

# Wet-chemical extractions to characterise pedogenic Al and Fe species – a critical review

Thilo Rennert 

Fachgebiet Bodenchemie mit Pedologie, Institut für Bodenkunde und Standortslehre, Universität Hohenheim, D-70593 Stuttgart, Germany. Email: [t.rennert@uni-hohenheim.de](mailto:t.rennert@uni-hohenheim.de)

**Abstract.** Wet-chemical extraction of soil is a standard procedure to characterise pedogenic aluminium (Al) and iron (Fe) species, especially oxides, allophanic minerals and metal–organic associations. This article critically reviews the suitability of commonly used extractants (e.g. dithionite, oxalate and pyrophosphate) and the potentials and restrictions in their use for species identification and in soil classification. None of the commonly used extractants is completely selective and quantitative. The degree of completeness differs between the extractants and depends on soil composition. Dithionite-based methods provide a ‘pseudo-total’ content of pedogenic Fe oxides, as they are not always completely dissolved. Oxalate may attack further non-target species, releasing additional Al and Fe. Therefore, the extraction of Al and Fe exclusively from poorly crystalline species is not always guaranteed. As a consequence of dispersion of aggregates, pyrophosphate solubilises both mineral particles and metals from organic associations. Thus, quantification of species based on these extractions and their implementation in pedogenic thresholds may be questionable. Alternative extractants such as citrate–ascorbate and dithionite–citrate–oxalate could be used in addition, as applicable and reliable wet-chemical extractions will be still demanded for research and practical applications. The examination of the effectiveness and selectivity of wet-chemical extraction methods by spectroscopic techniques is recommended.

**Additional keywords:** dithionite, organic complexes, oxalate, oxides, pyrophosphate, soil classification.

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## Introduction

During formation and development of soils, all solid phases, i.e. soil organic matter (SOM) as well as minerals, undergo continuous (trans)formation and decay to varying extents in the presence of water. Aluminium (Al) and iron (Fe) in primary minerals, especially silicates, undergo weathering during soil formation, forming pedogenic species. Most importantly, these species include oxides, hydroxides, secondary clay minerals and organic associations of Al and Fe, allophane and similar minerals (allophanic constituents), and Al and Fe in exchangeable and water-soluble form (e.g. Loeppert and Inskeep 1996; La Force and Fendorf 2000; Dai *et al.* 2011). Quantitatively less important in most soils are Al and Fe phosphates, siderite, schwertmannite and Fe sulfides (Postma 1980; Prietzel *et al.* 2016).

Knowing the chemical composition of soils is the key to understand how and to what extent soils may fulfil their functions both qualitatively and quantitatively. For instance, soil functions comprise the storage of water and nutrients, and filtering and transformation of contaminants. Apart from SOM, especially metal (i.e. Al, Fe and manganese (Mn)) oxides and hydroxides play a prominent role in (ad)sorbing and transforming organic and inorganic contaminants (e.g. Bradl 2004; Pereira *et al.* 2012; Remucal and Ginder-Vogel 2014). Further, these oxides and hydroxides, together with

organic associations of the metals, play an important role in storing and stabilising SOM (e.g. von Lützwow *et al.* 2006; Kleber *et al.* 2015). Thus, identification and quantification of these pedogenic soil constituents is a prerequisite to enlighten the processes on which important soil functions are based. Given the enormous spatial and material complexity of soils, the full or even partial chemical characterisation of soil constituents is a challenging but necessary task to understand soil development and the pedogenic species evolved. Consequently, several textbooks have been published, summarising the methods of characterising the chemical composition of soils (e.g. Sparks 2001; van Reeuwijk 2002; Pansu and Gautheyrou 2006; Soil Survey Staff 2014a).

A traditional and very popular approach for soil characterisation is to extract soil samples and subsequently analyse the supernatant or filtrate chemically. Extraction means to separate or to obtain a certain component from a mixture of different substances, i.e. the approach is destructive. The principle of chemical extraction is using extractants that break up chemical bonds. Thus, the optimal result of chemical extraction is the complete, specific solubilisation of the target substance. The species released by chemical extractions are elements in ionic form or molecules, which are constituents of the target substance. These wet-chemical extractions are common in soil analysis because they are mostly easy to

handle, even with a large number of samples, less time-consuming and less expensive than advanced spectroscopic methods. The techniques to quantify the analytical targets in the extracts are available also in less equipped laboratories, e.g. atomic absorption spectrometry for metal analysis. Therefore, wet-chemical extractions have become standard in soil analysis.

Results from chemical extractions are being used for soil classification, e.g. by defining diagnostic properties and horizons in the international WRB classification (IUSS Working Group WRB 2015) or the US Soil Taxonomy (Soil Survey Staff 2014b). For instance, the definition of Andosols (or Andisols) and Podzols (or Spodosols) is based, among other criteria, on the contents of Al, Fe and silicon (Si) in different fractions that are defined by chemical extraction. The idea behind this is that these extractions enable the quantitative and qualitative analysis of pedogenic species that are the characteristic results of soil-forming processes. These processes have led to the specification of Andosols and Podzols with short-range ordered (SRO) Fe and Al oxides, allophanic minerals and Al in organic complexes as typical pedogenic species (Lundström *et al.* 2000; Dahlgren *et al.* 2004).

Attempts to differentiate pedogenic species by wet-chemical extraction have a long history. For instance, van Bemmelen (1877) used different acids and bases for the extraction of 'hydrogels' from soil. Tamm (1922) used oxalate and oxalic acid to dissolve 'gel complexes' of Si, Al and Fe, and Galabutskaya and Govorova (1934) employed dithionite to dissolve Fe oxides by reduction of Fe(III). Later, other extractants were introduced, e.g. pyrophosphate for organic metal complexes (Bremner and Lees 1949; Aleksandrova 1960), and EDTA, Tiron and citrate-ascorbate for 'amorphous'/poorly crystalline (Fe) oxides (Borggaard 1976; Biermans and Baert 1977; Reyes and Torrent 1997). Apart from these single extractions, several sequential extraction schemes have been developed for several elements in soil, partially based on the single extractants – a sample is treated successively with different extractants, aiming at dissolving the target analyte in different chemical forms. Such schemes have been published for single elements in soil, e.g. for Al (Dai *et al.* 2011), Fe (La Force and Fendorf 2000) and Mn (Jarvis 1984).

Critical reviews on the principles and the informative value of wet-chemical extraction techniques to identify and to characterise pedogenic species were published by the end of the 20th century (e.g. Borggaard 1988; Parfitt and Childs 1988; Loeppert and Inskeep 1996). Therefore, details on the laboratory procedures will be mentioned only briefly and as shortly as possible in the following. However, since these reviews were published, several studies have followed that are useful to test extraction techniques in a variety of soil environments and by advanced techniques. Therefore, this review aims at critically reviewing wet-chemical extraction methods regarding their selectivity, their potential and restrictions to characterise pedogenic Al and Fe species in soil quantitatively and qualitatively, and the potentials to derive conclusions on identification of pedogenic species and soil classification.

## Nomenclature and definitions

As mentioned above, the development and application of wet-chemical extraction to characterise certain soil components began in the 19th century. Since then, several terms have been introduced and used in the soil-science literature. The terms used by early researchers such as van Bemmelen (1877) and Tamm (1922), 'hydrogels' and 'gel complexes', have disappeared from recent studies, as it became known that, for instance, poorly crystalline Fe oxides and allophanic minerals are dissolved by Tamm's method (Schwertmann 1964; Parfitt and Childs 1988), rather than gels. The use of further terms may be discussed in the following, considering and reflecting the dynamic increase in knowledge. Analogously to Cornell and Schwertmann (2003), Al and Fe oxides, hydroxides and oxide-hydroxides are collectively referred to as oxides in this review.

Jackson *et al.* (1986) defined 'free oxides' as a general term for oxides of Al, Fe, Mn, titanium (Ti) and Si in soil, irrespective of their degrees of crystallinity. 'Free' refers to compounds with a single species as the coordinating cation, in contrast to 'combined oxides' with two or more different coordinating cations. Similarly, Loeppert and Inskeep (1996) designated the total Fe oxides in soil as 'free'.

Most soil scientists are very likely familiar with the term 'sesquioxide', which is also used in modifications, like for instance 'sesquic podosol' in the Australian soil classification (Isbell and National Committee on Soil and Terrain 2016). It is still used in recent publications and in soil classification systems, including the WRB classification (definition of the spodic horizon and the Ferralsol), the US Soil Taxonomy (definition of the oxic horizon) and the Australian and German soil classifications (definition of the Bs horizon; Ad hoc Arbeitsgruppe Boden 2005). 'Sesqui' originates from Latin, meaning one-and-one-half times, i.e. the term 'sesquioxide' defines metal oxides in the form of  $Me_2O_3$ . Consequently, Fe oxides such as ferrihydrite, goethite and lepidocrocite are not sesquioxides in a strict application of this definition, but hematite is. This differentiation is very likely not intended in soil-science papers and classification systems. According to Chesworth (2008), 'sesquioxide' is a 'superannuated term for the oxides and hydroxides of trivalent metals, particularly Fe and Al'. Considering that 'sesquioxide' in a strict sense is exclusively defined by stoichiometry (metal to oxygen ratio of 2:3), and excluding many important Al, Fe and Mn hydroxides in soil, its further use does not seem helpful as a general term for metal oxides in soil.

A fraction of the total ('free') Al and Fe oxides in soil has been designated as 'active' (e.g. Schwertmann 1964; Blume and Schwertmann 1969). Thus, the proportion of active oxides in soil may theoretically range from zero to 100%. The quotient of the contents of Fe in 'active' form and that in total pedogenic oxides has been tagged as 'activity ratio' (Blume and Schwertmann 1969). In addition, Mizota and van Rееuwijk (1989) designated Al in allophane, (partly) imogolite, in organic complexes, in interlayers and in exchangeable form as active Al. According to Blume *et al.* (2011), active oxides are more easily mobilised than more crystalline oxides. Similarly, Loeppert and Inskeep (1996) equated active oxides with poorly crystalline

oxides. They proposed the argument that poorly crystalline oxides have small particle sizes and thus large specific surface areas, which makes them chemically very reactive. The term 'active' is imprecise for at least three reasons. First, minerals other than oxides are included (e.g. allophane; Mizota and van Reeuwijk 1989). Second, the reference to crystallinity may imply the inclusion or exclusion of certain minerals in or from the active fraction, but there is no definition of a threshold of activity or reactivity. Third, active oxides have been frequently operationally defined by their solubility in oxalate (e.g. Schwertmann 1964; Blume and Schwertmann 1969; Loeppert and Inskeep 1996), which will be discussed later.

Similar inaccuracy is connected with the use of the adjective 'amorphous' to describe certain phases in soil. The nomenclature regarding amorphous, poorly crystalline and SRO (order spanning some nanometres in at least one direction) minerals is not uniform in the soil-science literature. For instance, Schaeztl and Thompson (2015) equated 'amorphous' with 'noncrystalline'. In contrast, noncrystalline phases have been defined as including both SRO and amorphous phases (Jackson *et al.* 1986). Shang and Zelazny (2008) used the terms 'short-range order' and 'poorly crystalline' equivalently on the one hand, and 'amorphous' and 'noncrystalline' on the other hand. Loeppert and Inskeep (1996) equated all the terms 'active', 'noncrystalline', 'short-range ordered' and 'amorphous'. This inconsistent nomenclature applies for instance to ferrihydrite, which is a poorly ordered Fe(III) oxide that has been previously referred to as 'amorphous' (Schwertmann and Taylor 1989), but for which structural models are available (e.g. Michel *et al.* 2010; Hiemstra 2013). Schwertmann and Taylor (1989) stated 'The once common belief that the majority of Fe oxides in soils are amorphous was caused primarily by the difficulties in detecting small concentrations of poorly crystalline phases. As physical analytical methods have improved, it has become obvious that most of what was formerly thought to be amorphous is either ferrihydrite and/or one of the other common Fe oxides. Ferrihydrite has short-range, three-dimensional order and should not be considered amorphous. As ferrihydrite becomes even less ordered (i.e. only two-dimensional order), the distinction between what is crystalline and what is amorphous becomes arbitrary. Naturally, the transition between perfectly ordered structures and highly disordered ones is continuous.' Similarly, Shang and Zelazny (2008) pointed out that the boundary between the mineral phases with varying crystallinity is diffuse. Therefore, to circumvent the historically partially confusing use of the terms to describe poorly crystalline phases, I suggest using the terms 'short-range ordered' equivalent to 'poorly crystalline', but not equivalent to 'noncrystalline' and 'amorphous'. Amorphous materials exhibit no order, even in the local environment of the atoms (Harsh 2012). Consequently, minerals such as allophane, imogolite and ferrihydrite are not noncrystalline or amorphous, as short-range order (Shang and Zelazny 2008) and a continuum of varying degrees of crystallinity are given. This designation should be differentiated from 'X-ray amorphous', which refers to broad unresolved signals of ferrihydrite and allophane in X-ray diffractograms.

For associations of metals, especially  $Al^{3+}$ , with SOM, sometimes the term 'humate' has been used (e.g. Sakai and Kumada 1985; Farmer and Lumsdon 2001). It refers especially to the analysis of Andosols where Al associated with SOM may be quantitatively important, as reviewed by Takahashi and Dahlgren (2016). However, the ending '-ate' implies that a salt of a defined carboxylic acid has formed (Leigh *et al.* 1998). The use of this term regarding soil analyses has two weaknesses. First, humic acids extracted from soil do not have a uniform composition among different soil types and horizons, and the term itself does not give any chemical information (Schnitzer 2001). Thus, they cannot be treated in chemical nomenclature like a defined individual carboxylic acid. Second, the ending '-ate' determines that a salt has actually formed, which is mostly not proven by chemical means, and which would exclude other forms of metal-SOM interaction in soil, e.g. adsorption of a metal cation by varying mechanisms. Therefore, the problematic use of 'metal humate' to characterise the product of SOM-metal interactions in soil should be replaced by a more general term that does not have potentially wrong implications regarding the type of interaction, e.g. 'metal-SOM association' or 'metal-organic association'.

### Extraction methods

As pointed out before, chemical extraction methods are widespread, as they are feasible, inexpensive and do not require sophisticated laboratory facilities. Another aspect of using extraction methods is that physical separation of the target substances from the soil matrix is very laborious, if not quantitatively impossible. Magnetic soil minerals can be separated from the soil matrix by applying a strong magnetic field. However, recovery of these particles strongly depends on their size. Schulze and Dixon (1979) recovered 70–94% of the dithionite-citrate-bicarbonate (DCB) extractable Fe ( $Fe_{DCB}$ ) in the 0.2–2.0  $\mu m$  size fraction by magnetic separation, but only 11–40% in the size fraction  $<0.2 \mu m$ . The recently described method for magnetic separation of magnetite from soil (Ahmed and Maher 2018) is very laborious and time-consuming (14 days). In addition, a method for the complete and selective physical separation of non-magnetic phases in soil, for instance Al oxides or metal-SOM associations is not yet available.

The 'perfect' wet-chemical extraction and the subsequent analysis should fulfil several requirements. First, it is actually the target analyte being extracted, and it is completely and permanently extracted, i.e. it is not only temporarily released, and then again removed from solution by adsorption or precipitation. Second, the target analyte is selectively extracted, i.e. the analyte in forms other than the targeted one are not extracted. Third, separation of the solid and the liquid phase is complete. Fourth, substances accidentally released during extraction do not interfere with analysis of the target analyte. Optionally, independent techniques, e.g. spectroscopic methods, verify the quantitative and possibly qualitative results. In the following, frequently applied extraction methods are discussed against the background of these requirements. Several restrictions of the selectivity and applicability of extraction methods in soil originate from the

polyminerale mixture soil itself. Rate-limiting factors such as crystallinity and particle size for the dissolution of an oxide may vary within the soil matrix (Cornell and Schwertmann 2003). Large crystals are more difficult to dissolve than small imperfect crystals (Borggaard 1988). Further, the extractability of mineral soil constituents may vary depending on associations with other compounds, i.e. if the analytical target present as coating, as an association with SOM or as interlayer of phyllosilicates, and on the extent of substitution of one element by another, e.g. Fe by Al (Borggaard 1988; Shang and Zelazny 2008). Apart from this chemical distribution, the spatial distribution of a mineral phase also affects its extractability, as occlusion in aggregates may cause a large resistance to dissolution, relative to free individual crystals (Shang and Zelazny 2008). For instance, a particle size  $<50\ \mu\text{m}$  is demanded for a complete extraction of Fe from pedogenic oxides (Mizota and van Reeuwijk 1989). Thus, grinding of such samples is recommended (Mizota and van Reeuwijk 1989; Pansu and Gautheyrou 2006, Blume *et al.* 2011).

#### Dithionite–citrate(–bicarbonate)

Dithionite ( $\text{S}_2\text{O}_4^{2-}$ ) is a strong reductant at  $\text{pH} < 9\text{--}10$ , with an optimum at  $\text{pH} 7\text{--}8$  (Pansu and Gautheyrou 2006). Thus, it extracts Fe(III) from oxides in soil, which undergo reductive dissolution. For subsequent analyses, the reduced  $\text{Fe}^{2+}$  and concomitantly released  $\text{Al}^{3+}$  ions remain in solution in the presence of a complexing agent like citrate ( $\text{C}_6\text{H}_7\text{O}_7^{3-}$ ; DC method, for 16 h at room temperature; Holmgren 1967), and in the facultative presence of bicarbonate ( $\text{HCO}_3^-$ ) as buffer (DCB method, for 15 min at  $80\ ^\circ\text{C}$ ; Mehra and Jackson 1958). The amounts of Fe extracted by DC and by DCB ( $\text{Fe}_{\text{DC(B)}}$ ) are considered equivalent (Klamt 1985; Borggaard 1988; IUSS Working Group WRB 2015). Extraction with dithionite is presumed to remove both well crystalline and poorly crystalline Fe oxides from soil (McKeague and Day 1966; McKeague *et al.* 1971). Thus, dithionite-based methods are used to quantify total ('free') Fe oxides in soil (Loeppert and Inskeep 1996). Shang and Zelazny (2008) pointed out that the term 'free Fe oxides' is operationally defined, representing Fe extracted by dithionite-based methods. These methods have become standard in textbooks on soil analysis (e.g. Mizota and van Reeuwijk 1989; Pansu and Gautheyrou 2006; Blume *et al.* 2011).

Criteria to check the appropriateness of a method include complete extraction of the analytical target, which excludes extraction of non-target species. Thus, given the descriptions of the application area of dithionite-based methods, these methods should completely dissolve pedogenic Fe oxides such as goethite, hematite, lepidocrocite and ferrihydrite. Iron in organic associations, in silicates, especially clay minerals, in siderite, vivianite and sulfides should not be released by DC(B). As dithionite-based methods depend on the reduction of Fe(III), oxides containing Fe(II) are not necessarily completely dissolved. Magnetite itself did not dissolve upon DCB treatment, only hematite coatings were attacked in soil containing both Fe oxides (McKeague *et al.* 1971; Walker 1983). Taylor and Schwertmann (1974) found that maghemite did not dissolve during DCB extraction, but

Singer *et al.* (1995) did. In addition, Hunt *et al.* (1995) and van Oorschot and Dekkers (1999) found that fine-grained magnetite and maghemite were dissolved by DCB. However, the latter authors emphasised that the completeness of extraction is a function of extraction temperature and magnetite content. Both magnetite and maghemite may be inherited from the parent material or formed during soil development (Mullins 1977). Pedogenic magnetite forms distinctly smaller particles ( $\sim 50\ \text{nm}$ ; Maher *et al.* 2003) than lithogenic magnetite. Formation of soil magnetite and maghemite by transformation of goethite and ferrihydrite is favoured at elevated temperature in the presence of SOM (Childs and Wilson 1983; Hanesch *et al.* 2006). These conditions prevail during vegetation fires, which would explain pedogenic magnetite in steppe soils (Maher *et al.* 2003). Pedogenic maghemite occurs in highly weathered soils of the tropics and subtropics, but may also form in soils of temperate climate (Taylor and Schwertmann 1974; Zanelli *et al.* 2006). Apart from the impact of fire, maghemite may form from oxidation of (lithogenic or pedogenic) magnetite and dehydration of lepidocrocite (Mullins 1977). Although (pedogenic) magnetite and maghemite are usually considered less abundant in soil, they may be quantitatively significant in (sub)tropical soils and soils where the formation conditions especially apply. In these cases, the quantification of total Fe oxides by DC(B) extraction may not always be precise.

A critical issue of the effectiveness of the DCB extraction is grain size, which can be solved by grinding as pointed out before, and the potential need to repeat the extraction. Nonetheless, several studies have shown that DC(B) does not guarantee extraction of Fe from the entirety of pedogenic oxides. Gorbunov *et al.* (1961) applied the DCB method to concretions at  $80\ ^\circ\text{C}$  and found only partial dissolution of goethite and hematite. However, this may have been partially caused by the temperature prescribed in the original method, which should not exceed  $75\ ^\circ\text{C}$  to minimise the decomposition of dithionite and to limit the formation of colloidal sulfur (S) and Fe sulfides (Pansu and Gautheyrou 2006). Borggaard (1982) found that natural hematite and magnetite were not completely dissolved by DCB, while natural goethite and lepidocrocite and a synthetic ferrihydrite were. Vodyanitskii and Shoba (2014) reported that hematite and goethite in (sub-tropical) soils were not completely dissolved, which agrees with Ericsson *et al.* (1984), who detected incomplete dissolution of hematite, even after three DCB extractions, and Goswami *et al.* (1995). Coward *et al.* (2018) showed that especially poorly crystalline Fe oxides were resistant to reduction by dithionite, which was the consequence of protection by SOM (Eusterhues *et al.* 2014a). Similarly, allophane and Al oxides may prevent complete reduction and extraction by dithionite (Filimonova *et al.* 2016). These are examples of the importance of localisation of the species to be solubilised by extraction as indicated before. Vodyanitskii (2002) reviewed the use of DCB and detected problems in its application with volcanic, acid-sulfate, ferralitic and peat soils, which refer to incomplete dissolution, especially of hematite, magnetite and Al-substituted goethite, and formation of reduced S species.

Apart from the target oxides, mentioned earlier, that were not completely dissolved by DC(B), other non-target phases may be partially attacked. These include allophane

(Wada and Tokashiki 1972; Farmer *et al.* 1983; Campbell and Schwertmann 1985), trioctahedral-type layer silicates (Arshad *et al.* 1972), chloritic minerals (Mitchell *et al.* 1971), smectites (Borggaard 1982; Stucki *et al.* 1984), kaolinite (Stanjek 1987) and metal–SOM associations (Tokashiki and Wada 1975; Wada 1989). Thus, both Al and Fe ions from non-target phases may be analysed in DC(B) extracts and potentially wrongly attributed to target phases. Especially the Al analysed in these extracts may originate from various sources, as Al ions form soluble complexes with citrate. Unlike Fe(III), dithionite does not reduce Al(III), i.e. the presence of Al<sup>3+</sup> in DC(B) extracts is the consequence of the reductive dissolution of Fe oxides, where Al may have substituted Fe or was present in adsorbed form (e.g. Bigham *et al.* 1978; Childs and Wilson 1983; Parfitt and Childs 1988). In addition, Al<sub>DC(B)</sub> may result from the reduction of Fe(III) in the structure of aluminosilicates that was subsequently weakened (Kaufhold *et al.* 2010). Consequently, the content of Al<sub>DC(B)</sub> of a soil sample cannot be attributed to distinct Al minerals. In addition to partial dissolution, DCB was found to alter the surfaces and surface charge characteristics of allophane and imogolite (Su and Harsh 1996), which affects the results of spectroscopic and microscopic analyses of soil samples previously treated with DCB regarding allophanic constituents.

A further, yet seldom applied dithionite-based extraction method utilises the combination of dithionite, citrate and oxalate (DCO; Goswami *et al.* 1995; Varadachari *et al.* 2006). The results presented by these authors showed a greater quantitative effectiveness of DCO compared with DCB, when applied to soils, synthetic and natural goethite and hematite, and clay minerals. There was no clear trend of aqueous Al and Si concentrations in the DCO extracts that would point to decreased or increased unintended dissolution of clay minerals.

#### *Ammonium oxalate–oxalic acid*

Historically, extraction with ammonium oxalate–oxalic acid ((NH<sub>4</sub>)<sub>2</sub>C<sub>2</sub>O<sub>4</sub>–C<sub>2</sub>H<sub>2</sub>O<sub>4</sub>) in darkness (AOD) at pH 3 targets (by operational definition) ‘active’ oxides (Schwertmann 1964). Tamm’s original method (Tamm 1922) was carried out in the presence of light, which, however, induces reduction of Fe(III) and the dissolution of more crystalline Fe oxides such as goethite and hematite (Deb 1950). Both Al and Fe(III) ions form soluble complexes with oxalate. At pH < 3.5, oxide surfaces are protonated, which is the first stage of dissolution, followed by adsorption of oxalate and release of complexed Al<sup>3+</sup> and Fe<sup>3+</sup> ions. The pH is maintained by the oxalate–oxalic acid buffer (Pansu and Gautheyrou 2006). The method of Schwertmann (1964) has become the international standard (Pansu and Gautheyrou 2006) that aims to completely extract X-ray amorphous soil compounds like ferrihydrite. However, Jones *et al.* (2000) found that AOD extraction did not completely dissolve all X-ray amorphous phases from tropical soils (Andisols, Oxisols, Mollisols and one Ultisol).

The AOD extraction is a notably rate-limited process. The rate of dissolution is proportional to the specific surface area (Cornell and Schwertmann 2003). The duration of the extraction is 2 h (Schwertmann 1964) or 4 h (McKeague and Day 1966). Fischer (1976) found that, after 2 h, easily

extractable Fe oxides were dissolved, and continued extraction dissolved Fe from more crystalline oxides and partially from silicates (Schwertmann 1973). However, no general kinetics are derivable and so a precise separation of Fe species is not possible with the empirical method (Schwertmann 1973). This is especially true for the Fe oxides, and makes AOD extraction sample-specific. Apart from ferrihydrite, AOD dissolved magnetite (Walker 1983) and maghemite (Taylor and Schwertmann 1974). These are not SRO minerals, so the general equalisation of ‘SRO minerals’ and ‘AOD extractable’ is incorrect. In addition, tropical soils derived from volcanic materials and rich in magnetite, may have larger contents of AOD-extractable Fe (Fe<sub>AOD</sub>) than of Fe<sub>DC(B)</sub> (Algoe *et al.* 2012). Depending on its crystallinity, AOD may dissolve lepidocrocite completely or to very small extent (Schwertmann and Taylor 1972; Poulton and Canfield 2005). Similarly, small or poorly crystalline goethite and hematite particles are dissolved by AOD (Acebal *et al.* 2000; Mansfeldt *et al.* 2012). Childs and Wilson (1983) detected unexpectedly low amounts of Fe<sub>AOD</sub> in soils dominated by poorly crystalline lepidocrocite, ferrihydrite, magnetite and maghemite. In strongly reduced soil with exclusion of oxygen, fougèrite and green rust have been identified and may be present in considerable amounts (Trolard *et al.* 1997; Rennert *et al.* 2013). It is dissolved by DCB, but not by AOD (Trolard *et al.* 2007). In contrast, schwertmannite, a Fe-hydroxy sulfate is dissolved upon AOD extraction (Reyes and Torrent 1997).

Unlike in the DC(B) extraction, several Al-containing minerals are dissolved by AOD. These include hydroxy-interlayer Al, poorly crystalline Al oxides, allophane, imogolite and other poorly crystalline aluminosilicates (e.g. Higashi and Ikeda 1974; Parfitt and Childs 1988; Wada 1989). However, Dohrmann *et al.* (2002) reported that dissolution of allophane was not complete, when present at large contents. However, they detected partial dissolution of gibbsite and halloysite. Kaufhold *et al.* (2010) even designated the underestimation of the allophane content by AOD extraction as systematic. These contradictory findings may be explained by the composition of allophanes in soils, which form a continuum with variable Al:Si in the range of 1–2 and degrees of crystallinity (Dahlgren *et al.* 2004). In summary, the unambiguous assignment of Al and Fe ions in AOD extracts to certain minerals is not possible. Consequently, the calculation of the difference of Fe<sub>DC(B)</sub> and Fe<sub>AOD</sub> to quantify crystalline minerals is potentially unreliable (Vodyanitskii 2002).

Like the DCB extraction, undesired phases are attacked during AOD extraction and induce the release of Al or Fe or both. Both metals may be released from trioctahedral silicates such as biotite, chlorite, muscovite and illite (Arshad *et al.* 1972). The AOD extraction may also solubilise Al and Fe in organic associations (e.g. McKeague and Day 1966; Parfitt and Henmi 1982; Farmer *et al.* 1983). Skjemstad *et al.* (1992) assumed that DC is as effective as AOD to extract Al associated with SOM. The Al in AOD extracts also derives from Al that has substituted Fe in Fe oxides, from gibbsite and from hydroxy–Al interlayers (Parfitt and Henmi 1982; Parfitt and Childs 1988). Given the low pH during extraction, exchangeable Al will be desorbed from different surfaces and subsequently analysed in the extracts.

### Pyrophosphate

Extraction with pyrophosphate ( $P_2O_7^{4-}$ ) aims to extract Fe and Al present in soil in organic form (Bremner and Lees 1949; Aleksandrova 1960; McKeague 1967). Extraction at pH 10, which considerably exceeds that of the original approach (pH 7; Bremner and Lees 1949), has become standard (Pansu and Gautheyrou 2006). Pyrophosphate chelates polyvalent cations and peptises soil particles at pH 10. Thus, at least two mechanisms may be active during extraction and potentially attack different metal species: metal cations that have formed complexes with SOM, and metal oxides on which SOM has adsorbed (summarised by Parfitt and Childs 1988). Peptisation of aggregates and particles (metal oxides with adsorbed SOM) at high pH is possibly more important than ligand exchange of Fe and Al ions (Borggaard 1988), but the relation of these two fractions depends on the soil type and soil composition (Jarvis 1986; Parfitt and Childs 1988). In volcanic soils, the principle action of pyrophosphate was dispersion of SOM aggregates (Thompson *et al.* 2011). It cannot be excluded that Al and Fe present as small particles that have not interacted with SOM are released by peptisation and aggregate disruption during pyrophosphate extraction. The same applies for particulate SOM occluded in aggregates before their disruption. Thus, an unpredictable variety of organic and inorganic species is solubilised by pyrophosphate extraction, and the species do not necessarily have a common compositional and soil-scientific processual background apart from being commonly extracted by pyrophosphate.

Evidence that pyrophosphate does not selectively extract organically bound Fe, but also Fe from poorly crystalline Fe oxides was published in the late 1960s (Bascomb 1968; Grimme and Wiechmann 1969) and repeatedly confirmed (e.g. Higashi *et al.* 1981; Jeanroy and Guillet 1981; Evans and Wilson 1985; Skjemstad *et al.* 1990, 1992; Meijer *et al.* 2007). According to Parfitt and Childs (1988), pyrophosphate-extractable Fe ( $Fe_{py}$ ) does not specifically relate to any particular form of Fe in soils and it should not be used to estimate Fe in humus complexes. Evans and Wilson (1985) noted that  $71 \pm 46\%$  of  $Fe_{py}$  and  $21 \pm 13\%$  of  $Al_{py}$  were from inorganic sources, as deduced from precipitation of the extracted cations by  $NH_4OH$  (Bascomb 1968). Regelink *et al.* (2014) reported that pyrophosphate at pH 8.5 released not only Fe ions bound to SOM, but also Fe-oxide nanoparticles. Consistently, Kassim *et al.* (1984) detected the release of particles including ferrihydrite as a dispersed sol that remained in suspension under greater gravitational fields than normally used in routine determination of pyrophosphate-extractable Fe. Shuman (1982) questioned the use of pyrophosphate to extract the organic fraction of Fe, as Fe oxides were also dissolved. Klamt (1985) even 'denunciated' the pyrophosphate extraction of Fe from soil. In addition, the partial release of Al and Fe from silicates has also been known for a long time (Titova 1962; Kononova *et al.* 1964). Well crystalline Fe oxides were not attacked by pyrophosphate at pH 10 (Bascomb 1968). Apart from Al in organic associations, pyrophosphate attacked and partially dissolved poorly crystalline Al hydroxides, Al-hydroxy interlayers and to small extent gibbsite and allophane (Farmer *et al.* 1983; Kaiser and Zech 1996; Kleber *et al.* 2004) so that, like  $Fe_{py}$ ,  $Al_{py}$  did not

exclusively originate from organic associations (e.g. Jarvis 1986; Parfitt and Childs 1988). Paterson *et al.* (1993) designated the  $Al_{py}$  fraction as ill-defined, derived from single and sequential AOD and pyrophosphate extractions of Podzol horizons.

As particles of unknown size and composition are released during extraction, phase separation is a crucial step. This is the main reason for the poor reproducibility of the method (e.g. Borggaard 1988; Skjemstad *et al.* 1990; Pansu and Gautheyrou 2006; Shang and Zelazny 2008). Schuppli *et al.* (1983) showed that clear supernatants from extractants required the application of ultrafiltration. Supernatants centrifuged at lower speed contained suspended mineral particles, even when using a flocculant. Ultracentrifugation that helps to circumvent these problems is not routinely available in soil-science laboratories. This restriction may thwart the application of pyrophosphate extraction as an easy-to-use method.

### Further extractants

Ethylenediaminetetraacetic acid (EDTA;  $C_{10}H_{16}N_2O_8$ ) is a strong complexing agent, and was found to dissolve similar amounts of Fe from synthetic oxides (ferrihydrite, goethite and hematite) after 4–5 h as AOD (Borggaard 1976). Apart from poorly crystalline Fe oxides, EDTA solubilises additionally exchangeable Fe together with Fe in organic associations (Jeanroy and Guillet 1981; Borggaard 1988). However, the amounts of Fe and Al extracted by EDTA were distinctly smaller than those extracted by pyrophosphate (McKeague and Schuppli 1985). Dissolution of Fe from goethite, hematite, lepidocrocite, maghemite and especially magnetite by EDTA was less than that by AOD, and dissolution from silicates was distinctly less than that by DCB (Borggaard 1982). The major drawback of EDTA is the long time to reach equilibrium, which may be several months. The alkaline pH, range of 7.5–10, with 10 mostly used (Borggaard 1988), and the long extraction time make EDTA unsuitable as an extractant for poorly crystalline and organic forms of Al (McKeague and Schuppli 1985; Pansu and Gautheyrou 2006). A 0.05 M EDTA solution, adjusted to pH 7 with ammonia, solubilised organic Al, but did not largely attack imogolite-type minerals (Farmer *et al.* 1980).

Hydroxylamine ( $NH_2OH$ ) is a relatively weak reductant to solubilise Mn(IV) from oxides in soil, together with hydrochloric acid (HCl; Chao 1972). It was also used to extract Fe from 'amorphous oxides' and provided similar results to AOD (Chao and Zhou 1983). Qiang *et al.* (1994) reported smaller amounts of Fe extracted by  $NH_2OH-HCl$  than by AOD, and so did Suda *et al.* (2013), who used a modification ( $NH_2OH-HCl$  in acetic acid). Qiang *et al.* (1994) explained this by incomplete reduction, hindered by SOM that covered or occluded the oxides, similar to that found for DCB (Eusterhues *et al.* 2014a; Coward *et al.* 2018). Reduction of Fe(III) during  $NH_2OH-HCl$  treatment induced partial dissolution of clay minerals (Ryan *et al.* 2008). Lee *et al.* (1989) reported larger amounts of Fe extracted by AOD than by  $NH_2OH$ , probably due to the presence of magnetite, and no

significant differences in the amounts of Al and Si solubilised by the two extractants.

Tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate;  $C_6H_4Na_2O_8S_2$ ) is a complexing agent to extract 'amorphous' Al, Fe and Si oxides at pH 10.5 and 80 °C (Biermans and Baert 1977). Crystalline forms are also attacked, as gibbsite and nontronite release substantial proportions of Al, and illite of Fe (Biermans and Baert 1977). Tiron did not solubilise magnetite to large extent (Reyes and Torrent 1997). Its effectivity to extract Al and Fe is similar to that of AOD, but greater for Si (Kodama and Wang 1989). Like AOD, Tiron dissolves allophane and imogolite (Kodama and Ross 1991). As a strong complexing agent at alkaline pH, Tiron may solubilise Al and Fe from organic associations, as the contents of Tiron- and pyrophosphate-extractable Al and Fe from Histosols and Gleysols were very similar, and so were the correlations of these contents with the contents of organic carbon (C) (Höhn *et al.* 2008). Thus, Tiron is not restricted to oxides, as originally intended. For non-weathered materials lacking metal-SOM associations and containing Fe-Ti oxides, Algoe *et al.* (2012) suggested Tiron to quantify SRO-Fe oxides.

Ascorbic acid ( $C_6H_8O_6$ ) is capable of reducing Fe(III) in well crystalline oxides such as hematite and goethite (e.g. Zinder *et al.* 1986; Suter *et al.* 1991). Ascorbic acid (0.1 M) combined with oxalate (McKeague and Day 1966) extracted similar amounts of Fe and larger amounts of Al from soils compared with DCB (Shuman 1982). Thus, this extractant may be an alternative for DCB regarding Fe, and provides the sum of  $Al_{DC(B)}$  and  $Al_{AOD}$ . Reyes and Torrent (1997) suggested using 0.05 M ascorbic acid with 0.2 M citrate to determine Fe in poorly crystalline oxides (pH 6, 16 h). In contrast to AOD, allophane, imogolite, chlorite, magnetite and Fe sulfides were attacked to distinctly smaller extents by citrate-ascorbate (CA; Kostka and Luther 1994; Reyes and Torrent 1997). Especially Podzols and Andosols revealed larger contents of  $Al_{AOD}$ ,  $Fe_{AOD}$  and  $Si_{AOD}$  than the respective CA-extractable contents ( $Al_{CA}$ ,  $Fe_{CA}$  and  $Si_{CA}$ ; Reyes and Torrent 1997). Furthermore, the molar ratios of  $Al_{AOD} - Al_{CA}$  and  $Si_{AOD} - Si_{CA}$  were consistent with those in allophane, which could be used for allophane quantification, as both AOD and CA extract Al from poorly crystalline oxides and organic associations, but only AOD additionally from allophane and imogolite. Because citrate at pH 6 alone extracted only little Fe but Fe in organic associations (Gerke 1993), Reyes and Torrent (1997) suggested the difference in  $Fe_{CA}$  content and that of citrate-extractable Fe ( $Fe_C$ ) as a measure of poorly crystalline Fe oxides. Extraction with CA was more efficient in dissolving small particles than AOD, as shown by electron microscopy (Pizarro *et al.* 2008). In combination with other extractants, CA may be used to differentiate SOM sorbents (Wagai *et al.* 2013). Citrate combined with bicarbonate dissolved fougèrite and green rust (Trolard *et al.* 2007).

Extraction under alkaline conditions dissolved various pedogenic species. At a high concentration of NaOH (5 M), clay minerals, other silicates, gibbsite, poorly crystalline Fe oxides and metal-organic associations were dissolved so that more or less well crystalline Fe oxides remained, which can be used for further analyses (Norrish and Taylor 1961; Pizarro *et al.* 2003). However, as the extraction is carried out at elevated

temperature, 90 °C, alteration at least of Al-substituted goethite occurred during extraction (Kämpf and Schwertmann 1982). At lower concentration (0.5 M; Hashimoto and Jackson (1958)), NaOH dissolved amorphous Al species, poorly crystalline Al oxides, SRO silicates, halloysite and partly gibbsite (Kitagawa 1976; Barreal *et al.* 2003). Furthermore, extraction of Al-SOM associations cannot be excluded given the alkaline pH. Thus, a strict selectivity for Al species is not given. Hot  $Na_2CO_3$  solution did not completely dissolve allophanic constituents and is thus not applicable to quantify these minerals (Hashimoto and Jackson 1958).

#### *Extraction and spectroscopic techniques*

The brief and very likely incomplete summary of studies on extraction of Al and Fe in pedogenic species and their interpretation have illustrated several potential drawbacks considering the selectivity of the methods. These may be enlightened by the combination of extraction and spectroscopic data. Especially X-ray diffractometry (XRD) and Mößbauer, nuclear magnetic resonance (NMR) and X-ray absorption spectroscopy are powerful tools to characterise pedogenic Al and Fe species in soil. Identification and quantification of Fe oxides by XRD is difficult at low contents and low crystallinity (e.g. Kodama *et al.* 1977; Acebal *et al.* 2000). However, differential XRD can be used to study the effectiveness and selectivity of an extractant (e.g. Campbell and Schwertmann 1985). A sample with a suitable internal standard is analysed by XRD before and after extraction, and the diffractogram after extraction is subtracted from that before extraction. This method provides qualitative (like infrared spectroscopy) and at least semiquantitative information about the minerals. Recently, the performance of XRD was greatly enhanced by synchrotron-based high-energy XRD and evaluation of pair-distribution functions, which enable the characterisation of poorly crystalline species, e.g. of Al, Fe and Mn (Carrero *et al.* 2017; Wang *et al.* 2017, 2018). The technique has not yet been applied to check the applicability of extraction methods.

Mößbauer spectroscopy (MS) is a sensitive probe of the local electronic structure and of the local crystallographic, magnetic and chemical environments (Rancourt 1998). Thus, it can determine both the types and relative amounts of Fe oxides (e.g. Kodama *et al.* 1977; Bigham *et al.* 1978). However, restrictions in its application are given by low contents of oxides and overlapping of field values by small particles, increasing extent of Al substitution and simultaneous presence of magnetite and maghemite (Bigham *et al.* 1978; Singer *et al.* 1995; Saragovi and Mijovilovich 1997). Ericsson *et al.* (1984) applied MS to study the dissolution of Fe oxides in soil by DCB treatment. They found that goethite was completely dissolved after three subsequent extractions, while hematite was not, confirming that DCB extraction might not always dissolve all Fe oxides. Similarly, Parfitt and Childs (1988) deduced from MS that hematite and magnetite were only partially dissolved by DCB extraction. They also found that pyrophosphate mobilised and extracted goethite particles. Their results from extraction (DCB, AOD and pyrophosphate), XRD and MS showed that the successful assignment of certain forms of Al and Fe derived from extraction differed between soil types, having studied an Alfisol,

Andepts, Oxisols, Spodosols and Ultisols. Iron extracted by pyrophosphate in basaltic soils did not resemble monomeric Fe–SOM associations, but rather included Fe-nanocrystalline components, as detected by MS (Thompson *et al.* 2011). These components may be embedded in an organic matrix (Chorover *et al.* 2004; Thompson *et al.* 2006b), which does not necessarily imply chemical interaction between the minerals and the organic matrix. Thompson *et al.* (2006a) and Mansfeldt *et al.* (2012) showed by MS that in soils affected by repeated redox cycles, the majority of AOD-solubilised Fe oxides were not composed of ferrihydrite, but of nano- and micro-goethite particles. These findings challenge the universal validity of the calculation of the ferrihydrite content by multiplying the  $Fe_{AOD}$  content with 1.7 suggested by Parfitt and Childs (1988). Nano-goethites may not be completely dissolved by DCB (van der Zee *et al.* 2005).

X-ray absorption methods considering different regions of the spectrum – X-ray absorption near-edge spectroscopy (XANES) and extended X-ray absorption fine structure spectroscopy (EXAFS) – are useful tools especially for Fe species. Groups of Fe-bearing phases (e.g. oxides, Fe–SOM associations, silicates and sulfides) are successfully discriminated by XANES (e.g. Prietzel *et al.* 2007; Rennert *et al.* 2013). Similarly, EXAFS can differentiate these groups of species, and additionally quantify Fe in different oxides (e.g. Mikutta *et al.* 2008; Kiczka *et al.* 2011; Sun *et al.* 2018). In contrast, Prietzel *et al.* (2007) showed that different Fe oxides such as ferrihydrite and goethite cannot be distinguished in synthetic mixtures by linear combination fitting of XANES spectra. Using EXAFS and XRD data, Baker *et al.* (2010) confirmed that AOD does not always solubilise ferrihydrite and that the assignment of degrees of crystallinity to operationally defined extracted fractions is not universally valid. Karlsson *et al.* (2008) concluded from EXAFS data that pyrophosphate and AOD extraction of organic soils is rather unspecific. Sun *et al.* (2018) showed that EXAFS differentiates between ferrihydrite and micro-goethite, but the ferrihydrite contents determined by EXAFS were greater than those determined by MS and by extraction with  $NH_2OH-HCl$ . The total content of Fe(III) oxides in topsoils of a Swiss chronosequence determined by DCB extraction was in the same range as quantified by EXAFS (Kiczka *et al.* 2011). This again confirms that the suitability of standardised extraction procedures depends on the sample (soil type and soil horizon).

In general,  $^{27}Al$ -NMR spectroscopy is capable of distinguishing between octahedral and tetrahedral Al and may be used to determine the coordination of Al for instance in phyllosilicates, allophane and gibbsite (Kinsey *et al.* 1985; Ildefonse *et al.* 1994; Bardy *et al.* 2007). Apart from minerals, Bardy *et al.* (2007) and Basile-Doelsch *et al.* (2005) showed that identification of Al–SOM associations is possible with solid-state  $^{27}Al$ -NMR spectroscopy. In the clay fractions of the horizons of a tropical Podzol, Bardy *et al.* (2007) found both a good agreement of Al in organic association as determined by pyrophosphate extraction and by  $^{27}Al$ -NMR spectroscopy, and incomplete solubilisation by pyrophosphate. However, this is so far the only study to test the amounts of  $Al_{py}$  against NMR spectroscopy.

Quantification of allophane from AOD data alone is problematic in the presence of large amounts of ferrihydrite (Parfitt and Childs 1988). It was based on the contents of  $Al_{AOD}$ ,  $Si_{AOD}$  and  $Al_{py}$  and empirical factors (Mizota and van Reeuwijk 1989; Parfitt 1990). Alternatively, Si in allophanic constituents can be quantified by  $^{29}Si$ -NMR spectroscopy. Rennert *et al.* (2014) compared the results of  $^{29}Si$ -NMR spectroscopy and extraction data mentioned before and found a systematic overestimation by extraction, caused by mobilisation of non-allophanic Si, such as Si released from AOD-soluble ferrihydrite (Schwertmann *et al.* 1982) or amorphous silica (Tamm 1922). Similarly, Hiradate *et al.* (2006) found an overestimation of Si in allophanic constituents by  $Si_{AOD}$  in A horizons with rather low allophane contents compared with quantification by  $^{29}Si$ -NMR spectroscopy, but an underestimation in subsoil horizons rich in allophanic Si. They suggested that the classical AOD extraction does not dissolve all allophanic constituents in these accumulation horizons. Kaufhold *et al.* (2010) applied XRD and quantified allophane by the Rietveld technique. In accordance with Hiradate *et al.* (2006), they found an underestimation of allophanic Si by AOD extraction in allophane-rich samples. Thus, quantification of allophane by AOD extraction alone has been challenged by two non-destructive techniques. For a further characterisation of the development of pedogenic Al species in volcanic-ash soils, the relative proportion of tetrahedral Al, obtained by  $^{27}Al$ -NMR spectroscopy, may provide valuable information (e.g. Basile-Doelsch *et al.* 2005; Hiradate *et al.* 2006; Rennert *et al.* 2014).

Table 1 summarises the most important findings regarding the effectiveness of chemical extractions to characterise

**Table 1. Generalised effectiveness of selected chemical extractants regarding dissolution or mobilisation of pedogenic Al and Fe species**

Al oxides, poorly crystalline oxides, hydroxides and gibbsite; DC(B), dithionite–citrate–(bicarbonate); Py, pyrophosphate; CA, citrate–ascorbate; DCO, dithionite–citrate–oxalate; p, potential(ly); cd, complete dissolution; dse, dissolution to small extent (approximately <10%); dde, dissolution to distinct extent (up to ~50%); mp, mobilisation of particles; ?, unknown because of contrary results or insufficient number of data available

	Hematite	Goethite	Ferrihydrite	Lepidocrocite	Magnetite	Maghemite	Al oxides	Allophane	Silicates	Metal–SOM complexes
DC(B)	pcd	pcd	pcd	pcd	dse?	dde?	dde?	dde	dse	dde
AOD	pcd	pcd	pcd	pcd	pcd	pcd	pcd	pcd	dse	pcd
Py	mp?	mp	mp	mp?	mp?	mp?	dse	dse	?	pcd
CA	dse	dse	pcd	pcd	dse	pcd	dse?	dse	dse?	pcd
EDTA	dse?	dse?	pcd	dde	dde	dde	dse	dse	dse	pcd
Tiron	?	dse	pcd	?	dse	?	pcd	pcd	dde	pcd
DCO	pcd	pcd	pcd	pcd	?	?	?	?	?	?

pedogenic Al and Fe species. Details were given in the previous sections.

## Discussion

The preceding sections revealed several drawbacks and restrictions of chemical extraction methods to characterise pedogenic Al and Fe constituents. However, the total amount of Fe oxides can be determined by DC(B) extraction, when the sample is ground and extraction is repeated when necessary. In other cases, this is not possible, e.g. in the presence of large amounts of magnetite or when extraction with DCO indicates a fraction of Fe oxides that is not completely dissolved by DC(B), as shown by the quoted literature examples. Thus, the  $Fe_{DC(B)}$  content may be better interpreted in analogy to aqua regia extraction, concerning the total element contents in soil, as a ‘pseudo-total’ content. This term shall express that the extraction has the potential to be complete, but it is *a priori* unknown, whether completeness is given or not. Whether the  $Fe_{DC(B)}$  content actually provides the total content of Fe in oxides does not only depend on practical laboratory performance described before – it also depends on the sample itself and its composition. Regarding selective extraction of Fe species from soil, La Force and Fendorf (2000) pointed out that selectivity is soil-type specific, and extraction should be adapted accordingly. This, however, restricts the applicability of standardised extraction methods.

An educated guess on the composition of the sample to be studied, sound knowledge of soil formation and the phases evolved and of known restrictions of common extraction procedures will help to draw reasonable and careful conclusions. For instance, the ratio of  $Fe_{DC(B)}$  to total Fe might not always be a reliable indicator of the extent of weathering (derived from the transfer of Fe from silicate forms to oxides). This applies especially to tropical soils, the Fe-oxide fraction of which may contain a substantial proportion of maghemite and magnetite, or special soils in other climates, which may contain maghemite, as described previously. Here, additional DCO and CA extraction may be an alternative, together with additional spectroscopic studies. This also applies to soils with Fe oxides that are protected from dissolution by associated SOM, an aspect brought up only recently and not entirely studied or understood. Apart from this potential underestimation, the content of Fe oxides in soil, as derived from DC(B) extraction, may be overestimated by the contribution of Fe from non-oxide sources. The relative and absolute amount of non-oxide Fe is not predictable, if not by applying sophisticated spectroscopic techniques such as MS or EXAFS.

Previously mentioned studies have shown that the unambiguous allocation of Al and Fe to certain minerals is not possible, as the metals may be extracted from organic associations, silicates and oxides. Dissolution methods are mostly empirical, and their results based on operational definitions. They cannot be expected to sharply separate Fe in oxides from that in other phases and particularly the degree of crystallinity of Fe oxides, as they are part of a continuum (Schwertmann 1973). Iron oxides that alter under periodically changing redox conditions are an example. Munch *et al.* (1978)

reported an increase of the ratio of  $Fe_{AOD}$  and  $Fe_{DCB}$  contents ( $Fe_{AOD}:Fe_{DCB}$ ) in soil after treatment with Fe-reducing *Clostridia*. Subsequent studies have shown that the increase of this ratio cannot be interpreted as an increase in the content of a mineral defined as poorly crystalline like ferrihydrite at the expense of a mineral defined as well crystalline like goethite, but rather as the formation of AOD-soluble nano- and micro-goethites (Thompson *et al.* 2006a; Mansfeldt *et al.* 2012; Winkler *et al.* 2018). These findings contradict the historical interpretation of the nature of AOD-extractable Fe oxides, since the increase of the  $Fe_{AOD}:Fe_{DC(B)}$  ratio was considered as a decrease in crystallinity, expressed by mineral names. The consequence is that chemical methods cannot be expected to perfectly distinguish degrees of crystallinity, and a better understanding of ‘noncrystallinity’ is provided when AOD extraction is combined with more selective and accurate techniques (Soil Survey Staff 2014a). Similarly, Torrence and Percival (2003) concluded from their comparison of extraction of clays (by AOD, DC, Tiron and  $NH_2OH-HCl$ ) that selectivity for specific Fe oxides was neither good nor consistent, and that no procedure tested was unambiguously selective for ferrihydrite. Similarly, Wada and Tokashiki (1972) stated that extraction by DCB,  $NaCO_3$  and NaOH was far from a complete quantitative mineralogical analysis of volcanic-ash materials, but helped in the interpretation of the physical and chemical properties.

As pointed out earlier, AOD extraction may not allow for a definite allocation of Al to distinct minerals. Similar to the case of Fe, the extent of correct allocation depends on the soil type and the soil horizon under study. In the case of volcanic-ash soils, this aspect is the more important. As shown before, pyrophosphate does not selectively extract metals from organic associations. Andosols and Andisols are defined, among other criteria, by contents of  $Al_{AOD}$  and  $Fe_{AOD}$  (Soil Survey Staff 2014b; IUSS Working Group WRB 2015). Andic properties (WRB classification) are further differentiated by the contents of  $Si_{AOD}$  and  $Al_{py}$  with strict thresholds (e.g. silandic properties with  $Si_{AOD} > 6 \text{ g kg}^{-1}$ ; ratio of the contents of  $Al_{py}$  and  $Al_{AOD} < 0.5$ ). Surely, an allophane-containing soil sample will always have significant contents of  $Al_{AOD}$  and  $Si_{AOD}$ . However, the reverse conclusion is not necessarily correct, as further, non-allophanic, soil constituents are known to release Al and Si upon AOD extraction. Similarly,  $Al_{py}$  does not necessarily relate to Al-SOM associations. Thus, it is questionable whether methods, which give at best a rough estimation of the species’ content, should be used for the definition of strict thresholds. Alternatively, CA and AOD extraction could be used for an approximation of Al and Si in allophanic constituents as mentioned previously ( $Al_{AOD}-Al_{CA}$  and  $Si_{AOD}-Si_{CA}$ ). Uehara (2003) pointed out that not simply a criterion for andic properties is needed, but a method to quantify and characterise ‘noncrystalline’ components of soils, including Al- and Fe-SOM associations, poorly crystalline oxides and allophanic constituents. He suggested determining the total content of X-ray amorphous materials by spiking a soil sample with a known amount of crystalline material and XRD analysis with the Rietveld technique (Jones *et al.* 2000). Further methods are available, as presented in *Extraction and spectroscopic techniques* above.

As pointed out earlier, extraction with pyrophosphate solubilises metals by two processes: (i) by chelating metal ions that have previously formed complexes with organic species and (ii) by peptising soil (micro)aggregates. As recently reviewed by Takahashi and Dahlgren (2016), the classical view on 'Al-humus complexes' is based on complexation of  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions by carboxylic and phenolic groups of humic substances. The degree of 'metal-humus' complexation is quantified by ratios of Al, C and Fe determined in pyrophosphate extracts. Although  $\text{Al}^{3+}$  and  $\text{Fe}^{3+}$  ions doubtlessly form complexes with carboxylic and phenolic groups, the explanatory value of Al, C and Fe in pyrophosphate extracts might be a subject for reconsideration on a mechanistic basis. Apart from metal ions that were solubilised by ligand exchange (pyrophosphate against organic functional groups), further organic and inorganic species may be solubilised during extraction. These include particulate organic matter (POM), Al and Fe oxides, and allophanic constituents in aggregates that have been disrupted during pyrophosphate extraction, and SOM that was adsorbed on mineral surfaces, in addition to that desorbed by pyrophosphate. Depending on the extent of phase separation, also the potentially nano-sized particles (Calabi-Floody *et al.* 2011) are subsequently analysed and allocated to an operationally defined fraction, irrespective of their actual chemical association. Removing POM and water-extractable C before extracting the mineral soil with pyrophosphate (e.g. Kaiser *et al.* 2011, 2012) represents great progress in the application of pyrophosphate extraction, but has not yet become standard. Nonetheless, there is a demand to clarify the nature and the properties of metal-SOM associations in soil on a mechanistic basis, transcending the classical view of metals that form complexes with functional groups of humic substances. Aluminium and Fe ions might react with functional groups of further SOM constituents, which are not necessarily humic substances that are defined by their solubility in alkali. In addition, the processes by which metals interact with SOM differ, as they form complexes with organic functional groups of varying strength (e.g. Goodman 1988; Driscoll and Schecher 1990; Skjemstad 1992; Masion *et al.* 2000; Sundman *et al.* 2014). Finally, metals in minerals that have formed by co-precipitation with SOM (Scheel *et al.* 2007, 2008; Eusterhues *et al.* 2011) may be considered as present in a metal-SOM association, but this mechanistic difference has not yet been considered to large extent.

Metal ions that have formed complexes with SOM may be extractable with neutral citrate (Reyes and Torrent 1997) so that an extractant other than pyrophosphate could be tested. The characterisation of Al-SOM associations in soil by spectroscopic techniques is still a large challenge. The  $^{27}\text{Al}$ -NMR approach might be promising, but its application is so far restricted to tropical Podzols. An extension to Podzols developed in different climates and especially to Andosols is desirable. Identification of Fe-organic associations is possible with X-ray absorption methods (e.g. Sundman *et al.* 2014; Bhattacharyya *et al.* 2018) and with MS (e.g. Goodman 1988), and the same applies to other pedogenic Fe species in soil.

Identification and characterisation of soil constituents that derive from interactions of metals and SOM is not only of academic interest. The SOM adsorbed on metal-oxide surfaces,

co-precipitated with metal oxides and metal ions shows retarded degradation, and is stabilised (e.g. Mikutta *et al.* 2007; Scheel *et al.* 2007, 2008; Schneider *et al.* 2010; Eusterhues *et al.* 2014b). The processes thus play a prominent role in the terrestrial part of the global C cycle and interconnected processes. For instance, this is expressed in the so far incompletely understood SOM storage in Andosols by interactions of SOM in allophanic minerals and formation of Al-SOM associations (Takahashi and Dahlgren 2016). Andosols store the largest amounts of SOM among all terrestrial mineral soil types (Zehetner 2010). Another example is the dynamic composition of Fe phases formed under dynamic redox conditions, inducing the formation of either more or less crystalline phases (e.g. Chen *et al.* 2018; Winkler *et al.* 2018). Adequate techniques are demanded, if possible by chemical extraction, to characterise these important pedogenic species. Alteration and ageing of these species may not only occur under variable redox conditions in periodically water-saturated soils, but also on a smaller spatial scale in aerated soils, which commonly have anaerobic microsites (Keiluweit *et al.* 2016, 2018). Thus, appropriate characterisation techniques help to broaden our understanding of processes and formation of pedogenic species in soil.

### Synthesis: conclusions and research directions

Borggaard (1988) suggested avoiding operational definitions of metal fractions in soil by certain extractants, and to simply designate for instance Fe extracted by AOD 'oxalate-extractable Fe', instead of adding a designation that would imply selectivity, which is not always given. The continued validity of Borggaard's suggestion is surely a conclusion of this review. The general identification of individual species by extraction, irrespective of soil type or soil horizon has been shown to be impossible. At best, this might be possible with groups of species. Similarly, further terms are still in use, although they are imprecise (e.g. 'sesquioxide') or proven wrong (e.g. 'amorphous oxide').

The problems with potential restrictions regarding the suitability of chemical extraction techniques are not the application of these techniques themselves, but the danger of improper and careless interpretations, e.g. regarding selectivity (allocation of extracted Al and Fe fractions to certain minerals or organic species, quotients and differences of the extracted contents) and completeness as pointed out in the previous sections. Nonetheless, there is a demand to develop and to apply extraction methods for instance for soil classification and standard soil analyses other than those that have been identified as disputable such as pyrophosphate regarding exclusively metal-SOM associations (the nature of which require further research), and AOD regarding allophane quantification. Obviously, when the definition of, for example, diagnostic horizons, properties, complexing cations for SOM and weathering indicators is based on chemical extractants, then the extraction procedure should provide explicit results. This is not the case at the moment.

Although spectroscopic tools are at least partially available for the identification of pedogenic Al and Fe species, they cannot completely replace extraction methods because of high

costs, restricted availability and laborious data evaluation. Alternative extraction methods could include CA and DCO. Spectroscopic studies should be carried out to identify the species that have been removed, as detailed, and comprehensive studies regarding the removal of species by CA and DCO are still lacking. This applies especially to redoximorphic soils, which reveal a multi-faceted and dynamic composition of Fe oxides (e.g. Thompson *et al.* 2006a; Mansfeldt *et al.* 2012; Chen *et al.* 2018; Winkler *et al.* 2018). These studies are a prerequisite for possible integration of new extractants. Finally, the results of these comprehensive studies might be considered in soil classification systems.

### Conflicts of interest

The author declares no conflicts of interest.

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