

## The impact of desiccation of a freshwater marsh (Garcines Nord, Camargue, France) on sediment–water–vegetation interactions

### Part 1: The sediment chemistry

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#### Abstract

The impact of desiccation on a marsh sediment was studied both in the laboratory and in the field.

Changes in the sediment chemistry of a homogenized sediment suspension during desiccation were studied in the laboratory. FeS was oxidized completely. A considerable mineralization of organic phosphate took place, from both the acid soluble organic phosphate fraction and from the residual organic phosphate fraction, but no significant mineralization of organic matter was observed. The o-P formed during the mineralization was recovered partly in the Fe(OOH)≈P fraction and partly in the CaCO<sub>3</sub>≈P fraction. An upward flux was found.

During spring and summer 1990 the water inlet to a shallow permanent freshwater marsh with a surface of about 1.5 hectares was blocked, in order to desiccate the marsh by evaporation. The sediments initially consisted of a black anoxic organic top layer and a less organic anoxic gray layer. During the desiccation of the sediment a brown oxic surface layer was formed from the black layer and an increase of pH and Eh occurred. Subsequent rainfall made the Eh increase further but caused a decrease in pH indicating an increase in bacterial activity.

A progressive oxidation of FeS was observed. An increase in Tot-P in the surface layer and a decrease in the gray and the black layer of the sediment occurred, probably due to a capillary upward flux. A mineralization of organic matter was observed in the two deeper layers. In the upper brown layer this mineralization was less evident, probably because it has been masked by the capillary movement. A net C loss of 40% was calculated to have occurred in the layer 0–40 cm. In the deeper layers a decrease in Tot-N was observed, whereas no important increase occurred in the top layer. Over a sediment layer of 40 cm a N loss of 50% was calculated. C- and N losses occurred simultaneously, suggesting the importance of mineralization as a source of inorg-N for denitrification. The chemical and physical changes in the sediment during desiccation affected layers down to 40 cm. This means that not only the top layer of a sediment but also deeper layers are active in systems of which part of the sediment dries occasionally.

Fractionation of the surface sediment phosphate showed an increase of Fe(OOH)≈P in the top layer due to the oxidation of FeS to Fe(OOH), enlarging the P-adsorption capacity of the sediment. A mineralization of about 50% of acid soluble organic phosphate occurred. After rainfall, a net increase in

residual organic phosphate occurred presumably due to an increase of bacterial activity.

Drying may therefore be utilized as a tool, in wetland management, to eliminate organic nitrogen and carbon from the sediment. In rice culture, it may be used to make part of the organic nitrogen available to the rice.

## Introduction

In subtropical and tropical regions many shallow water bodies desiccate from the end of spring or beginning of summer, due to evaporation and lack of rain. This desiccation can be expected to have an impact on the sediment chemistry, as well as on the vegetation. In the Camargue (Rhône-delta; South of France), marshes normally desiccate in May or June depending on the meteorological conditions. Consequently, an oxidation of reduced substances, such as  $\text{NH}_4^+$ ,  $\text{Fe}^{2+}$ ,  $\text{Mn}^{2+}$  and  $\text{S}^{2-}$ , as well as a mineralization of organic matter may be expected.

During the last decade many marshes have been kept permanently flooded artificially with Rhône water, to create a habitat which is favourable to water birds and fish. This has resulted in an increase of maximum standing crop of submerged and aquatic macrophytes. Consequently an accumulation of organic matter in the sediments occurred, causing anoxic conditions. In several marshes  $\text{Fe}^{2+}$  or  $\text{S}^{2-}$  were found in the interstitial water, as well as an accumulation of FeS in some sediments (Van Wijck *et al.*, 1992). FeS has been shown to accelerate denitrification (Golterman, 1992). Its formation will affect the distribution of phosphate over the different pools in the sediment (Golterman, 1988; De Groot, 1992), by diminishing the quantity of Fe(OOH) present in the sediment.

High concentrations of  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$  have been shown to have a negative effect on the growth of emergent macrophytes (Ernst, 1990) and on submerged macrophytes (Van Wijck *et al.*, 1992). Changes in species composition as well as in maximum standing crop were observed in several marshes, after years of permanent flooding (Grillas, pers. comm.).

Rice fields are irrigated from April until Sep-

tember, after which the sediment gradually dries, depending on the meteorological conditions. After the germination of the rice the irrigation is stopped for about one week to stimulate rooting, during which period the ricefield desiccates. Nitrogen fertilizer is essential to obtain a reasonable harvest. Over 80% of the nitrogen, however, may be lost due to denitrification (Minzoni *et al.*, 1988).

The objectives of this study were:

- (1) To measure the chemical and physical changes in the sediment during desiccation.
- (2) To determine vertical fluxes of org-C, N, P and Cl between the different sediment layers.
- (3) To determine changes in the fractional composition of the sediment phosphate.
- (4) To determine to what extent the changes observed remain in the long term.
- (5) To determine whether desiccation may be used as part of the management regime of wetlands and rice fields.

During spring and summer 1990 a shallow freshwater marsh with surface of about 1.5 ha and a maximum water depth of 32 cm was allowed to desiccate by evaporation. During desiccation, sediment cores were taken and pH, Eh, water content, concentrations of Tot-P, Tot-N, Tot-Fe, Tot- $\text{S}^{2-}$ , interstitial concentrations of o-P,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$  were measured in the different sediment layers. In order to study changes in the distribution of sediment phosphate over the different fractions, sediment phosphate in the top layer was fractionated by means of sequential extraction. Changes in the fractional composition of the sediment may affect the quantity of bioavailable  $\text{P}_{\text{sed}}$ .

In 1991 some samples were analysed to see whether the changes induced by the desiccation remain in the long term.

## Material and methods

The Garcines is a freshwater marsh with a surface of 1.5 hectares and a maximum depth of 0.3 m, situated in the Camargue (South of France). It was kept flooded from spring 1987 onwards. The sediment surface consisted of two layers: a liquid organic black top layer of about 20–25 cm thickness, rich in FeS, Org-C and Tot-N and a more compact deeper gray layer which was less rich in Org-C (Table 2). This is probably the bed of an ancient arm of the Rhone (Rhone d'Ulme).

### Laboratory experiment

A surface sediment sample was taken from the edge of the Garcines on 9 April 1990. A sediment suspension was prepared containing 250 g dw l<sup>-1</sup>. After homogenizing and sieving, over 500 µm mesh size, 5 l of the suspension was put into a crystallization dish (diameter = 25 cm, height = 15 cm), placed in a glasshouse. After 0, 10, 18, 24 and 27 days samples were taken. The samples were analysed for Tot-P, Tot-Fe, Tot-N, Org-C and Tot-S(II-) and the sediment phosphate was fractionated. At t = 27 days a surface (first 5 mm) sample and a deeper (> 5 mm) sample were analysed. In the two layers Cl<sup>-</sup> was measured.

### Field experiment

A sampling station was chosen in the shallow part about 15 m from the border (water depth approximately 20 cm). Samples were taken within a radius of one meter around a wooden pole marking the station.

The marsh was left to desiccate. From 22 June to 28 August samples were taken regularly. On each sampling date two sediment cores (Ø = 12 cm; depth = 40 cm) were taken and separately analysed. The different sediment layers were separated. Each layer was analysed after mixing. In February and May 1991 further sam-

ples were taken. In all samples pH, Eh, water content, Tot-P, Tot-N, Tot-Fe, Tot-S(II-), interstitial o-P, NH<sub>4</sub><sup>+</sup>, Fe<sup>2+</sup> and S<sup>2-</sup> were measured. Interstitial water was obtained by centrifugation of the sediment while excluding oxygen. Different forms of P<sub>sed</sub> found in the surface layer, were fractionated by means of sequential extraction (details below).

### Chemical analysis

pH and Eh were measured in the field, directly after sampling.

All chemical analyses were carried out according to the IBP Manual Nr 8 (Golterman *et al.*, 1978): Tot-Fe was determined as Fe<sup>2+</sup> (method 4.5.1) and Tot-P as o-P (method 5.6.2) after digestion of a measured quantity of sediment with H<sub>2</sub>SO<sub>4</sub> and H<sub>2</sub>O<sub>2</sub> (De Groot, 1990). For all colorimetric methods absorbances were measured using a Philips PYE Unicam PU 8600 spectrophotometer. Assuming C<sub>5</sub>H<sub>7</sub>NO<sub>2</sub> as general formula of organic matter (Golterman, 1975), Org-C was calculated from COD which was determined by measuring Cr<sup>3+</sup> after digestion with K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> in H<sub>2</sub>SO<sub>4</sub> (method 7.3.2). After alkalisation, Tot-N was measured acidimetrically as NH<sub>3</sub> (method 5.2.2) after distillation from the same digestion mixture. Interstitial NH<sub>4</sub><sup>+</sup> was determined using a direct Nessler reagent (Golterman, 1991). Interstitial S<sup>2-</sup> and Tot-S<sup>2-</sup> were determined with a back-titration of the excess I<sub>2</sub> with 0.1 M 1/6As<sub>2</sub>O<sub>3</sub>, using a Mettler DL 40 RC Memo Titrator. Cl<sup>-</sup> was titrated with Ag<sup>+</sup> in acid medium (method 4.6.2), using a Mettler Memo Titrator.

During the entire period water level and temperature were measured. Sediment phosphate was fractionated by means of a sequential extraction (Golterman & Booman, 1988; De Groot & Golterman, 1990). Fe(OOH) ≈ P is extracted with a TRIS-buffered solution of Ca-NTA (0.02 M) plus dithionite (0.045 M), CaCO<sub>3</sub> ≈ P with Na-EDTA (0.05 M), Acid Soluble Organic Phosphate (ASOP) (De Groot, 1990) with H<sub>2</sub>SO<sub>4</sub> (0.25 M) and Residual Organic Phosphate (ROP)

Table 1. Thickness of the sediment layer, water level and pH of the sediment on desiccation during the laboratory experiment.

Days	Sediment thickness (cm)	Water level (cm)	pH
0	9.5	0.0	7.2
1	9.1	0.5	
2	9.0	0.8	
3	9.0	0.9	
4	8.6	0.7	
6	8.2	0.2	6.7
8	7.7	0.0	

was determined after digestion with  $H_2SO_4$  and  $H_2O_2$ .

## Results

### Laboratory experiment

The sediment in the crystallization dish desiccated rapidly; the overlaying water completely evaporated within eight days and the sediment was completely dry after 27 days (Table 1). The pH decreased from 7.2 to 6.7 and a decrease in sediment height of 1.8 cm was observed (Table 1). After 27 days a 5 mm thick, solid top layer had formed, existing of thin brown and gray layers; the sediment underneath was gray, homogeneous and porous. After 27 days  $0.24 \text{ mg g}^{-1} \text{ Cl}^-$  was found in the top layer against  $0.04 \text{ mg g}^{-1}$  in the bottom layer (Table 2).

The changes in the chemical composition of the homogenized sediment during the experiment are presented in Table 1. An increase in Tot-N, Org-C, Tot-P and Tot-Fe is observed over the first 18 days of the experiment.

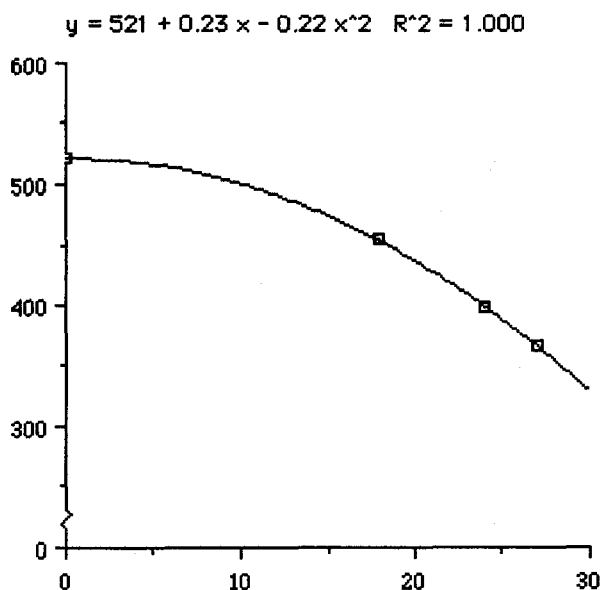


Fig. 1. Changes in total Org-P: ASOP + ROP ( $\text{mg g}^{-1}$ ) with time (days)-laboratory experiment.

### Sediment phosphate

During the desiccation a considerable hydrolysis of Org-P took place, indicated by the decrease of ASOP and ROP and the increase in  $\text{Fe(OOH)} \approx \text{P}$  and  $\text{CaCO}_3 \approx \text{P}$  compared to  $t = 0$  (Table 1). In the first 18 days the Org-P/inorg-P quotient decreased from 3.3 to 1.6, which corresponds to a mineralization of approximately 35% of the Org-P. The time-curve is a convex curve (Fig. 1). The o-P formed during the mineralization is recovered partly in the  $\text{Fe(OOH)} \approx \text{P}$  fraction and partly in the  $\text{CaCO}_3 \approx \text{P}$  fraction; adsorption of o-P onto  $\text{Fe(OOH)}$  and precipitation of  $\text{CaCO}_3 \approx \text{P}$  have apparently occurred simulta-

Table 2. Chemical characteristics on a dry mass basis of a homogenized sediment suspension during desiccation.

Days	$\text{Fe(OOH)} \approx \text{P}$ $\mu\text{g g}^{-1}$	$\text{CaCO}_3 \approx \text{P}$ $\mu\text{g g}^{-1}$	ASOP $\mu\text{g g}^{-1}$	ROP $\mu\text{g g}^{-1}$	$\text{Fe(OOH)}$ $\text{mg g}^{-1}$	Org-C $\text{mg g}^{-1}$	Tot-N $\text{mg g}^{-1}$	Tot-Fe $\text{mg g}^{-1}$	Tot-P $\mu\text{g g}^{-1}$	Tot-S(II-) $\text{mg g}^{-1}$	C/N	Org-P/Inorg-P
0	68.0	91.1	260	261	5.8	32.7	3.6	24.4	673	0.46	9.1	3.3
10						36.3	3.8	27.5	764	nd	9.6	
18	92.5	194	172	282	5.1	38.2	4.0	28.2	816	nd	9.6	1.6
24	101	138	215	182	5.4	35.4	4.1	26.0	722	nd	8.6	1.7
27 surface	128	187	186	182	5.8	36.8	4.0	26.3	793	nd	9.2	1.2
27 > 5 mm	136	192	176	217	6.0	36.4	3.5	26.8	771	nd	10.4	1.2

Table 3. Thickness of different sediment layers, sediment  $\text{Cl}^-$  and sediment level relative to a local arbitrary datum, at seven times during summer 1990.

Date	Thickness of layer (cm)			Sediment level (cm)	$\text{Cl}^-$ ( $\text{mg g}^{-1}$ )		
	Brown	Black	Gray		Brown	Black	Gray
22-June-90	0.0	30	10	0.0		0.15	0.055
3-July	0.0	26	14	0.0			
12-July	0.2	25	15	- 5.8		0.31	0.005
18-July	5.0	15	15	- 6.0	0.260	0.21	0.023
----- rainfall ----- rainfall ----- rainfall -----							
31-July	5.0			- 5.0	0.136		0.050
7-Aug	11.0	6.0	10	- 14.0	0.065	0.034	0.014
----- rainfall ----- rainfall ----- rainfall -----							
21-Aug	8.0	8.0	10	- 9.0			

neously. The main increase in  $\text{CaCO}_3 \approx \text{P}$  occurs between  $t = 0$  and  $t = 18$  days, simultaneously with the main mineralization of ASOP.

#### Field experiment

From 22 June till 28 August 1991, the marsh progressively dried from the border to the deeper

central part, although the sediment was wetted twice by rainfall: on 29 July 15.6 mm and on 13 and 14 of August 26.8 mm. At the end of August the marsh was filled by heavy rainfall: on 29 and 30 August 71.6 mm.

During the desiccation of the sediment an oxic brown surface layer was formed from the black layer. The brown layer will be numbered 1a, the

Table 4. Physical characteristics of the different sediment layers during desiccation.

Date	pH			Eh (mV)			Water content (% of d.w.)		
	Brown	Black	Gray	Brown	Black	Gray	Brown	Black	Gray
22-June-90		6.6	6.6		- 267	- 286		65.1	41.7
		6.6	6.6		- 300	- 260		58.8	30.7
3-July		7.8	7.6		- 178	- 185		64.5	39.3
		8.0	8.1		- 200	- 180		60.6	52.0
12-July		8.7	8.6		- 110	- 165		59.0	30.9
		8.5	8.6		- 199	- 142		59.9	24.3
18-July	8.3	8.7	8.3	32.0	- 144	- 121	7.6	11.7	17.6
	8.2	8.5	8.3	5.0	- 198	- 138	5.9	18.5	21.0
----- rainfall ----- rainfall ----- rainfall -----									
31-July	6.7	6.7		27.0	43		58.2	53.3	
	6.6	6.7		55.0	- 112		56.3	49.4	
7-Aug	8.1	7.1	7.1	67.0	- 174	- 181	48.9	44.8	36.9
	7.7	6.9	7.2	53.0	- 182	- 127	50.9	46.0	27.3
----- rainfall ----- rainfall ----- rainfall -----									
21-Aug	6.9	6.9	7.0	19.0	- 160	- 150	54.8	34.9	24.1
	7.0	7.1	7.1	- 165.0	- 198	- 121	57.2	51.5	23.1
19-Feb-91		9.2	8.1		- 194	- 200			
		8.4	8.1		- 188	- 198			
28-May		8.2	7.9		- 189	- 170			
		8.3	7.7		- 175	- 155			

black layer 1b and the gray layer 2. When 'the surface layer' is mentioned without a number it means the top layer, regardless of whether it is black or brown.

The thickness of the different layers is given in Table 3. During the desiccation a decrease in sediment level, compared to a local datum in the marsh, occurred (Table 3). The first decrease of water content of the layers 1a and 1b occurred between 12 and 18 July, whereas the first decrease in water content of layer 2 occurred between 3 and 12 July (Table 4). An increase in  $\text{Cl}^-$  was observed in the surface layer between 22 June and 12 July (Table 3). The desiccation of the sediment caused an increase in pH and Eh in all sediment layers (Table 4).

Both between 18 and 31 July and 7 and 21 August the sediment was wetted by rainfall, giving a considerable increase in sediment water content and Eh and a decrease of pH (Table 3) and  $\text{Cl}^-$  (Table 2) in the surface layer.

An increase in interstitial  $\text{Fe}^{2+}$  was observed in all layers (Table 5), between 18 and 31 July.

During the desiccation a progressive oxidation of sediment  $\text{S}^{2-}$  was observed in the black and

the gray layer (Table 6). Layer 1a initially contained no  $\text{S}^{2-}$ , but after the rainfall some  $\text{S}^{2-}$  was found.

Again  $\text{S}^{2-}$  was formed after the marsh was filled with rainwater and the layer 1a disappeared. However, in May 1991 the FeS had not yet reached 25% of the concentration measured at the beginning of the experiment (Table 6).

### Phosphate

During the desiccation an increase in Tot-P was observed in the top layer; in the deeper layers a decrease was observed, suggesting an upward flux (Table 6). Between 3 July and 12 July a considerable decrease in  $\text{Fe}(\text{OOH}) \approx \text{P}$  and a simultaneous increase of  $\text{CaCO}_3 \approx \text{P}$  occurred (Table 7). Over the period of 12 July to 28 August an increase in  $\text{Fe}(\text{OOH}) \approx \text{P}$  occurred. No net decrease in Org-P (ASOP + ROP) occurred in the top layer of the sediment (Table 7). A net mineralization of ASOP occurred over the period of 3 July to 28 August, which was compensated by a net increase of ROP. Between 22 June and 28 October

Table 5. Concentrations of o-P,  $\text{Fe}^{2+}$  and  $\text{NH}_4^+$  in the interstitial water of the different sediment layers.

Date	[ $\text{NH}_4^+$ ] ( $\text{mg l}^{-1}$ )			[ $\text{Fe}^{2+}$ ] ( $\text{mg l}^{-1}$ )			[o-P] ( $\mu\text{g l}^{-1}$ )		
	Brown	Black	Gray	Brown	Black	Gray	Brown	Black	Gray
22-Jun									
3-Jul					2.9	7.5		35.0	29.0
12-Jul	3.4		1.1	4.3		12.4	28.0		
	2.7		1.2	6.0		8.0			
18-Jul	18.5	1.7	2.7	0.3	0.3	0.3	32.3	29.0	25.8
	17.3	1.5	2.9	0.0	3.0	0.0	29.0	19.4	
	rainfall			rainfall			rainfall		
31-Jul	14.2	7.1		13.0	13.8		59.7	48.4	
	8.5	5.9		10.0	8.0		48.4	27.4	
7-Aug				1.8	1.8	2.9			
				1.8	1.8	1.3			
	rainfall			rainfall			rainfall		
21-Aug	6.0	5.6	6.2	5.8	6.0	3.0	32.3	41.9	
	4.6	5.6	6.2	6.3	7.0	2.8	32.3		
19-Feb-91		4.2	5.0		7.6	10.4		7.7	nd
		2.3	2.8		4.0	7.3		nd	nd
28-May		1.7			1.4			5.7	
		2.0			1.0			4.0	

Table 6. Concentrations of total N, total P, total organic C and total sulphide in the different sediment layers.

Date	Total N (mg g <sup>-1</sup> )			Total org-C (mg g <sup>-1</sup> )			Total P (μg g <sup>-1</sup> )			Total S <sup>2-</sup> (mg g <sup>-1</sup> )		
	Brown	Black	Gray	Brown	Black	Gray	Brown	Black	Gray	Brown	Black	Gray
22-Jun		3.23	2.80		28.7	17.6		617	534		2.20	0.33
		2.92	3.16		27.5	36.6*		574	548		1.97	0.72
3-Jul		2.40	1.88		23.7	16.9		551	572		1.92	0.34
		2.39	0.84		23.8	9.2		531	509		2.97	0.71
12-Jul		3.62	0.50		32.8	6.1		709	486		1.32	0.29
		2.94	0.48		28.2	5.9		721	518		1.21	0.38
18-Jul	3.12	1.99	1.11	27.4	23.3	11.0	754	570	507	0.00	1.06	0.27
	3.89	1.75	1.08	31.8	22.1	10.9	693	527	459	0.00	1.11	0.16
	rainfall			rainfall			rainfall			rainfall		
31-Jul	3.31	2.46		27.6	23.3		647	554		0.24	0.38	
	2.92	2.15		26.8	20.0		637	514		0.23	1.92	
7-Aug	2.41	1.91	0.77	23.8	17.9	7.8	638	621	530	0.00	0.70	0.35
	2.73	1.49	0.50	26.8	19.8	6.1	830	562	558	0.27	1.58	0.27
	rainfall			rainfall			rainfall			rainfall		
21-Aug	2.93	1.60	0.56	32.0	18.5	7.5	660	488	442	0.09	0.92	0.10
	3.03	1.49	1.16	28.9	19.2	6.7	655	535	465	0.01	0.72	0.12
19-Feb-91		2.71	1.64		23.9	14.1		649	494		1.01	0.87
		2.73	1.69		24.1	15.7		660	574		0.45	0.62
28-May		2.64			25.9			595			0.43	
		1.86			22.1			564			0.23	

Table 7. Different fractions of sediment phosphate in the upper layer of the sediment.

	Colour	Fe(OOH)≈P (μg g <sup>-1</sup> )	CaCO <sub>3</sub> ≈P (μg g <sup>-1</sup> )	ASOP (μg g <sup>-1</sup> )	ROP (μg g <sup>-1</sup> )	Tot inorg-P (μg g <sup>-1</sup> )	Tot org-P (μg g <sup>-1</sup> )	Org-P/Inorg-P	Σ fractions (μg g <sup>-1</sup> )	
3-Jul	Black	118	172	171	167	290	338	1.17	628	
12-Jul	Black	76	251	151	167	327	319	0.97	646	
18-Jul	Brown	107	204	139	166	311	305	0.98	616	
	rainfall		rainfall		rainfall		rainfall		rainfall	
21-Aug	Brown	115	226	152	196	340	348	1.02	688	
28-Aug	Brown	174	154	80	254	327	333	1.02	700	
19-Feb	Black	65	236	176	170	302	346	1.15	648	

50% of ASOP was mineralized. From 3 to 18 July ROP remained constant. Between 18 July and 28 August a considerable increase in ROP occurred.

### Nitrogen

Between 12 and 31 July an increase in interstitial NH<sub>4</sub><sup>+</sup> occurred in layer 1a. On 31 July the interstitial NH<sub>4</sub><sup>+</sup> in layer 1a was significantly higher

than in the layers 1b and 2 (Table 5). Between 22 June (3.1 mg g<sup>-1</sup>) and 3 July (2.4 mg g<sup>-1</sup>) a net decrease in Tot-N occurred, followed by an increase between 3 (2.4 mg g<sup>-1</sup>) and 18 July (3.5 mg g<sup>-1</sup>), which was the last sampling date before the first rain. Between 22 June (3.0 mg g<sup>-1</sup>) and 18 July (1.1 mg g<sup>-1</sup>) a net decrease in Tot-N occurred in the layer 2. The increase in the surface layer could not completely account for the decrease in the layer 2.

### Carbon

During desiccation Org-C decreased in the layers 1b and 2. No significant decrease in Org-C occurred in the layer 1a.

### Balance calculations

An attempt was made to calculate N, C and P balances for the entire sediment layer. In the calculation we have supposed that: 1) in all layers one gram of sediment has the same volume at the same water content, 2) only vertical movements of water and compounds occur, 3) at  $t=0$  the gray layer has a thickness of 10 cm and 4) the total mass of the sediment column is constant (corrections being made by varying the thickness of the gray layer). The sediment mass of one layer was calculated from the layer thickness and water content, supposing that 1 ml of water has a weight of 1 g and 1 ml of dry sediment 1.5 g. The calcu-

lations were repeated with a sediment weight of  $2.5 \text{ g ml}^{-1}$ , but as the results were very similar, they are not presented. The 31 July could not be taken into account because no data on the gray layer were available.

Except for 18 July, where a negative thickness of the gray layer was calculated, the calculated gray layer did not vary much, indicating that the estimation of the mass as a function of the water content was not unrealistic (Table 8a). The balance calculations indicate that a considerable net loss of Tot-N and Org-C occurred between 22 June and 3 July and between 12 July and 7 August (Table 8a,b). No changes occurred between 3 and 12 July and between 7 and 21 August. The net loss of Org-C is estimated (Table 8b) at 40% and the net loss of Tot-N at 50% (Table 8a) over a column depth of 40 cm.

As phosphate is not lost in transformations in the sediment the P-balance was used as a check of the calculation. The calculations showed in-

Table 8a & 8b. Balances of Tot-N, Org-C and Tot-P. The thickness of the gray layer has been calculated in order to obtain a constant sediment mass ( $\text{g cm}^{-2}$ ).

Date	Thickness layer (cm)			Mass ( $\text{g cm}^{-2}$ )			N ( $\text{mg cm}^{-2}$ )			Total N	
	Brown	Black	Gray	Brown	Black	Gray	Brown	Black	Gray	$\text{mg cm}^{-2}$	% of $t=0$
22-Jun	0.0	30.0	10.0	0.0	11.9	7.3	0.0	36.6	21.8	58.5	100
3-Jul	0.0	25.0	15.7	0.0	9.8	9.5	0.0	23.4	12.9	36.3	62
12-Jul	0.2	25.0	9.7	0.3	10.7	8.3	0.0	35.0	4.1	39.1	67
18-Jul	5.0	15.0	-2.7	6.0	15.9	-2.7	21.1	29.8	-3.0	47.9	82
	----- rainfall -----			----- rainfall -----			----- rainfall -----			----- rainfall -----	
7-Aug	11.0	6.0	12.1	6.0	3.6	9.6	15.4	6.2	6.1	27.7	47
	----- rainfall -----			----- rainfall -----			----- rainfall -----			----- rainfall -----	
21-Aug	8.0	8.0	11.2	3.8	5.1	10.3	11.2	7.9	8.9	28.0	48

Date	C ( $\text{mg cm}^{-2}$ )			Toal C		P ( $\text{mg cm}^{-2}$ )			Total P		
	Brown	Black	Gray	$\text{mg cm}^{-2}$	% of $t=0$	Brown	Black	Gray	$\text{mg cm}^{-2}$	% of $t=0$	
22-Jun	0	335	129	464	100	0.00	7.10	3.96	11.1	100	
3-Jul	0	233	123	356	77	0.00	5.29	5.11	10.4	94	
12-Jul	0	326	50	376	81	0.00	7.63	4.17	11.8	107	
18-Jul	179	361	-30	510	110	4.36	8.73	-1.30	11.8	107	
	----- rainfall -----			----- rainfall -----			----- rainfall -----			----- rainfall -----	
7-Aug	152	67	67	287	62	3.83	2.15	5.23	11.2	101	
	----- rainfall -----			----- rainfall -----			----- rainfall -----			----- rainfall -----	
21-Aug	114	97	73	285	61	2.47	2.63	4.70	9.8	89	



deed that there was no change in Tot-P on a unit area basis (Table 8b).

## Discussion

The increase in Tot-P, Tot-N, Org-C and Tot-Fe, occurring in the laboratory experiment, was probably not an effect of the desiccation, but more likely caused by the sedimentation of sand in the suspension, giving a relative increase in all sediment components except for SiO<sub>2</sub>.

As the evaporation will mainly take place at the surface of the sediment this will give rise to an upward flux. Compounds, dissolved in the interstitial water, will crystallize at the sediment surface and therefore give rise to an accumulation of salts in the top layer. In the laboratory experiment a considerable increase in surface Cl<sup>-</sup> occurred. Since in the field, the increase in Cl<sup>-</sup> observed in the surface layer occurred between 22 June and 12 July. It seems that the main upward flux of water occurred over this period. Between the 22 June and 3 July an decrease of water content occurred only in layer 2. This means that, during this period, a net upward flux of water occurred; the losses at the surface being compensated by water from the layer 2. After the first rainfall a decrease in sediment Cl<sup>-</sup> occurred in layer 1a. This decrease could partly be explained by a downward flux of rain water into the deeper layers of the sediment. The low values found in all sediment layers on 7 August suggests that a vertical movement occurred as well washing part of the Cl<sup>-</sup> to the lower central part of the marsh.

### *Sediment phosphate*

The increase in Tot-P in the surface layer, found in the field experiment, was probably caused not only by an upward water flux but also by the increase in phosphate adsorption capacity of the top layer (De Groot & Fabre, 1993). The formation of Fe(OOH) after the oxidation of Fe<sup>2+</sup> may be of importance as well in inducing the upward flux by creating a chemical potential. Fabre (1992) found an increase in inorg-P<sub>sed</sub> in the surface sediment of the bank of the Garonne on desic-

cation. The increase was suggested to be caused by an accumulation of phosphate rich particles, stimulated by the growth of attached algae. The [o-P]<sub>int</sub> was found to increase as well. It is likely that an upward flux has occurred as well; the hydrological conditions however did not allow this hypothesis to be tested (Fabre, pers. comm.).

In our laboratory and field experiments a mineralization of ASOP occurred. In the laboratory experiment the mineralization of ASOP (between  $t=0$  and  $t=18$  days) was followed by a mineralization of ROP (between  $t=18$  days and  $t=24$  days). On drying of moist soil samples Sparling *et al.* (1985) found a decrease of bacterial biomass C of 11 to 68%, depending on the soil. Biomass C was calculated from respiration rate measured under standard conditions. This indicated that a lot of bacteria died. They found a Tot-P<sub>bact</sub> varying between 3.9–55.1  $\mu\text{g g}^{-1}$  of which they estimated that between 0.4 and 15.8  $\mu\text{g g}^{-1}$  was released on drying of the soil. In the days following cell lysis P<sub>bact</sub> will to a large extent be hydrolysed by the cell enzymes, just as it is in algal cells (Golterman, 1960). Bacteria have been reported to account for a considerable quantity of Tot-P<sub>sed</sub> in certain sediments (Gächter, 1987). P<sub>bact</sub> will for a large part be recovered in the ROP fraction (De Groot & Fabre, 1992). The decrease in ROP may be explained by bacterium mortality.

In the field experiment an increase in ROP occurred after rainfall. This may be caused by an increase of bacterial activity after rewetting of the sediment. A strong increase in bacterial activity was observed by Barlett and James (1980) on rewetting dried soil samples. In oxic conditions bacteria were shown to be able to stock 'luxury' phosphate (Gächter, 1987), this may be in the form of poly-phosphate as well as in the form of inositol phosphate (Stevenson, 1982). Therefore an o-P uptake by bacteria should be considered as a possible cause of the increase in ROP.

It seems that mineralization of ASOP by bacteria occurred. De Groot & Fabre (1993) found that ASOP was the main active Org-P fraction, which, on desiccation, became bioavailable after mineralization. Changes in ROP seem to be re-

lated to changes in the size and the state of the bacterial population; changes in the inert Org-P which makes part of ROP do not seem to have been important in our experiments.

Golterman (1988) calculated a solubility diagram for the  $\text{Fe}(\text{OOH}) \approx \text{P} / \text{CaCO}_3 \approx \text{P}$  system. In the sediment  $\text{Fe}(\text{OOH}) \approx \text{P}$  is positively related to the  $\text{Fe}(\text{OOH})$  and the  $[\text{o-P}]_{\text{int}}$  and negatively to the pH. The formation of  $\text{CaCO}_3 \approx \text{P}$  is positively related to  $[\text{o-P}]$ ,  $[\text{Ca}^{2+}]$  and pH. The observed decrease in  $\text{Fe}(\text{OOH}) \approx \text{P}$  and simultaneous increase of  $\text{CaCO}_3 \approx \text{P}$  is in agreement with the solubility diagram as an increase in pH of more than one pH unit occurred over this period. The increase in  $\text{Fe}(\text{OOH})$  due to the oxidation of FeS, is not large enough to compensate the pH effect.

The increase in  $\text{Fe}(\text{OOH}) \approx \text{P}$  which occurred between 12 July and 28 August was probably due to an increase in  $\text{Fe}(\text{OOH})$  as a consequence of FeS oxidation and an increase in  $[\text{o-P}]_{\text{int}}$  due to the water flux.

The increase in  $[\text{Fe}^{2+}]_{\text{int}}$  after rainfall may originate from: (1)  $\text{Fe}(\text{II}^+)$  salts going into solution or (2) iron reduction by bacteria.

During the oxidation of  $\text{S}^{2-}$ ,  $\text{Fe}^{2+}$  concentrations in the interstitial water increase, which may cause the formation of  $\text{Fe}(\text{II})$  salts. Since  $\text{Fe}^{2+}$  is very sensitive to oxidation by  $\text{O}_2$  this has probably not been of quantitative importance. Nevertheless, the dissolution of  $\text{Fe}(\text{II})$  salts may explain the interstitial  $\text{Fe}^{2+}$  as the quantity of  $\text{Fe}(\text{II}^+)$  required to cause the observed increase in  $[\text{Fe}^{2+}]$  is negligible compared to Tot-Fe. Since the increase in interstitial  $\text{Fe}^{2+}$  occurs simultaneously with the expected increase in bacterial activity, iron reduction may also explain the increase in  $[\text{Fe}^{2+}]$ . Although the  $[\text{Fe}^{2+}]$  is unimportant from point of view of Tot-Fe, it may be of ecological significance as interstitial  $\text{Fe}^{2+}$  has been found to be toxic to many aquatic macrophytes (Ernst, 1990) and certain submerged macrophytes (Van Wijck *et al.*, in press). Golterman (1992) showed that FeS can be used by sediment bacteria as electron donor for denitrification. With FeS a significantly higher denitrification rate was observed than with organic matter as the only electron

donor. Since the desiccation of the marsh sediment resulted in a long-term decrease in both FeS and organic matter, a decrease in denitrification capacity may be expected, as well as a decrease in sulphate reduction capacity. Several factors may have attributed to the significantly lower FeS the year after drying.

- (1) The FeS found in the sediment and oxidized by the desiccation had accumulated over years and therefore several years will be required to reach the FeS concentration found before desiccation again.
- (2) During the desiccation a significant mineralization of organic matter took place, reducing the quantity of organic matter available for iron and sulphate reduction or both.
- (3) Due to the desiccation the biomass production in the marsh was lower than in previous years, resulting in a lower input of fresh organic matter into the sediment, thus reducing the quantity of organic matter available for iron and sulphate reduction.

#### *Balance calculations*

The values calculated for the 18 July seem doubtful. This is probably due to fact that at low water content of the sediment part of the interstitial space is filled with air, which means that supposition 1 (in all layers one gram of sediment has the same volume at the same water content) does not hold for samples with a very low water content. Therefore 18 July was not taken into account for the balance.

The first decrease in Org-C coincided with the mean increase in redox in both the black and the gray layer and was probably due to the penetration of  $\text{O}_2$  into the sediment. The second decrease occurred after the first rainfall. Since explained above, a strong increase of bacterial activity may be expected to occur some days after rewetting of the sediment, resulting in an acceleration of mineralization. The decrease in Tot-N observed coincided with the decrease in Org-C. The inorg-N which is liberated during the mineralization evidently serves as N-source to the denitrification, thus controlling N loss due to denitrification,

while  $\text{NH}_3$  volatilization may have been of some importance as well. The N loss between 22 June and 3 July may have been stimulated by the flux of  $\text{NH}_3$  to the surface, where it is lost after nitrification and subsequent denitrification. The second decrease occurred after the first rainfall; here two factors may have been of importance: denitrification, as a consequence of the observed increase in mineralization, and vertical losses due to a washing of ions to the deeper part of the marsh. Several authors have found an increase in mineralization of organic matter in soils subjected to alternating drained and flooded conditions (Gooding & McCalla, 1945; Stephenson, 1956; Birch, 1960; Reddy & Patrick, 1975); high N loss was shown to occur in the same conditions (Wijler & Delwiche, 1954; Russell, 1961; Patrick & Wyatt, 1964; Reddy & Patrick, 1975).

As phosphorus is an element with a closed cycle,  $P_{\text{sed}}$  could be used to test the validity of the balance calculations made for Org-C and Tot-N. Since neither decrease, nor increase of  $P_{\text{sed}}$  occurred it can be concluded that the calculated Tot-N- and org-C losses should be considered as reasonable estimates of the losses which have occurred.

In many studies on sediment-water interactions only the upper centimetres of the sediment are assumed to be active. During and after desiccation important changes were observed in our work down to a depth of about 40 cm and there was a flux of water from the deeper layers to the sediment surface. This means that for all sediment systems which (partly) desiccate occasionally, such as rivers, marshes, coastal lagoons, edges of shallow lakes and reservoirs this supposition does not hold. When making predictions about the development of the trophic state of such systems after reduction of the external nutrient loading an active sediment layer of several tens of centimetres should be taken into account.

As desiccation has a long lasting impact on the surface sediment it may serve as a tool in wetland management. It may find applications both in the management of natural water bodies and in rice culture.

Many natural water bodies are subject to an

enrichment with nutrients. These nutrients enter either with the inflowing water, or by means of wet or dry precipitation. In the longer term this may lead to an increase in biomass production, changes in the vegetation, and eventually to a replacement of macrophytes by algae. Inorg-N may be lost from the system due to denitrification and ammonium volatilization. Part of the inorg-N entering a system will be stocked in the sediment as Org-N, which may become available after mineralization. In contrast, phosphate entering a water body will accumulate in the sediment in both inorganic and organic form, where it may be inactivated temporarily, but not permanently, as demonstrated in this study. Phosphate present in a system will remain present unless it is removed with the outflowing water, or by human action. Furthermore, an accumulation of organic matter will occur, due to the increase in biomass production, favouring anoxic conditions. Since  $\text{Fe}^{2+}$  and  $\text{S}^{2-}$  are toxic to many macrophytes (Ernst, 1990), this may cause changes in the vegetation.

As drying will cause important losses of Tot-N and Org-C from the sediment it may be applied to restore oligotrophic conditions in marshes and other manageable water bodies, **if these systems are nitrogen limited**. In phosphate limited systems drying will activate phosphate due to a mineralization of Org-P and the upward flux of water. It will therefore favour eutrophic conditions. In systems with a short retention time drying may be applied to speed up the elimination of phosphate from the sediment after reduction of the phosphate input.

In rice fields up to 80% of the fertilizer-N applied, is lost due to denitrification before it can be taken up by the rice (Minzoni *et al.*, 1988). On the other hand, enough nitrogen for several years of culture is present in the surface sediment in the form of Org-N. In our experiments it was shown that desiccation caused a considerable mineralization of Org-N. The  $\text{NH}_3$  liberated was lost to denitrification, as no vegetation was present (Van Wijck & De Groot, 1993). The  $\text{NH}_3$  has to be oxidized at the sediment surface prior to denitrification, which means that it will be present in the sediment for a certain time. During this time

plants may take up part of it. Therefore a water regime with alternating submersion and desiccation of the soil, just before the period in which the rice plants need nitrogen, may improve the yield. Fertilizer should be applied afterwards, at the moment that the rice plants need the nitrogen (about 6 weeks after germination). Since this water regime will not only result in a mineralization of Org-N, but also in an oxidation of FeS and Org-C, it should be expected to slow down denitrification and thus the loss of fertilizer.

In the Camargue the rice plants are burned in the fields after the harvest. This means a considerable loss of Org-N (about 150 kg N hectare<sup>-1</sup>), as the Inorg-N formed will surely be lost before the next culture. When the rice plants are ploughed into the soil, the Org-N will partly remain present. When the field is managed correctly, next years' culture may benefit from part of this N.

Further research should be conducted to test and optimize the application of desiccation for both wetland management and rice culture.

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