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Prediction of reducible soil iron content from iron extraction data

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Abstract. Soils contain various iron compounds that differ in solubility, reducibility and extractability. Moreover, the contribution of the various iron compounds to total iron (Fe) and total Fe concentrations differs highly among soils. As a result, the total reducible Fe content can also differ among soils, and so does the dynamics of iron reduction. These factors complicate the prediction of reducible Fe based on Fe extraction data and hamper the application of process-based models for reduced or waterlogged soils where redox processes play a key-role. This paper presents a theoretical analysis relating reducible to extractable Fe reported in the literature. Predictions made from this theoretical analysis were evaluated in soil incubations using 18 rice paddy soils from all over the world. The incubation studies and the literature study both show that reducible Fe can be related to Fe from some selected, but not all, iron extractions. The combination of measurements for labile Fe(III)oxides (derived from oxalate-extractable Fe) and stabile Fe(III)oxides (derived from dithionite-citrate-extractable Fe) shows highly significant correlations with reducible Fe with high coefficients of determination ($r^2 = 0.92–0.95$ depending on the definition of stabile Fe(III)oxides). Given the high diversity in rice soils used for the incubations, these regression equations will have general applicability. Application of these regression equations in combination with soil database information may improve the predictive ability of process-based models where soil redox processes are important, such as CH_4 emission models derived for rice paddies or wetlands.

Introduction

Redox sequence processes are among the dominant processes in anoxic environments. Iron reduction is a dominant process within the redox sequence in all types of anaerobic systems (e.g., Reddy et al. (1980)). In rice paddies, iron reduction contributes dominantly to the electron capture released from organic compounds: 58–79% (Yao et al. 1999), 66–84% (Inubushi et al. 1984) and 14–58% (van Bodegom and Stams 1999). Several authors suggested that 0.5 N HCl extracts all of the reduced iron (Fe) and no oxidised forms (e.g., Lovley and Phillips (1986) and Ratering and Schnell (2000)). The use of 0.5 N HCl extraction to estimate reducible Fe is relatively new, needs prolonged incubation periods -to reduce all reducible Fe- and is infrequently used in soil surveys. Unfortunately, there is no clear relationship available between soil reducible Fe and measurements of extractable Fe that are commonly available in soil databases (e.g., in profile data belonging to the FAO soil map of the world or the WISE database (Batjes 1995)). The absence of a validated relationship between extractable Fe and the amount of reducible Fe in soils seriously hampers the predictive capacity of various early diagenesis models and, among others, of models that predict emissions of the greenhouse gas methane from reduced or waterlogged soils.

The present study evaluates available information on iron compounds, its extractability and its reducibility. Based on this information, predictions of reducible Fe based on iron extractions were made. Reducible Fe is defined as the fraction of soil Fe that can be reduced by microorganisms during a prolonged period of anoxic conditions. The relationship between reducible Fe and various measurements of extractable Fe was quantified further by long-term anoxic incubations of 18 highly different rice paddy soils from all over the world. The reducible Fe content -as determined by 0.5 N HCl- and different fractions of extractable Fe were determined in these incubations.

Theory of iron extraction and iron reduction

Reducibility of soil iron compounds

Soil iron occurs in various compositions. For modelling of soil redox processes only those forms of Fe that can be reduced (partly) need to be quantified. These are in order of reducibility:

1. Water-soluble Fe is fully and directly available for reduction, but is generally found in very low concentrations only, e.g., ∼ 4% of the total Fe content (Gotoh and Patrick 1974).
2. Exchangeable Fe is the part of the iron that is directly exchangeable with the soil adsorption complex. This Fe is also fully reducible. The quantity of exchangeable Fe usually depends upon the Cation Exchange Capacity of the soil.
3. Amorphous Fe(III)oxides are presumably the predominant iron source for iron reduction (Lovley 1991), but are only partly reducible. Across various studies, a similar fraction of about 35–50% of the amorphous Fe(III) oxide was found to be reducible (Lovley and Phillips (1986, 1988); Roden and Zachara 1996). Amorphous iron reduction might have been limited by acetate in the measurements of Lovley and Phillips (1986, 1988), but such a limitation will not have occurred in the experiments of Roden and Zachara (1996) given their experimental set-up. Ferrihydrite, which is usually also assumed to be amorphous, had

a smaller reducibility: 19.8% (Roden and Zachara 1996).

4. Crystalline Fe(III)oxides are much less available for iron reducers. Reducibilities are 2.5% for lepidocrocite (γFeOOH) (Elsgaard and Jørgensen 1992), 1.5% for magnetite (Fe_3O_4) (Lovley and Phillips 1988), vary for akagenite (β-FeOOH) from 3% (Lovley and Phillips 1988) to 4% (Lovley and Phillips 1986) and vary for goethite (α-FeOOH) from 1% (Lovley and Phillips 1988) via 1.5% (Lovley and Phillips 1986) to 1.5–12.5% (Roden and Zachara 1996). The reduction of hematite is even less than that of goethite and equalled 0.25% (Lovley and Phillips 1988) and 0.64% (Roden and Zachara 1996), respectively.

The differences in reducibility between the various Fe(III) oxides can be explained by differences in reactive surface area and follows the same order as the order in reactivity of these minerals with respect to sulphidication, which was: amorphous Fe >>lepidocrocite> goethite> hematite (Raiswell et al. 1994; Canfield 1989). The exception is magnetite with a reactivity with respect to sulphidication that is much smaller than that of goethite and hematite (Raiswell et al. 1994).

Although the reducibility of crystalline Fe(III) oxides is much less than that of amorphous Fe(III) oxides, the contribution of crystalline phases to total iron reduction can be highly significant, up to 10–20% in some soils (Roden and Zachara 1996). Jakobsen and Postma (1999) also suggested that less reactive Fe(III) oxides, like crystalline oxides, may be important for iron reduction. This is probably caused by the larger amount of crystalline Fe(III)oxides compared to amorphous Fe(III)oxides present in some soils. The reactivity of iron containing reactive silicates and plate silicates is too low to contribute to iron reduction (Raiswell et al. 1994). Unfortunately, no literature describing the reducibility of siderite ($FeCO_3$) could be found.

Extraction methods for soil iron

Numerous iron extraction methods are available, but we only discuss the extraction methods for the iron phases that contribute to the total amount of reducible Fe. The relevant methods are listed in Table 1 and discussed below.

At present, extraction with 0.5 N HCl is commonly used to quantify iron reduction (e.g., Klüber and Conrad (1998) and Ratering and Schnell (2000), Roy et al. (1997), Yao et al. (1999)) and supposed to extract all reducible Fe and only reducible Fe, although Heron et al. (1994) discusses that extraction with cold 5 M HCl may be more appropriate to estimate reducible Fe at longer time scales of several years. Given that most surface soils in wetlands are not anaerobic for such long periods, extraction with 0.5 N HCl is used hereafter for comparison with other iron extraction methods. Both HCl extraction methods are, however, inappropriate in sediments with high calcite or carbonate concentrations, due to interferences and acid neutralisation during extraction (Amirbahman et al. 1998). As indicated in the introduction, 0.5 N HCl extractions only provide information on total reducible Fe after prolonged incubation of the soil sample. This makes the method not very applicable for soil surveys and is unavailable in soil databases. It should therefore not be seen as a replacement of iron extraction methods used in routine soil analysis of

Table 1. The percentage of various soil Fe-compounds that is extractable with a particular method and the average percentage that is reducible based on literature data (references and discussion are given in the section on 'extraction methods for soil iron').

Extraction methods	*Dissolved iron*	*Exchangeable iron*	*Amorphous iron oxides*	*Crystalline iron oxides*	*Magnetite*	*Siderite*	*Iron-silicates*
0.5 N HCl	?	?	?	?	?	?	?
Water	100	0	0	0	0	0	0
NH_2OH	100	100	100	< 1	?	?	0
Oxalate	100	100	100	0	? (but > 0)	? (but > 0)	0
Ammonium acetate	100	100	100	0	? (but > 0)	? (but > 0)	0
Dithionite-citrate	100	100	100	54–100	4	0	0
12 N HCl	100	100	100	100 (?)	?	40	2
Reducible percentage	100	100	42	3	1.5	?	0

air-dried samples, but merely as a method to validate the estimates obtained by these iron extraction methods.

Sometimes, extraction with water has been used to quantify iron reduction (e.g., Jugsujinda and Patrick (1996)), but water extracts only water-soluble Fe and thus underestimates total reduced Fe. Several extraction methods exist for the combination of water-soluble Fe and amorphous iron oxides and can be applied on air-dried soil samples:

1. 'Total free Fe' is an extraction of 0.25 M hydroxylamine (NH_2OH) hydrochloride in 0.25 N HCl, incubated at 60 °C for 2 hours (Lovley and Phillips 1988; Roden and Zachara 1996). It extracts 100% of the amorphous iron, 11.5% of the ferrihydrite and < 1% of the goethite and hematite (Roden and Zachara 1996). Data from this extraction method are not generally available in soil databases.
2. A mixture of 0.113 M oxalate and 0.086 M oxalic acid (hereafter called 'oxalate') extracts 100% of the amorphous iron, 2% of the ferrihydrite and < 1% of the goethite and hematite (Roden and Zachara 1996). Similar results were obtained by Canfield (1989), who mentioned that 100% of the ferrihydrite and 100% of the lepidocrocrite was extracted, while goethite, hematite and iron-silicates remained unaffected. Magnetite was also extracted efficiently (McKeague et al. 1971; Canfield 1989) and siderite was also supposed to be extracted (Jakobsen and Postma 1999). Results obtained with the extraction by 1 M ammonium acetate, e.g., used by Satawathananont et al. (1991) are similar to those by oxalate, although ammonium acetate is a less effective complexing agent than oxalate and mainly works via proton-promoted dissolution, which is a relatively slow process.

3. Dithionite-citrate extraction extracts Fe more effectively than the above-mentioned extractions (Roden and Zachara 1996). Amorphous iron oxides are extracted for 100%, while siderite and iron silicates are hardly extracted (Raiswell et al. 1994; Canfield 1989). Extractability of crystalline iron oxides is less clear. Canfield (1989) mentions that crystalline iron oxides were extracted completely, whereas Raiswell et al. (1994) mentioned that lepidocrocite, goethite and powdered hematite were extracted for 54–70%, whereas ankerite (2%) and magnetite (4%) were extracted much less effectively.
4. Several extraction methods exist for the total Fe content. Most commonly used is 12 N HCl boiled for 1 minute (Roden and Zachara 1996). However, even this method does not seem to extract all Fe: pyrite is relatively insoluble in this extraction and is thus not (fully) measured (Rickard 1975; Luther et al. 1982). In addition, Raiswell et al. (1994) mention that the extraction effectiveness of siderite (40%), ankerite (17%) and Fe-silicates (2%) was not high. Similar results were obtained with a 8 N HCl extraction (Jakobsen and Postma 1999), which neither extracted all iron silicates. Results obtained with a cold 1 M HCl were in reasonable close agreement with the Fe extracted by 12 M HCl (Leventhal and Taylor 1990).

Relating extractable iron to reducible iron

The reducibility of various iron compounds is presented in Table 1. It was assumed that both ferryhydrite and lepidocrocite behave similarly as amorphous iron oxide, based on their reactivity for sulphidication and their extractability. Siderite is, based on the extraction data, expected to be partly reducible. However, siderite is omitted from the discussion due to limited data availability and because no good extraction method is available (Christensen et al. 2000). Since siderite is generally only a small fraction of soil Fe, such an omission does not lead to large errors.

Extractions with water and 0.5 N HCl can only be used to estimate reducible Fe after a prolonged anaerobic incubation during which all iron is reduced. After such an incubation, water-extractable Fe severely underestimates reducible Fe (Table 1), whereas 0.5 N HCl will match reducible Fe. All other extraction methods can be -and are- performed on air-dried soils. Comparison of the extracted fractions by different methods using air-dried soils and the contribution of various iron compounds to reducible Fe content in the soil (Table 1) reveals that none of the listed methods exactly matches reducible Fe.

Depending on the composition of soil Fe in a particular soil, one extraction method may be a better indicator than another, but this may be reversed in a different soil. For example, the assumption that reducible Fe equals 42% of oxalate extractable Fe (Table 1) is only correct if soil reducible Fe iron comes predominantly from amorphous iron oxides. In soils dominated by crystalline phases no correlation between reducible iron and NH_2OH- or oxalate extractable Fe was found (Roden and Zachara 1996).

Diverging results are also obtained when using dithionite-citrate as single Fe extraction. Data provided by Wassmann et al. (1998) and Yao et al. (1999), Yao and

Conrad (1999) yield a significant linear relationship between dithionite-citrate extractable Fe and reducible Fe with a regression coefficient (i.e. slope of the regression) of 0.25–0.42 for Philippine soil samples. In a study by Canfield and Thamdrup (1996), 49% of the soil dithionite-citrate extractable Fe was reduced. On the contrary, no significant correlation was found between dithionite extractable Fe and reduced Fe in data by Tsutsuki and Ponnamperuma (1987) and Satawathananont et al. (1991). The latter study comprised mostly acid-sulphate soils, dominated by Fe-S clusters that are indeed extracted by dithionite-citrate, but which are not reducible.

This brings us to the heart of the matter: Reducible Fe is an important parameter in early diagenesis models. Analytical data for different soils based on a single Fe extraction method as present in soil databases show large deviations in predicted reducible Fe among different soils and cannot be used with acceptable reliability: dithionite-citrate extractable Fe is only a good predictor in soils dominated by crystalline Fe phases, whereas oxalate extractable iron is a good estimator of soil reducible Fe if amorphous iron oxides are dominant. However, it can be deduced from Table 1 that it should be possible to get a better estimate for reducible Fe if at least two extraction methods are used simultaneously. This hypothesis was explored by incubating a range of different rice soils to exactly determine their reducible Fe content and to analyse these same soils by a range of Fe extraction methods. The aim was to derive an empirical formula relating measured reducible Fe with extractable Fe using multiple regression analysis. Given the diversity in incubated soils, such a relationship may be applied successfully to predict soil reducible Fe from Fe extraction data in soil databases.

Materials and methods

Incubation experiments

Samples from 18 soils from East Asia (6), West Africa (5), Europe (1) and the USA (6) were incubated and monitored for changes in reduced and extractable iron. Some general characteristics of these soils are presented in Table 2. More characteristics for various of these soils are given elsewhere (Holzapfel-Pschorn et al. 1986; Sass et al. 1994; Wassmann et al. 1998). All soil samples had been air-dried and stored at 4 °C before use. Soil slurries were prepared in 500-ml serum bottles by mixing 50 g soil with 125 ml sterilised distilled water. The bottles were closed with butyl rubber stoppers and were repeatedly (7×) evacuated and flushed with N_2 gas to a final gas pressure of 140 kPa. The anoxic slurries were incubated in the dark at 30 °C while shaken continuously at 125 rpm. All soils were incubated in quadruple of which two replicates had an extra addition of 2.5 ml thick culture of *Shewenella putrefaciens* in the log-phase. *S. putrefaciens* is a well-known iron reducing bacterium and was added to make sure that soil storage had not hampered the soil iron reducing capacity. *S. putrefaciens* had been pregrown as described by

Table 2. Measured characteristics of the rice soils used in the incubation study

		%sand	*%clay*	*%C*	*RMC*[1]	*%N*	*pH*[2]
East Asia	Beijing	22	34	0.99	28.4	0.08	8.34
	Gapan	76	8	1.67	39.7	0.14[3]	6.36[3]
	Maahas	20	30	2.3	28.1	0.19[3]	6.43[3]
	Bugallon	34	18	2.55	46.9	0.17[3]	6.91[3]
	Luisiana	6	42	2.11	27.8	0.16[3]	4.59[3]
	Pila	53	15	3.3	46.5	0.18[3]	7.48[3]
West Afrika	Foum Gleita	35	27	0.78	9.6	0.06	7.44
	Niomo	86	9	0.27	6.7	n.d.	n.d.
	Fanaye	32	24	0.78	3.9	n.d.	n.d.
	Ndiaye	39	22	1.14	6.5	n.d.	n.d.
	Burkina Faso	67	14	1.11	3.8	n.d.	n.d.
Europe	Vercelli	72	8	1.67	13.2	0.15[4]	6.0[4]
USA	Beaumont	10	39	1.06	19.0	0.09	5.5[5]
	Bernard	74	9	1.64	6.1	0.13	5.5[5]
	Charles 5.4	82	7	1.37	21.0	0.1	5.4
	Charles 7.2	19	39	1.63	11.0	0.13	7.2
	Edna	68	9	0.99	5.4	0.07	n.d.
	Katy	60	13	0.92	6.3	0.08	n.d.

[1] RMC = Readily Mineralisable Carbon (Yagi and Minami 1990) in μmol C g d.w.$^{-1}$
[2] pH was determined in air-dried soil
[3] Wassmann et al. (1998)
[4] Holzapfel-Pschorn et al. (1986)
[5] Sass et al. (1994)
n.d. = not determined

Roden and Zachara (1996). The slurries were incubated and analysed weekly (including at t = 0) for extractable and reduced iron. Incubations were stopped when the amount of reduced Fe, as determined by 0.5 N HCl extraction, remained constant, which was in practice after 2–3 months. During this period, ferric iron reduction was the dominant electron scavenging reaction (as was shown by the correlation between (CO_2 + CH_4) production and ferric iron reduction, results not shown) and will have dominated the changes in redox potential (Eh) in time. Given that Eh itself provides a measure of the redox status only and not of the reduction capacity, which is needed to estimate the rate of ferric iron reduction, Eh was not measured, but Eh will have been similar in its dynamics as measured by Wassmann et al. (1998).

Analytical techniques

The initial moisture content of the air-dried soil was determined gravimetrically by oven drying. Air-dried samples from each soil were analysed for oxalate extractable Fe (McKeague and Day 1966). Well-mixed slurry samples of 1-ml from the incubated soil slurries were taken anoxically by syringes. All subsequent handling until obtaining the supernatant occurred at anoxic conditions. Water-soluble Fe was determined by directly centrifuging 0.2 ml slurry sample at 16,000 g. The supernatant was collected and stored at −20 °C for subsequent analysis of Fe^{2+} and Fe^{3+} (described below). Adsorbed Fe was determined by re-suspending the soil pellet in 0.5 ml 1 M $CaCl_2$ solution and shaking it for 2 hours. The extracts were centrifuged at 13,000 rpm and the supernatant was collected and stored at −20 °C for analysis of Fe^{2+} and Fe^{3+}. Reduced Fe was measured using another 0.2 ml slurry sample and adding the sample to 4.8 ml 0.5 N HCl (Lovley and Phillips 1986). Dithionite extractable Fe was determined by adding 4.8 ml 50 g/l sodium dithionite in 0.35 M acetic acid/0.2 M sodium citrate at pH = 4.8 to 0.2 ml slurry sample. Total Fe extraction was done by adding 4.8 ml 12 N HCl to 0.2 ml slurry sample. Amorphous soil Fe was quantified by adding 4.8 ml 1 M NH_4-acetate at pH = 4.0 to the remaining 0.2 ml slurry sample. These last 4 extractions were shaken at 150 rpm for 2 hours and were centrifuged at 16,000 g afterwards. The supernatant was collected and stored at −20 °C for analysis of Fe^{2+} and Fe^{3+}.

All supernatants were analysed in the same way: 0.1 ml supernatant was added to 0.9 ml 1 g/l ferrozine in 50 mM HEPES buffer of pH = 4.0. The absorbance was measured immediately at 562 nm on a photospectrometer and yields Fe^{2+} in solution. After measurement, 0.25 ml 0.25 M hydroxylamine in 0.25 M HCl was added and after 30 minutes the absorbance was measured again. This final measurement yields the initial amount of Fe^{2+} and Fe^{3+} in solution. This procedure avoids interference of iron speciation on the measurements, which may be a potential problem (Christensen et al. 2000).

Results and discussion

Results with and without the addition of *S. putrefaciens* were not significantly different in any soil at any moment (paired student's t-test, $P > 0.05$), indicating that soil storage had not significantly affected the soil iron reduction rates or the reducible iron content. Therefore, the incubation data were combined to produce 4 replicates.

The rate and maximum of iron reduction were highly soil dependent (Figure 1), because the dynamics of iron reduction in time depends upon the amount of reducible Fe present and the amount of easily degradable organic matter (providing the electron donor). The amount of easily degradable organic matter was quantified by the Readily Mineralisable Carbon (RMC; Table 2) which is the amount of C mineralised after 28 days (Yagi and Minami 1990). RMC was significantly correlated to the reducible iron content (Pearson correlation coefficient = 0.64, $P = 0.003$), because iron reduction was the dominant electron accepting reaction in all soils and, most importantly, because iron reduction proceeded almost linearly in time during the first 28 days of the incubation. Soils in which iron reduction stopped earlier or later than average were significant outliers in this correlation with RMC, because

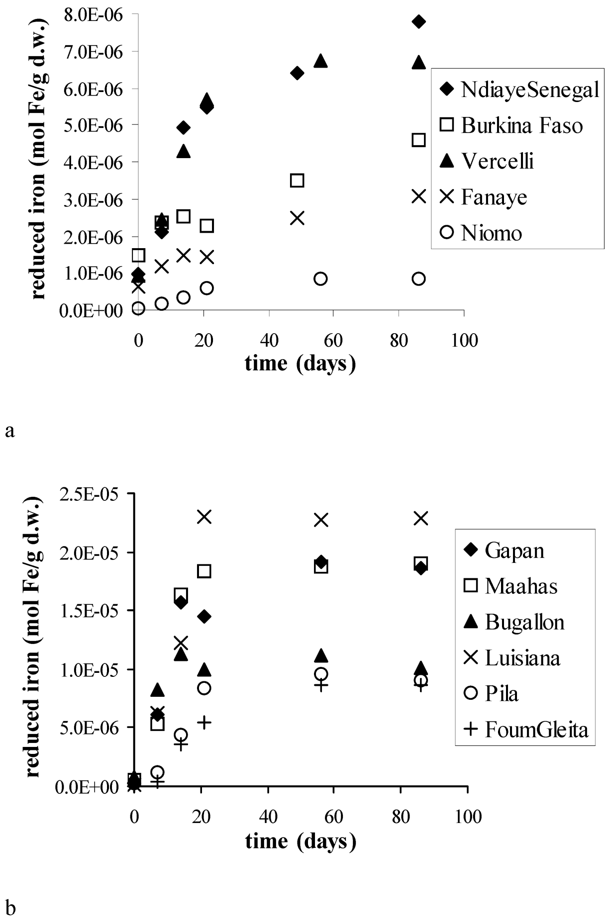


Figure 1. Iron reduction dynamics (as determined by Fe extracted with 0.5 N HCl) in 11 selected soils. Note the different y-axes.

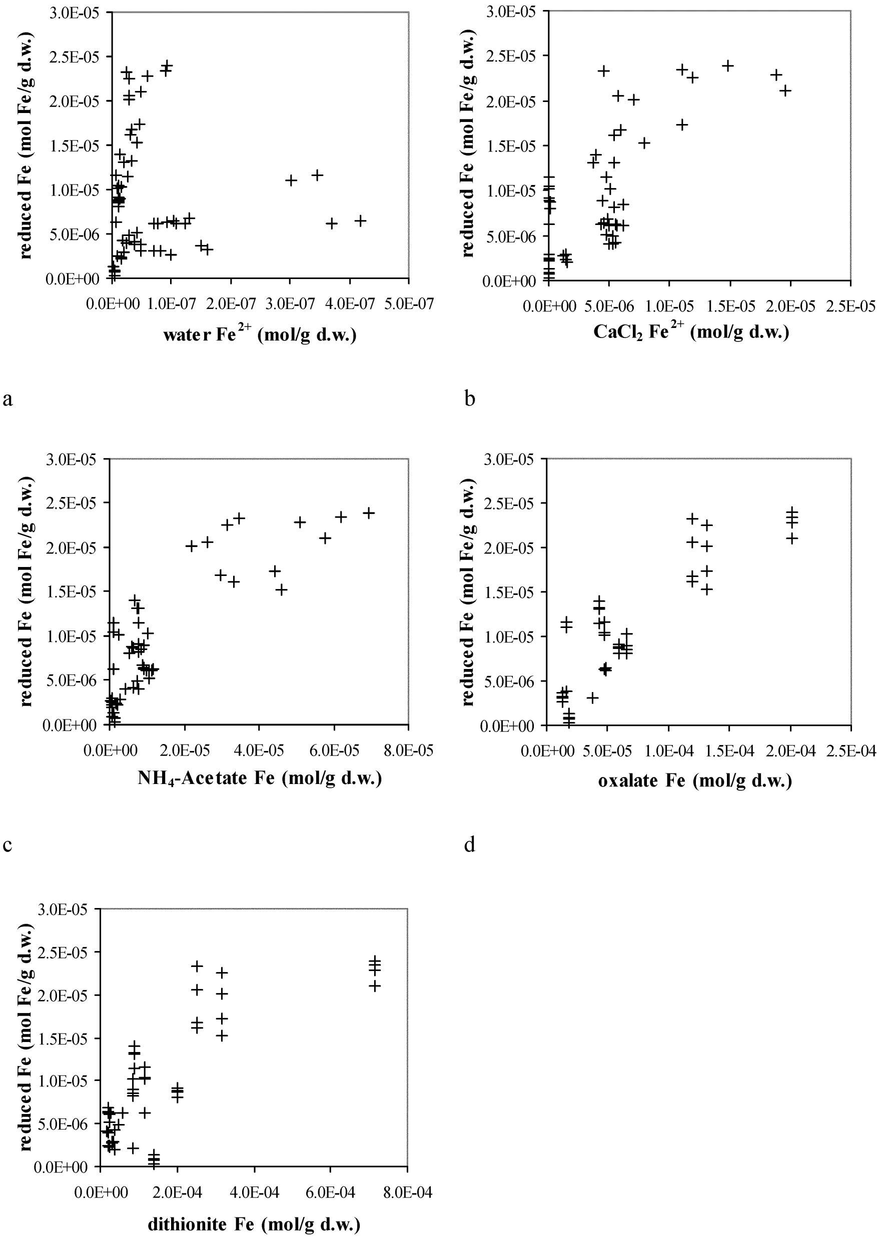
in those soils a different fraction of the reducible iron was reduced during the first 28 days. The reducible iron content was also significantly correlated to %C (Pearson correlation coefficient = 0.51, P = 0.026), but this correlation was less strong because of differences in organic matter quality among soils.

The variability in total reducible Fe is reflected in the variability in extractable Fe by various extraction methods. The amount of Fe^{2+} in the soil solution was highly variable, but unrelated to the total reduced iron at the end of the incubation (Figure 2a) and was neither related to soil texture (results not shown). On average, the amount of soil particle exchangeable Fe^{2+} (extracted using 1 M $CaCl_2$) was related more closely to total reduced Fe (Figure 2b). Also the absolute amounts extracted by 1 M $CaCl_2$ were of the same order of magnitude as the reduced amounts of iron. However, at low adsorbed Fe^{2+} concentrations, the amount of reduced Fe was severely underestimated by $CaCl_2$-extractable Fe^{2+}. The two extraction methods for labile iron oxides, NH_4-acetate and oxalate, both extracted more Fe than was actually reduced (Figure 2c, 2d), indicating that not all labile iron oxides were reduced in these soils or that the extractions pulled Fe from a different pool. The correlation between reduced Fe and iron extracted by these methods was however quite strong (treated below), indicating that most reduced iron came from labile iron oxides. The final extraction method, sodium dithionite (an important method for both labile and crystalline iron oxides), extracted about 18 times more iron than was reduced, suggesting that most of the crystalline iron remained untouched by iron reduction. The correlations between dithionite-extractable iron and reduced iron (treated below) were not as strong as those for the methods extracting labile iron oxides: the variability was higher and reduced Fe was virtually unrelated to dithionite-extractable Fe at high dithionite-extractable Fe contents (Figure 2e).

All extracted iron fractions, except water soluble iron, were significantly correlated to reduced iron at the end of the incubation ($P < 0.001$). The r^2 for the various extractions did however vary considerably; 0.76, 0.77, 0.80 and 0.91 for $CaCl_2$, dithionite-citrate, NH_4-acetate and oxalate extraction, respectively. Multiple regression analysis was carried out to determine whether combinations of extractions, as anticipated in the theoretical section above, would yield significantly better estimates of reducible Fe as determined by the amount of reduced Fe at the end of the incubation. Only one combination of extractions was shown to be significantly better than a single predictor, being the combination of oxalate and dithionite-citrate extraction ($P < 0.001$, $r^2 = 0.92$). Interestingly, the regression coefficient relating dithionite-citrate extracted iron to reducible iron was negative in this multiple regression. Multiple regression analysis was also carried out after defining dithionite-citrate extractable Fe minus oxalate extractable Fe as the stabile iron oxide fraction. Defining such a fraction improved the multiple regression and the combination of oxalate extracted iron and stabile iron oxides (Equation 1) was significantly better than a single predictor ($P < 0.001$, $r^2 = 0.95$):

$$\begin{aligned}\text{Reducible Fe} = {} & 0.19 * \text{oxalate extractable Fe} \\ & - 0.028 * (\text{dithionite-citrate extractable Fe} \\ & - \text{oxalate extractable Fe}) \qquad (1)\end{aligned}$$

A single regression between oxalate extractable Fe and reducible Fe had a regression coefficient of 0.14. The regression coefficients from both the single and the multiple regression were considerably lower than anticipated based on theory (Table 1) and the regression coefficient of the stabile fraction was even correlated negatively to reducible iron. The negative regression coefficient can only be explained chemically if oxalate extracts also significant amounts of stable iron oxides which are not reduced. The introduction of dithionite-citrate extractable Fe minus oxalate extractable Fe subsequently corrects for this overestimation of the contri-



a

b

c

d

e

Figure 2. Relationship between reduced iron (determined by 0.5 N HCl-extraction) at the end of the incubation with a) water-extractable Fe^{2+}, b) 1 M CaCl$_2$-extractable Fe^{2+}, c) NH$_4$-acetate-extractable total iron, d) oxalate-extractable total iron and e) dithionite-extractable total iron.

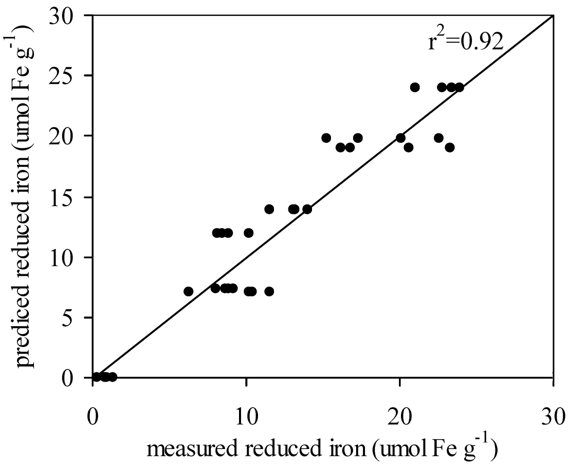


Figure 3. Predicted reduced iron based on Equation 1 compared to measured reduced iron (determined by 0.5 N HCl-extraction) at the end of the incubation.

bution of crystalline Fe phases to reducible Fe. The predictive power of Equation 1 is reasonably good over a large range of reducible Fe contents (Figure 3).

If NH_4-acetate extractable Fe instead of oxalate-extractable Fe is used as an approximation for labile iron oxides, the following equation is obtained (r^2 = 0.81):

$$\begin{aligned}\text{Reducible Fe} = {} & 0.31 * NH_4\text{-acetate extractable Fe} \\ & + 0.017*(\text{dithionite-citrate extractable Fe} \\ & - NH_4\text{-acetate extractable Fe})\end{aligned} \qquad (2)$$

Equation 2 is closer to our expectation based on Table 1, but its predictive capacity is slightly poorer than Equation 1. A single parameter regression between NH_4-acetate extractable Fe and reducible Fe had a regression coefficient of 0.47, which is again more closely related to the theoretically predicted value of 0.42. This may imply that iron extracted by NH_4-acetate is more closely related to reducible labile iron oxides than iron extracted by oxalate. No crystalline Fe phases are extracted by NH_4-acetate. All crystalline Fe phases are therefore incorporated in the second part of Equation 2, which now yielded a positive regression coefficient. The regression coefficient is close to the theoretically predicted value of 0.03 (Table 1). These results also imply that soil crystalline Fe phases have a small surface area, because up to 12.5% of synthetic crystalline iron oxides with a high surface area were reduced (Roden and Zachara 1996).

This regression analysis thus provides two regression equations that combine data on labile and stable iron oxides in slightly different ways and that can be determined by extractions on air-dried soils. Both equations gave reasonably good predictions of reducible Fe over a large range of Fe contents and a large range of Fe compound characteristics.

Conclusions

Rice paddy soils from all over the world show a high variability in both Fe concentration and in characteristics of the soil Fe compounds. As a result, the total reducible iron content can also differ among soils. The dynamics of iron reduction also differed by the combination of different total reducible iron content and different amounts of readily mineralisable carbon. This was clearly exemplified in the soil incubations presented in this study. The incubation studies also showed that reducible iron can be related to iron from selected iron extractions determined on air-dried soil samples. Especially the combination of measurements for labile Fe(III)-oxides and stabile Fe(III)oxides gives a highly significant correlation with high coefficients of determination with the amount of reducible Fe present. This was anticipated by our theoretical analysis. Given the high variability in soil conditions used in our incubations, we hypothesise that these regression equations have general applicability. A better estimate of reducible Fe than could be obtained so far can be calculated with these regression equations in combination with information on extractable Fe found in soil databases. This better estimate of reducible Fe will improve the predictive ability of process-based model in which soil reducible Fe is an important input parameter. Examples of such models are early diagenesis models and other models in which soil redox processes play a key-role, like CH_4 emission models derived for natural wetlands or rice paddies.

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