

Enregistrement scientifique n° : 880

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Présentation : poster

**Iron sulphates formation in acid sulphate soils
of the Lower Casamance (Senegal)**
**Formation de sulfates de fer dans les sols sulfatés acides de
Basse-Casamance (Sénégal)**

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Formation of acid sulphate soils is preceded by a reduced stage, generally in tidal marshes and in mangrove environments. Periodic flooding of these soils causes either acidification (due to pyrite oxidation) or deacidification of the surface horizons. In this work, we present the main results of a field study carried out in an acid sulphate soils environment of the lower Casamance (Senegal). The formation of iron sulphates is discussed on the basis of geochemical and mineralogical interpretations.

The soils of the Djigoumou valley are highly acid and saline with a wide range of salinity. They are clayed and the dominant clay mineral is kaolinite. Surface waters were collected in rainy season when the upstream part of an anti-salt dam was filling. Groundwaters were sampled with a piezometric network at the beginning and the end of the rainy season. Complete chemical analyses for 71 surface waters and 63 ground waters were done and field measurements were carried out for pH and electrical conductivity. Free-ion and ion-pair activities were computed from these analytical data by the PC-Wateq model. Saline efflorescences and iron oxide deposits were collected in different parts of the valley during the dry season. Powder X-ray diffractometry and scanning electron microscopy were used for the identification of mineral phases.

The salinity of groundwaters increases from the limit of the lowlands to the river axis and reaches an electrical conductivity of 100 dS m⁻¹. The surface waters are more diluted. Three types of chemical composition are determined for the groundwaters. The waters bordering on the valley are sulphated whereas chlore ion is dominant in other waters. The sulphate activity of waters is fairly constant and is set at 10⁻² mol L⁻¹. The pH is also constant and is ranged from 3 to 4. White-ochrous efflorescences form ferrous sulphates (rozenite) which are bordering on the valley and sometimes associated with mixed ferrous-aluminium sulphates such as halotrichite. In the central part of the valley where soil water is more concentrated, jarosite precipitates. Surface waters are saturated with respect to this mineral whereas groundwaters are undersaturated. Schwertmannite occurs in a fine ochrous surface deposit.

The iron sources are the pyritic sediment in mangrove environment and the ferrallitic environment of the watershed. In acid sulphate soils, iron is mobilized under different forms which depends of environmental conditions. The ferric sulphates, jarosite and schwertmannite, are formed when pH-Eh conditions are required. The specific localization of ferrous sulphates

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Introduction

The drought in West Africa has salinized surface waters and acidified mangrove soils in Lower Casamance. Huge bare surfaces of saline and acid sulphate soils have extended and mangrove vegetation has declined (MARIUS, 1985).

In valleys where an anti-salt dam was built (BOIVIN 1990 ; MONTOROI, 1996a), river hydrology was modified. Valleys are no more flooded with tidal rhythm whereas runoff waters are stored by dam in rainy season. During dry season, upstream sulfidic sediments were oxidized undergoing biogeochemical acidification and acid sulphate soil formation. These lowlands soils are also affected by salinization and the intensity of this process depends on soil localization in regard to the old riverbed. In dry season, saline efflorescences were formed close to the valley border (LE BRUSQ and *al.*, 1987 ; MONTOROI, 1996a and b).

Formation of acid sulphate soils is preceded by a reduced stage, generally in tidal marshes and in mangrove environments. Periodic flooding of these soils causes either acidification (due to pyrite oxidation) or deacidification of the surface horizons (Van BREEMEN, 1993).

In this work, we present the main results of a field study carried out in an acid sulphate soils environment of the lower Casamance (Senegal). The formation of iron sulphates is discussed on the basis of geochemical and mineralogical interpretations.

Materials and methods

The Djigoumou valley is located on the right bank of the Casamance river, 15 km northeast of Ziguinchor. The annual rainfall is about 1100 mm per year during the last twenty years period (**Figure 1**).

The soils of the Djigoumou valley are highly acid ($\text{pH} < 4$) and saline with a wide range of salinity. They are clayed and the dominant clay mineral is kaolinite. They are submerged during the rainy season from June to October, and the surface water has evaporated during the dry season from November to May.

Surface waters were collected in rainy season when the upstream part of an anti-salt dam was filling. Groundwaters were sampled with a piezometric network at the beginning and the end of the rainy season. Complete chemical analyses for 71 surface waters and 63 ground waters were done and field measurements were carried out for pH and electrical conductivity. Free-

ion and ion-pair activities were computed from these analytical data by the PC-Wateq model (TRUESDALL and JONES, 1974).

Saline efflorescences and iron oxide deposits were collected in different parts of the valley during the dry season. Powder X-ray diffractometry and scanning electron microscopy were used for the identification of mineral phases.

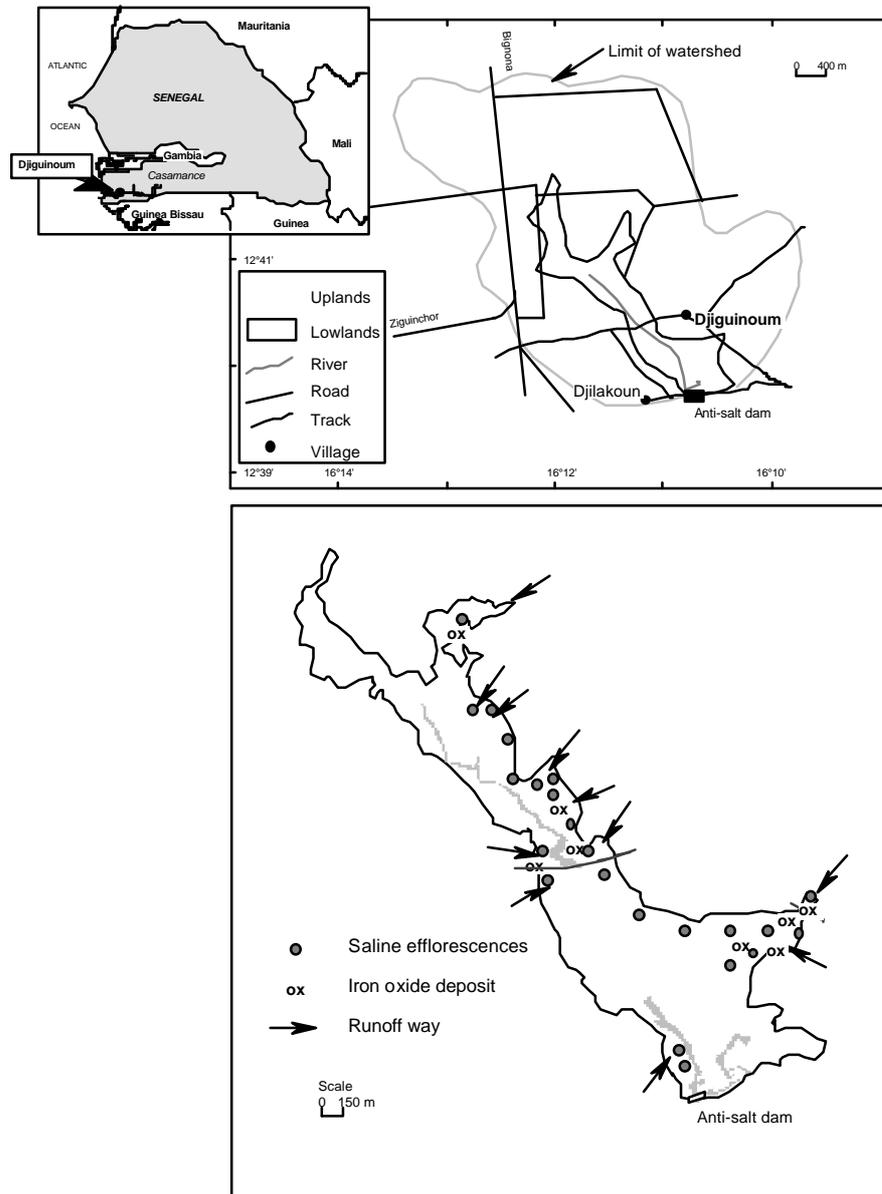


Figure 1

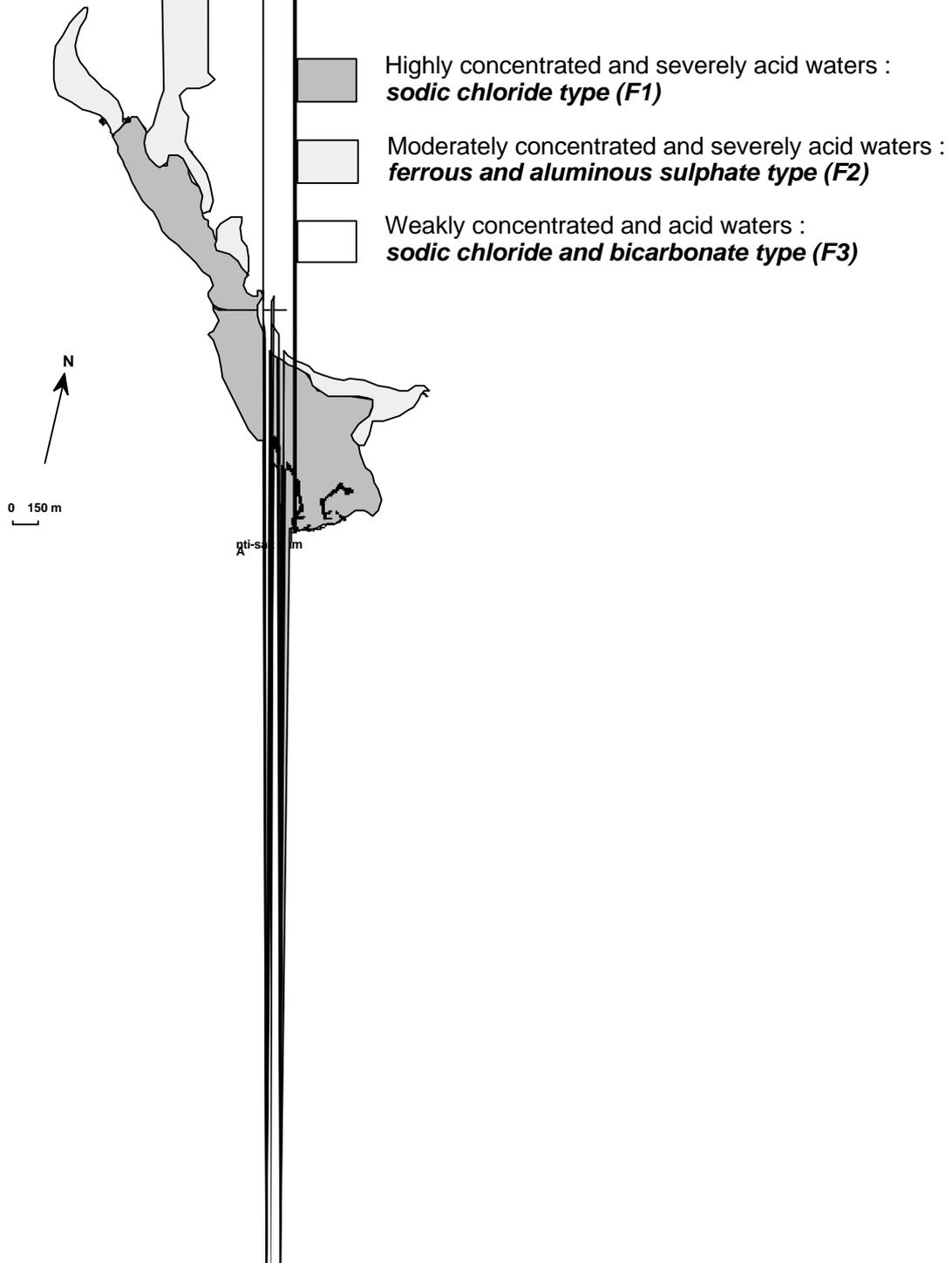
Study site of Djiguinoum valley and sampling localization for mineralogical characterization

Results

● *Chemical composition of waters*

The salinity of ground waters increases from the limit of the lowlands to the river axis and reaches high values of electrical conductivity close to 100 dS m⁻¹. The surface waters are more diluted.

Three types of chemical composition are determined for the ground waters (**Figure 2** and **Table 1**).



increases. They are close to the seawater for the most concentrated waters. However, in diluted waters, significant amounts of aluminium are present.

Table 1
Average chemical composition of ground waters at two periods of the year
(in anionic and cationic ratio)

Faciès chimique (dS m ⁻¹)	CE	pH	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	H ⁺	Al ³⁺	Fe ^{3+/2+}	Ca+Mg	Na+K	Al+Fe+H
<i>Fin de la saison sèche</i>															
F3	0,2	5,1	67,3	17,2	15,5	21,4	14,0	44,6	2,7	1,5	7,1	8,5	35,4	47,4	17,2
F2	3,1	3,7	12,2	87,0	0,8	24,6	17,7	9,0	0,9	1,4	20,7	25,7	42,3	9,9	47,8
F1	44,8	4,2	87,3	12,7	0,0	5,2	20,8	69,9	1,2	0,1	1,2	1,6	25,9	71,1	2,9
<i>Début de la saison sèche</i>															
F3	0,4	4,9	62,6	22,2	15,2	20,9	12,9	47,7	3,4	1,6	8,4	5,1	33,8	51,1	15,1
F2	2,1	3,5	14,5	85,3	0,2	29,1	16,2	11,3	1,0	3,1	24,0	15,3	45,4	12,3	42,4
F1	25,4	3,6	84,0	16,0	0,0	5,5	19,2	70,0	1,5	0,4	2,7	0,7	24,7	71,5	3,8

● Identification of salts

The saline efflorescences form different types of microcrystalline crusts on the soil surface. They are located on bare areas where evaporation is intense. Some of them are continuous and have included soil particles. The evolution of these crusts in dry conditions transform the soil surface in a layer of saline powder. Other crusts appear like irregular spots, often associated with ferric oxide deposit. Their color is white with sometimes yellowish or reddish tinge. Their size is variable and is assumed to be related with the microtopography and the particle redistribution before flooding. Salts are very soluble.

White-ochrous efflorescences form ferrous sulphates (rozenite) which are bordering on the valley. The rozenite looks like aggregates of granular crystals with a smooth shape (1 to 3 mm in diameter). Its formula is Fe^{II}(SO₄), 4H₂O. Sometimes this mineral is associated with mixed ferrous-aluminium sulphates, such as halotrichite (Fe^{II}Al₂(SO₄)₄, 22H₂O), and with others aluminium sulphates, especially alunogen (MONTOROI, 1995). In the central part of the valley where soil water is more concentrated, jarosite (KFe^{III}₃(SO₄)₂ (OH)₆) precipitates.

Schwertmannite occurs in a fine ochrous surface deposit (MONTOROI and HERBILLON, *in prep.*). This mineral is a very poorly crystallized mineral (SCHWERTMANN 1988; SCHWERTMANN and FITZPATRICK 1992) formed by biogeochemical oxidation of Fe(II) (BIGHAM *et al.*, 1992 ; BIGHAM and MURAD, 1997). Its formula is ranged from Fe₁₆O₁₆(OH)₁₂(SO₄)₂, 10 H₂O to Fe₁₆O₁₆(OH)₉(SO₄)₃, 10 H₂O depending of the saturation degree by SO₄ anion (BIGHAM *and al.*, 1990).

● Formation of iron sulphates

Surface waters are oversaturated with respect to jarosite whereas ground waters are undersaturated (**Figure 3**). F3 type ground water is only saturated with respect to goethite. The chemistry of this groundwater is influenced by water percolation through ferrallitic soils. Surface waters are saturated with respect to schwertmannite which is consistent with recent results presented by BIGHAM and *al.* (1996).

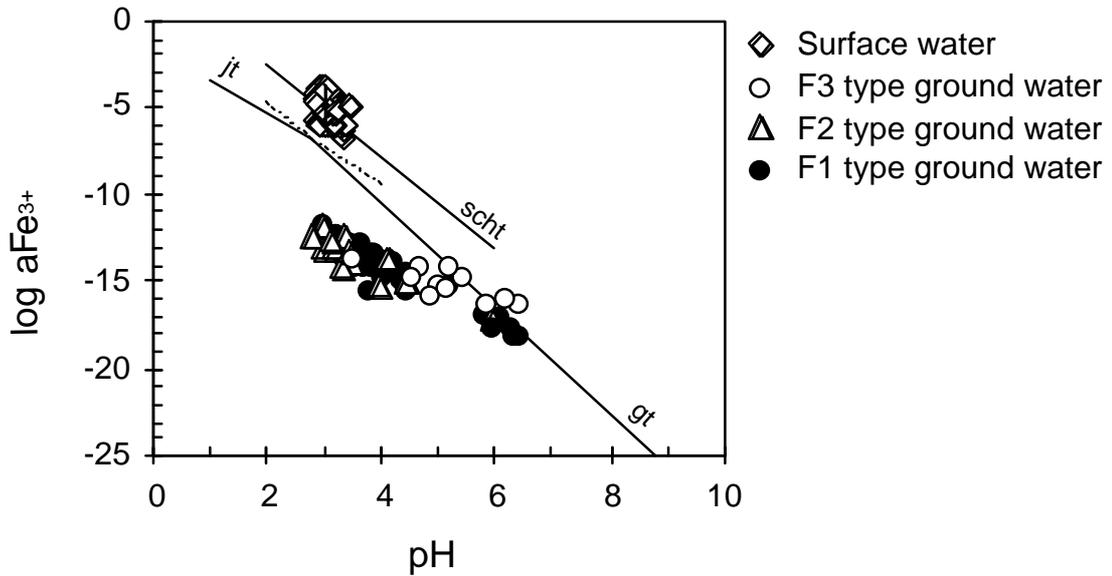


Figure 3

Solubility diagram of jarosite (jt), schwertmannite (scht) and goethite (gt). Solubility lines are calculated as given by BIGHAM and *al.* (1996)

As shown in **figure 4**, a lateral ground water flow through acid sulphate soils combined with a concentration by evaporation would also lead to ferrous sulphate precipitation (MONTOROI and RIEU, 1997).

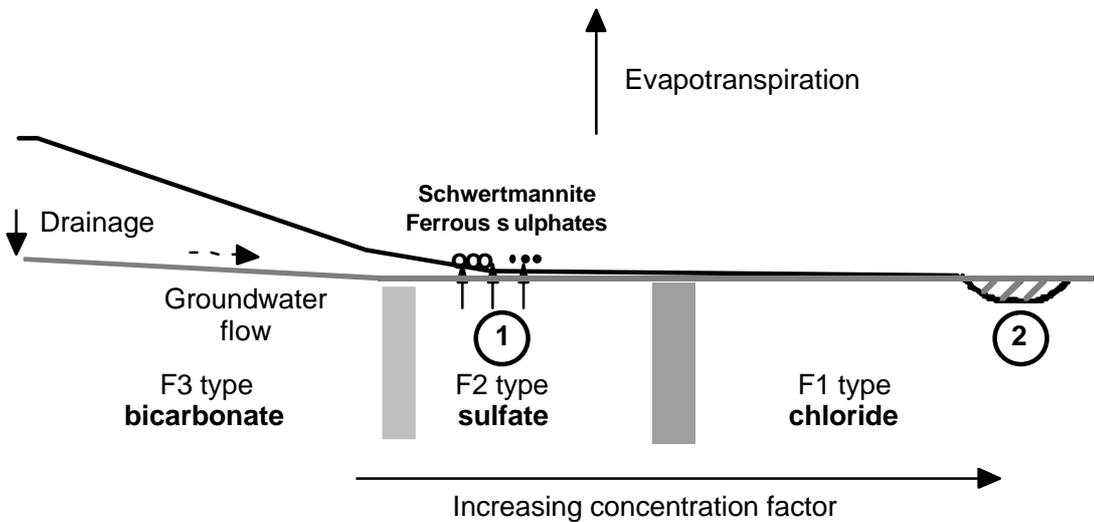


Figure 4

Formation mode of iron sulphates during lateral transfer of ground water

Initially bicarbonated (F3 type), ground water is enriched in sulphate, aluminium and iron ions and evolves into F2 type. Then, during its flow towards river axis, ground water concentrates by evaporation which undergoes aluminium and iron sulphate précipitation and F1 type formation.

Conclusion

The iron sources are the pyritic sediment in mangrove environment and the ferrallitic environment of the watershed. In acid sulphate soils, iron is mobilized under different forms which depends of environmental conditions.

The iron sulphates, such as ferrous sulphates (rozenite, halotrichite), ferric hydroxysulphate (jarosite) and ferric oxyhydroxysulphate (schwertmannite), are formed when pH-Eh conditions are required. The specific localization of ferrous sulphates on the border of the valley and the particular pattern of the efflorescences, which are in relation with the distribution of surface soil particles, agree with the adsorption properties of soil colloids in extrem acid conditions and the lateral ground water flow through acid sulphate soils combined with a concentration by evaporation.

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Mots clés : Sulfate de fer, Sol sulfaté acide, Minéralogie, Géochimie, Casamance, Sénégal.

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