

Processes driving soil solution chemistry in a flooded rice-cropped vertisol: analysis of long-time monitoring data

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Abstract

Senegal river water has positive alkalinity (0.55 meq l^{-1}) and positive calcite-residual alkalinity (0.30 meq l^{-1}). Without leaching, this water presents a possible alkalization and sodication hazard for the soil. The effect of flooding on soil solution chemistry in an irrigated nondrained vertisol under rice was monitored during 3 years in northern Senegal. During flooding, soil solution redox potential dropped to about -0.15 V , and alkalinity increased to 15 meq l^{-1} . Mg content increased as well, from about 1 to 5 meq l^{-1} , whereas Cl and SO_4 contents decreased to very low levels at the end of the growing season (0.05 meq l^{-1}). After the fallow, nonflooded period between two crop cycles, the soil solution composition returned to its initial neutral sulfate and chloride composition. The observed cycle in soil solution chemistry could not be explained by water and solute transfer because infiltration rates were very low, due to air entrapment in the soil profile. Geochemical control by calcite and gypsum was excluded during irrigation. Mössbauer spectroscopy showed that iron oxides were both well- and poorly crystallized goethite. Goethite dissolution was assessed by pH–Eh stability diagrams.

We explained the increase in alkalinity and Mg concentration in the soil solution partly by the composition of the irrigation water, and partly by the reduction and dissolution of Fe oxides, and Fe^{2+} fixation on exchange sites of the clay minerals. These processes were reversed as soon as the soil oxidized. The decline in Cl concentration was attributed to geochemical control through the formation of a GR-Cl^- mineral around the porous cups. In that case, Cl should not be used as a

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natural tracer. Carbonates accumulate in soil solution not only due to iron reduction, but also because of the positive residual alkalinity of the irrigation water. When the soil dries at the end of crop cycle, the carbonate concentration of topsoil will increase and calcite will precipitate. This ongoing process may result in calcium control and ultimately soil alkalinization over the years.

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1. Introduction

Rice, wheat and maize supply more than 50% of all calories consumed by the entire human population (IRRI, 1993). In West Africa, rice (*Oryza sativa* L.) is rapidly gaining importance, a development driven by changing consumer preferences and higher consumption levels in urban centers. It is the major crop grown under irrigation in West African Sahelian countries, where surface water resources are scarce in relation to arable land. A major concern in these potentially high yielding (e.g. Häfele et al., 2000) systems in an arid climate is the danger of soil degradation due to soil salinization processes (Boivin, 1997; Wopereis et al., 1998). Soil salinization is induced by evaporation, poor drainage and low water quality. It is considered to affect more than 10% of irrigated lands (Cheverry and Robert, 1998; Rhoades, 1997; Szabolcs, 1994).

In West Africa, irrigated rice cultivation has been linked directly with soil salinization (Madeley, 1993). However, Ceuppens and Wopereis (1999) showed that rice actually decreases salinity in naturally saline soils in the Senegal river delta. More insight is still needed into potential soil alkalinization and sodication processes under irrigated rice in the arid climate of the West African Sahel. But these processes are generally slow and may interact with many others. Simulating and foreseeing soil evolution in time is, thus, very complex.

Irrigated rice is cropped on clayey soils. In dry periods, clayey soils and particularly vertisols shrink and often crack at low water content (Wilding and Puentes, 1988). During land preparation and flooding, cracks allow preferential or bypass flow to occur (Favre et al., 1997; Mitchell and Genuchten, 1993; Tuong et al., 1996; Van Stiphout et al., 1987). Favre et al. (1997) demonstrated very rapid crack closure under irrigation or simulated rain. Shallow water table and surge flooding may cause air entrapment (Dixon and Linden, 1972) potentially blocking infiltration (Touma, 1984). Under prolonged flooding, the topsoil may become reduced, leading to reduction of iron oxides and iron in the clay structure (Fe_{SUR}), which can greatly modify proton and cation balances and CEC (e.g. Favre et al., 2002; Stucki, 1988). These processes are not well known or even observed under field conditions. They are neglected in most solute and water transfer simulation models.

Nutrient uptake by rice is very important in root zone, particularly for Si, N, P, Cl and Mg, Cl being a balance ion (Matsuo et al., 1995; Yoshida, 1981). Plant available nutrients are to a large extent determined by the extent of soil reduction upon flooding. Cations are released through adsorption of ferrous iron on the exchange complex (Brinkman, 1970; Genon et al., 1994; Ponnampereuma, 1965). Phosphorus is released by dissolution of oxides (Husin et al., 1987). NO_3^- turns into NH_4^+ upon reduction, and NH_4^+ can be fixed on the soil's cation

exchange complex (Ernstsen, 1996; Schneiders and Sherer, 1998). Khaled and Stucki (1991) showed irreversible fixation of potassium on reduced iron bearing smectites.

The evolution of soil quality underirrigation, therefore, results from complex interactions between a lot of processes. Field monitoring should address water and solute transfer, precipitation and dissolution of salts, cation exchange, geochemical equilibria, redox reactions and plant uptake. Most of these phenomena are related to rapid changes in temperature, microbial activity or plant growth. Only a few studies have reported extensive data sets. Soil solution evolution is generally investigated through simplified laboratory soil models, and only a reduced number of factors are taken into account. Ponnampetuma (1972) focused on redox processes, providing little information on geochemical equilibria or transfer processes. Other studies discussed plant nutritional aspects (e.g. Husin et al., 1987; Narteh and Sahrawat, 1999) in laboratory experiments, or described soil solution evolution without interpretation at process level (Ferreira and Coelho, 1984). The study reported here was carried out on an irrigated rice cropped vertisol in the Senegal River Valley, West Africa, as part of a multiyear research program on the evolution of sahelian soils under irrigation.

The objectives of this study were to (1) monitor the changes in soil solution chemistry under irrigated rice over a period of 3 years, (2) check the matching between observations and current knowledge on related soils and processes and (3) discuss the relative importance of solute transfer, geochemistry, redox processes and plant nutrient uptake on soil solution composition changes.

2. Material and methods

2.1. Study site and soil

Field experiments were conducted in an irrigated laser-leveled, but undrained paddy field, representative for rice growing conditions in the Senegal valley, near Donaye, Podor, northern Senegal (16°40'N, 15°00'W). Farmers have grown two crops of rice per year on this field since 1986. The first crop is sown during the hot dry season (DS, from March to June) and the second crop during the wet season (WS, from July to October). Experiments were conducted in 1996, 1997 and 1998. During this period, the farmer used transplanting as the crop establishment method and short-duration cultivar Sahel108 (IR13240-108-2-2-3).

The area has an arid climate with an average rainfall of about 280 mm, 95% of which falls between July and November (Albergel et al., 1993). Average Class A pan evaporation exceeds average rainfall in each month and by over 2000 mm annually (Brunel and Bourron, 1992). The soil is an arid vertisol (INRA, 1998), Xerert (USDA, 1998), locally known as Hollaldé soil.

Rice fields are flooded for more than 100 days during each growth cycle (Boivin et al., 1995). Irrigation water from the Senegal River is supplied to the field by gravity from an elevated channel using siphons. Farmers commonly apply about 200 kg urea ha⁻¹ and 100 kg diammonium phosphate (18% N, 20% P) ha⁻¹, but no potassium fertilizer (Wopereis et al., 1999).

The main soil characteristics of the Ap horizon (0–25 cm depth) at the experimental site are given in Table 1. Soil texture, CEC, total carbon content and pH values are close to

Table 1

Main soil characteristics at 0–25-cm depth: texture, total carbon, CEC and pH

Clay (%)	Fine silt (%)	Coarse silt (%)	Fine sand (%)	Coarse sand (%)	C total (mg/g)	N total (mg/g)
57.4	15.9	15.2	11.4	1	5.28	0.46
CEC (cmol _c /kg)	Exchangeable cations (cmol _c /kg)				pH	
	Ca	Mg	Na	K	H ₂ O	KCl
26.6	13.2	10.5	0.8	0.4	6.8	5.5

average values for vertisols (Ahmad, 1983). Topsoil bulk density was about 1.5 g cm^{-3} when dry and 1.3 g cm^{-3} when saturated. The clay fraction was composed of smectite (about 70%) and kaolinite (about 30%). Dithionite extractable Fe content ranged from 41.4 to 46.0 cmol Fe kg⁻¹ of air-dried soil. The Fe_{Str} content of smectite was 114.0 cmol Fe kg⁻¹ of smectite and Fe oxides are goethite, part of it being poorly crystallized (Favre et al., 2002).

2.2. Water quality and water balance

Water of the major Sahelian rivers has a low salt content (class conductivity 1; sodium hazard 1), according to Richards (1954), but upon concentration it may become hazardous (Vallès et al., 1989), as it often possesses a positive residual alkalinity. The composition of Senegal River water was analyzed weekly during 1997.

At the study site, the soil surface is cracked prior to first irrigation, but cracks close very quickly after irrigation, as described in a neighboring site by Favre et al. (1997). Between two crop cycles, Boivin et al. (1999) estimated the in situ saturated hydraulic conductivity of the field-dried topsoil, using suction infiltrometer to avoid preferential flow in the cracks. Saturated hydraulic conductivity values ranged from 3 to 30 mm day⁻¹. However, Boivin (1997) and Boivin et al. (1998a,b) established the water balance of the field and found that after crack closure, the soil infiltration rate was less than 1 mm day⁻¹. We used the same methods as Boivin et al. (1998a) to determine field water balance components. Fluctuations in ponded water depth are determined by evapotranspiration and irrigation rates. Water delivery was calculated from direct measurement of siphon inflow rate and by calculation of water volume in the field from sloping gauge readings and krigged estimates of field topography. Depth of flooding water was monitored twice daily, and before and after irrigation. The shallow water table fluctuates from 1.8 m depth to topsoil, due to Senegal river raw in rainy season (Diaw, 1996).

2.3. Soil solution monitoring

The chemical composition of the soil solution was monitored daily during the 1996 WS, the 1997 WS and the 1998 DS, using porous cups installed at 0.2 m depth. To evaluate the influence of water and solute transport processes on soil solution chemistry, a second set of porous cups was installed. Vertical and lateral water fluxes to and from these cups were blocked by a polyethylene film inserted horizontally in the soil, 0.2 m below the

porous cup and at a distance of 0.3 m all around. This second set was monitored during the 1996 WS and 1997 WS only. Soil solution was collected every 2 days, stored at 4 °C, filtered and analyzed for EC, pH, Al, Si, K, Mg, Ca, Na, NO₃, HPO₄, HCO₃, CO₃, SO₄ and Cl. HCl titration was used for carbonates; ICP, capillary electrophoresis and absorption spectrophotometer for cations; and ionic chromatography and capillary electrophoresis for anions. Data from porous cups where water transfer was blocked are referred to as NT (no transfer) observations; others are referred to as T observations. Alkalinity was equal to HCO₃ + CO₃ in the collected solutions. Fe²⁺ in the porous cups was not measured due to difficulties in preventing reoxidation during sampling. Fe²⁺ was, however, measured by Besson (2001) on the soil solution extracted from soil samples using centrifugation under nitrogen atmosphere. Centrifugation was chosen to prevent sharp changes in pCO₂, and Besson (2001) found Fe²⁺ concentrations ranging from 0.3 to 0.9 meq l⁻¹ for Eh values ranging from 0.15 to 0.05 V.

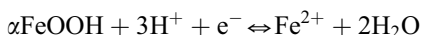
2.4. Soil reduction monitoring

Soil reduction status was monitored in situ during the 1998 DS as redox potential (Eh), pH and Fe^{II}/Fe^{III} ratio. Because of the high Fe_{Str} content, CEC was also measured during soil reduction. The Eh was monitored using platinum probes (Schott Geräte Metal Elektrode PT 1800) at 0.2 and 0.4 m depth. Three probes were placed at each depth and the Eh was then measured daily throughout the whole crop cycle. In situ soil pH was monitored daily using pH combination glass membrane probes with a Calomel internal reference system (Schott Geräte, pH Einstabmesskette H 9080) at 0.2 and 0.4 m depth. Two probes were installed at each depth. The pH probes allowed periodic renewal of the internal solution during monitoring, without removing the probe. The CEC and Fe^{II}/Fe^{III} ratio changes upon reduction were analyzed on soil samples collected at different Eh during the cropping cycle. Methods and results of this experiment are presented in Favre et al. (2002). In situ redox potential and pH measurements were continued after the 1998 DS, i.e. during the ‘interseason’ (the fallow period between two crops) and the 1998 WS.

2.5. Mineral equilibria

The KINDIS (Madé, 1991) and PHREEQC (Parkhurst and Appelo, 1999) programs were used to calculate mineral equilibria for soil solutions taken during the 1998 DS. Ionic speciation was evaluated by an iterative procedure and ionic activity calculated from the extended Debye–Hückel relation. The ionic product (*Q*) was then calculated and compared to the solubility product (*K*) of each of the following minerals: calcite, gypsum, magnesite and for some silicates: i.e. sepiolite, kaolinite and beidellite. The two latter minerals are present in the soil profile.

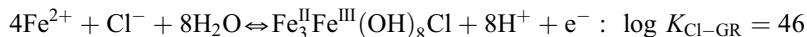
Eh–pH stability Pourbaix diagrams were built for goethite (αFeOOH), using the following equilibrium reaction and log*K* value:



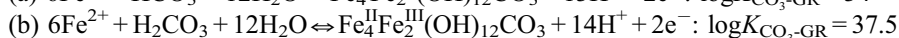
log*K* = 14.44 (Cornell and Schwertmann, 1996).

Eh and $p\text{CO}_2$ of the soil solutions may change when sampling with the porous cups prior to analysis. Therefore, we also discussed equilibrium with green rusts (GR) because it is very sensitive to pH. Because chloride and carbonates were the major anions, Cl-GR and CO_3 -GR equilibrium was considered using the reactions given by Génin et al. (1998):

Cl-GR:



CO_3 -GR:



with $\text{pe} = \text{Eh}(V)/0.05916$.

2.6. Crop growth

Crop components were monitored each cropping season. Crop yields were 6.3, 5.5 and 6.4 t ha⁻¹ of paddy for the 1996 WS, the 1997 WS and the 1998 DS, respectively.

3. Results

3.1. Water balance study

Cumulated water delivery was about 1000 mm during the wet season, and about 1500 mm during the dry season. Fig. 1 shows fluctuations in ponded water depth during the

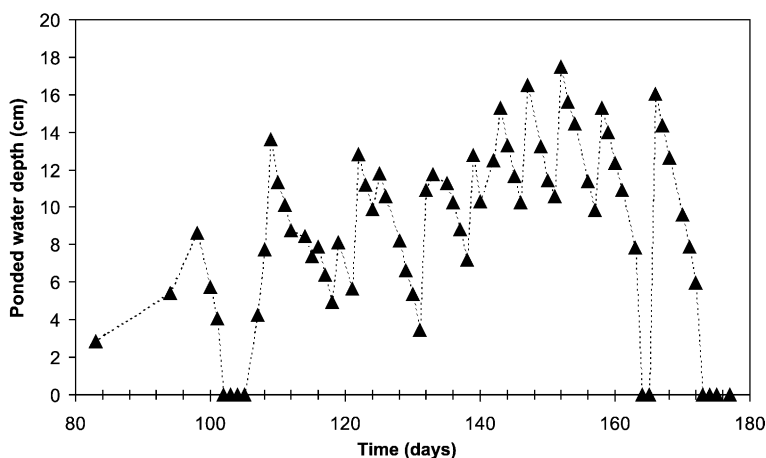


Fig. 1. Fluctuations in ponded water depth (1998 DS).

1998 DS. The field was left to dry during 5 days at the beginning of the crop cycle, i.e. at around 20 days after transplanting (DAT) for weed control. During the growth cycle, ponded water depth gradually increased from 2 to about 15 cm in the reproductive phase of the rice crop. Sudden increases in ponded water depth are due to renewed irrigation. In accordance with Boivin et al. (1998b), cumulated evapotranspiration equalled cumulated irrigation, as infiltration and surface water losses were negligible. A mean topsoil gravimetric water content of 60% was reached after 8 days of flooding (data not shown).

Irrigation water quality remained nearly constant over time. An average analysis is presented in Table 2, showing positive alkalinity (0.55 meq l^{-1}) and positive calcite-residual alkalinity (0.30 meq l^{-1}). Without leaching, this water presents an alkalinization and sodication hazard for the soil.

3.2. Soil solution monitoring

Evolution of electrical conductivity (Ec), Mg, Ca, Na and K during the three cropping seasons at 0.2 m depth are shown in Fig. 2. Evolution of alkalinity, Cl and SO_4 at the same depth are presented in Fig. 3. Correlation coefficients between Ec, Eh, cations and anions are reported in Table 3. No significant differences were observed between T and NT sampling sites.

Ec increased with duration of flooding. At the beginning of the cropping cycle, Ec ranged from 0.3 (1998 DS) to 0.5 dS m^{-1} (1997 WS). At the end of the cropping cycle, Ec ranged from 0.9 (1996 and 1998) to 1.2 dS m^{-1} (1997). Ec increased rapidly to 1.4 dS m^{-1} at the beginning of 1997 WS, and remained constant afterwards, probably due to rainfall that diluted flooding water during this time period. Mg was significantly correlated with Ec; it increased more rapidly, from about 1 to 5 meq l^{-1} at the end of the growing season. Ca and Na were poorly correlated with Ec except during the 1998 DS. In 1996 and 1997, Ca values fluctuated between 0.5 and 6 meq l^{-1} without a clear trend and Na values remained relatively constant with time. K values were very low and tended to decrease

Table 2
Irrigation water quality: average values and standard deviations for 18 analyses (1997)

	Average values	S.D.
pH	7.26	0.3
EC (dS/m)	0.06	0.02
Cl^- (mmol/l)	0.06	0.05
SO_4^{2-} (mmol/l)	0.02	0.01
NO_3^- (mmol/l)	0.01	0.01
HPO_4^{2-} (mmol/l)	0.00	0.00
Alkalinity (mmol/l)	0.55	–
Ca^{2+} (mmol/l)	0.25	0.04
Mg^{2+} (mmol/l)	0.21	0.04
Na^+ (mmol/l)	0.11	0.04
K^+ (mmol/l)	0.07	0.03
SiO_2 (mg/l)	1.01	2.00
Al (mg/l)	5.65	2.60

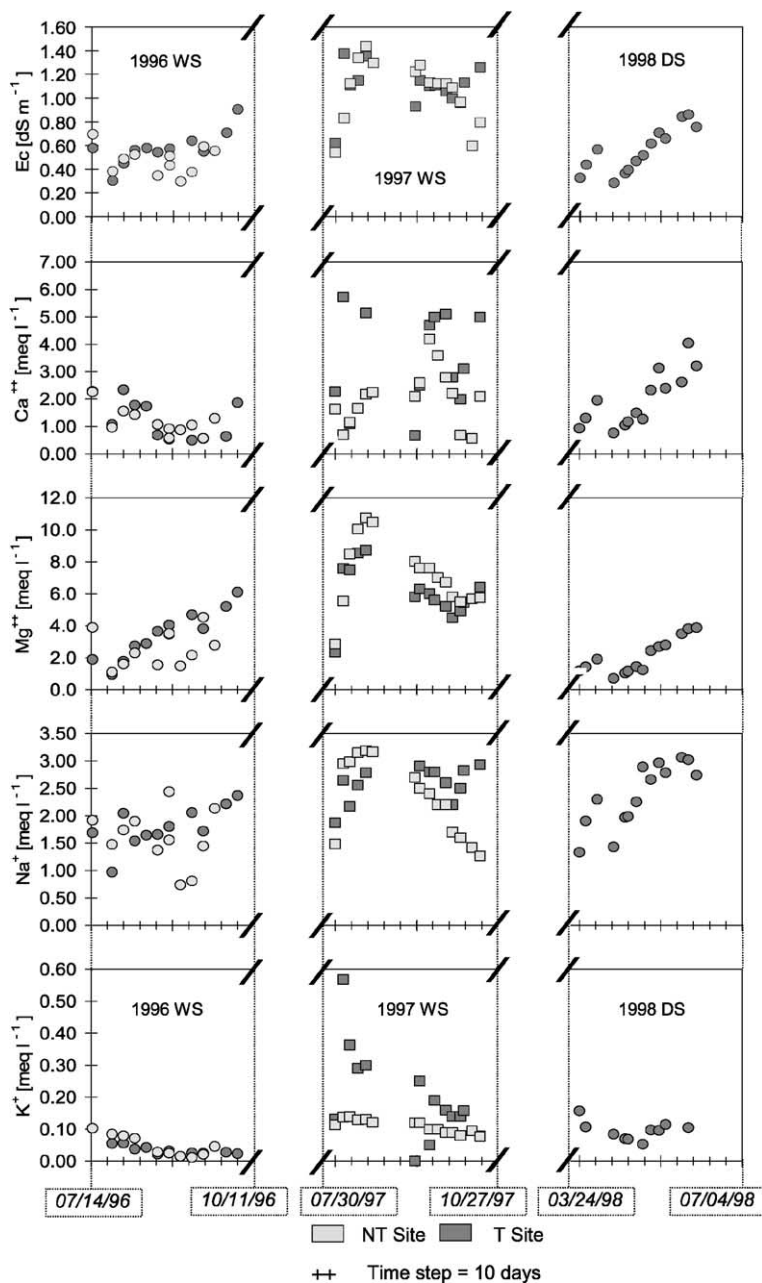


Fig. 2. Electrical conductivity (Ec), calcium, magnesium, sodium and potassium in soil solution during the three cropping seasons (1996 DS, 1997 WS and 1998 DS).

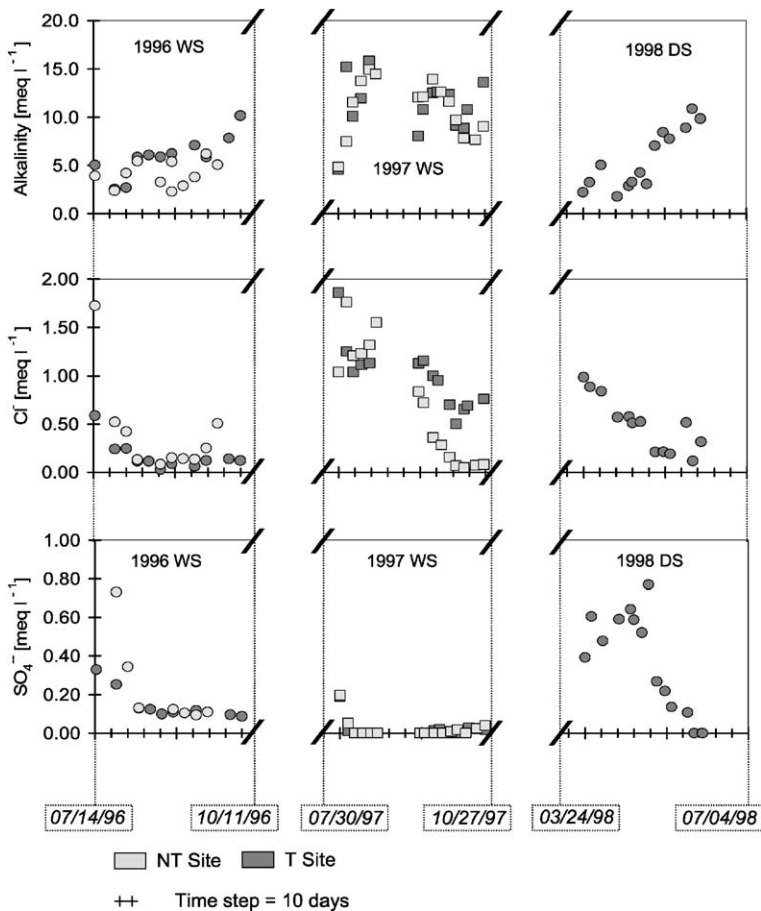


Fig. 3. Alkalinity, chloride and sulfate in soil solution during the three cropping seasons (1996 DS, 1997 WS and 1998 DS).

with time. Alkalinity behaved like magnesium, increasing over time from about 2 to about 15 meq l⁻¹, and strongly correlated with Ec.

Cl and SO₄ values decreased with time. Cl values decreased strongly from a maximum value of 2 meq l⁻¹ to a minimum value close to 0. The soil solution cannot be sampled between two crop cycles, but Cl content at the beginning of each crop cycle was back to values higher than 1 meq l⁻¹ and the soil solution content seemed to run in cycles (Figs. 2 and 3). The changes observed in soil solution composition during one crop cycle were, therefore, reversible and this was true for both the T and NT sites. Boivin et al. (1998b) made similar observations on the same site for the 1994 WS and DS, and for two other rice fields in the region (unpublished results). The decrease in Cl content is surprising because it suggests that chloride is adsorbed or fixed; now chloride is usually considered as a nonfixed reference element in soils and, thus, used as a tracer or for calculating water concentration ratio in many experiments. This result will be discussed below.

Table 3

Correlation coefficients between EC, Eh, cations and anions during three crop seasons (1996, 1997 and 1998) on T and NT sites

Ions	Eh	EC				
	1998 T	1996 T	1996 NT	1997 T	1997 NT	1998 T
Ca ²⁺	− 0.780	0.014	0.485	0.565	0.439	0.975
Mg ²⁺	− 0.848	0.888	0.755	0.839	0.878	0.957
Na ⁺	− 0.879	0.823	0.557	0.678	0.750	0.895
K ⁺	− 0.623	0.369	0.478	0.553	0.373	0.098
Alc	− 0.826	0.958	0.640	0.947	0.915	0.972
Cl [−]	0.874	− 0.209	0.654	− 0.307	0.284	− 0.734
SO ₄ ^{2−}	0.933	− 0.497	− 0.235	− 0.668	− 0.711	− 0.815

3.3. Eh and pH monitoring

In situ Eh and pH values monitored at 0.2-m depth during the 1998 DS, 1998 WS and the fallow period in-between are presented in Fig. 4. All probes showed the same trends. Slight differences are probably due to short-range spatial Eh variability, a common observation in rice fields (Ponnamperuma, 1965). The in situ Eh decreased during flooding to values indicating the onset and continuation of reduced soil conditions (Fig. 4). The three Ap horizon probes (0.2 m) showed a drop in Eh with duration of flooding, from 0.6 to − 0.15 V. The Eh in the AB horizon, (0.4-m depth) also decreased with time, to values ranging from 0.26 to − 0.07 V (data not shown). At these Eh, nitrate and oxides of Fe and Mn will be reduced (Van Breemen, 1988). The Ap horizon was more rapidly reduced. This is most likely due to the fact that rice roots mainly develop in the Ap horizon, leading to higher root and microbial activity (Sharma et al., 1994).

Upon flooding, in situ soil pH decreased rapidly as well, and stabilised to approximately 5–5.5 for Eh values below 0.45 V. The low pH values are due to high $p\text{CO}_2$. The soil solution pH values raised to alkaline values (close to 8) in a few hours when equilibrated with atmosphere.

Fig. 5 shows the Eh–pH stability diagram. Stability areas are calculated for $p\text{Fe}^{2+} = 3$. This activity value is common in rice fields (e.g. Genon et al., 1994; Ponnamperuma et al., 1967). It was actually measured in the same field at the end of cropping season 2000 (unpublished results) and is close to values found by Besson (2001). The data points are distributed in two clouds corresponding respectively to fallow and irrigation period. The fallow period (Eh > 0.45 V) shows positive correlation between Eh and pH, with increasing Eh and pH values with time (Fig. 4) in the goethite αFeOOH stability zone. The irrigation period contains the reduced samples, in the goethite and Fe^{2+} stability zone. It shows no correlation between Eh and pH. Eh drops, while pH remains constant. In the lower Eh values, many points are located on the goethite equilibrium line, and a few others are below the line in the Fe^{2+} zone. This is in agreement with the results of Favre et al. (2002), who found using Mössbauer spectra (Fig. 6 and Table 4) that Fe oxides were constituted of poorly crystallized goethite and using transmission electron microscopy observations that Fe oxides were almost completely dissolved in the more reduced samples. The geochemistry of iron should, therefore, be mainly ruled by the αFeOOH –

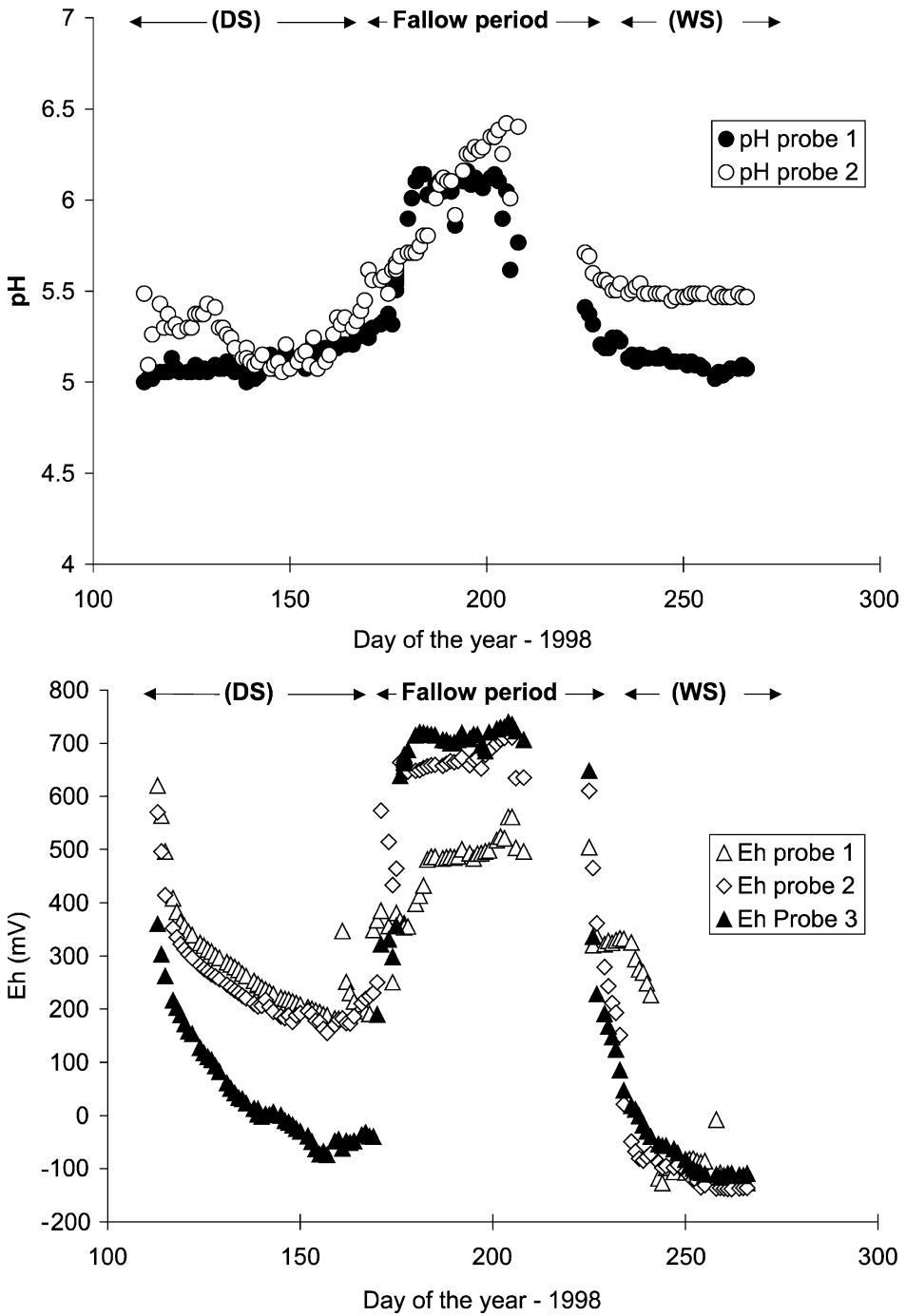


Fig. 4. In situ redox potentials and pH values monitored at 0.2 m depth in 1998.

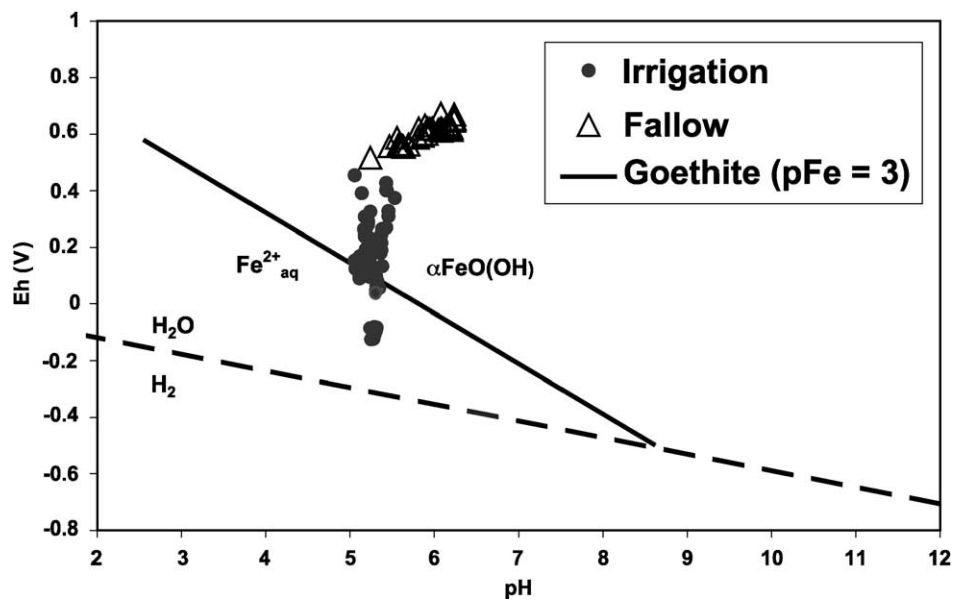


Fig. 5. Eh–pH stability diagram. Stability area of goethite relative to Eh, pH and an aqueous Fe²⁺ activity of 1 mmol at 25 °C. Open triangles: fallow period. Black points: irrigation period (1998).

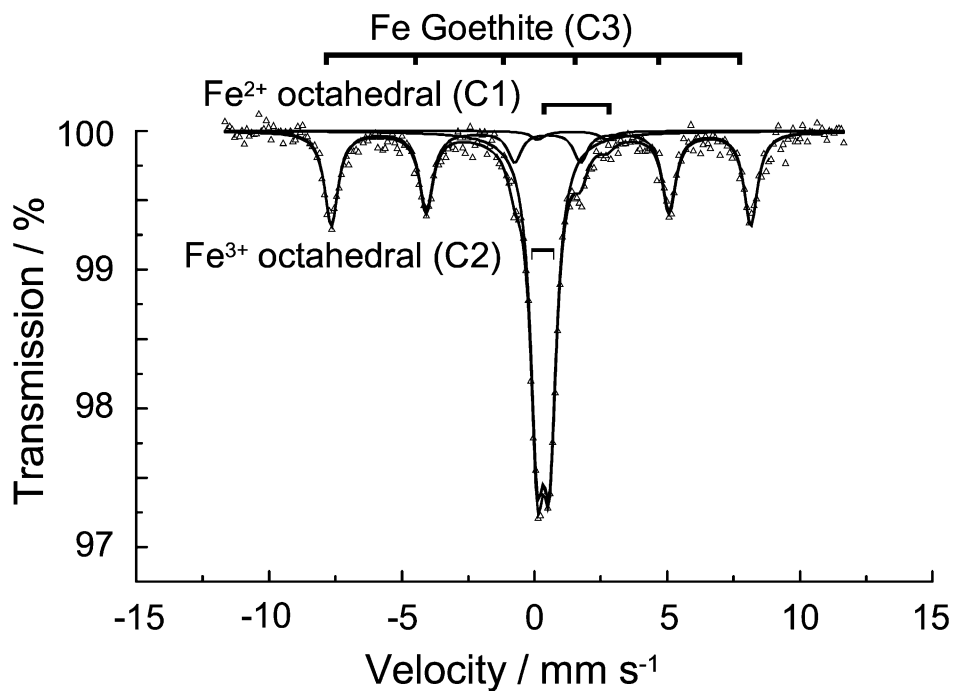


Fig. 6. Mössbauer spectra of oxidized soil sample from Favre et al. (2002).

Table 4

Hyperfine parameters of Mössbauer spectra of oxidized soil sample from Favre et al. (2002)

Iron form	δ^a relative fer α (mm s ⁻¹)	H (kOe) ^b	ΔE_Q^c (mm s ⁻¹)	RA ^d (%)
C1	1.57		2.59	2
C2	0.49		0.47	57
C3	0.48	490	-0.25	41

^a Isomer shift with respect to metallic α -Fe at room temperature.^b Hyperfine field.^c Quadrupole splitting.^d Relative area.

Fe^{2+} system in the irrigation period and a negative correlation between Eh and pH was, thus, expected. The null correlation between Eh and pH can be due to (i) increasing $p\text{CO}_2$ that drops pH upon flooding, (ii) nonequilibrium continuous dissolution of goethite slowly converging to goethite- Fe^{2+} equilibrium under high $p\text{CO}_2$ conditions and (iii) Fe_{Str} reduction. Chemical nonequilibrium is very common in such soils (Condom, 2000). Goethite is generally not considered by authors (Genon et al., 1994) for temporarily waterlogged soils. Note that goethite and lepidocrocite form by oxidation GR (Génin et al., 1998). Reductive dissolution of goethite occurs at lower Eh, for a given pH and $p\text{Fe}^{2+}$ value, than ferric or ferrosferric hydroxides reductive dissolution. In this soil, Favre et al. (2002) showed that Fe_{Str} in the smectite and iron in oxides are simultaneously reduced with time. However, the redox potential for Fe_{Str} reduction and the Eh-pH relation for these reactions are not documented. Since the Fe_{Str} content of the soil equals the oxide iron content (Favre et al., 2002), part of the observed Eh-pH relation might be explained by continuous reduction of Fe_{Str} in smectite. This should be documented in further research.

3.4. Soil solution mineral equilibria

Evolution of saturation index Q/K for some common minerals during the cropping period have been calculated using both in situ (Fig. 7) and laboratory pH (Fig. 8) values. Soil solution is continuously oversaturated with respect to kaolinite and beidellite, both being present in soil. In field conditions where high $p\text{CO}_2$ values induce a low pH, soil solution is mostly undersaturated with respect to other minerals likely to crystallize in these conditions (like sepiolite, calcite, magnesite). However, when laboratory pH (i.e. lower $p\text{CO}_2$) values are considered in calculations (Fig. 8), soil solution concentrations were near to saturation with respect to calcite and sepiolite. When the soil profile dries up and reoxidizes, $p\text{CO}_2$ drops and these minerals probably crystallize and accumulate in the soil profile during fallow period. This is in agreement with calcite precipitation observed on TEM images of the surface of test minerals reported by Audergon (2000) for the same field.

In field conditions with low pH values, soil solution is oversaturated towards CO_3 -GR due to high HCO_3^- concentration (results not shown). Nevertheless, Legrand et al. (2001) showed that the CO_3 -GR synthesised by Génin et al. (1998) probably does not precipitate under natural conditions. As we observed continuous increase in alkalinity with time, we, therefore, think that this CO_3 -GR does not precipitate in the soil. However, vacuum was applied when collecting the soil solution. Then $p\text{CO}_2$ dropped to low values and pH

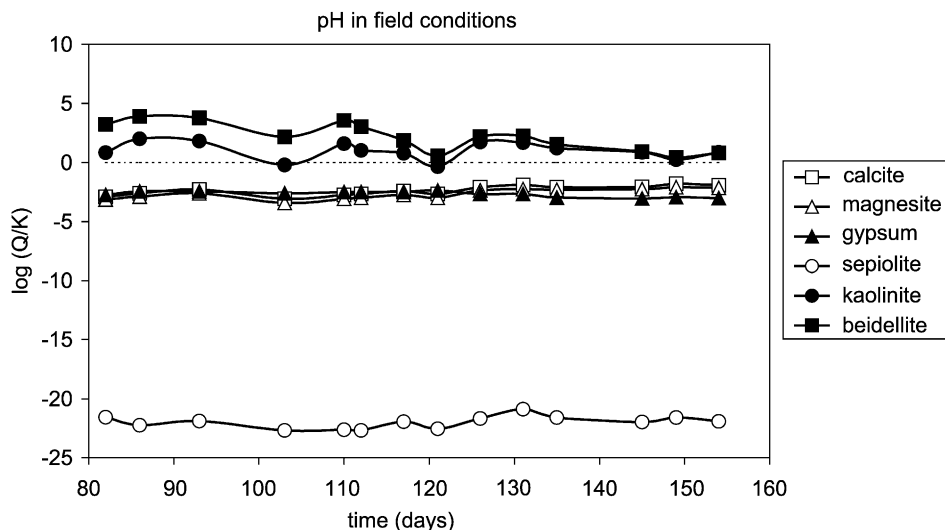


Fig. 7. Evolution of saturation index for calcite, magnesite, gypsum, sepiolite, kaolinite and beidellite in soil solution collected by porous cups during 1998 dry cropping season (DS), using field-monitored pH.

increased, as studied by [Suarez \(1987\)](#). Evolution of Cl-GR saturation index with time is illustrated in [Fig. 9](#) for 1998 DS. Saturation index are calculated for field and laboratory pH, for pFe values of 4. Saturation index values for $pFe = 3$ are also presented for the last three sampled points where Eh reached the lowest values. Due to low field pH values, the soil solution is undersaturated with respect to Cl-GR. At laboratory pH however,

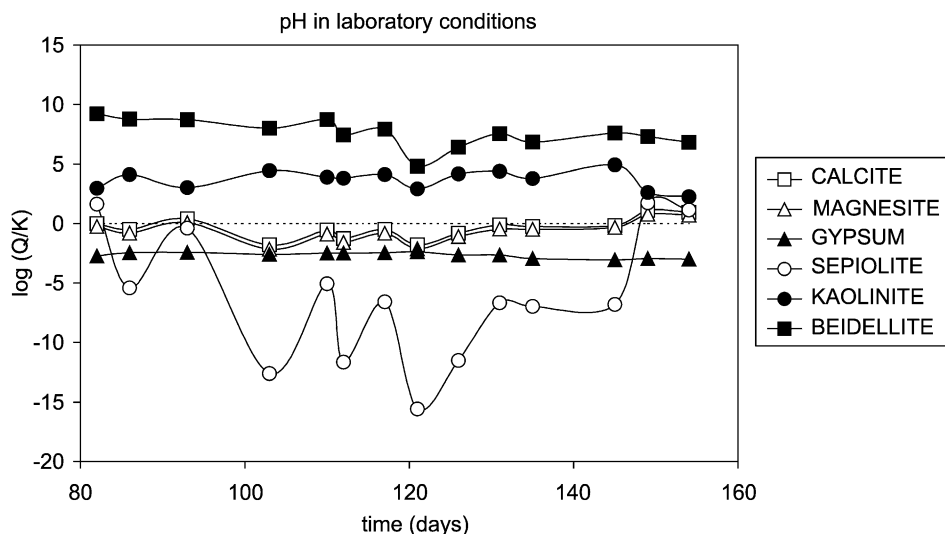


Fig. 8. Evolution of saturation index for calcite, magnesite, gypsum, sepiolite, kaolinite and beidellite in soil solution collected by porous cups during 1998 dry cropping season (DS), using laboratory-measured pH.

4.1. Water transfers

Water transfers can occur downward during flooding, and upward between two cropping cycles upon drying of the soil. We found no significant differences in soil solution composition between T and NT sites, indicating that the influence of water and solute transfers is negligible. Infiltration rates were much lower than saturated hydraulic conductivity. Favre et al. (1997) showed that crack closure allowed air entrapment in the AB horizon of the soil, which was confirmed by air bubbling even one month after flooding. We conclude that the very low infiltration rate is due to air entrapment, induced by surge flooding and shallow water table. Air entrapment lowers or even stops infiltration (Touma, 1984) and changes in soil solution composition are not influenced by water and solute fluxes. This conclusion is in agreement with the low drop in redox potential in the AB horizon (0.4 m depth), and with results of Dommergues (1961) and Moureaux (1968), who showed that under natural flooding, the microbial activity in the AB horizons of those soils remained aerobic even after 40 days of flooding. Hammecker et al. (in press) came to the same conclusion using tensiometer readings and modelling in the same field.

4.2. Rice uptake and ions balance

If water transfer is blocked, solutes supplied by the irrigation water accumulate in the top soil. Assuming that irrigation water does not infiltrate deeper than 0.3 m, we have reported in Table 5 the amount of cations and anions brought into the topsoil per hectare and per irrigation cycle. The amount of cations per hectare that are present in the soil solution can be estimated, considering a mean gravimetric water content of 60% in topsoil during flooding. The difference between mean soil solution composition at the beginning and at the end of crop cycles was then calculated and reported in Table 5.

Nutrient uptake by rice has been widely studied (DeDatta, 1981; Matsuo et al., 1995; Yoshida, 1981). It depends, among others, on rice variety and yield. Table 5 shows the

Table 5

Comparison between nutrient uptake, nutrient supply by irrigation and changes in soil solution composition

Nutrient	Chloride uptake in monitored field (Besson, 2001) (mol/ha)	Total uptake for variety IR8 and 6 t h ⁻¹ paddy yield (Yoshida, 1981) (mol/ha)	Total uptake for variety Peta and 6 t h ⁻¹ paddy yield (Yoshida, 1981) (mol/ha)	Average difference in soil solution ^a (mol/ha)	Supply by irrigation (1998 DS) (mol/ha)	Supply by irrigation (1996 and 1997 WS) (mol/ha)
N		8100	10071	n.m.	–	–
P		1001	1095	n.m.	–	–
K		5450	7770	– 162	1050	700
Ca		470	730	0	1875	1250
Mg		985	1306	5400	1575	1050
S		317	517	– 450	150	100
Cl	>340 to <990	1895	3250	– 1800	900	600
Si		21800	35680	0	–	–
Na		n.m.	n.m.	0	1650	1100

^a Difference=(mean values in soil solution at the end of the three monitored cropping seasons) – (mean values in soil solution at the beginning of the three monitored cropping seasons).

amount of nutrient taken up by rice straws and panicles at the end of the growing season, for a 6 t ha^{-1} paddy yield, and using literature data on nutrient content of two rice cultivars (Yoshida, 1981). Besson (2001) found Cl uptakes ranging from 340 mol ha^{-1} in the monitored field to 990 mol ha^{-1} in more saline fields of the same region for 6 t ha^{-1} of paddy.

Table 5 allows, therefore, comparison of changes in soil solution, nutrient supply from the irrigation water and nutrient uptake by the rice plant. For Si, K, Cl and S, rice uptake exceeds supply by the irrigation water. Si is present in unlimited quantity in the soil, and K is available as an exchangeable cation. Cl and S are only present in the soil solution. Chloride is mainly fixed in rice straws and roots (Matsuo et al., 1995; Yoshida, 1981). But Cl uptake is passive, i.e. it is dependent on soil solution content and evapotranspiration rate. The amount of Cl removed from soil solution can be estimated at 1800 mol ha^{-1} (Table 5), and the amount of Cl brought in by irrigation water is about 900 mol ha^{-1} in dry season and 600 mol ha^{-1} in wet season. The total amount of Cl removed ranges, therefore, from 2400 to 2700 mol ha^{-1} . This is compatible with the higher uptakes reported in the literature, but not in agreement with the observed Sahel108 chloride content. In addition, Cl content drops regularly during the crop cycle, whereas 90% of nutrients uptake occurs before flowering (DeDatta, 1981), that is to say before the 65th day of the rice crop. We, therefore, conclude that Cl decrease in soil solution cannot be explained by rice uptake.

Ca and Mg supply by the irrigation water was larger than calculated plant uptake. This would imply that Ca concentration would increase. However, it remained about constant over time, while Mg increased much faster (Fig. 2). As discussed before, it is possible that calcite precipitated in the porous cups, which would explain the low Ca concentration in our analyses. But the increase in Mg concentration and in alkalinity remain unexplained and are discussed below.

4.3. Oxydoreduction and exchanges

Oxidation–reduction reactions and cation exchanges on clays should also be taken in account. As reported in Favre et al. (2002), CEC increased upon reduction, due to both oxide coatings dissolution and Fe_{Str} reduction. Iron reduction increases soil alkalinity (Van Breemen, 1988) and adsorption of Fe^{2+} on the exchangeable sites is considered to replace exchangeable cations (e.g. Brinkman, 1970; Narteh and Sahrawat, 1999). It may be the case for Mg if the selectivity coefficient of the clay for Fe^{2+} is higher than for Mg, as exchangeable Mg is very high (Table 1). This is, however, not documented. The cation release is, however, limited due to CEC increase, and is reversible because CEC increase is reversible when Fe_{Str} oxidises (Favre et al., 2002). This is different from ferrollysis (Brinkman, 1970) because the release of cations is limited, and because no leaching of the released cations occurs during flooding. Ferrollysis probably cannot occur in such clayey and shrinking soils. Reduction of iron forms is similarly responsible for the high increase in alkalinity observed, though in situ pH values remained constant due to high $p\text{CO}_2$ values.

Rice straw from the previous harvest is generally burned before land preparation, and consequently K and Cl are returned to the soil. Iron oxidation releases protons and consequently reduces alkalinity. This may partly explain the chemical cycles observed.

The cyclic evolution of the soil solution is due to combination of (i) air entrapment blocking infiltration, (ii) nutrient uptake by rice, and release when straw is burned and (iii) oxidation–reduction cycles and exchanges with clays. It is, thus, difficult to determine if a general trend occurs. Favre et al. (2002) reported a general weathering of the soil when studying iron forms during crop cycles. Carbonates are accumulating in soil solution not only due to iron reduction, but also because of the positive residual alkalinity of Senegal river water. When the soil dries at the end of the crop cycle, the topsoil $p\text{CO}_2$ will decrease, the carbonate concentration will increase and calcite will precipitate. This ongoing process may, thus, result in calcium control and ultimately soil alkalization over the years.

5. Conclusions

Changes in soil solution chemistry were cyclic from one cropping season to the other. The soil solution had a neutral sulfate and chloride composition at the beginning of the cropping season, and an alkaline composition at the end, but was back to neutral at the beginning of the next cropping season. Chloride content decreased sharply upon flooding. This was not induced by transfers, because infiltration rates were very low or null, due to air entrapment.

In situ Eh and pH monitoring showed that the soil solution reached the Fe^{2+} stability zone during irrigation period, in good agreement with previously reported results. In contradiction with other studies, the iron system was ruled by Goethite dissolution, but showed non equilibrium in part of the flooding time, due to continuous increase in $p\text{CO}_2$. The high $p\text{CO}_2$ pressure lowered in situ soil pH though the soil solution alkalinity increased sharply. The part of structural iron reduction in Eh–pH relation should be further documented.

The decrease in Cl was not explained by rice nutrient uptake. We hypothesized that unstable Cl-GR formed in the soil around the porous cups during solution collection and resulting drop in $p\text{CO}_2$. Hence, Cl should not be used as a reference element for calculating concentration ratios of water when sampled under vacuum atmosphere in partly reduced soils. Moreover, Cl control in soils with low $p\text{CO}_2$ might occur without vacuum apply, and should, therefore, be tested.

The processes driving soil solution chemistry described here are related to flooding and redox processes but are different from ferrolysis. An accumulation of carbonates and resulting alkalization of the topsoil is likely to occur if irrigation is maintained without leaching or reclamation.

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