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Chemical extraction of sedimentary iron oxy(hydr)oxides using ammonium oxalate and sodium dithionite revisited – an explanation of processes in coastal sediments

Extracción química de oxi(hidrox)óxidos sedimentario utilizando oxalato de amonio y ditionito sódico revisado - una explicación de los procesos en sedimentos costeros

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ABSTRACT

Iron oxides promote aggregation, adsorb nutrients and pollutants and serve as electron acceptor; hence it is desirable to understand the composition of the soil and sedimentary iron pool. Here we tested if existing chemical extraction approaches using solely ammonium oxalate and sodium dithionite deliver consistent information on the allocation of amorphous and crystalline iron oxides for coastal sediments, which experience alternating redox conditions. For that purpose iron was extracted using citrate dithionite solution buffered with sodium bicarbonate and acid ammonium oxalate solution (pH 3.25). The content of dithionite extractable iron (Fe_d) and oxalate extractable iron (Fe_o) ranged from 1.7 to 7.4 g kg^{-1} and 1.0 to 11.3 g kg^{-1}, respectively. We calculate the content of crystalline iron oxide as usual from the difference between Fe_d and Fe_o, however, we failed for nearly half of the investigated soil samples, because the Fe_o content exceeded Fe_d. It is assumed that the oxidation of Fe(II) phases into oxalate extractable Fe(III) phases as well as the catalyzed dissolution of Fe(III) minerals by Fe(II) oxalate complexes sophisticate the results gained by chemical extractions using only ammonium oxalate and dithionite as leachates, but that these interferences do not account for oxalate in excess of dithionite extractable iron. Likely, dissolution of magnetite contributed to excess oxalate extractable iron. We conclude that conventional Fe_o and Fe_d extraction schemes may be misleading for coastal soils, i.e., more research is needed that can assign standardized Fe extraction schemes to defined mineral phases including the rapid physicochemical changes in such environments to attain reliable and comparable Fe data, particularly in the transition to terrestrial environments.

RESUMEN

Los óxidos de hierro promueven la agregación, adsorción de nutrientes y contaminantes, y también sirven como receptores de electrones; por lo tanto, es relevante comprender la composición de los pooles de hierro del suelo y sedimentos. Aquí analizamos si las aproximaciones de extracción química existentes, utilizando únicamente oxalato de amonio y ditionito sódico, entregan información consistente sobre la asignación de óxidos de hierro amorfos y cristalinas para los sedimentos costeros, los cuales sufren condiciones redox cambiantes. Se extrajo hierro usando una solución de ditionito citrato tamponado con bicarbonato de sodio y una solución de oxalato de amonio ácido (pH 3,25). El hierro extraído en ditionito (Fe_d) y hierro extraído en oxalato (Fe_0) varió de 1,7 a 7,4 g kg^{-1} y de 1,0 a 11,3 g kg^{-1}, respectivamente. Calculamos el contenido de óxido de hierro cristalino a partir de la diferencia entre Fe_d y Fe_o, con errores en casi la mitad de las muestras de suelo investigadas pues Fe_o excedió a Fe_d. Se asume que tanto la oxidación de la fase Fe(II) en la fase de hierro extraído en oxalato Fe(III) y la disolución catalizada de minerales Fe(III) por complejos de oxalato de Fe(II), sofistican los resultados obtenidos mediante extracciones químicas usando sólo oxalato de amonio y ditionito como lixiviados, pero que esas interferencias no dan cuenta del oxalato en exceso de ditionito de hierro extraíble. Probablemente, la disolución de magnetita contribuyó al exceso de oxalato de hierro extraíble. Concluimos que esquemas convencionales de extracción Fe_o y la Fe_d pueden entregar resultados erróneos para suelos costeros, necesitándose más investigación que asigne esquemas estandarizados de extracción de Fe para fases minerales definidas incluyendo los rápidos cambios fisicoquímicos en estos ambientes, para lograr datos Fe fiables y comparables, especialmente en la transición a ambientes terrestres.

Palabras clave: Óxidos de hierro, geoquímica sedimentaria, disolución selectiva, extracción secuencial.

INTRODUCTION

Iron is the fourth most abundant element of the lithosphere, and Fe(II) and Fe(III) minerals and its dissolved species are ubiquitous in the Earth´s crust, hydrosphere, biosphere and atmosphere (Cornell and Schwertmann, 2003). In most rocks, iron is present as Fe(II) and is released by chemical weathering. Pedogenic Fe(III) oxides, -hydroxides and -oxyhydroxides, hereafter for simplicity referred to as iron oxides, are formed by oxidation of ferrous iron, hydrolysis of ferric iron solutions or inter-conversion between the iron oxides (Schwertmann and Taylor, 1989; Cornell and Schwertmann, 2003). In soils and sediments, iron oxides control the mobility of plant nutrients (e.g. phosphate), the degradation, conversion and (im)mobilization of inorganic and organic pollutants and serve as an electron acceptor during dissimilatory Fe(III) reduction under anoxic conditions (Cornell and Schwertmann, 2003; Kappler and Straub, 2005). Additionally, iron oxides promote cementation and aggregation, although the aggregating effect seems to vary with different soils (Schwertmann and Taylor, 1989).

The most common iron oxides in soils and sediments are ferrihydrite (Fe_5HO_8 x 4 H_2O), lepidocrocite (γ-FeOOH), goethite (α-FeOOH), hematite (α-Fe_2O_3) and maghemite (γ-Fe_2O_3), which are composed of $FeO_3(OH)_3$ octahedrons and only differ in terms of linkage and spatial arrangement of this structural unit (Cornell and Schwertmann, 2003). Redox reactions and the associated dissolution and precipitation as well as mobilization and redistribution of iron are induced by chemical and microbial processes. Where the oxidation of Fe(II) under oxic conditions is catalyzed by microorganisms (Kappler and Straub, 2005), the reduction of Fe(III) by microorganisms in anoxic environments is mandatory (Ottow, 2011). However, the transformation of iron depends primarily on pH, redox potential (Eh), temperature and moisture (Cornell and Schwertmann, 2003).

Also in tidal marsh sediments iron oxides are prevailing electron acceptors (Kostka and Luther, 1994; Kostka *et al.*, 2002). Besides sulfate, iron oxides function as terminal electron acceptors for the degradation of organic matter in marine environments (Canfield *et al.*, 1993; Kostka *et al.*, 2002). In the absence of sulfate microbial Fe(III) reduction may account for 21 – 78 % of the anaerobic organic matter oxidation (Canfield *et al.*, 1993). Upon Fe(III) reduction, either dissolved Fe(II), which may be adsorbed onto mineral particles, or nonsulfidic Fe(II), i.e. Siderite ($FeCO_3$) is formed (Canfield *et al.*, 1993). However, in sulfidic milieus, liberated Fe(II) may precipitate with dissolved sulfide to produce FeS, removing Fe(II) from solution (Canfield *et al.*, 1993; Poulton, 2003). Moreover, coastal sediments are characterized by rapid cycling of Fe, overall each iron atom is involved in redox cycles approximately 100 to 300 times before being buried in the sediment (Canfield *et al.*, 1993).

To estimate the amount of amorphous or poorly crystalline Fe in soils and sediments the acid ammonium oxalate extraction method (Schwertmann, 1964; McKeague and Day, 1966; Blume and Schwertmann, 1969) is widely used. Actually, oxalate-extractable Fe (Fe_o) is a measure of the free (x-ray) amorphous iron oxides (Schwertmann, 1959, 1964), which are basically ferrihydrite and small amounts of organically-bound Fe (Cornell and Schwertmann, 2003). Schwertmann (1964) modified the method proposed by Tamm (1922) by using a 0.2 M NH_4-oxalate/ oxalic acid as extracting reagent, a pH of 3.0 and 2 h shaking time in the dark. Darkness is essential, since light prompts the dissolution of crystalline iron oxides (Schwertmann, 1964). Together with citrate-bicarbonate-dithionite (CBD) extractable Fe (Fe_d) (Mehra and Jackson, 1960), which quantifies the total amount of iron oxides (Cornell and Schwertmann, 2003), Fe_o does not only provide useful information on soil genesis (using the activity ratio Fe_o/Fe_d) (Blume and Schwertmann, 1969), but it also allows the differentiation of Fe pools depending on their degree of crystallization (Schwertmann, 1964). Nevertheless, these extraction schemes assume stable Fe(II) phases and it remains unclear how far, due to the rapidly changing physicochemical compositions both under in situ and under lab conditions, these chemical extraction methods allow to obtain reliable data regarding amorphous and crystalline iron oxides on which basis meaningful statements can be made about e.g. the exchange capacity of the iron oxide pool for pollutants and nutrients or the potential to stabilize the soil structure by cementation. Furthermore, only with reliable data solid interactions on pedogenetic processes from the activity ratio can be derived.

Hence, we reviewed existing chemical extraction approaches for coastal sediments using solely ammonium oxalate and dithionite in order to elucidate their reliability for iron speciation and deriving information on pedogenic processes from Fe_o/Fe_d ratios.

MATERIALS AND METHODS

Twenty-four soil samples were collected from top soils of Fluvic Gleysols and Tidalic Fluvisols with eutric or salic and/or calcaric properties from several tidal sites of the River Elbe estuary, Northern Germany. Disturbed soil samples were taken from each site in 10 cm and 30 cm depth. Some sites were inundated twice a day; usually a pronounced reed belt can be found here. Higher situated sites were just flooded during storm surges; these extensively managed areas are generally grasslands.

Table 1 summarizes means and ranges of some representative soil properties subdivided according to salinity. The corresponding physicochemical analyses were conducted according to the methods described by Blume *et al.* (2011) and Schlichting *et al.* (1995).

For extracting both the amorphous and well crystallized iron oxides, 2 g homogenized, sieved (< 2 mm) and air-dried samples were digested with 0.3 M Na-citrate solution, 1 M $\mathrm{NaHCO_3}$ solution and Na-dithionite in a water bath (75 – 80 °C) according to the method described by Mehra and Jackson (1960). The extraction steps were carried out twice. Finally, the sediment was washed with 10 ml 0.1 N $\mathrm{MgSO_4}$, the supernatant was added to the extract and mixed well. To selectively extract amorphous and poorly crystallized iron oxides 2 g homogenized, sieved (< 2 mm) and air-dried samples were added to a mixture of 0.2 M $\mathrm{NH_4}$-oxalate and 0.2 M oxalic acid at pH 3.25 corresponding to Schwertmann (1964). The suspensions were shaken for 1 h in the dark. For both extractions iron was determined by atomic absorption spectrometry.

Table 1. Mean and extreme values of some physicochemical properties of the studied soils.

Tabla 1. Valores medios y extremos de algunas propiedades físico-químicas de los suelos estudiados.

	Physicochemical property	Mean	Range
fluvial	pH ($\mathrm{CaCl_2}$)	6.4	4.2 – 7.2
	$\mathrm{CaCO_3}$ (%)	3.7	0.0 – 7.2
	organic matter (g kg^{-1})	46	21 – 87[†]
	sand (%)	36	1 – 89
	silt (%)	41	6 – 65
	clay (%)	24	5 – 40
	ECEC (cmol$_c$ kg^{-1})	21.8	10.7 – 39.3
brackish	pH ($\mathrm{CaCl_2}$)	6.6	5.1 – 7.3
	$\mathrm{CaCO_3}$ (%)	4.0	0.0 – 8.0
	organic matter (g kg^{-1})	43	8 – 140[†]
	sand (%)	52	10 – 70
	silt (%)	36	21 – 53
	clay (%)	12	5 – 37
	ECEC (cmol$_c$ kg^{-1})	15.9	8.9 – 29.1
marine	pH ($\mathrm{CaCl_2}$)	7.4	7.1 – 7.6
	$\mathrm{CaCO_3}$ (%)	10.0	0.0 – 37.3[‡]
	organic matter (g kg^{-1})	37	10 – 66
	sand (%)	24	4 – 60
	silt (%)	53	29 – 61
	clay (%)	23	8 – 36
	ECEC (cmol$_c$ kg^{-1})	20.3	8.3 – 29.7

[†] due to detritus, [‡] due to fractured shells

RESULTS

The contents of oxalate and dithionite extractable iron ($\mathrm{Fe_o}$ and $\mathrm{Fe_d}$ respectively) ranged from 1.0 to 11.3 g kg^{-1} for $\mathrm{Fe_o}$ and from 1.7 to 7.4 g kg^{-1} for $\mathrm{Fe_d}$ with an average of 5.0 g kg^{-1} and 4.3 g kg^{-1}, respectively (Table 2). On average, the highest $\mathrm{Fe_d}$ and $\mathrm{Fe_o}$ values were found for the fluvial zone. The lowest values were found in the brackish section.

Table 2. Dithionite and oxalate extractable solid phase iron ($\mathrm{Fe_d}$ resp. $\mathrm{Fe_o}$) of the sampled estuarine sediments plus the content of crystalline iron oxides ($\mathrm{Fe_{d\text{-}o}}$) and the activity ratio ($\mathrm{Fe_o/Fe_d}$). Values for $\mathrm{Fe_d}$, $\mathrm{Fe_o}$ and $\mathrm{Fe_{d\text{-}o}}$ in g kg^{-1}.

Tabla 2. Ditionito y oxalato de hierro extractable en fase sólida ($\mathrm{Fe_d}$ resp. $\mathrm{Fe_o}$) de los sedimentos de estuarios muestreadas más el contenido de óxidos de hierro cristalino ($\mathrm{Fe_{d\text{-}o}}$) y la relación de actividad ($\mathrm{Fe_o/Fe_d}$). Valores para $\mathrm{Fe_d}$, $\mathrm{Fe_o}$ y $\mathrm{Fe_{d\text{-}o}}$ en g kg^{-1}.

	sample ID	$\mathrm{Fe_d}$	$\mathrm{Fe_o}$	$\mathrm{Fe_{d\text{-}o}}$	$\mathrm{Fe_o/Fe_d}$
fluvial	211	5.0 ± 0.5	4.5 ± 0.2	0.5	0.9
	213	5.1 ± 0.0	4.7 ± 0.2	0.4	0.9
	221	4.1 ± 0.2	3.7 ± 0.2	0.4	0.9
	223	5.5 ± 0.2	5.9 ± 0.1	-	1.1
	421	4.6 ± 0.2	5.8 ± 0.2	-	1.3
	423	5.2 ± 0.0	4.0 ± 0.2	1.2	0.8
	521	4.8 ± 0.0	10.4 ± 0.2	-	2.2
	523	5.2 ± 0.0	11.3 ± 0.1	-	2.1
	811	4.2 ± 0.1	5.6 ± 0.4	-	1.3
	813	7.4 ± 0.0	9.8 ± 0.4	-	1.3
brackish	1121	5.6 ± 0.1	5.7 ± 0.2	0.0	1.0
	1123	4.3 ± 0.0	3.6 ± 0.2	0.7	0.8
	1511	2.7 ± 0.0	2.7 ± 0.0	0.0	1.0
	1513	3.7 ± 0.1	3.1 ± 0.0	0.6	0.9
	1521	3.6 ± 0.0	2.9 ± 0.0	0.7	0.8
	1523	2.4 ± 0.1	1.2 ± 0.0	1.2	0.5
	1813	4.6 ± 0.0	3.5 ± 0.0	1.1	0.8
	1823	1.7 ± 0.3	1.0 ± 0.4	0.7	0.6
marine	2011	4.6 ± 0.3	6.2 ± 0.2	-	1.3
	2013	2.6 ± 0.0	4.1 ± 0.0	-	1.6
	2021	3.8 ± 0.3	4.0 ± 0.1	0.0	1.0
	2023	3.9 ± 0.0	3.2 ± 0.1	0.7	0.8
	2211	4.5 ± 0.0	7.0 ± 0.3	-	1.6
	2213	6.0 ± 0.0	7.2 ± 0.0	-	1.2
	2221	3.5 ± 0.3	4.6 ± 0.1	-	1.3
	2223	3.5 ± 0.2	3.4 ± 0.0	0.1	1.0

To calculate the content of crystalline iron oxides (Fe_{d-o}), the difference between the contents of Fe_d and Fe_o was generated, as earlier suggested by Blume and Schwertmann (1969). Intriguingly, for ca. 45 % of the samples this difference yielded a negative value for Fe_{o-d}, because the Fe_o content exceeded that for Fe_d. Hence, the ratio Fe_o/Fe_d that is generally used to indicate changes in the Fe oxide signature during pedogenesis and that by definition can reach a maximum value of 1 (Blume and Schwertmann, 1969), reached values > 1 for nearly half of the samples. Despite multiple repetitions of these analyses this discrepancy persisted, therefore errors in performing the chemical extractions were excluded. For the other samples the Fe_o/Fe_d value ranged between 0.5 and 1 (Table 2).

DISCUSSION

General analytical processes and explanations

The dithionite extraction has been extensively tested and often been used to extract the amount of pedogenic iron oxides from soils by reductive dissolution (Mehra and Jackson, 1960; Schwertmann, 1964; McKeague and Day, 1966). Similarly the acid ammonium oxalate extraction is well-established and commonly used for the determination of amorphous and poorly crystalline iron oxides (Schwertmann, 1964; McKeague and Day, 1966; Blume and Schwertmann, 1969).

Also for coastal and marine sediments these chemical extractions have been applied in previous studies to evaluate the properties of the solid phase iron content (Phillips and Lovley, 1987; Canfield, 1989; Oenema, 1990; Canfield *et al.*, 1993; Kostka and Luther, 1994; Poulton and Canfield, 2005; Zhu *et al.*, 2012; Zhu *et al.*, 2013; Luo *et al.*, 2014). The content of amorphous iron oxides (Fe_o) analyzed in this work (Tab. 2) was basically of the same magnitude as those found in other estuarine and coastal sediments (Kostka and Luther, 1994; Taillefert *et al.*, 2002; Zhu *et al.*, 2012; Zhu *et al.*, 2013; Luo *et al.*, 2014). However, the content of crystalline iron oxides (Fe_{d-o}) was relatively lower than in the coastal sediment studied previously (Kostka and Luther, 1994; Zhu *et al.*, 2012; Luo *et al.*, 2014), except when compared to the study of Taillefert *et al.* (2002), who found crystalline iron oxide contents of < 1 g kg^{-1} in the uppermost 10 cm of Berry´s Creek (Hackensack River, New Jersey, USA).

However, Canfield (1989) and Oenema (1990) also stated an overlapping of oxalate and dithionite extractable iron in the Long Island Sound and Eastern Scheldt profile, respectively. Oenema (1990) explained this phenomenon with the fact that most iron oxides were not well crystallized, what seems reasonable, since in systems with frequently changing redox conditions most iron oxides are present as ferrihydrite. Additionally, marshland soils can be considered as young soils in which the transformation of amorphous into more stable compounds has not yet proceeded as in sites with advanced pedogenesis (Cornell and Schwertmann, 2003).

Potential interferences during chemical extraction

In marshland soils various interferences during the chemical extraction of the solid iron pool may occur, affecting the obtained findings. These interferences may result, for example, from Fe associations with acid volatile sulfides (AVS) or oxidation of Fe(II) during sample preparation and are discussed below.

For instance, Canfield (1989) and Oenema (1990) mentioned that iron bound in AVS oxidizes during drying procedure into oxalate extractable iron phases. AVS is common in many sedimentary environments and represents the operational pool of sedimentary depositions including, among others, dissolved sulfide and FeS generating H_2S following HCl addition (Rickard and Morse, 2005).

As coastal and marine sediments are sensitive to changes in redox conditions, oxygen entry during sampling, storage and extraction may bias the results. Extractions made in ambient air differ up to 70 % from extractions conducted under anoxic conditions, due to the shift to more oxidized forms (Cauwenberg and Maes, 1997). Obviously, a distinct interpretation of oxalate extractable iron is not possible in environments where Fe(III) as well as Fe(II) phases coexist. To distinguish between ferrous and ferric iron phases Phillips and Lovley (1987) developed an anaerobic oxalate extraction method that was later on applied by Canfield *et al.* (1993) for Danish coastal sediments. However, the fact that Fe(II) phases are oxidized during sample preparation provides no explanation why the samples under study partially attain considerably higher contents of oxalate than of dithionite extractable iron, since dithionite dissolves the entire reactive iron pool in salt marsh sediments (Kostka and Luther, 1994).

Furthermore, there may be substantial readsorption and redistribution of extracted metals thus lowering their true amounts: up to 2.2 g kg^{-1} of extracted iron could be removed from the solution by readsorption, particularly in sediments with many available exchange places (Roychoudhury, 2006).

An additional release of Fe by oxalate may be related to both catalytic effects and the specific mineralogy. Earlier studies have suggested that Fe(II) oxalate complexes catalyze the dissolution of Fe(III) minerals (Kostka and Luther, 1994; Poulton and Canfield, 2005). Such dissolved Fe(II) may be produced during oxalate extraction from AVS and/or magnetite.

Another potential source of Fe(II) is the partial dissolution of silicates and pyrite oxidation during extraction, even though pyrite is not extractable in oxalate (Kostka and Luther, 1994). The extent of catalyzed dissolution of iron oxides depends on the concentration of Fe(II) present (Suter *et al.*, 1988) and becomes greater, the higher the Fe(II) concentration is (Poulton and Canfield, 2005). Thus, Kostka and Luther (1994) concluded that using oxalate extractions may underestimate crystalline Fe(III) minerals and overestimate amorphous Fe(III) minerals in saltmarsh and marine sediments. Furthermore, Heron *et al.* (1994) reported that dithionite extracts partly siderite ($FeCO_3$) and FeS producing dissolved Fe(II), suggesting that dithionite may be of little use for Fe(III) determination in sediments that contain both Fe(II) and Fe(III) phases. In this regard, all interpretations on reactive iron pools have to be done with care in sedimentary environments when oxalate and/or dithionite were the used extractants. Yet, these findings also cannot explain why we found oxalate extractable iron in excess to dithionite extractable one.

One of the minerals potentially contributing to high sources of additional Fe in the oxalate extract is magnetite. It is mostly of lithogenic origin, but may also be synthesized by microorganisms. While magnetotactic bacteria in soils were detected the first time by Fassbinder *et al.* (1990), Blakemore identified magnetotactic bacteria in marine muds already in 1975. Since magnetite is soluble in oxalate (Heron *et al.*, 1994; Kostka and Luther, 1994), but only to a small extent in dithionite (Fine and Singer, 1989; Poulton and Canfield, 2005), this fraction of the iron pool may cause the apparent excess in oxalate extractable iron.

Specific dissolution of Fe(III) and Fe(II) phases

In order to emphasize the importance of accurately identified Fe(III) and Fe(II) phases in the iron cycle of coastal sediments Kostka and Luther (1994) proposed an improved extraction scheme for the solid iron phase of salt marsh soils. An even more accurate differentiation including the evaluation of magnetite and Fe carbonate phases such as siderite and ankerite was suggested by Poulton and Canfield (2005). These extraction schemes, calibrated with standard Fe(III) minerals, has been used partly or completely by many researchers, to distinguish between the various solid iron phases occurring in estuarine and marine sediments (Wijsman *et al.*, 2001; Kostka *et al.*, 2002; Otero and Macias, 2002; Taillefert *et al.*, 2002; Zhu *et al.*, 2012; Zhu *et al.*, 2013; Luo *et al.*, 2014). The precise distinction of the different iron phases is relevant because iron oxides are important protagonists in buffering dissolved sulfide, which is produced during bacterial dissimilatory sulfate reduction (Canfield, 1989; Wijsman *et al.*, 2001; Poulton, 2003; Zhu *et al.*, 2012). Reactivity towards reaction with dissolved sulfide varies substantially due to widely varying mineralogy, crystallinity and morphology of iron oxides (Zhu *et al.*, 2012). Ferrihydrite and lepidocrocite are more reactive towards reduction by sulfide than well crystallized phases (Taillefert *et al.*, 2002; Poulton and Canfield, 2005; Zhu *et al.*, 2012). Since dissolved sulfide is toxic for benthic organisms, the fixation of sulfide via iron sulfides (FeS, FeS_2) is an essential detoxifying mechanism for the macrofaunal community (Wijsman *et al.*, 2001).

At this point remains an open question, what kind of extraction methods are the most relevant and precise ones. Apart from the two schemes of Kostka and Luther (1994) and Poulton and Canfield (2005), a number of other extraction schemes have been reported in the literature. But they differ from each other in many aspects, including sample preparation, time of extraction, single step or sequential extraction and type and strengths of the applied extractants (Roychoudhury, 2006). To date, a standardized method is not defined, which includes all mentioned processes and the rapid changes in coastal soils.

This study, however, reveals that the common Fe_o/Fe_d extraction methods may not be useful for coastal sediments, therewith challenging the understanding of Fe oxide dynamics of sedimentary environments. Furthermore, this work raises complex questions: where is the intercept, when Fe extraction methodology must change, as we approach coastal systems? Do the conventional extraction schemes provide reliable data for soils in which potentially changing redox conditions if only in niches may occur? How can we interpret Fe data from different localities if assessed by different methods? The methodological integration of reliable and comparable data of the iron pool in estuarine and coastal sediments into the global Fe cycle remains thus an interesting research challenge.

CONCLUSIONS

Estuarine and coastal sediments contain various forms of iron oxides combined with Fe(II) compounds that may dissolve during extraction. This study shows that in almost half of the samples under study, ammonium oxalate even extracted more Fe than dithionite. As this opposes common knowledge, we conclude that Fe_o and Fe_d cannot be used for the reliable determination of pedogenic iron oxides in mixed Fe(II)-Fe(III) sediments.

There are a lot of possible interferences during common extraction routine like, for example, the oxidation of Fe(II), the catalyzed dissolution of Fe(III) minerals by Fe(II) oxalate complexes or the ambiguous specificity of the extractants, therefore we recommend that all interpretations on the reactive iron pool of sedimentary environments have to be done with special diligence when oxalate and dithionite were the extractants of choice.

Although there is a variety of extraction schemes described in the literature, which differ in many aspects, a standardized method is still required to attain reliable and comparable information about the solid iron phases in sedimentary environments.

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