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SOME ASPECTS OF NUTRIENTS CYCLES IN THE CAMARGUE (FRANCE)

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RESUM

S'estudien alguns processos químics i biològics que tenen a veure amb els cicles dels nutrients en aiguamolls, i se centra l'atenció en tres aspectes importants com són la desnitrificació, la mineralització dels macròfits i l'absorció de fosfat als sediments. Els resultats provenen de treballs portats a terme a la Camarga, al delta del Rhone (Sud de França).

ABSTRACT

Some chemical and biological processes involving nutrient cycles in wetlands are studied, focussing in three major items which are denitrification, mineralization of macrophytes and phosphate absorption onto sediments. Results come from works carried out in the Camargue (Rhone delta, S. France).

Plant nutrients are of considerable interest in the protection of wetlands. Not only will an increased input of nutrients cause problems of eutrophication such as a shift from one type of vegetation to another, less desirable, even an increased growth of desired community (both its quantity and its growth rate) may cause an increased overgrowing or filling in of the wetland.

In wetlands the chemistry of the water is largely controlled by the sediments, therefore the interactions between sediment layers of wetlands and the most important plant nutrients become significant. Unfortunalely sediment chemistry is more complicated than just setting up flow diagrams or simple budgets; it demands sophisticated techniques and interpretations.

In the kind of wetlands considered here, we agree on the importance of maintaining macrophytes, i.e. submerged and emergent types of vegetation. Competition against phytoplankton growth is weakened by increased nutrient input, because as soon as phytoplankton starts winning in the competition it has a competitive advantage by intercepting the light.

For primary production macrophytes need less nutrients per unit biomass than phytoplankton. While for the latter the P content is about 0,5-1% of the dry weight and N about 10%, for the macrophytes these figures tend to be 4-5 times higgher biomass of macrophytes can be build up although at a much lower growth rate. As long as all incoming nutrients can be absorbed by macrophyte vegetation can absorb, the phytoplankton will increasingly absorb excess nutrients. The consequent increase in phytoplankton biomass will result in competitve loss by macrophytic vegetation.

The difference in nutrients demand for phytoplankton and macrophytes can be roughly described as follows

for phytoplankton:

$5\ CO_2 + 2H_2O + NH_3 \longrightarrow C_5H_7NO_2\ (P1/30) + 5\ O_2$
(based on about 50-60% of algal material being protein)

For macrophytes:

$25\ CO_2 + 22\ H_2O + NH_3 \longrightarrow C_{25}H_{47}NO_{22}(P1/30) + 25\ O_2$

(assuming that for 1 CO_2 taken up protein formation as in phytoplankton, in macraphytes about 4 CO_2´s are taken up for extra carbohydrates, e.g. cellulose).

Due to the difference in chemical composition, the mineralization processes of phytoplankton and of macrophytes are different. While due to the high nitrogen content of the phytoplankton the mineralizing bacteria will release free NH_3 into the water (using only a small part of the biomass for the build-up of their own biomass and the larger part for their energy), bacteria decomposing macrophytes need extra N in order to convert organic matter with a high C/N, into their own proteins (often around 40-60 %) with a lower C/N. Furthermore while phytoplankton death occurs more small input of organic matter into the sediments, the macrophytes die off more abruptly during the late autumn, causing a single, large input of organic matter into the sediments, which during winter will only slowly desompose. Anoxic conditions in the sediments are therefore more often found in waterlogged soils than in not-polluted, phytoplankton dominated lakes.

A special problem in the study of eutrophication of wetlands is the complexity of the drainage system. Agricultural fields are often interwoven with the natural marshes. Drainage systems exits for irrigation, withdrawal of exces water and even for water supply to the natural marshes; which in the Mediterranean environment often have to receive water to prevent them from drying out. Both in the natural marshes, as in the cultured fields (where rice is often one of the major crops) important interfaces are present, where N and P will be transferred from water to soil, from water and soil into the plant, into the atmosphere and vice versa. Monitoring these fluxes in order to achieve a «nutrient budget» requires a major effort, and thus a significant financial budget, which is rarely available.

In this paper, which is not meant to the synthesys, I will discuss a few of the major processes, which play a role in wetland nutrient chemistry. The discussion will primarily focus upon our own work in the Camargue (Rhone delta, S. France). A synthesis is in preparation and will be published elsewhere.

The major processes which will be considered are:

1. Denitrification
2. Mineralization
3. Phosphate adsorption onto sediments.

DENITRIFICATION

If nitrate is added to waterlogged soils, it will rapidly disappear, usually linearly related with time (Golterman, 1990). We followed this disappaerance in enclosures (diameter 44 cm), placed in normally cultivated rice-fields. Some typical results are depicted in Figure 1. The high initial nitrate concentration is related to the high input of N-fertilizer, as used in plant uptake alone. In order to proof that denitrification, indeed played a role, several experiments were carried out with the acetylene inhibition technique, by which technique not N_2, but N_2O is formed which can be measured with simple gas chromatography (Minzoni et al., 1988).

Nitrate was therefore added to enclosures placed in a rice-field. The first results were disappointing, the recovery as N_2O was only about 30 % (Fig. 1). We realized that not only does the N_2O diffuse upwards into the water and the overlying air space, but also into the deeper water layers. We therefore added N_2O to similar enclosure and noticed that there was a very constant disappearance rate. After correction for this disappearance we found a recovery of the added N-NO_3 lost of

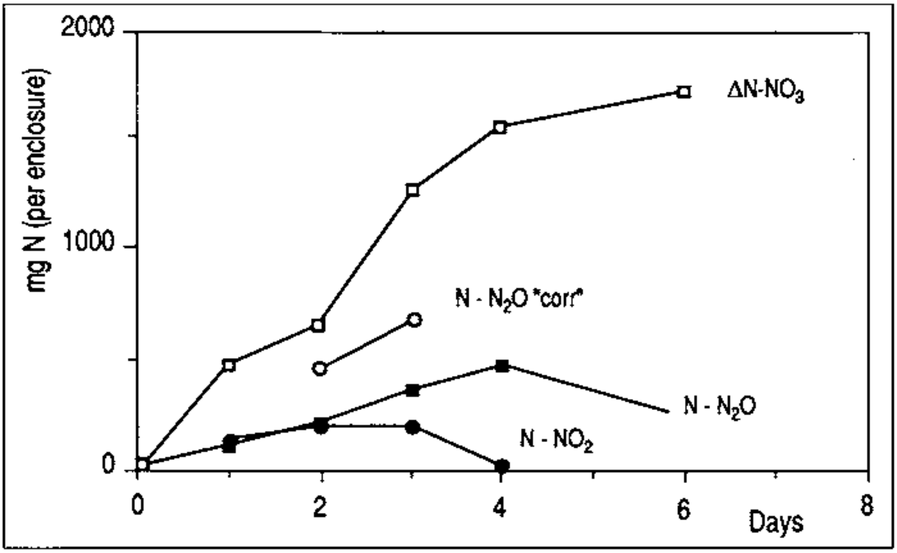

Figure 1. Decrease of nitrate and nitrite and N_2O production (also after correction for losses) in enclosures in rice-fields. Drawn after data from Minzoni et al. 1988.

about 70% as N_2O (Figure 1). As further proof of the large losses which occur in these waterlogged soils, we added $K^{15}NO_3$ to another enclosure. Depending on whether rice was already present or not we could recover only 5% and 10% respectively of added $K^{15}NO_3$ in the vegetation (Minzoni, 1988). This experiment points again to the important loss by denitrification.

Concomitant with the nitrate disappearance, high concentrations of nitrite were formed, often up to 20-30% of the added nitrate; the flux through this compound may be even more significant. Although in rice-fields this probably does no harm (as long as one does not try to culture e.g. fish as well) in marshes this migh become an important toxic compound if the river water used for irrigation contains considerable quantities of nitrate production, production of N_2, would yield much more energy.

Temperature and organic matter seem to be the factors controlling the rate of denitrification and nitrite formation. Recently, however, we noticed that FeS could also serve as a hydrogen donor and stimulated denitrification at a much higher rate an organic matter alone (Golterman, 1990). During this denitrification high concentration of nitrite was formed. It seems likely therefore that bacteria other than only the heterotrophic ones must be taken into account.

There is a general belief that denitrification is a process protecting the environment against eutrophication. This is partially true, but it should be realized that while the bacteria do indeed release a considerable quality of nitrogen into the air, nevertheless by their own metabolism accumulate nitrogen in the sediments. It has been shown (Muller, 1977, for discussion see Golterman, 1984) that nitrogen builds up slowly in the sediments of eutrophying lakes and is strongly related to the increase of primary production. Denitrification should therefore not be seen as a panacea against an unlimited N input.

MINERALIZATION

There are few studies on mineralization of higher aquatic plants, neither of cultured plants like rice, nor of the naturally occurring macrophytes. Comin (1988) carried out experiments in litter bags and followed the disappearance rate of the bulk material and that of P, N and C. His experiments show an increase of the N% of the degrading material, as seems to be necessary before a complete mineralization can take place. The mineralization of macrophytes containing a high C/N ratio is, however, quantitatively still poorly understood. Previously, when farmers were adding a «green manure» to their fields, they knew that nitrogen had to been added in order to achieve mineralization. In preliminary experiments we noticed that the mineralization proceeded better under anoxic conditions, where CH_4 will be formed. This may be a means by which the bacterial ecosystem get rid of the excess carbon; it seems likely that the eventually added nitrogen inder these conditions will be largely denitrified. The disppearance of carbon is, however, not the only important variable to follow mineralization. For the growth of the vegetation nitrogen seems to be more important.

I think that are needed experiments in which the fate of the carbon and the nitrogen is followed during the mineralization. Unfortunately we are dealing with too many compounds. We have tried therefore, to distinguish different nitrogen fractions in the soil. As specific extractions are not yet possible we tried an operative fractionation (Bonetto et al., 1988). Usually 0,1 M NaOH at 20°C (e.g. for 17 hrs) or 6 M HCl (or H_2SO_4) at 100°C (3 hrs) are used, in which no real plateau is usually reached. We found a better plateau using 0,1 M NaOH during at least three days; after this extraction the H_2SO_4 yielded a better, although not a complete plateau. Experiments are now underway to see in which compartment the mineralized N will appear.

We know nothing of the fate of the remineralized nitrogen during the non growing season. Firstly NH_3 will be formed, which will be partially adsorbed onto the sediments, and therefore be oxidized very slowly. Low temperature do not protect the nitrate produced against denitrification as this process will proceed even at 0°C (El Habr & Golterman, 1989). Only field studies under well controlled conditions will enable us to quantify the rates of these processes in the field. Laboratory experiments will always remain too far from the real situation to permit an extrapolation.

PHOSPHATE ADSORPTION ONTO SEDIMENTS

The adsorption of phosphate onto sediments is today a frequently studied phenomenon. Recent reviews appeared by Golterman (1984) and Bostrom et al. (1982). The process can well be described with the Freundlich adsorption isotherm.

P_{sed} = A* (0-Pw)B
where P_{sed} = amount of phosphate adsorbed per unit dry weight
0-Pw= concentration of ortho-phosphate in the overlying water

Furumai & Ohgaki (1989) described the 0-P adsorption by the Langmuir isotherm. Golterman (1990), however, demostrated that the available experimental data do not permit a choice between the Langmuir and Freundlich adsorption isotherms, and demostrated that a choice can only be made using experiments carefully designed for that purpose.

The question remains as to what extent the reducing conditions in the sediments have an influence on the adsortion of 0-P on the iron system and on the distribution of 0-P over the Fe (00HO) and Ca CO_3 systems.This problem can be tackled as we (Golterman & Booman, 1989, De Groot & Golterman, 1990) developed a separation of Fe (OOH)~P and $CaCO_3$ ~P using specific (chelating) extractants in stead of operative extractants such as NaOH and HCl. As a first result we demostrated that the organic pool is much larger than is generally believed, as NaOH and HCl hydrolyse a large part of the org-P, (which is then measured as inorganic P).

As Fe (OOH) plays an important role in the adsorption process, formation of

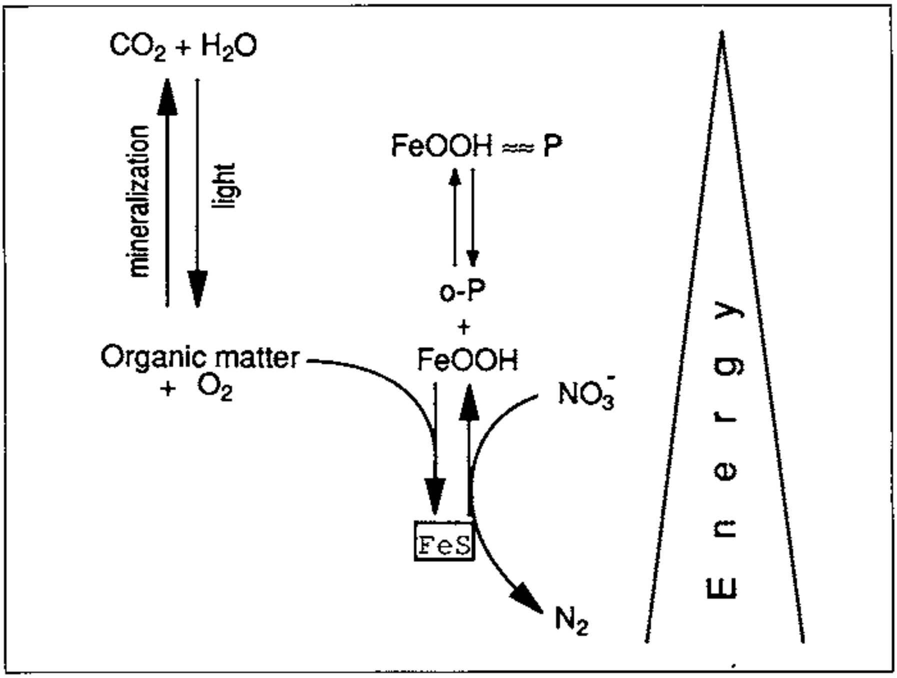

Figure 2. Schematic representation of FeS formation, its influence on P adsorption onto sedimens and denitrification.

FeS may negatively influence phosphate adsorption (De Groot, 1990). Golterman (1984) calculated that this can only play a minor role in deeper lakes. In shallow water bodies it will be more important. Here the input of organic matter does not take place day by day (as caused by the rain of dead phytoplancton in deeper lakes), but after the death of the macrophyte vegetation, followed by mineralization as soon as the temperature start rising in spring. Marshes and rice-fields indeed contains large amounts of FeS. Oxidation of FeS by denitrification may restore the adsorption capacity. Figure 2 gives a simplified scheme relating the role of FeS in the nutrient chemistry in those systems where FeS is a major part of the Fe being present. In this respect wetlands differ from deeper lakes, where the amount of Fe (OOH) converted to FeS is less and which conversion occurts less suddenly (de Groot, loc. cit.).

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