

Nutrient dynamics in the floodplain ponds of the Paraná River (Argentina) dominated by the water hyacinth *Eichhornia crassipes*.

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Abstract. Some aspects of nutrient status and dynamics prevailing during low and high water conditions in the fringing floodplain ponds of the Paraná River dominated by the floating macrophyte *Eichhornia crassipes* are described. During summertime low water conditions, low DIN:DRP ratios (0.16–1.0) and low DIN (0.5–4.8 $\mu\text{mol.liter}^{-1}$) in the root-zone of the floating meadows suggest that macrophyte growth is limited by nitrogen. DRP concentrations appear to be controlled more by abiotic sorption-dissolution than by biological reactions. Preflood nutrient fluxes from the sediments, as estimated from pore-water profiles, show that a minimum of 1.19 and 0.38 $\text{mmol.m}^{-2}.\text{d}^{-1}$ of DIN and DRP were regenerated from the sediments, respectively. Heterotrophic N_2 fixation is primarily associated with decaying litter (0.4 to 3.2 $\mu\text{mol.N}_2.\text{g}^{-1}.\text{d}^{-1}$). Nutrient recycling from sediments and meadow-litter, and heterotrophic N_2 fixation (1.4 $\text{mmol.N.m}^{-2}.\text{d}^{-1}$) appear sufficient to sustain high floating macrophyte productivity for long periods of time, without invoking large inputs from the river. The high water and early isolation periods are characterized by a very dynamic behavior of DIN, reflecting marked imbalances between N supply and demand by the biota. After hydrologic isolation of the ponds, DIN rapidly decreases to undetectable levels and stays low for the following 3 weeks, presumably as a result of high demand by phytoplankton and sediment bacteria. DIN increases again to high values 3–8 weeks after the flood, following the re-establishment of NH_4^+ fluxes from the sediments. Compared to DIN, DRP concentrations remain relatively high and change little during and after the flood. Because of their small amplitude and short duration, floods do not appear to stimulate floating macrophyte production in the Paraná.

Introduction

The Paraná River drains the second largest watershed in South America after that of the Amazon, covering an area of $3.1 \times 10^6 \text{ km}^2$ shared by five countries: Brazil, Argentina, Paraguay, Bolivia and Uruguay. For a large part of its course, the Paraná is bordered by a $\approx 120,000 \text{ km}^2$

(Welcomme 1990), 10–50 km wide floodplain occupied by sub-tropical gallery forest, wetlands and meadows water bodies delimited by a complex network of alluvial leveés. Fish lakes and oxbow lakes formed by meandering tributaries entering the floodplain are also common. At the latitude of Corrientes (Argentina), water bodies are typically linear to crescent-shaped (100 to 500 m wide, 500 to 3,000 m long), shallow (1 to 5 m), turbid (Secchi depths of 0.2 to 1 m), and rarely have direct hydrologic contact with the river. Compared to the Amazon and the Orinoco, the Paraná has an irregular hydrologic regime. Floods may occur 1–3 times per year for periods of 2 wk to 3 mo, and water level fluctuations are relatively small (2–6 m, Fig. 1). This behavior is apparently unrelated to the damming history of the Upper Paraná, which only began in the early 1960s.

Ponds smaller than about 20 ha normally sustain relatively high biomasses of the floating macrophytes *Eichhornia crassipes*, *Sabnia herzogii* and *Pistia stratiotes*. Rooted macrophytes (*Eichhornia azurea*, *Victoria cruziana*, *Ludwigia peploides*, *Paspalum repens* and *Panicum elephantipes*) are occasionally present (Neiff 1986). Of these species, *E. crassipes*, the water hyacinth, is by far the most important in terms of coverage, biomass and productivity. It normally forms cohesive floating meadows which may cover 20–100% of the available surface, with standing stocks (dry weight) ranging from 5 to 30 metric tons per hectare (tha^{-1}), (Perez del Viso et al. 1968, Neiff & Poi de Neiff 1984). The meadows are normally not anchored, and often accumulate on windward sides of the ponds. Production shows a pronounced seasonality. Biomass usually increases from October to March, and declines to about 50% of its annual maximum during the cool season (April to September). Net biomass increments of 10–15 tha^{-1} are observed during the growth period (Lallana 1980; Neiff & Poi de Neiff 1984). Between exceptional floods (5–10 years), *Eichhornia* meadows may develop a floating organic soil and become colonized by other rooted hydrophytes.

Because of the absence of direct connections with the main channel, their low drainage ratio (drainage arealake area of 0.5 to 1), and the importance of *E. crassipes* meadows, these water bodies differ markedly from previously described floodplain lakes in the Amazon and the Orinoco (Devol et al. 1984; Fisher & Parsley 1979; Fisher et al. 1988; Hamilton and Lewis 1987; Howard-Williams & Junk 1976; Lenz et al. 1986; Melack & Fisher 1990; Forsberg et al. 1988; Hamilton & Lewis 1990). Factors such as climate, flood regime and nutrient supply from the river, watershed and atmosphere may control the amplitude and periodicity of macrophyte production in floodplain lakes, but their relative

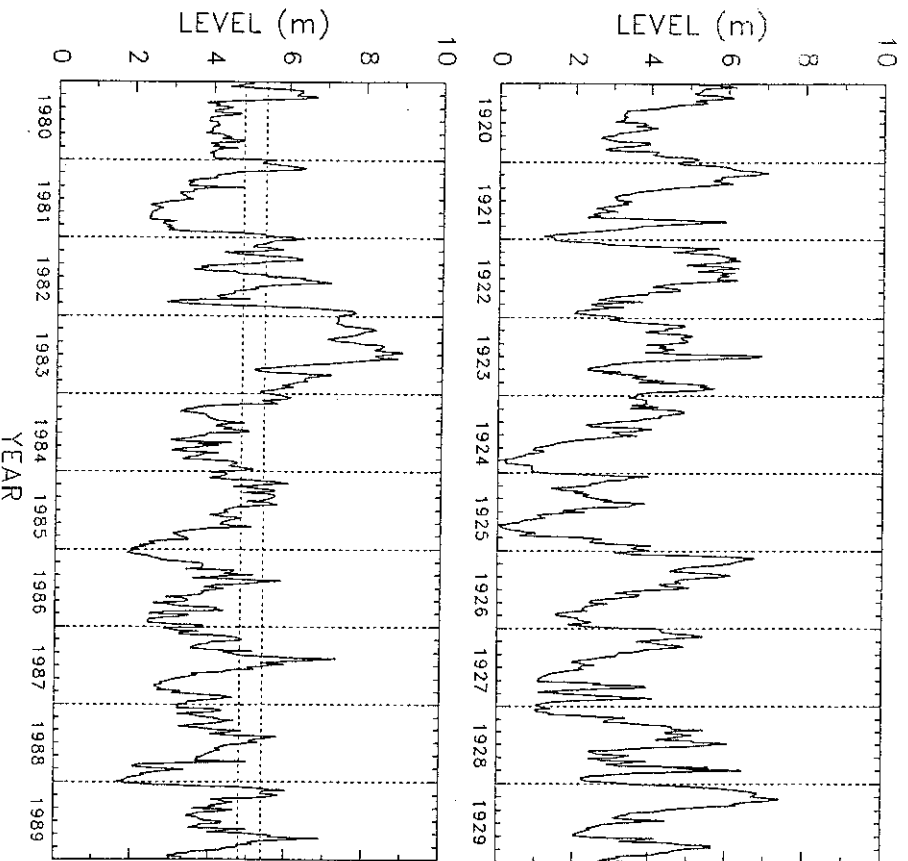


Fig. 1. Hydrometric level of the Paraná River at Corrientes during the 1920–1930 and 1980–1990 decades (source: unpublished data from the Argentina Direction of Navigation and Harbours). The horizontal lines show the approximate water ingestion levels in Ponds San Nicolas South (4.8 m) and North (5.4 m).

importance in different floodplains is unclear. In the Paraná, the high seasonal growth rates observed in the ponds implies the existence of large nutrient sources. Nutrient supply from the river, during floods, has been invoked to explain the apparently high productivity of floodplain ponds and floodplains in general (e.g. Junk et al. 1989). The flood pulse hypothesis may, however, not apply to all floodplain systems, as internal and external sources may contribute substantially to support macrophyte production. The present report characterizes some of the major nutrient

sources and pathways during low and high water conditions in the floodplain ponds of the Paraná and addresses the relative importance of river-derived nutrients vs other possible nutrient sources.

Study site

The study was conducted on the west bank of the Paraná River in Pond San Nicolas and four other nearby ponds on the fringing floodplain opposite the City of Corrientes (Argentina), 30 km downstream from the confluence of the Paraguay and Paraná Rivers (Fig. 2). Pond San Nicolas (27°27'S, 58°55'W; width \approx 150 m, length \approx 2 km) is located about 2 km from the river; it belongs to a complex of several similar ponds that are oriented parallel to the river. They are delimited by \approx 50 m wide, 1–2 m high alluvial levées occupied by gallery forest. A road divides P. San Nicolas into two water bodies (San Nicolas North and San Nicolas South) which are chemically distinct at low water. Plant cover is usually more developed in the South (90–95% cover in 1984–1989) than in the North (50–80%). The depth of both segments is uniform, but varies with time from 1 to 5 m, depending on the river level. The ponds are indirectly connected to the river 1–3 times per year, when the water level of the Paraná reaches or exceeds the 4.8 m datum at Corrientes (Fig. 1). Water and fine particulate matter are exchanged with the outside during floods, but *E. crassipes* normally remains trapped by trees and shrubs growing on the levées. Significant macrophyte flushing to the river, as described by Bonetto (1986), appears to occur only during exceptional floods such as that of 1983.

The open water sections of the ponds are characterized by low Secchi depths (25–100 cm), a pH of 6.0 to 6.7, and low oxygen levels (0–50% of saturation). Mean monthly air temperatures vary seasonally between 16 °C in July and 27 °C in January. The phytoplankton of the open water is dominated by small green, cryptophycean and dinoflagellate algae and cyanobacteria (e.g. *Sphaerocystis*, *Microactinium*, *Rhodomonas*, *Peridinium*, *Merismopedia*, *Anabaenopsis*). Planktonic heterocyst-bearing cyanobacteria are notably rare. Planktonic primary production rarely exceeds 1 gC·m⁻²·d⁻¹ (Zalocar et al. 1982), due to alternating light and nitrogen limitation (Carignan & Planas, unpubl.). The surrounding soil is composed of a superficial (0–50 cm) permeable layer of sandy silt underlain by ca. 2 m of compact reddish to grayish loam which is nearly dry to the touch. In the ponds, the loam is covered by 20–35 cm of dark, organic (5–10% C) and porous ($\phi = 0.8–0.95$) sediments. The limited thickness of organic

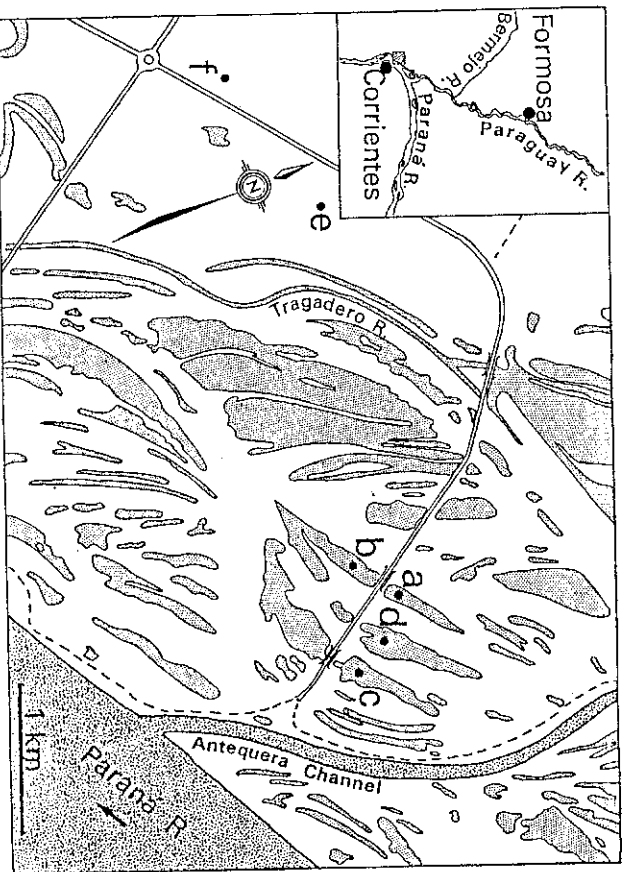


Fig. 2. Location of the study site, on the West bank of the Paraná River, Argentina: "a"; Pond San Nicolas North; "b"; Pond San Nicolas South; "c"; Pond Puente North; "d"; Pond Baltazar North; "e" and "f" are high water sampling stations.

sediments indicates that long term accumulation of organic matter does not presently occur in the ponds.

Methods

Water column, pore water and sediments

The site was visited during the warm season, between December and February 1988–1990, when macrophyte growth and nutrient demand are at maximum, and in April 1989 and 1990, when *E. crassipes* meadows are declining. The water column in floating meadows was sampled in December 1988 and April 1989 at four stations in Pond San Nicolas using passive equilibration devices ("peepers", Hessein 1976; Carignan 1984) with a vertical resolution of 2 cm. Biologically inert polysulfone membranes (Gelman DM-200, 0.2 μm pore size) were used. The samplers were initially de-aerated by keeping them for at least 12 h in

polyethylene bags inflated with 20 liters of nitrogen. They were positioned at least 50 m inside the meadows, and were left in place for one week in order to minimize disturbances resulting from their installation. Because this type of sampler requires about 24 h to reach equilibrium with the outside turbulent water, the chemical profiles thus obtained represent average conditions over 1–2 days. Horizontal profiles were taken at meadow edges to verify the existence of possible nutrient gradients between the open water and root environments. These profiles were taken at a depth of about 10 cm with 3 cm-wide diffusion samplers designed to penetrate the root mat without damaging the roots. Sediment porewater samples were obtained with a 1 cm vertical resolution by leaving diffusion samplers for 12–15 d in sediments; these samplers were carefully positioned by divers.

Dissolved inorganic carbon (ΣCO_2) and pH were measured following Carignan (1984). Samples for dissolved organic carbon (DOC), nutrients and major ions were collected in pre-acidified polystyrene tubes (1N Ulrex HCl, final pH \approx 3, stored at 4 °C) and analyzed within 2 weeks. DOC was measured by conductivity after UV-persulfate oxidation. Sulfate was measured by ion chromatography; NH_4^+ , NO_3^- + NO_2^- (henceforth called NO_3^-) and dissolved reactive phosphorus (DRP) were measured by automated methods (Stanton et al. 1977); total dissolved Fe, Mn, Na, K, Ca and Mg were measured with a Jarrell AtomScan 25 plasma emission spectrometer. Dissolved oxygen was measured with a YSI polarographic probe.

In January–April 1990, nutrients and major ions (unacidified samples) in surface waters were followed during and after an exceptional flood event during which the water-level reached the 8 m datum at Corrientes. On average, such floods occur only every 5–10 yr. Duplicate water samples were collected between 10:00 and 12:00 every second day in the floodplain and the river, and kept for 2–3 h on ice in polyethylene bottles. Samples were filtered through pre-washed Gelman HT-450 (0.45 μm) membranes for DRP, and Gelman AE glass fiber filters for NH_4^+ and NO_3^- manual determinations (Stanton et al. 1977) with five or ten cm cuvettes. Total P was measured after autoclaving (45 min at 120 °C) 50 ml samples with 0.5 g of potassium persulfate. We have not determined the efficiency of this procedure, but Engle and Sarnelle (1990) have reported that a 30 min digestion time with a smaller quantity (0.3 g) of alkaline persulfate (Valderrama 1981) underestimated TP in turbid waters of the Amazon.

Vertical temperature profiles were recorded every 15 min at 10–20 cm intervals during low-water between November 1989 and January 1990, and between December 1990 and January 1991 using thermistor

chains assembled with YSI 46032 glass-encapsulated thermistors set with epoxy in 25 × 4 mm steel shells. YSI cable and Electro Oceanics connectors were used to connect the cables to Licor LI-1000 data loggers enclosed in submersible aluminum cases. Precision and absolute accuracies were 0.02 °C and 0.05 °C, respectively. Sediment cores were collected by divers at the same site in Pond San Nicolas N before (January 1989) and after (April 1990) the flood using 10 cm diameter tubes. The cores were sectioned at 2 cm intervals and freeze-dried. Total C and Total N were measured with a Carlo Erba CNS analyzer.

Heterotrophic N₂ fixation

Heterotrophic N₂ fixation was measured in April 1990 (acetylene reduction) and in January 1991 (acetylene and ¹⁵N₂; Knowles 1980, 1982). In April, samples were collected in the field (San Nicolas N, high DIN concentration), and from an established (6 mo.) *E. crassipes* colony kept in a 8 × 2 × 1 m outside concrete tank (low DIN) located in Corrientes. Because Pond San Nicolas had been experimentally fertilized with DIN in January 1991 (Carignan and Planas, unpubl.), samples were collected in adjacent Pond Baltazar (Fig. 2), where DIN was undetectable (<0.05 μmol.liter⁻¹). Water, live roots and submersed decaying leaves and petioles of *E. crassipes* (0.5–1 g DW) were sampled underwater with clean 500 ml Mason jars, well inside the meadows. The type of litter assayed varied from cohesive to highly decomposed leaves and petioles. One hundred ml of C₂H₂-saturated pondwater was slowly injected at the bottom of the jars with a long needle; displaced water was evacuated through a second shorter needle, and the jar was gently mixed. This procedure allowed C₂H₂ introduction with no visible disturbance of the microbial assemblage attached to the decaying vegetation. Alternatively, we found that 50 ml of C₂H₂-gas could be slowly injected with a fine hypodermic needle through the septum and completely dissolved by gentle agitation, with little disturbance of the attached microbial assemblage.

Incubations were carried out in the dark, at 21–32 °C, within 1 °C of ambient temperatures, for periods of 1.5–4 h. Subsamples (25 ml) were taken from the jars with a 50 ml glass syringe and dissolved C₂H₄ was stripped by vigorous agitation for 90 s using a 1:1 sample:air ratio. Five ml of the gas phase were then injected into vials, and C₂H₄ measured with 10 d with a gas chromatograph equipped with a Porapak N column and a flame ionization detector. Proper temperature corrections and gas partition coefficients (Flett et al. 1976) were used to calculate C₂H₄ reduction rates. In all experiments, control jars containing litter and

pondwater were run to measure natural C_2H_4 levels. Care was taken to avoid accidental contamination of samples with NH_4^+ and NO_3^- which inhibit N_2 fixation. The absence of detectable contamination was systematically verified by measuring initial and final NH_4^+ and NO_3^- concentrations in the jars.

Calibration of the C_2H_2 reduction technique was performed by injecting 5.00 ml of 99% $^{15}N_2$ in water-filled jars, incubating ≈ 2 h, after which time C_2H_2 was added, thereby inhibiting further uptake of $^{15}N_2$, and the jars incubated for another 2 h. Vigorous sample agitation for ≈ 60 s after injection of the $^{15}N_2$ was unavoidable here since immediate isotopic exchange with dissolved $^{14}N_2$ had to be insured. At the end of the C_2H_2 incubation, C_2H_4 was sampled as above, and the loose particulate matter was resuspended and subsampled for filtration through Gelman AE glass fiber filters. Litter material was dried at 65 °C, weighed, finely ground and analyzed for total N (Carlo Erba). ^{15}N in filters and plants was measured by mass spectrometry (VG SIRA-12) after combustion at 900 °C with CuO. The isotopic ratio of N_2 in the experimental vessels was calculated assuming that they were initially saturated (Weiss 1970) with atmospheric N_2 having a 0.3663% ^{15}N content. Total N (TN) and total dissolved N (TDN) were measured by persulfate oxidation (D'Elia et al. 1977) followed by direct reading of the ultra-violet absorbance of NO_3^- at 220 and 275 nm (Smith et al. submitted).

Denitrification

Denitrification within the *E. crassipes* meadow was assayed only once in the field in April 1989, at a water temperature of 22 °C, using acetylene to inhibit the final $N_2O \rightarrow N_2$ reaction (Chan and Knowles 1979). Ten to twelve plants were gently lifted from the water and placed in duplicate 100-liter, 0.22 m², plastic containers to which 80 liters of surface pond-water had been added. Plant density in the containers was similar to natural surrounding values. Ten liters of C_2H_2 -saturated pondwater were then distributed within the root zone using plastic tubing. The containers were immediately covered with 1.5 m high, airtight tents made of two layers of 5 mil translucent polyethylene. The tents were tightly secured around the containers below the water-level; they enclosed 200–220 liters of air, to which 20 liters of C_2H_2 were added. The enclosed atmosphere and water column were then periodically sampled at three levels through lateral ports for the next 46 h. After 30 h, KNO_3 solutions were added through the lateral ports to raise NO_3^- concentrations to 9.8 in one container, and 98 $\mu\text{mol liter}^{-1}$ in the other. The low NO_3^- vessel was, however, damaged during a storm. Dissolved nitrous oxide was extracted

by vigorous agitation (90 s) of equal volumes of air and water in 50 ml syringes. Gas samples were collected in vacutainers and analyzed within one week by chromatography using a Porapak Q column and an electron capture detector. Water samples for NO_3^- analysis were taken before and after the experiment, and measured within 2 h of collection.

Results and discussion

Major ions, nutrients and vertical mixing within floating meadows during the isolation phase

Vertical profiles of major ions, taken in December 1988 through the ≈ 50 cm thick floating *E. crassipes* root-mat, show that the ionic composition of San Nicolas N and S ponds is dominated by sodium and bicarbonate (e.g. San Nicolas S, Table 1). Major ions in both ponds bear the signature of the Paraguay River where $\text{Na} > \text{Ca} > \text{Mg} > \text{K}$ compared to that of the Upper Paraná where $\text{Na} \approx \text{Ca} \approx \text{Mg} > \text{K}$ (Bonetto & Lancelle 1981). This is to be expected since the waters of both rivers usually remain well separated at the level of Corrientes, 30 km below their confluence. The vertical distribution of several constituents (ΣCO_2 , Ca, Mg, Na, Fe, Mn) is constant with depth which implies frequent mixing of the water column, at least over the upper 70 cm. Temperature profiles obtained during 94 days of the warm season (e.g. Fig. 3) show a complex mixing pattern dependent on daily wind and insolation. In open waters during sunny days, stratification typically begins around 10:00 AM and persists until 4:00 AM the following day. Complete mixing persists during cloudy and windy days. In the meadows, stratification tends to occur earlier and persists longer; complete mixing and upward dispersion of sediment-derived nutrients may occur only once every 1–2 weeks, during strong storms.

Although Ca, Mg and Na have orthograde profiles, NH_4^+ , DRP, K and SO_4^{2-} maintain pronounced vertical gradients in meadows (Table 1 and Fig. 4) attributable to an intense biological activity taking place within the root-zone. The persistence of higher K concentrations within the root-mat may be due an exchange for NH_4^+ by the root system, as we have observed equivalent release of K during NH_4^+ uptake experiments with *Eichhornia* (Carriagan et al. unpubl.). Nitrate was normally not detectable (at the $0.05 \mu\text{mol liter}^{-1}$ level) at any time or depth in the floating meadows. The disappearance of SO_4^{2-} around 15 cm, and the presence of high dissolved Fe concentrations, defines an anoxic and reducing environment confirmed by the absence of detectable dissolved oxygen below 5–10 cm. Compared to plant-covered areas, open waters are characterized by the presence of

Table 1. Vertical profiles of SCO_2 , DOC and major ions through the floating meadow in Pond San Nicoias South in December 1988. Data for the Upper Paraná and Paraguay Rivers are from Bonetto and Lancelli (1981)

Depth (cm)	SCO_2	DOC	Ca	Mg	Na	K	Fe	Mn	SO_4^{2-}
			(mmol.liter ⁻¹)						
0	1.32	2.74	0.29	0.22	1.03	0.14	0.005	0.001	0.0278
2	3.50	1.77	0.33	0.24	1.03	0.08	0.053	0.009	
4	3.63	1.74	0.34	0.25	1.03	0.10	0.070	0.010	0.0195
6	3.58	1.82	0.35	0.25	1.01	0.11	0.058	0.011	
8	3.58	1.74	0.35	0.25	0.98	0.11	0.056	0.011	
10	3.61	1.80	0.35	0.25	1.03	0.11	0.053	0.011	0.0140
14	3.57	1.87	0.35	0.25	1.05	0.11	0.056	0.011	
18		1.72	0.36	0.25	1.05	0.10	0.057	0.010	0.0003
20		1.73	0.35	0.25	1.05	0.10	0.054	0.009	
24		1.70	0.35	0.25	1.03	0.08	0.054	0.009	0.0000
26	3.72	1.70	0.35	0.25	1.01	0.07	0.057	0.009	
30		1.25	0.34	0.25	1.07	0.07	0.058	0.009	0.0000
34	3.83	1.57	0.35	0.25	1.01	0.05	0.063	0.009	
43		1.46	0.34	0.24	1.05	0.04	0.056	0.008	0.0000
49		1.44	0.33	0.24	1.01	0.03	0.054	0.007	
52		1.47	0.33	0.24	1.01	0.03	0.054	0.007	0.0000
58	3.40	1.44	0.33	0.24	1.01	0.03	0.054	0.007	
64		1.52	0.33	0.24	1.01	0.03	0.053	0.007	
Paraguay			0.32	0.20	0.84	0.08			
Upper Paraná			0.11	0.11	0.11	0.03			

3—6 ppm of dissolved oxygen at the surface, higher turbidity, and generally undetectable DIN concentrations (Carignan et al. 1992).

Vertical nutrient profiles taken through and below the root zone in summer (Fig. 4) suggest that DIN concentrations may limit the growth of *E. crassipes*. No comparable profiles for the floating meadows of the Amazon or Orinoco could be found in the literature. Ammonium levels (0.5—4.8 $\mu\text{mol.liter}^{-1}$) within the ≈ 50 cm-thick root zone in both ponds are much lower than those generally reported for environments where this plant is abundant, and orders of magnitude lower than concentrations previously used to establish relationships between growth and nutrient concentrations for tropical floating macrophytes (Gopal 1987). Low (0.1—0.6 $\mu\text{mol.liter}^{-1}$) DIN concentrations were also observed within the root-zone of floating meadows in two other ponds (Carignan et al. 1992). The success of *E. crassipes* in the Paraná shows that it can adapt to low nutrient concentrations and that supply is more important than concentra-

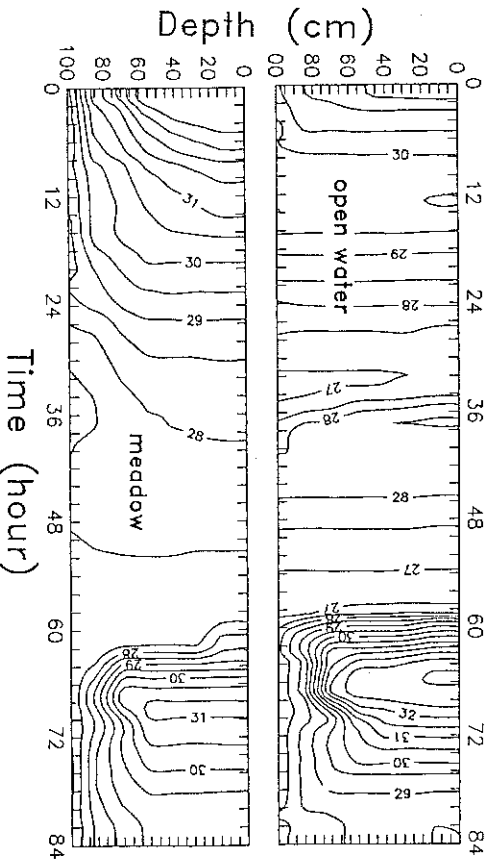


Fig. 3. Temperature isopleths in open waters and under an *E. crassipes* meadow from January 9 to 12, 1990; t_0 is midnight, January 9. January 8 was calm and sunny, and was followed by two cloudy and windy days; sunny and calm conditions returned on January 11. The vertical thermistor chains were placed about 100 m apart, on each side of the open water/meadow boundary.

tion in determining its growth in natural systems. The low DIN:DRP ratios (0.16–1.0) observed within the root zone are far from the $\approx 16:1$ proportion required by plants, and rule out P as a potential limiting nutrient in these ponds. We have experimentally verified (Carignan et al. 1992), using 20 m² limnocorals, that production by *E. crassipes* is in fact N-limited during the warm season. Dissolved organic nitrogen concentrations in open- and meadow-water range between 50 and 70 $\mu\text{mol.liter}^{-1}$. The origin, lability and fate of this pool are presently unknown.

Even if temperature and major ion data indicate that the upper 40 cm of water column is well mixed (Fig. 3), closely spaced NH_4^+ maxima and minima are present in the upper 10 cm (Fig. 4). The presence of steep NH_4^+ gradients strongly suggest that organic-N mineralization occurs concurrently with reassimilation within this zone. Established meadows thus appear to recycle NH_4^+ rapidly within the upper root mat, where decaying litter (leaves and stems) is abundant (Neiff & Poi de Neiff 1984).

During the cool season, nutrient concentrations under the plants increase by a factor of 10 (Fig. 4). This increase is likely attributable to the coincident decline in plant biomass which normally begins in April. The reasons behind the timing of the plant decline are unclear, but probably involve increasing grazing by insects, decreasing insolation, and lower temperatures, which decrease below the optimal 20–30°C range reported

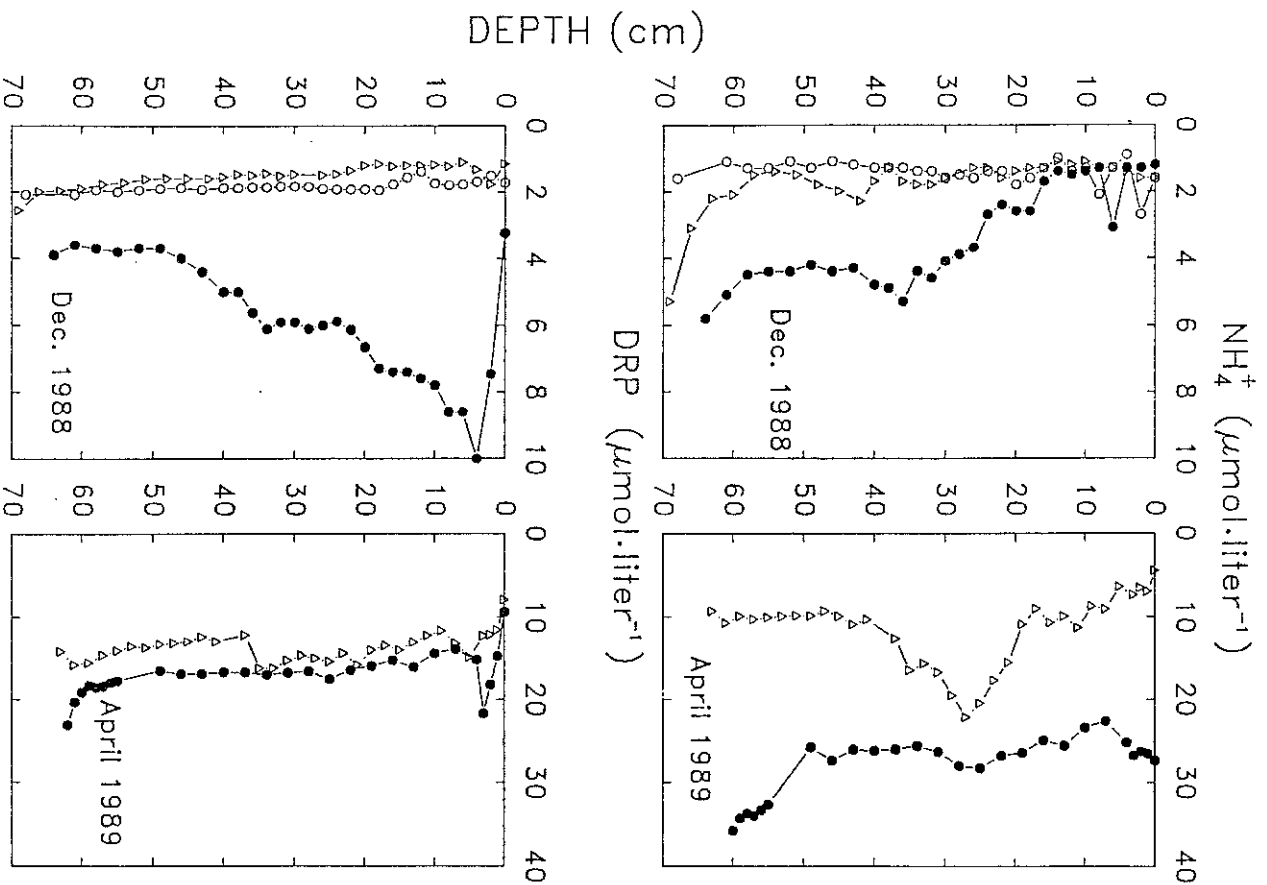


Fig. 4. Vertical profiles of NH_4^+ and DRP through the ≈ 50 cm thick root-zone of *E. crassipes* meadows in ponds San Nicolas North (open symbols) and San Nicolas South (filled symbols) in summer (December 1988) and winter (April 1989).

for *E. crassipes* by Sato (1988). Although no data are available, nutrient concentrations are expected to reach even higher values in July–August, when biomass reaches its annual minimum.

Horizontal NH_4^+ and DRP profiles taken at a depth of 10 cm across the open water/root zone interface during the growing season show further evidence of spatial heterogeneity in nutrient production and uptake within the litter and upper root zone (Fig. 5). DRP and NH_4^+ tend to be present in higher concentrations inside the root zone than in open water. Although actual nutrient fluxes across this interface cannot be evaluated, the profiles suggest that dissolved nutrients are lost from the upper root zone to the open water, even during periods when macrophyte growth and nutrient

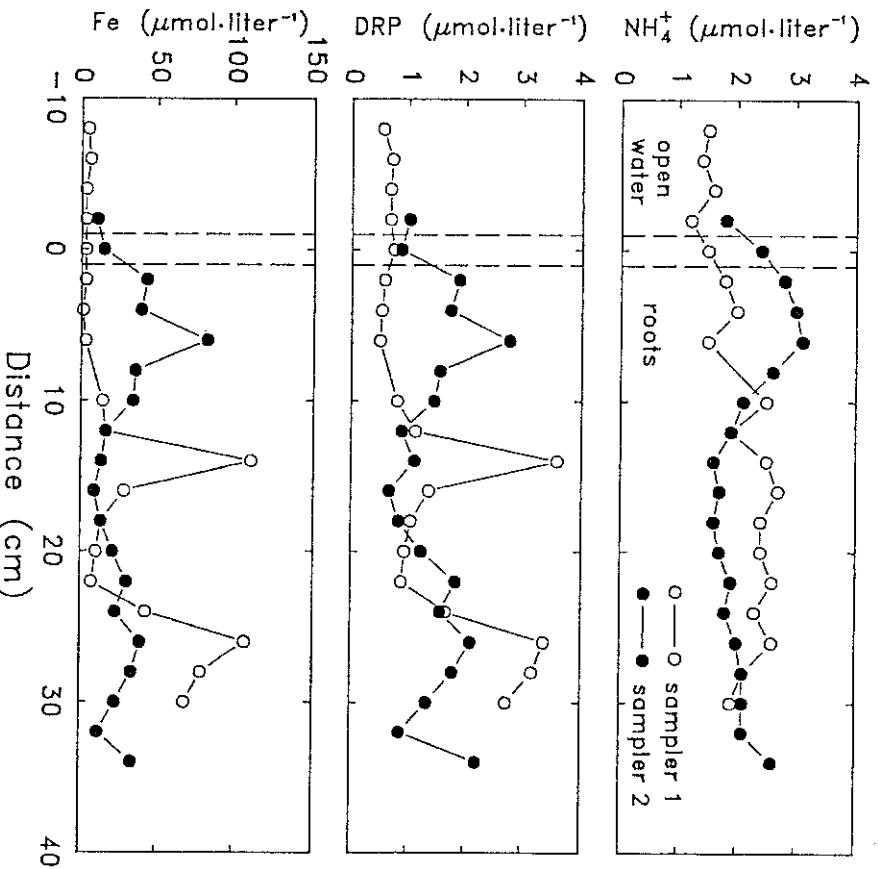


Fig. 5. Horizontal profiles of NH_4^+ , DRP and total dissolved Fe across the open-water/root zone boundary of the floating meadow in Pond San Nicolas North in December 1988.

demand are high. A strong linear relationship is observed between DRP and dissolved Fe for the horizontal profiles (DRP = 0.029 Fe + 0.61, $r^2 = 0.94$, $n = 38$). The high Fe concentrations most probably arise from the reduction of Fe-oxyhydroxides which are frequently visible on root hairs and plant debris near the water surface. The DRP-Fe regression suggests that 0.029 moles of P is liberated for each mole of Fe reduced. This ratio (1.7% by weight) is well within the range of reported values for phosphate adsorption onto iron oxyhydroxides (Sholkovitz & Copeland 1982). A similar relationship (DRP = 0.029 Fe + 0.073, $r^2 = 0.86$, $n = 97$) is maintained when the summertime vertical profiles through the root zone in San Nicolas N are added to the analysis. Thus, DRP concentrations in the root zone appear to be strongly influenced by phosphate adsorption onto Fe oxyhydroxides. Such a behavior is expected in systems where P is supplied in large excess of biological demand.

Pore water chemistry and internal nutrient fluxes

We used the chemical gradient approach to estimate nutrient fluxes at the sediment-water interface, and summed that transport was due to molecular diffusion only. Fluxes were calculated as:

$$J|_0 = -\phi D_s \frac{dC}{dx} \quad (1)$$

where $J|_0$ is the flux at the interface ($\text{mol.cm}^{-2}.\text{s}^{-1}$), dC/dx is the concentration gradient (mol.cm^{-3}), ϕ is the sediment porosity, and D_s is the coefficient of molecular diffusion ($\text{cm}^2.\text{s}^{-1}$) corrected for tortuosity using $D_s = D_m/\phi F$ (Berner 1980) with $F = \phi^{-3}$ for fine-grained sediment (Andrews & Bennett 1981; Ullman and Aller 1982), where D_m is the temperature-corrected self-diffusion coefficient (Li & Gregory 1974). It should be stressed that fluxes calculated in this manner probably underestimate true fluxes since bioturbation, bioirrigation and methane ebullition may have contributed to solute transport. Nevertheless, the exercise provides a first estimate of the importance of nutrient recycling from the sediments in such systems.

The results (Fig. 6, Table 2) suggest that on average, at least $1.10 \text{ mmol.m}^{-2}.\text{d}^{-1}$ of NH_4^+ and $0.27 \text{ mmol.m}^{-2}.\text{d}^{-1}$ of DRP were released from the sediments before the exceptional flood of January-February 1990. The low N:P flux ratio of 4.1 shows that, relative to biological demand, P is internally supplied in large excess to N in the ponds. Release is more variable for DRP than for NH_4^+ , but no clear seasonal differences are observed.

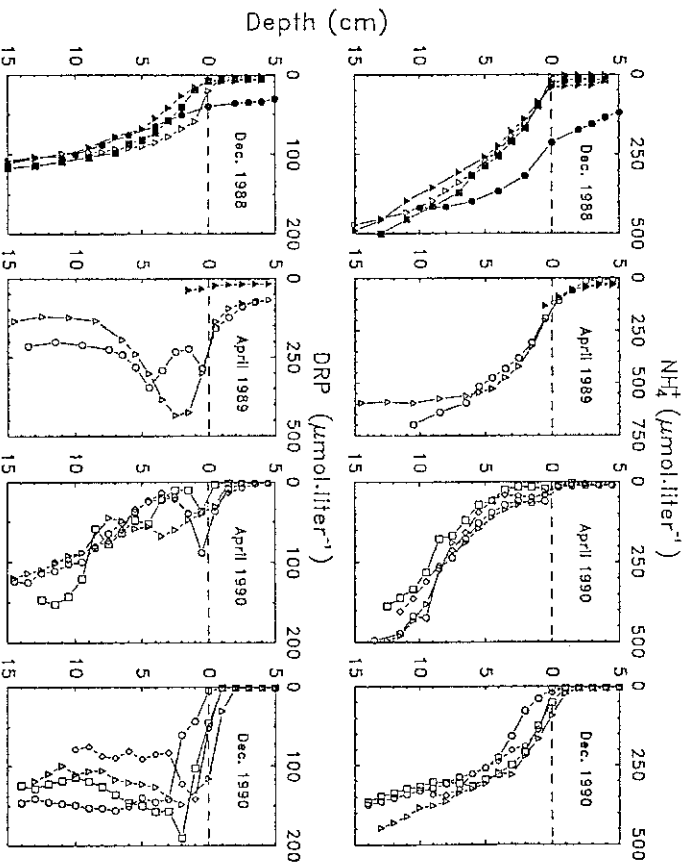


Fig. 6. Concentrations of NH_4^+ and DRP in the sediment pore-waters of ponds San Nicolas North and South under floating meadows (filled symbols) and in open water (open symbols).

The April 1990 profiles, taken 60 d after the flood differ markedly from those observed on other dates, and suggest a decrease in NH_4^+ flux at the interface compared to earlier dates. Two possible causes may explain the peculiar concave-upward shape of the NH_4^+ profiles (Fig. 6): biological disturbance or irrigation of the upper ≈ 8 cm, or the recent deposition of about 5–10 cm of NH_4^+ -absorbing material. There is no reason to believe that invertebrate activity should have been particularly high at that time, compared to December 1990, when the ponds still had a very reduced macrophyte cover and oxygen was present in the water column. The transient relaxation of pore-water NH_4^+ following a major, flood-induced disturbance of the upper 10 cm appears more plausible. Two different mechanisms may be invoked here. First, because NH_4^+ is subject to reversible adsorption in soils and sediments, the possible rapid deposition of 5–10 cm of new sediments during the flood may have left a NH_4^+ -depleted surficial layer; pore-water NH_4^+ originating from decomposition would then tend to increase with time, but adsorption onto the NH_4^+ -depleted solid phase would slow the process. Secondly, it is also possible

Table 2. Concentration gradients and NH_4^+ and DRP fluxes and ratios across the sediment-water interface in ponds San Nicolas North and South. The fluxes are based on bottom temperatures of 20 °C and 26 °C in April and December, respectively. A sediment porosity of 0.95, calculated assuming a density of 2.6 for the sediment solids, was used. Diffusion coefficients used in DRP flux calculations assume that DRP is equivalent to orthophosphate, and are composite coefficients taking into account the relative proportions and specific diffusion coefficients (Li & Gregory 1974) of H_2PO_4^- and HPO_4^{2-} at *in situ* pH

Station	Date	Plants	Gradient ($\mu\text{mol.cm}^{-4}$)		D_s ($\text{cm}^2.\text{s}^{-1}$)		Flux ($\text{mmol.m}^{-2}.\text{d}^{-1}$)		DIN:DRP
			NH_4^+	DRP	NH_4^+	DRP	NH_4^+	DRP	
South-1	15 Dec 1988	yes	0.053	0.0054	1.83E-5	7.77E-6	0.80	0.03	23.1
North-1	15 Dec 1988	no	0.096	0.0391	1.83E-5	7.69E-6	1.44	0.25	5.8
North-2	15 Dec 1988	yes	0.070	0.0208	1.83E-5	7.69E-6	1.05	0.13	8.0
North-3	15 Dec 1988	yes	0.053	0.0113	1.83E-5	7.69E-6	0.80	0.07	11.2
North-8	20 Apr 1989	no	0.117	0.1280	1.56E-5	6.55E-6	1.50	0.69	2.2
North-9	20 Apr 1989	no	0.123	0.1250	1.56E-5	6.55E-6	1.58	0.67	2.3
South-2	20 Apr 1989	yes	0.044	0.0102	1.56E-5	6.61E-6	0.56	0.06	10.2
North-1	30 Apr 1990	no	0.044	0.0517	1.56E-5	6.55E-6	0.56	0.28	2.0
North-2	30 Apr 1990	no	0.008	0.0290	1.56E-5	6.55E-6	0.10	0.16	0.7
North-3	30 Apr 1990	no	0.023	0.0179	1.56E-5	6.55E-6	0.29	0.10	3.0
North-4	30 Apr 1990	no	0.009	0.0352	1.56E-5	6.55E-6	0.12	0.19	0.6
North-1	16 Dec 1990	no	0.080	0.0813	1.83E-5	7.69E-6	1.20	0.51	2.3
North-2	16 Dec 1990	no	0.073	0.0984	1.83E-5	7.69E-6	1.10	0.62	1.8
North-3	16 Dec 1990	no	0.115	0.0892	1.83E-5	7.69E-6	1.73	0.56	3.1
North-4	16 Dec 1990	no	0.085	0.0874	1.83E-5	7.69E-6	1.28	0.55	2.3
Mean flux (1988—1989)							1.10	0.27	4.1
Mean flux (excluding April 1990)							1.19	0.38	3.1
Mean flux (April 1990 only)							0.27	0.18	1.5
Mean flux (December 1990)							1.33	0.56	2.4

that the shape of the profiles is partly due to the deposition of new, N-deficient organic sediments whose initial biological demand for N was so high that NH_4^+ release and accumulation in the pore-water and transport to the overlying water was reduced for several weeks after the flood. As will be seen below, this latter mechanism appears to have been important.

It is noteworthy that the NH_4^+ fluxes and profiles observed 10 months after the exceptional January-February 1990 flood are comparable to those found before. During the flood, water completely submerged the area shown in Fig. 2 and surface currents of the order of 10–20 cm.s^{-1} were observed for several days in the ponds, which become preferential flow channels when the water-level is changing rapidly. The fact that nutrient regeneration recovered 10 months after the flood indicates that even a flood of such magnitude is insufficient to scour the labile organic sediments of the pond. The two pre-flood and single post-flood sediment cores taken at the same site suggest that total C and total N increased after the flood (Fig. 7), and that new allochthonous organic matter had been deposited into the ponds. The lack of replication provides only weak evidence, however. Total C in the sediments of P. San Nicolas is within the range (3–16%) reported by Devol et al. (1984) for two Amazon flood-plain lakes.

The observation that NH_4^+ fluxes measured before and 10 mo after the flood are similar imply comparable NH_4^+ regeneration rates in the sediment column. This observation can be used to verify, qualitatively, whether the unusual April 1990 profiles are due to the relaxation of pore-water NH_4^+ after a major disturbance of the upper 10 cm, or if additional biological demand is involved. Indeed, if porosity, NH_4^+ regeneration rate (R , $\mu\text{mol per cm}^3$ of sediment per day) and adsorption coefficient (K) are known, non-steady-state diagenetic modeling can be used to predict the evolution of the pore-water profiles. If we assume that R and ϕ are constant with depth, the rate of change in pore-water NH_4^+ concentration (C) is given by (Bernier 1980):

$$\frac{dC}{dt} = \left(\frac{D_s}{1+K} \right) \left(\frac{d^2C}{dx^2} \right) + \left(\frac{1}{1+K} \right) \left(\frac{R}{\phi} \right) \quad (2)$$

where:

$$K = \frac{1-\phi}{\phi} sK' \quad (3)$$

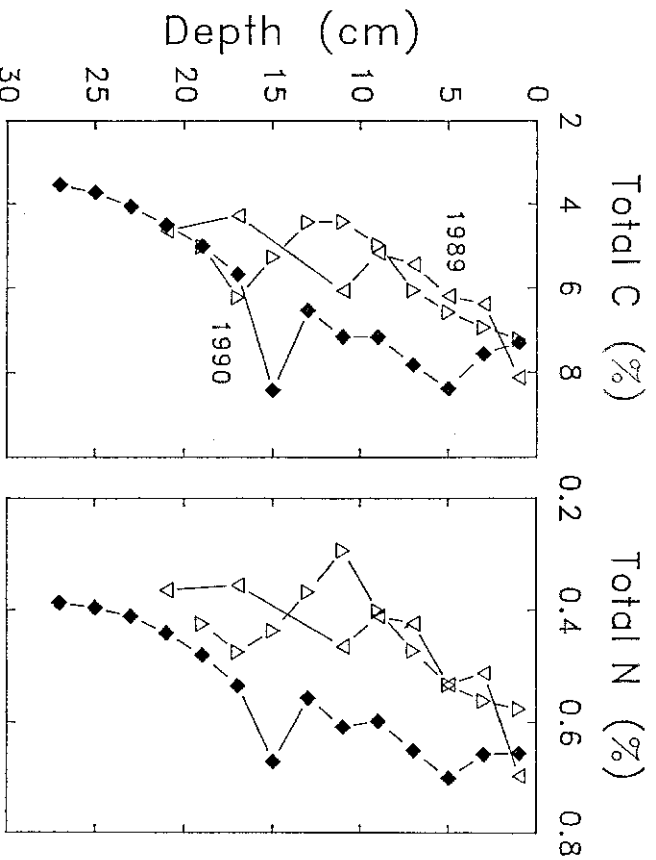


Fig. 7. Total sediment carbon and nitrogen vs. depth before (January 1989, open symbols) and after the flood (April 1990, filled symbols) in Pond San Nicolas North.

K' is the linear adsorption coefficient of NH_4^+ ($\text{liter}\cdot\text{g}^{-1}$), and s is the density of solids. Eq. (2) was integrated numerically by finite difference between $t = 0$ and $t = 100$ d using a Crank-Nicolson algorithm (Gerald & Wheatley 1984) with the following assumptions and boundary conditions. R was assumed to be constant with time and distributed homogeneously in the upper 10 cm, and its integrated value set equal to the diffusive flux observed at the interface on December 1990 (this is a minimum estimate since an important proportion of the labile organic matter deposited during the flood may have decayed). K' ($0.020 \text{ liter}\cdot\text{g}^{-1}$) was measured by centrifugation of a 0–10 cm bulk sample followed by extraction of the pellet with 2N KCl for 2 h and measurement of NH_4^+ in both extracts. Initial and boundary conditions are:

$$t = 0, x < 10 \text{ cm: } C = 0$$

$$t = 0, x > 10 \text{ cm: } C(x, 0) = 0.52(1 - \exp(-0.156x)), (\mu\text{mol}\cdot\text{cm}^{-3}),$$

$r^2 = 0.99$, the non-linear least-squares fit of the December 1988 profiles.

Time-dependent solution of $C(x, t)$ show that the NH_4^+ profile should regain a convex-upwards shape within 10–15 d following the flood (Fig. 8). Therefore, a model assuming positive R and simple abiotic adsorption cannot explain the persistence of a concave profile after 60 days. An additional strong NH_4^+ sink must have been present in the upper 5–10 cm of the sediments. This conclusion is consistent with the rapid disappearance of DIN in the ponds shortly after their hydrologic isolation (see below).

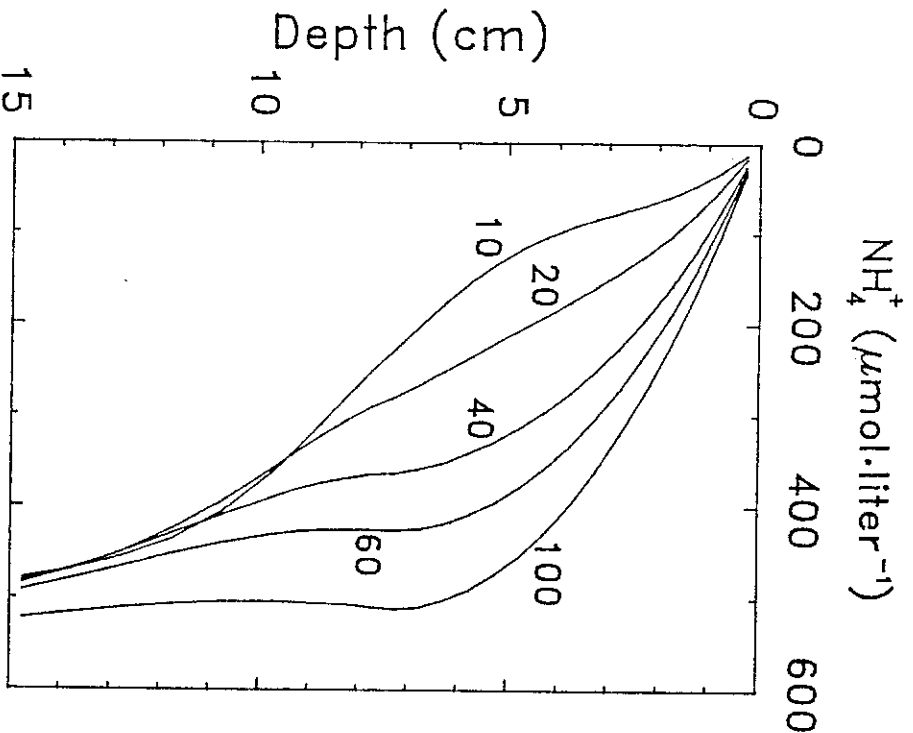


Fig. 8. Theoretical relaxation of pore-water NH_4^+ during the first 10–100 days after a flood-induced erosion of the upper 10 cm of the sediments followed by the sudden deposition of 10 cm of new sediments in Pond San Nicolae North. The model assumes that NH_4^+ production, diffusion and adsorption are the only important reactions.

Heterotrophic N₂ fixation

Heterotrophic nitrogen fixation is primarily associated with decaying litter in these systems, and appears to be strongly inhibited by DIN (Table 3). The molar ratio of ethylene formed to N₂ fixed varied considerably, from 4.3:1 to 22.6:1, among the 12 litter samples on which both measurements were made. The average C₂H₂:N₂, calculated as the sum of C₂H₂ produced divided by the sum of N₂ fixed in all experiments was 8.0:1, which is significantly higher than the 3:1 value often used to convert acetylene reduction to N₂ fixation rates. However, linear regression of C₂H₂ produced against N₂ fixed gives:

$$C_2H_4 = 3.82 \pm 1.2 \text{ } ^{15}N_2 + 12.66 \pm 4.5, r_2 = 0.50; n = 12; \quad (4)$$

with both slope and intercept significantly different from zero ($p < 0.01$). The slope is thus close to 3:1 ratio, and lower than the 10:1 to 100:1 values reported for heterotrophic fixation in the sediments of Narragansett Bay (Seitzinger & Garber 1987). Ethylene production in samples to which no acetylene was added was insignificant. Thus, we interpret the significant positive intercept as an indication that some acetylene reduction was also mediated by non-nitrogen-fixing organisms. These results provide further caution against the use of the acetylene reduction assay of heterotrophic N₂ fixation. Eq. (4) was used to convert C₂H₄ production to N₂ fixation for dates or samples for which only acetylene reduction rates are available (Table 3). In January 1991, individual N₂ fixation rates varied considerably, from 0.32 to 7.72 $\mu\text{mol.g}^{-1}.\text{d}^{-1}$. We presume that variability in both the ratio of C₂H₄ produced to N₂ fixed and fixation rate is attributable to the heterogenous nature of the litter samples assayed.

Few values of N₂ fixation by heterotrophs associated with decaying aquatic vegetation in natural systems have been reported in the literature. Our average rates of 1.99 and 3.18 $\mu\text{mol.g}^{-1}.\text{d}^{-1}$ found under low to undetectable DIN concentrations in April 1990 and January 1991 are 2–10 times higher than those found by Dierberg & Brezonik (1981) in a cypress dome swamp, and, to our knowledge, are the highest reported so far. The high N-demand by decaying vegetation is also apparent from the rapid decreases of inorganic N in the experimental vessels during incubation (Table 3). Fixation is undetectable in the open water, where cyanobacteria are normally a very minor component of the phytoplankton, but reaches the appreciable level of 0.07 $\mu\text{mol. liter}^{-1}.\text{d}^{-1}$ in surface water collected in the floating meadow. Roots fixed relatively little N₂ (0.03–1.23 $\mu\text{mol.g}^{-1}.\text{d}^{-1}$) and most of it may have been associated with fine litter caught in the roots.