soil iron minerals in different regions [54]. The reducible iron mineral ferrihydrite is usually the major component of weathered soils yielded in cold and dry environments, such as Antarctica [55] and alpine regions [56]. In contrast, in tropical and sub-tropical areas, such as the studied area of Guangdong province, South China, the ferric oxide from the weathering processes is composed entirely, or almost entirely, of crystallized iron oxides [57], which is a significantly less reducible soil iron mineral [15]. The second factor that contributed to the inhibition effect was the kinetic control of the reductive dissolution of Fe(III) hydro(oxides) in soils by the detachment of Fe centers from the iron oxide surfaces. Prior to the detachment step, the reduction of Fe(III) in the nearest-neighbor oxide and hydroxide must take place if rapid Fe(III) reduction processes occurred [40]. However, soil weathering processes involved high Fe-O bond energies, resulting in the difficult association with Fe detachment. Consequently, the availability of limited reduction sites on iron oxides inhibited Fe(III) reduction reactions.

5. Conclusions

The dependence of the reduction efficiencies of Fe(III) in the 21 iron-rich soils on soil geochemical properties and land use was systematically evaluated in this study. Our results clearly suggested that (i) Fe(III) in iron-rich soils underwent steady reduction processes with the supplementation of carbon sources in the soils, which further increased the Fe(III) reduction rates, (ii) human activities, such as the tillage of soils, can accelerate Fe(III) reduction processes, ascribe to the increased contents of soil organic ligands, and enhance the activities and enrichment of iron reducing bacteria, and (iii) the Fe(III) reduction rates of soils were highly corelated with the soil weathering degree. Our findings also suggested that the properties of soil, such as the parent materials, land-use types, and weathering degree, can be used to predict the reduction susceptibility of soil Fe(III) and further be used to evaluate the reductive transformation of soil pollutants according to the Fe(III) reduction rates in anoxic soil subsurface conditions.

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TABLES

Table1 The background of the studied soils.

ID	Parent Materials	ST(GREAT GROUP)	CST(subgroup)	Land-use types
G-A	Granite	Hapludult	Xanthic Ali-Udic Argosols	Forest
G-C1	Granite	Hapludult	Xanthic Ali-Udic Cambosols	Forest
G-C2	Granite	Hapludult	Xanthic Ali-Udic Cambosols	Forest
G-C3	Granite	Hapludult	Xanthic Ali-Udic Cambosols	Forest
A-A1	Alluvial deposit	Paleaquult	Typic Fe-accumuli-Stagnic Anthrosols	Paddy Field
A-A2	Alluvial deposit	Paleaquult	Typic Gleyi-Stagnic Anthrosols	Paddy Field
A-A3	Alluvial deposit	Albaquults	Albic Hapli-Stagnic Anthrosols	Paddy Field
A-A4	Alluvial deposit	Umbraquults	Typic Gleyi-Stagnic Anthrosols	Paddy Field
A-A5	Alluvial deposit	Chromuderts	Recalcaric Hapli-Stagnic Anthrosols	Paddy Field
A-A6	Alluvial deposit	Palehumult	Typic Fimi-Orthic Anthrosols	Paddy Field
A-A7	Alluvial deposit	Albaqualfs	Typic Hapli-Stagnic Anthrosols	Paddy Field
B-F	Basalt	Acrorthox	Typic Rhodi-Udic Ferralosols	Forest
B-C	Basalt	Acrorthox	Typic Ali-Udic Cambosols	Forest
Q-F1	Quaternary Period red earth	Rhodudult	Rhodic Hapli-Udic Ferrosols	Forest
Q-F2	Quaternary Period red earth	Rhodudult	Typic Hapli-Udic Ferrosols	Forest
S-A1	Sediments	Halaquepts	Typic Fe-leachi- Stagnic Anthrosols	Paddy Field
S-A2	Sediments	Halaquepts	Typic Fe-leachi- Stagnic Anthrosols	Paddy Field
S-A3	Sediments	Ochraquults	Typic Fe-leachi- Stagnic Anthrosols	Paddy Field
L-A	Limestone	Haplaquepts	Typic Hapli-Stagnic Anthrosols	Paddy Field
L-F1	Limestone	Hapludult	Leachic Carbonati-Udic Ferrosols	Forest
L-F2	Limestone	Hapludult	Leachic Carbonati-Udic Ferrosols	Forest

Table 2 The geochemical properties (unit: mol/kg dry soil).

Soils	pH	Na_2O	K_2O	CaO	MgO	SiO_2	Al_2O_3	Fe_2O_3	DCB-Fe	A-Fe[a]	C-Fe[b]	TOC[c] (%)
G-A	4.57	0.037	0.291	0.015	0.119	8.18	3.39	0.449	0.128	0.008	0.073	1.45
G-C1	4.76	0.039	0.314	0.010	0.035	8.42	3.37	0.256	0.087	0.033	0.239	4.66
G-C2	4.59	0.039	0.185	0.018	0.030	7.08	3.89	0.404	0.134	0.006	0.112	3.02
G-C3	4.15	0.028	0.223	0.019	0.024	9.68	2.36	0.226	0.062	0.014	0.547	3.43
A-A1	5.89	0.076	0.256	0.144	0.255	8.43	2.53	0.510	0.144	0.053	0.446	7.49
A-A2	6.14	0.109	0.245	0.096	0.243	10.78	2.40	0.503	0.147	0.051	0.170	4.27
A-A3	5.21	0.048	0.107	0.035	0.043	13.98	0.94	0.103	0.017	0.007	0.746	3.56
A-A4	5.58	0.026	0.015	0.026	0.008	14.17	0.79	0.073	0.020	0.012	1.541	2.66
A-A5	6.92	0.048	0.196	0.101	0.064	11.30	1.84	0.322	0.096	0.045	0.520	6.76
A-A6	6.22	0.089	0.269	0.088	0.145	9.40	2.03	0.334	0.086	0.074	1.081	5.29
A-A7	5.53	0.072	0.270	0.041	0.093	10.95	2.17	0.276	0.075	0.051	0.488	4.27
B-F	4.90	0.037	0.029	0.019	0.023	4.55	3.93	1.113	0.381	0.014	0.090	3.87
B-C	6.98	0.067	0.047	0.083	0.037	3.63	4.08	1.550	0.434	0.025	0.026	3.08
Q-F1	4.94	0.041	0.144	0.021	0.050	8.62	2.48	0.956	0.346	0.013	0.078	1.95
Q-F2	4.00	0.033	0.131	0.016	0.072	8.72	2.11	0.336	0.117	0.012	0.494	6.87
S-A1	4.57	0.130	0.280	0.039	0.263	9.53	2.49	0.493	0.084	0.036	0.283	3.32
S-A2	3.80	0.072	0.220	0.028	0.113	10.53	1.95	0.434	0.151	0.051	0.714	3.32
S-A3	4.73	0.089	0.238	0.049	0.173	9.62	2.21	0.388	0.075	0.065	0.446	4.88
L-A	6.02	0.052	0.185	0.069	0.153	11.28	1.48	0.469	0.095	0.018	0.243	1.62
L-F1	4.63	0.043	0.168	0.029	0.105	10.68	1.87	0.322	0.103	0.012	0.410	4.97
L-F2	6.99	0.037	0.224	0.096	0.209	10.77	1.79	0.389	0.151	0.015	0.134	3.03

[a] A-Fe: Amorphous-Fe;

[b] C-Fe: Complex-Fe;

[c] TOC: Total organic carbon.

Table 3 μ of the reduction rate of Fe(III) ($mM \cdot d^{-1}$)

Soils	μ_1 [a]	R^2	μ_2 [b]	R^2
G-A	0.09	0.998	0.50	0.995
G-C1	0.17	0.999	0.38	0.998
G-C2	0.15	0.986	0.57	0.993
G-C3	0.18	0.977	0.21	0.978
A-A1	0.74	0.998	1.30	0.999
A-A2	0.54	0.999	1.26	0.999
A-A3	0.11	0.999	0.14	0.999
A-A4	0.07	0.999	0.08	0.999
A-A5	0.51	0.999	0.58	0.994
A-A6	0.57	0.993	0.64	0.996
A-A7	0.60	0.999	0.82	0.999
B-F	0.13	0.989	0.26	0.993
B-C	0.15	0.966	0.22	0.862
Q-F1	0.13	0.951	0.51	0.997
Q-F2	0.15	0.992	0.43	0.977
S-A1	0.97	0.997	1.88	0.999
S-A2	0.98	0.992	1.84	0.999
S-A3	1.12	0.999	1.89	0.999
L-A	0.29	0.999	0.42	0.999
L-F1	0.15	0.999	0.35	0.999
L-F2	0.22	0.999	0.39	0.980

[a] The maximal Fe(III) reduction rate of soil without adding carbon sources.

[b] The maximal Fe(III) reduction rate when adding glucose.

Table 4 The calculated weathering indices of the studied soils (Mole ratio).

Soils	PA[a]	V[b]	CIA[c]	WIP[d]	BA[e]	CIW[f]	MWPI[g]
G-A	0.10	21.53	90.81	269.31	0.19	87.66	4.00
G-C1	0.11	43.86	90.28	278.80	0.17	86.38	3.50
G-C2	0.06	46.84	94.14	176.19	0.25	81.55	3.10
G-C3	0.11	36.38	89.73	199.78	0.11	90.93	2.29
A-A1	0.19	5.87	84.17	297.13	0.40	79.20	6.37
A-A2	0.19	5.90	84.21	299.00	0.37	80.68	5.02
A-A3	0.20	8.31	83.19	122.81	0.38	76.13	1.56
A-A4	0.08	13.42	92.18	31.46	0.14	88.59	0.51
A-A5	0.19	9.56	84.21	205.77	0.20	85.53	2.92
A-A6	0.22	7.14	81.99	294.74	0.30	81.36	4.81
A-A7	0.18	11.84	85.00	273.33	0.32	79.33	3.62
B-F	0.02	50.11	97.88	49.61	0.04	96.94	1.28
B-C	0.05	22.07	95.39	91.85	0.08	93.82	2.81
Q-F1	0.08	23.43	92.33	147.18	0.14	89.76	2.22
Q-F2	0.09	18.52	92.14	133.94	0.16	89.49	2.33
S-A1	0.18	6.41	84.72	333.08	0.41	79.60	5.74
S-A2	0.16	10.19	85.90	233.70	0.36	79.20	3.44
S-A3	0.17	7.87	85.46	267.48	0.20	88.09	4.14
L-A	0.21	6.08	82.87	204.57	0.27	84.84	3.35
L-F1	0.13	11.51	88.63	174.78	0.28	83.64	2.76
L-F2	0.20	5.89	83.37	237.28	0.20	88.72	3.91

[a] PA: potassium-sodium-calcium to aluminum, $(K_2O + Na_2O + CaO) / Al_2O_3$;

[b] V: Vogt's residual Index, $(Al_2O_3 + K_2O)/(MgO + CaO + Na_2O)$;

[c] CIA: chemical index of alteration, $100 \times Al_2O_3/(Al_2O_3 + CaO + Na_2O + K_2O)$;

[d] WIP: weathering index of Parker , $100 \times (2Na_2O/0.35 + MgO/0.9 + 2K_2O/0.25 + CaO/0.7)$;

[e] BA: BA, base to alumina, $(K_2O + Na_2O + CaO + MgO) / Al_2O_3$;

[f] CIW: chemical index of weathering, $100 \times Al_2O_3/(Al_2O_3 + CaO + Na_2O)$;

[g] MWPI: modified weathering potential index, $100 \times (K_2O + Na_2O + CaO + MgO)/(SiO_2 + Al_2O_3 + Fe_2O_3 + K_2O + Na_2O + CaO + MgO)$.

Table 5 Statistical correlations between the μ of the reduction rate of Fe(III) and the soil weathering indices.

Weathering indices or Reductases		μ_1	μ_2
PA	Pearson Correlation	**0.558(**)**	0.419
	Sig. (2-tailed)	0.009	0.059
V	Pearson Correlation	**-0.503(*)**	-0.411
	Sig. (2-tailed)	0.020	0.064
CIA	Pearson Correlation	**-0.561(**)**	-0.427
	Sig. (2-tailed)	0.008	0.054
WIP	Pearson Correlation	**0.644(**)**	**0.652(**)**
	Sig. (2-tailed)	0.002	0.001
BA	Pearson Correlation	**0.571(**)**	**0.586(**)**
	Sig. (2-tailed)	0.007	0.005
CIW	Pearson Correlation	**-0.460(*)**	**-0.452(*)**
	Sig. (2-tailed)	0.036	0.039
MWPI	Pearson Correlation	**0.660(**)**	**0.687(**)**
	Sig. (2-tailed)	0.001	0.001

**. Correlation is significant at the 0.01 level (2-tailed).

*. Correlation is significant at the 0.05 level (2-tailed).

Table 6 The parameter estimates, standard errors, and statistics obtained from multiple linear regression analysis of the soil physiochemical properties with respect to the reduction rates of Fe(III) under different conditions.[a]

	u_1			u_2		
	value	std error	P	value	std error	P
intercept	0.46	0.22	<0.05	1.35	0.47	<0.05
A-Fe	13.84	1.94	<0.001	21.02	4.15	<0.001
pH	-0.09	0.04	<0.05	-0.24	0.09	<0.05
r^2	0.74	0.18		0.61	0.38	

[a] A-Fe = content of amorphous Fe in mol/kg, pH in a 2:1 DI H_2O:soil ratio.

FIGURE CAPTIONS

Fig. 1. A map of the sampling locations of the studied soils.

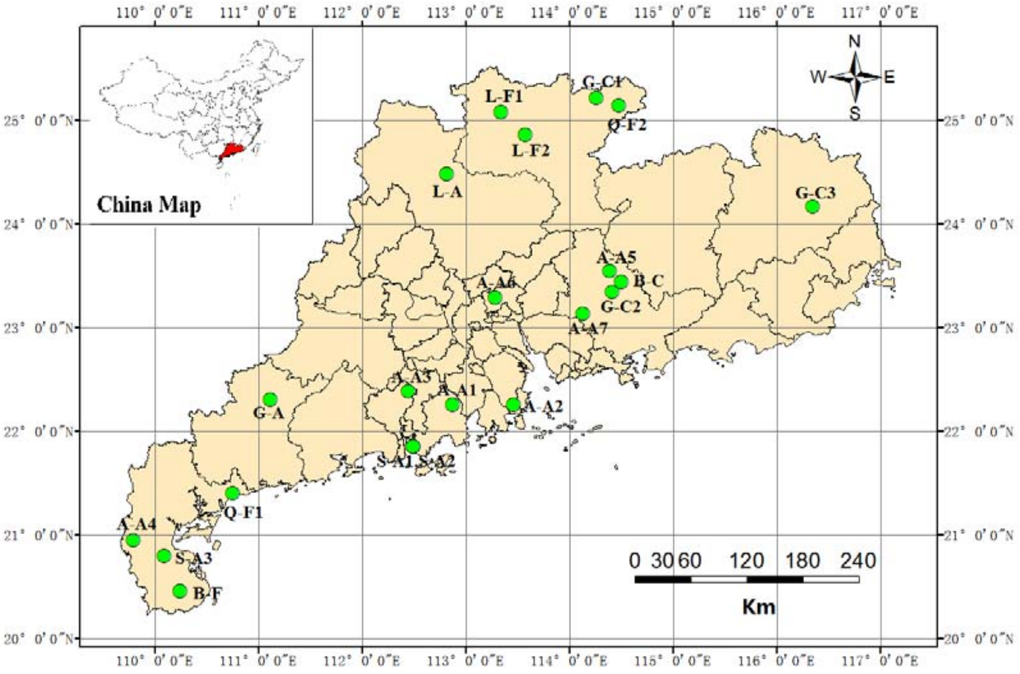
Fig. 2. The soil Fe(III) reduction kinetics with glucose (open markers) or not (closed markers) for 40 d in the studied soil samples (0.5 g) under anaerobic conditions controlled at pH 7.0 ± 0.5 with 30 mM PIPES buffer solution at 25 ± 1°C. Error bars represent the standard deviation of the mean from triplicate samples and are smaller than the symbol if not shown.

Fig. 3. The Fe(III) reduction rates in 40 days under anoxic conditions, controlled at pH 7.0 ± 0.5 with 30 mM PIPES buffer solution at 25 ± 1°C: (A) The average Fe(III) reduction rates under the four treatments, (B) the average Fe(III) reduction rates in the soils from different land use types, and (C) the average Fe(III) reduction rates in the soils from different CST soil orders. Error bars represent the standard deviation of the average Fe(III) reduction rates from all the samples in the same type. The average value within the same treatment that has different lowercase letters (i.e., a or b) are significantly different at $p < 0.05$ and $p < 0.01$, whereas the average value within the same treatment that has identical lowercase letters is not significantly different at $p = 0.05$.

Fig. 4. The average Fe(III) reduction rates in the various soil parent materials in 40 days under anoxic conditions, controlled at pH 7.0 ± 0.5 with 30 mM PIPES buffer solution at 25 ± 1 °C. Error bars represent the standard deviation of the average Fe(III) reduction rates

from all the samples from the same parent material. The average value within the same treatment that has different lowercase letters (i.e., a or b) are significantly different at $p < 0.05$ and $p < 0.01$, whereas the average value within the same treatment that has identical lowercase letters is not significantly different at $p = 0.05$.

Fig. 5. Principle Component Analysis (PCA) of the different soil physicochemical properties with the two series of Fe(III) reduction rates.



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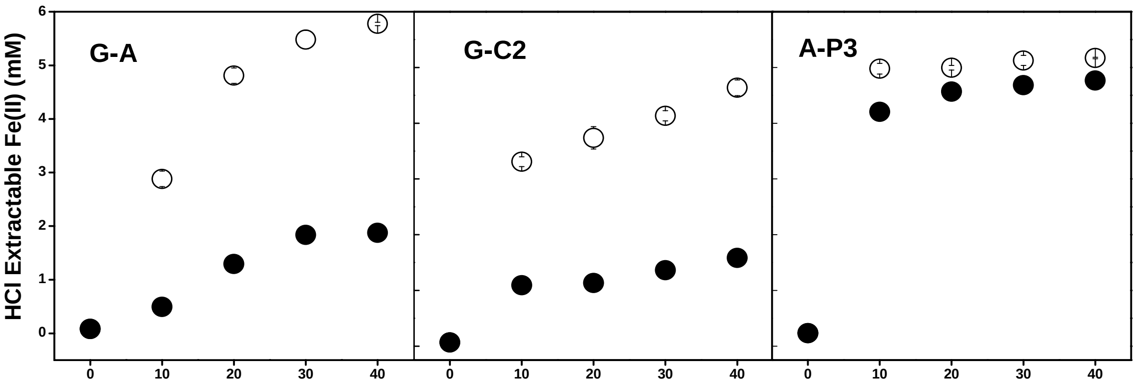
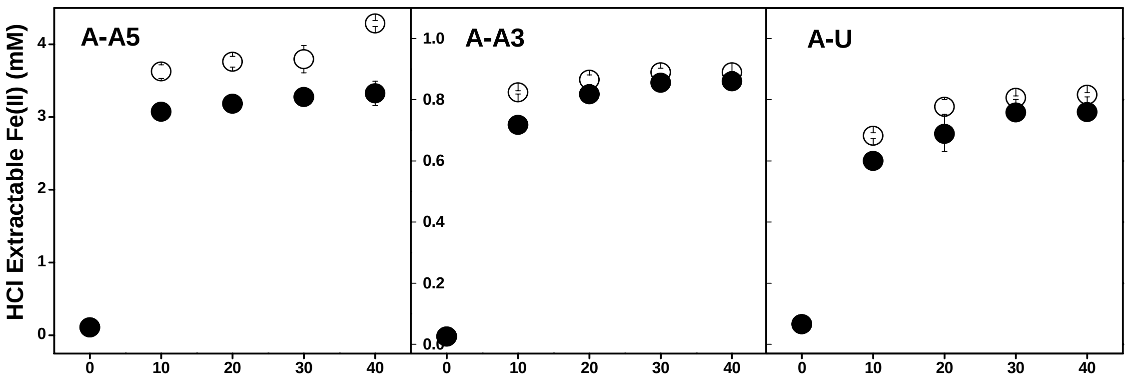
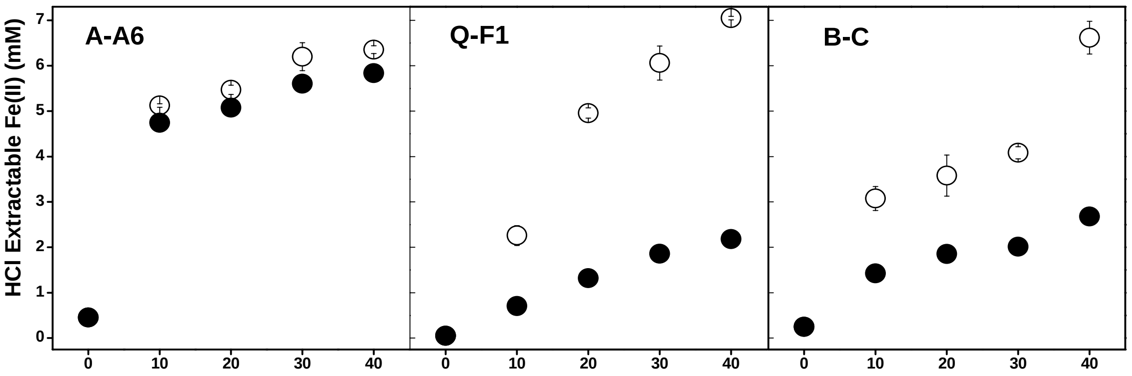
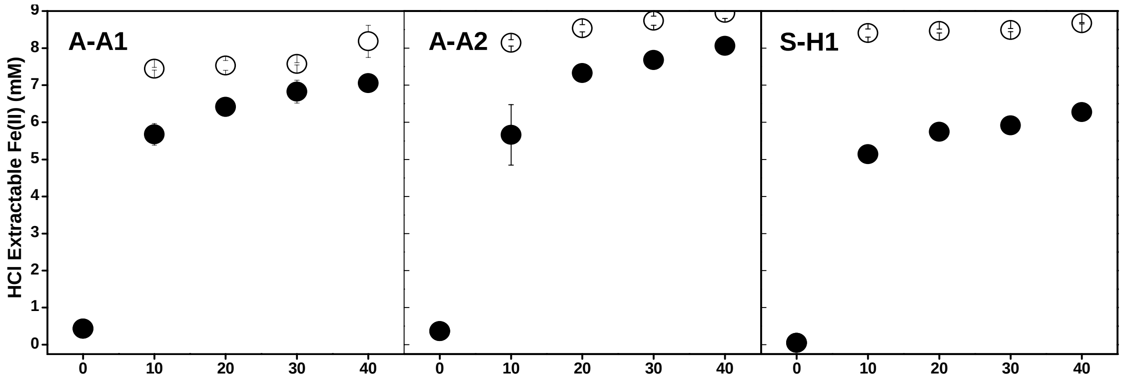

HCl Extractable Fe(II) (mM)
G-A
G-C2
A-P3
0
1
2
3
4
5
6
0
10
20
30
40


HCl Extractable Fe(II) (mM)
A-A5
A-A3
A-U
0
1
2
3
4
0.0
0.2
0.4
0.6
0.8
1.0
0
10
20
30
40


HCl Extractable Fe(II) (mM)
A-A6
Q-F1
B-C
0
1
2
3
4
5
6
7
0
10
20
30
40


HCl Extractable Fe(II) (mM)
A-A1
A-A2
S-H1
0
1
2
3
4
5
6
7
8
9
0
10
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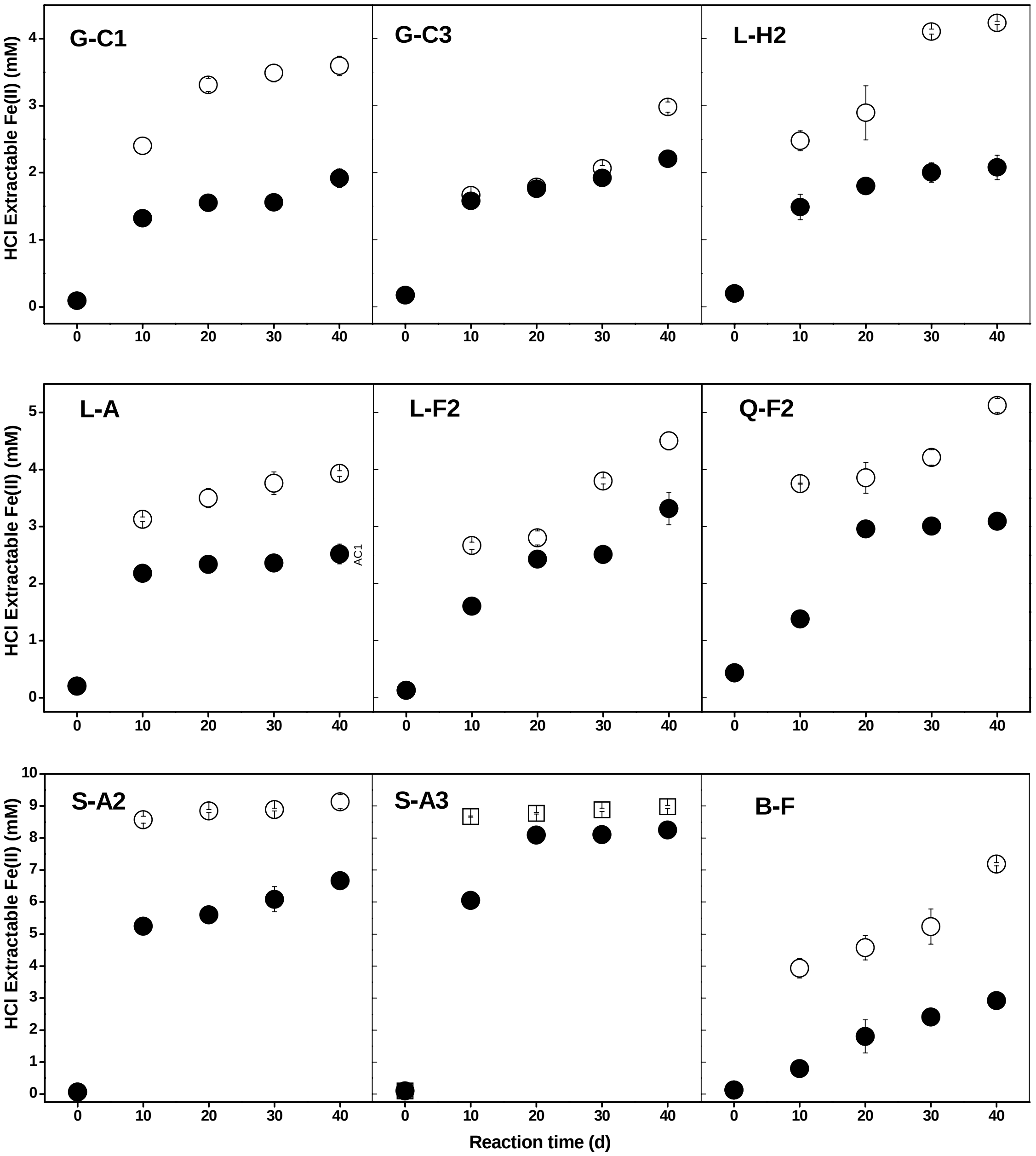
30
40



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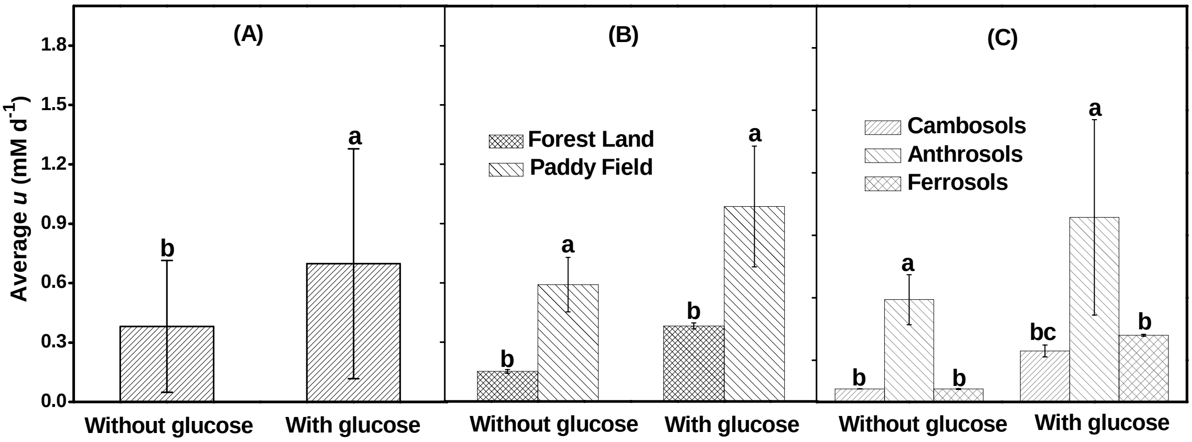

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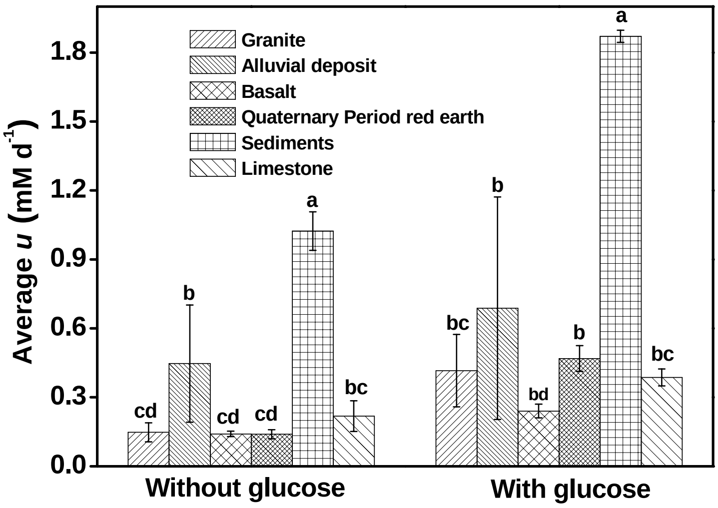

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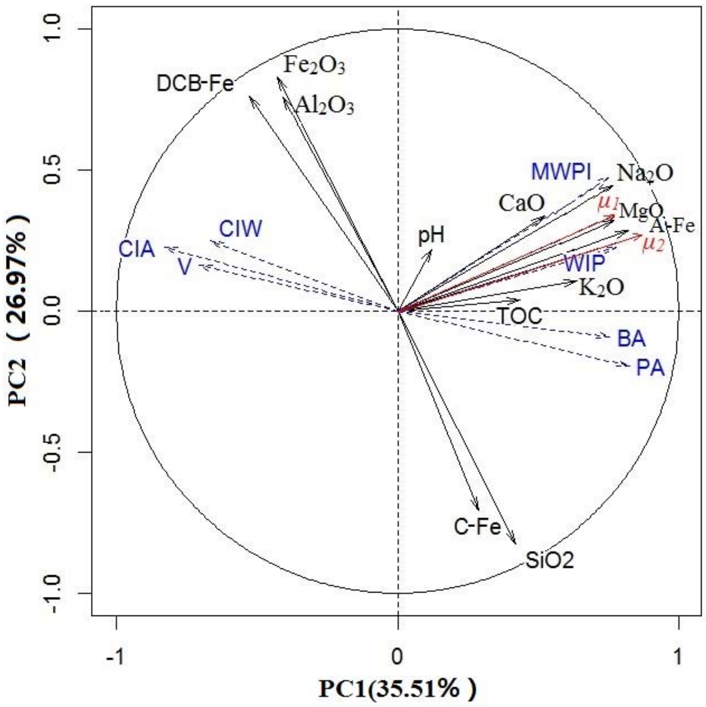

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