In situ Mössbauer spectroscopy and soil solution monitoring to follow spatial and temporal iron dynamics

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Abstract: Green-blue colours, characteristic of hydromorphic soils, have been recognized to be due to green rust minerals, for which the name "Fougerite" has been proposed. In reducing conditions, iron activity in soil solution is controlled by the dissolution and precipitation of iron oxides and especially of these transient, but well crystallised, green rust minerals. Recent study by EXAFS has suggested the partial substitution of Fe^{2+} by Mg^{2+}. Consequently, the general formula is:
$[Fe(II)_{(1-x)}\ Mg(II)_y\ Fe(III)_x\ (OH)_{(2+2y)}]^{x+}\ [x/n\ A^{n-}\ \ (1-x+y)\ H_2O]^{x-}$
where A^{n-} is the interlayer anion and x is the mole ratio Fe^{3+} / Fe_{total} (Refait et al., 2001).
The aim of this study is to follow the spatial and temporal iron dynamics by using *in situ* instruments. For the first time, a field Mössbauer spectrometer, adapted to the Earth's conditions from the instrument developed for Mars missions has been used to obtain spectra directly in a soil. MIMOS-II is operating in back-scattering geometry measuring the 14.41 keV Mössbauer radiation and the 6.4 keV Fe X-rays. The sensor head has been installed on an Archimedes screw into a PVC tube equipped with plexiglass windows through which spectra can be acquired at a given depth (± 0.4 mm). A printing circuit board carries the digital electronics for instrument control, communication, data acquisition and storage. No sample preparation is needed, the measurement is non-destructive and the volume probed is about 1-2 cm diameter and 100 to 200 µm depth. A spectrum is acquired in about 2-3 days. The tube was placed in hydromorphic soils in Fougères (Brittany, France). For the analysis of the soil solution, we have installed a multiparametric probe with a measurement cell at 80 cm depth, isolated from the atmosphere. In this cell, several parameters (pH, Eh, dissolved oxygen, temperature, conductivity) are directly measured and samples are collected with tubings. Dissolved Fe(II) and S(-II) are immediatly measured in the field with a portable spectrometer after filtration. The chemical analysis is completed in the laboratory.
The first results show both spatial and temporal mineralogical variations. The first evidence is the spatial variation of the x ratio of the green rust mineral at a given time. In the deepest horizon (approximately 100 cm), the green rusts are more reduced (x = 0.33) than at 50 cm (x = 0.65). The second evidence, obtained by resetting the instrument exactly at the same vertical position, is that the x ratio changes with time. This shows that the green rust minerals are highly reactive solid phases. These mineralogical varia-

tions can be correlated with fluctuations of the water table and the development of oxidoreduction processes in the soil solution.

keywords: hydromorphic soils – oxidoreduction – iron oxides – Mössbauer – green rusts

I Introduction

Iron in soil is one of the five most important chemical elements in abundance. It plays a major role in biogeochemical cycles as electron donor and acceptor in oxidoreduction reactions, the main source of energy for life. Soil genesis and soil properties are influenced by iron in minerals (Schwertmann, 1988) and in solutions (Ponnamperuma, 1972). Iron minerals occur mainly as fine particles which develop a large specific area, and closely associate to other colloidal particles (De Boodt et al., 1991). Mössbauer spectroscopy has emerged as a key tool to study precipitations, transformations, substitutions, reactivities, etc. of iron minerals (Schwertmann and Cornell, 1991), and to define the conditions of synthesis of GRs (Drissi et al., 1995; Hansen and Koch, 1995). GRs have been shown to be precursors of goethite and lepidocrocite (Refait and Génin, 1993; Schwertmann and Fechter, 1994). It has been shown that several iron phases, especially GRs and ferrous clay minerals are very reactive because Fe can be oxidized or reduced in their structures. However, their lability makes difficult the study and the conservation of these minerals from the field to the laboratory, for which special care must be taken (Badaut et al., 1985; Trolard et al., 1996). The first studies realised at Fougères (Brittany, France) in hydromorphic soils under forest have shown, by Raman and Mössbauer spectroscopies and kinetic selective extraction, that the major iron mineral is a GR, the "Fougerite" (Trolard et al., 1996; 1997). However, the mole *x* ratio, Fe^{3+} / $Fe_{tot.}$ of this mineral changes with depth (Abdelmoula et al., 1998). This suggests that there could exist temporal variations of this *x* ratio. But the preceding studies have been performed in the laboratory, either on synthetic minerals or on soil samples, and destructive sampling precludes the repetition of measurements at the same place.

In order to monitor in situ transformations of iron minerals in soils, a miniaturized Mössbauer spectrometer, designed for Mars missions, was adapted to Earth's conditions (Klingelhöfer et al., 1999), and installed in the field. It is mobile with depth in a PVC tube, and used to characterize and follow *in situ* iron minerals in soils.

The aim of this presentation is thus to show the first results obtained on iron dynamics, and the first evidence for *in situ* variations of the mole *x* ratio, Fe^{3+} / $Fe_{tot.}$ in soils with time and space under natural conditions.

II Materials and methods

II.1 Sampling site

The soil catena studied is localised in the domanial forest of Fougères. Many thalwegs cut a hill into small watersheds, about 800 m long. The site is located near a spring area upslope, at about 200 m from the top of the hill. The soils are developed in a granitic sand-silty saprolite (several meter depths) derived from weathering of granodiorite with cordierite. This saprolite is covered by two different silty formations (Van Vliet-Lanoë et al., 1995). The deeper one is the result of in situ saprolite evolution and the shallower one is a loess formed during the last glaciation (Weichselian). The soil catena is made of acid brown soil (ALOCRISOLS) upslope and hydromorphic reductic soils (REDOXISOLS-

REDUCTISOLS) downslope (Baize and Girard, 1995). This soil is acid attested by a pH_{H_2O} from 4 to 5.1 and a pH_{KCl} from 3.4 to 4 according with depth.
In the site where the instruments were placed, the different horizons observed are:

- 0 – 15 cm: a black histic horizon above an organo-mineral horizon with a diffuse transition.
- 15 – 50 cm: a redoxic silty horizon with some decolorations along roots and numerous oxido-reduction mottles; structure is massive and the watertable piezometric level is most frequently present in this horizon.
- 50 – 80 cm: a reductic silty horizon, homogeneous in colour and clearly blue (5BG 6/1), almost permanently waterlogged (10 months per year), without roots. Texture changes progressively to sand-silty from 60 cm to 80 cm.
- 80 – 120 cm: the reductic granitic saprolite with bluish-green color, permanently waterlogged. Texture is sand-silty.

II.2 In situ measurements and instrumentations

Mössbauer spectroscopy is a nuclear spectroscopy, whose applications in soil science are quasi-exclusively restricted to iron mineralogy. Being specific of iron, it is a very sensitive technique to identify and quantify iron minerals in soils, with a detection limit of about a few percents. Depending on their magnetic properties, iron minerals give doublets or sextets. From the spectra, informations about iron valence (Fe^{2+} or Fe^{3+}) and crystallographic environment (tetra or hexa-coordinations, for example) can be gained. In the following, we are only concerned with doublets, which are characterized by their isomer shift δ and their quadrupole splitting ΔE_Q.
The isomer shift δ is the abscissa of the middle of the doublet, measured with respect to a α-Fe foil reference, and is determined by the electron density at the nucleus. Thus, δ reflects specifically the oxidation states (Fe^{2+} or Fe^{3+}) of iron. The quadrupole splitting ΔE_Q is the distance between the peak doublets and originates from non-uniform charge density and electric field gradient interactions with the iron nucleus. Thus, ΔE_Q is influenced by the crystallographic environment.
The miniaturized Mössbauer spectrometer originally developed for Mars spatial mission with NASA and European Spatial Agency supports (Klingelhöfer et al., 1996) has been adapted to the Earth's conditions. This new prototype, called MIMOS-II, has been especially designed to study iron mineralogy in soils (Klingelhöfer et al., 1999). It works in backscattering geometry. Its total mass is less than 400 g and the power consumption of approximately 2 W is supplied by a battery, wih an autonomy of *ca*. 10 days. The instrument contains:

- a γ ray source, with an initial activity of 150 mCi, embedded in a rhodium matrix. The γ rays are emitted at 14.4 keV by the disintegration of ^{57}Co to ^{57}Fe. The resonance absorption by the sample is due to ^{57}Fe, whose natural abundance is 2.245 % of total iron.
- a drive generating by Doppler effect, a variation of the incident wavelength. Thus, Mössbauer spectra are presented with the velocity of the source in $mm.s^{-1}$ in abscissa and the number of γ rays emitted by the sample in ordinate.
- two detectors associated with amplifiers measuring the γ ray emitted by the absorbing solids at 14.4 keV and the X rays emitted at 6.4 keV.

The spectrometer is fixed on a 18 cm diameter platform inside a PVC tube (figure 1). It is mobile with depth with the help of a threaded rod (1.75 mm per turn). The tube is watertight and five large windows are drilled on a vertical. The instrument is placed in front of a window to acquire a spectrum. The investigation depth of the incident γ ray radiations is approximately 0.5 mm and the circular field of view is 2 cm diameter. Two or three days are sufficient to acquire a good quality spectrum. The accuracy of the depth is about 1.0 mm. A good physical contact between the soil and the windows was observed and noise was small. Temperature was not controlled but it was constant near 283 K. A series of reference positions was defined: 106 cm, 103 cm, 100 cm, 98 cm, 87 cm, 83 cm, 78 cm, etc. and about twice a week the spectrometer was moved to one of them. Quality of spectra depends essentially on iron concentration in the samples and the time of acquisition. Lorentzian are fitted to the spectra and the relative abundance of components is obtained by integration of the corresponding areas. The precision obtained on the *x* ratio is better than the precision on each individual doublet, as errors partly compensate, and can be estimated as ± 0.01 (Refait et al., 2001).

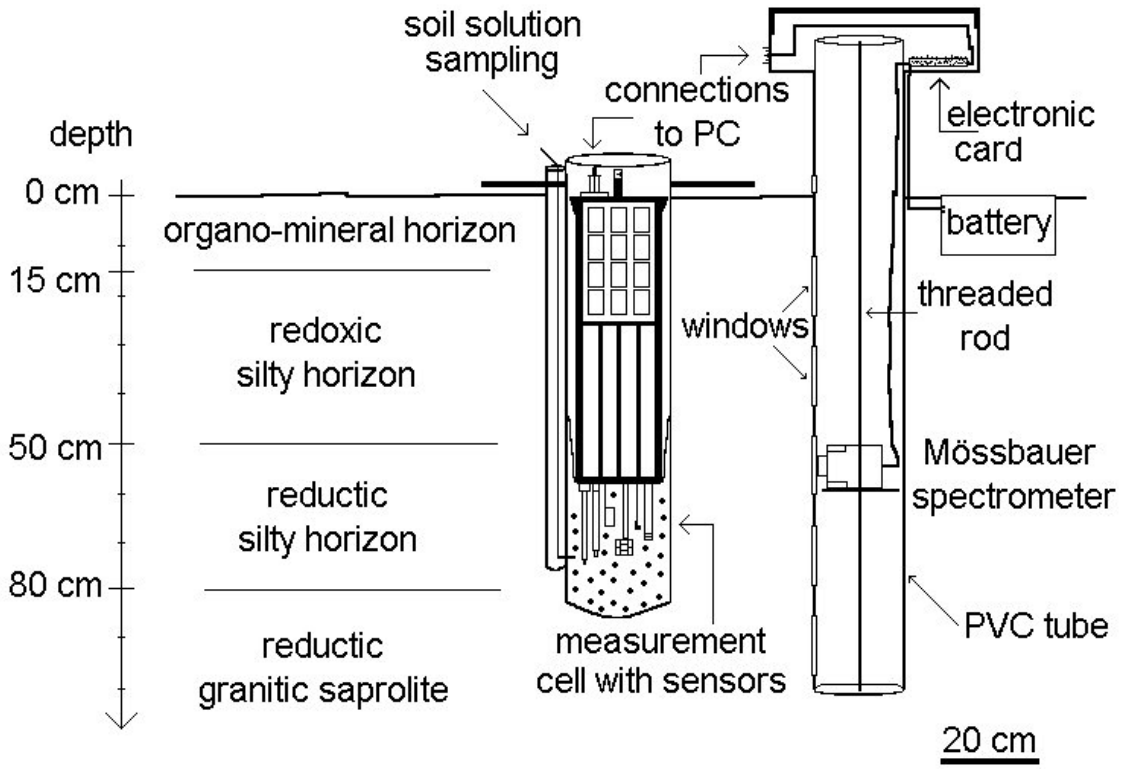

Figure 1: Soil catena and devices for *in situ* monitoring: Mössbauer spectrometer and multiparametric probe.

A multiparametric probe designed for oceanic measurements in sea water by Meerestechnik Electronik was adapted to monitor *in situ* changes of physical and chemical parameters in soil solution (Feder et al., 1998). No battery changes or sensor maintenance are required during several weeks. The probe is put into another PVC tube about 80 cm length and 12 cm diameter (figure 1). The lower extremity remains open to ease the entry and the circulation of soil water in the cell of the pipe where the measurements are performed, at 70 cm depth. To avoid the penetration of particles, the cell was wrapped in a synthetic and inert cloth. Precaution was taken to avoid preferential outflow along the tube and to isolate thoroughly the measurement cell from the atmosphere. The instrument is completed with external tubings to sample the soil solution precisely in the cell, free from contact with oxygen from the external atmosphere ; pH, oxido-reduction potential, dissolved oxygen, electric conductivity and temperature are measured every hour and directly and continuously stored in the internal memory of the probe.
After filtration at 0.45 µm, dissolved iron of soil solution samples are analyzed immediately *in situ* by colorimetry at 660 nm after DPKBH complexation (Suarez Iha et al., 1994; Bourrié et al., 1999) with a portable spectrometer Hach DR/2010.
In addition, the watertable level is followed with a piezometer. It was observed that the watertable level stays generally at around 40 cm depth during winter and moves down to 80 cm during the driest summers.

III Results and discussion

III.1 *In situ* mineralogical transformations of iron oxides

Natural GR, the "fougerite" mineral (Trolard et al., 1996; 1997), is the only iron oxide identified by Mössbauer spectroscopy in the field (figures 2 and 3 and table 1). The quality of Mössbauer spectra is similar in situ to that of spectra acquired in the laboratory by classical transmission Mössbauer spectroscopy on the same sample, and hyperfine interaction parameters are characteristic of GRs (Génin et al., 1998).
The variation with depth of the x ratio is large, from 0.34 to 0.64 (table 2), and much larger than the estimation error on x (± 0.01).
For example, at 106 cm depth, x ratio is equal to 0.36, close to x = 1/3 for which the corresponding chemical formula for GR is: $Fe(II)_2\ Fe(III)\ (OH)_7$.
At 48 cm depth, where x ratio is 0.62, close to x = 2/3 for which the chemical formula for GR is: $Fe(II)\ Fe(III)_2\ (OH)_8$.
The variation of x observed is monotonous between these limits.
At some depths, 48, 87, 98 and 106 cm, x ratio variations are of the same order of magnitude or only slightly larger than the estimation error (± 0.01). In these horizons, x can be considered as constant. On the opposite, sharp x ratio variations are observed with time at 83, 100 and 103 cm in soil (figure 4): for example at 100 cm depth, x ratio is initially equal to 0.39 and then increases to 0.48 one week later, suggesting that the $x = Fe^{3+} / Fe_{tot.}$ ratio of the mineral can change quickly, i.e. in a few days, in soil.
A special phenomenon is observed at 78 cm depth: the first recorded spectrum does not show any iron minerals (see arrow on figure 4) but one month later, a significant signal of GR appears, suggesting that GR has precipitated meanwhile.

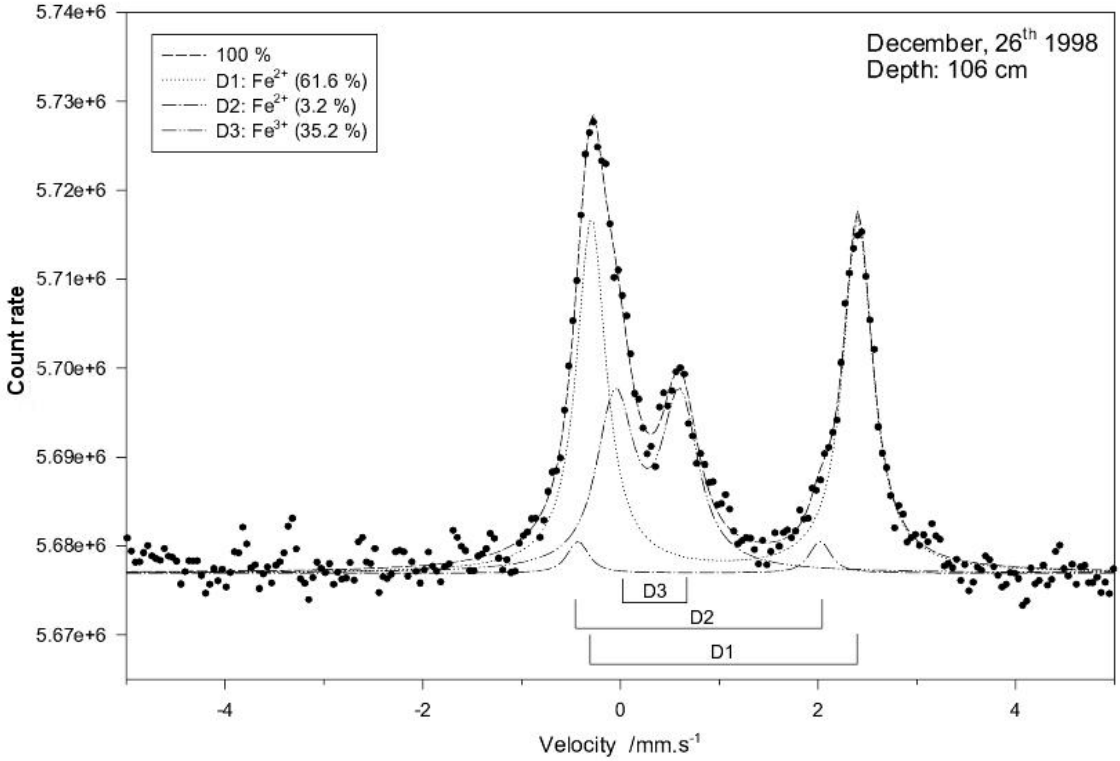

Figure 2: Backscattered Mössbauer spectrum measured *in situ* at 106 cm depth in the soil. The field temperature is *ca.* 283 K and the hyperfine interaction parameters are reported in table 1.

Table 1: Hyperfine interaction parameters of two *in situ* Mössbauer spectra (figures 2 and 3) obtained at 283 K at different depths. δ is the isomer shift (in $mm.s^{-1}$) with respect to that of a α-Fe foil reference; ΔE_Q is the quadrupole splitting (in $mm.s^{-1}$); RA is the Relative Area of the components (in %).

	December, 26th 1998			January, 22th 1999		
	106 cm depth			98 cm depth		
	δ	ΔE_Q	R A	δ	ΔE_Q	R A
D1: Fe^{2+}	1.05	2.70	61.60	1.05	2.71	49
D2: Fe^{2+}	0.79	2.46	3.20	0.83	2.33	5.90
D3: Fe^{3+}	0.27	0.66	35.20	0.26	0.67	45.10

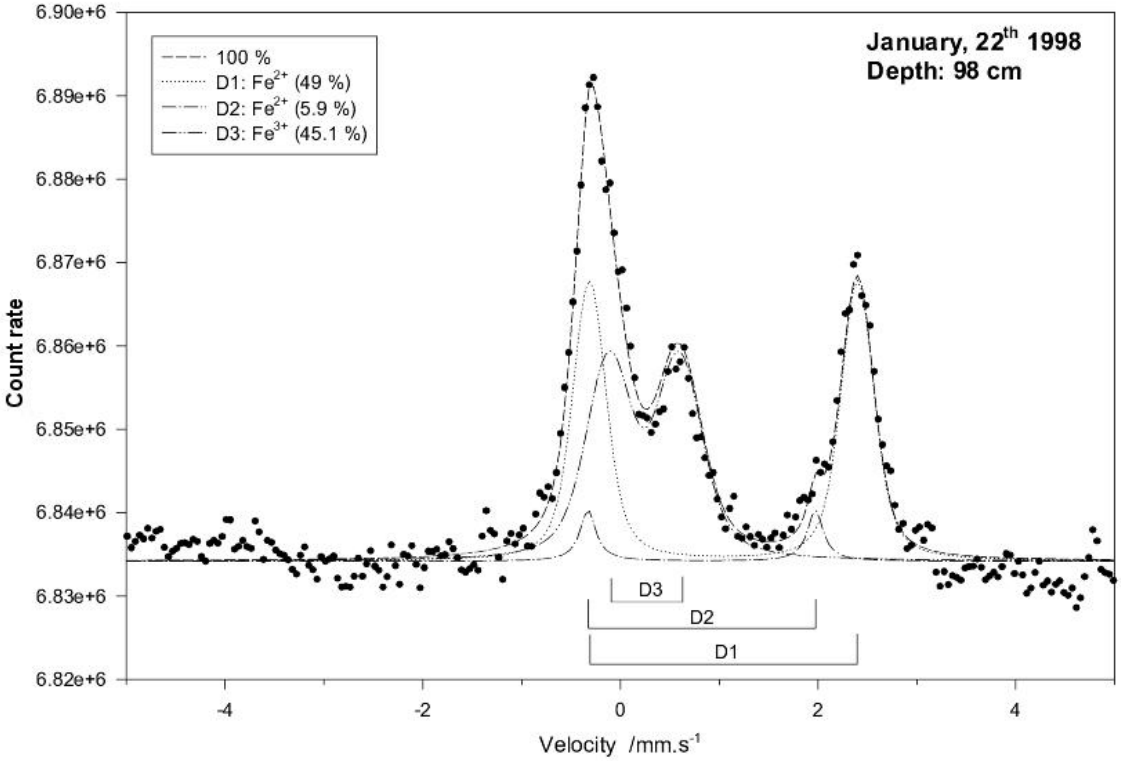

Figure 3: Backscattered Mössbauer spectrum measured *in situ* at 98 cm depth in the soil. The field temperature is *ca.* 283 K and the hyperfine interaction parameters are reported in table 1.

Table 2: Extreme values and average of $x = Fe^{3+} / Fe_{tot.}$ at different depths in soil (see also figure 4)

Depth	$x_{min.}$	$x_{max.}$	x_{mean}
48 cm	0.61	0.64	0.62
78 cm	0.59	0.61	0.60
83 cm	0.49	0.53	0.51
87 cm	0.49	0.52	0.50
98 cm	0.45	0.47	0.46
100 cm	0.39	0.48	0.43
103 cm	0.37	0.43	0.41
106 cm	0.34	0.37	0.36

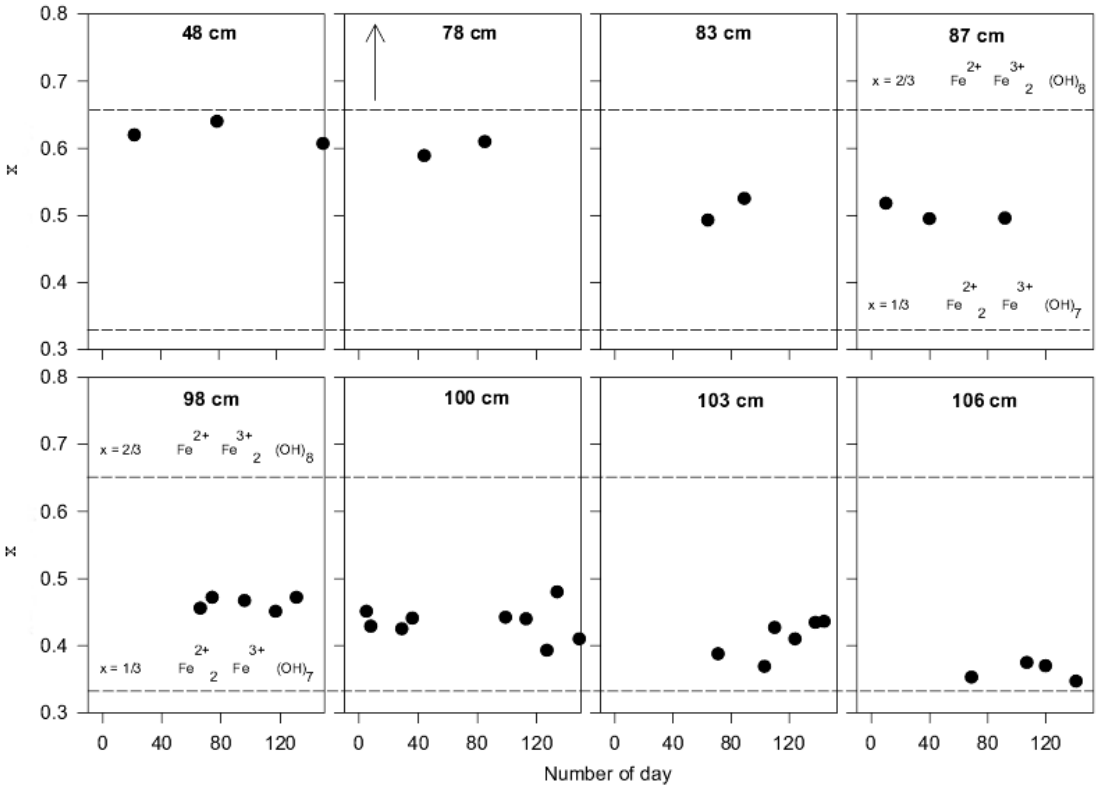

Figure 4: Variations of $x = Fe^{3+} / Fe_{tot.}$ with time at different depths. The short dashed lines correspond to *x* ratios equal to 1/3 and to 2/3 with corresponding abridged chemical formula. The arrow in the 78 cm diagram indicates the absence of GRs Mössbauer spectrum at this time (see text).

III.2 Discussion

All the *x* ratios observed in the field range between 1/3 and 2/3. No GRs have been found out of these limits. This is in agreement, first, with the thermodynamic equilibria computations performed by Bourrié et al. (1999), and secondly with the model of the regular solid solution proposed by Génin et al. (2001) and Bourrié et al. (2002, this volume).

The variation with depth of the *x* ratio is consistent with field observations: *x* is minimum in the deeper reductic horizons, and maximum in the upper redoxic horizons (table 2).

The most frequent pe and pH values coincide with the common part of the stability fields of the three GRs corresponding to *x* ratios 1/3, 1/2 and 2/3; this strongly suggests that the GRs act as a buffer to poise oxido-reduction potential.

IV Conclusions

A portable Mössbauer spectrometer has been used for the first time *in situ* to study iron oxide mineralogy in an hydromorphic soil. Spatial variation of $x = Fe^{3+} / Fe_{tot.}$ ratio were observed with depth:

- more ferric GR $Fe(II)\ Fe(III)_2\ (OH)_8$ is present in the upper redoxic horizons;
- more ferrous GR $Fe(II)_2\ Fe(III)\ (OH)_7$ is present in the lower reductic horizons.

Rapid temporal variations of *x* ratio have been observed by recording spectra at the same point at different times during the year. These variations are correlated to the fluctuations of the watertable and to the development of alternating aerobic and anaerobic conditions.

This is a means to follow the influence of anaerobic and aerobic alternations, in which iron plays the role of electron donor or acceptor. Natural GR is an essential actor in this interplay of biogeochemical cycles.

Acknowledgments: This work was supported by the Institut National de la Recherche Agronomique (INRA), the région Bretagne, the German Space Agency (DLR) and the French National Program on Soil and Erosion (PNSE).

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