Natural attenuation processes of nitrate in a saline lake-aquifer system: Pétrola basin (Central Spain)

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Introduction

Nitrate (NO_3^-) is considered as one of the most significant contaminants that could prevent reaching the goals of the Water Framework Directive 2000/60/EC. Excessive use of fertilizers in agriculture, and wastewater spill out, are the principal sources of NO_3^- in the environment. High NO_3^- concentrations in groundwater are a matter of concern due to its negative effects on health and on the eutrophication of surface water bodies. Saline wetlands under intense agricultural land use in semi-arid to arid climates are among the most vulnerable environments to NO_3^- pollution.

A representative example is the Pétrola Basin in High Segura River Basin (Central Spain) (Fig. 1). It was declared vulnerable to NO_3^- pollution in 1998, due to the inputs of pollutants from agricultural sources and urban waste waters without proper treatment. NO_3^- inputs are derived from nitrification of synthetic NH_4^+ fertilizers. The quantification of natural NO_3^- attenuation processes provides information about the systems' capacity for water resource renewal. Previous studies showed that denitrification is considered the main process at the saltwater-freshwater interface around the lake, with nitrogen reduction rates (NRRs) in lacustrine sediments about 1.25 mmol d^{-1} L^{-1} under flow-through conditions (Carrey et al., 2014). The pattern of NO_3^- reduction in recent lake sediments is currently not known. In this study, the potential of NO_3^- attenuation linked to the sediment-water interface was studied.

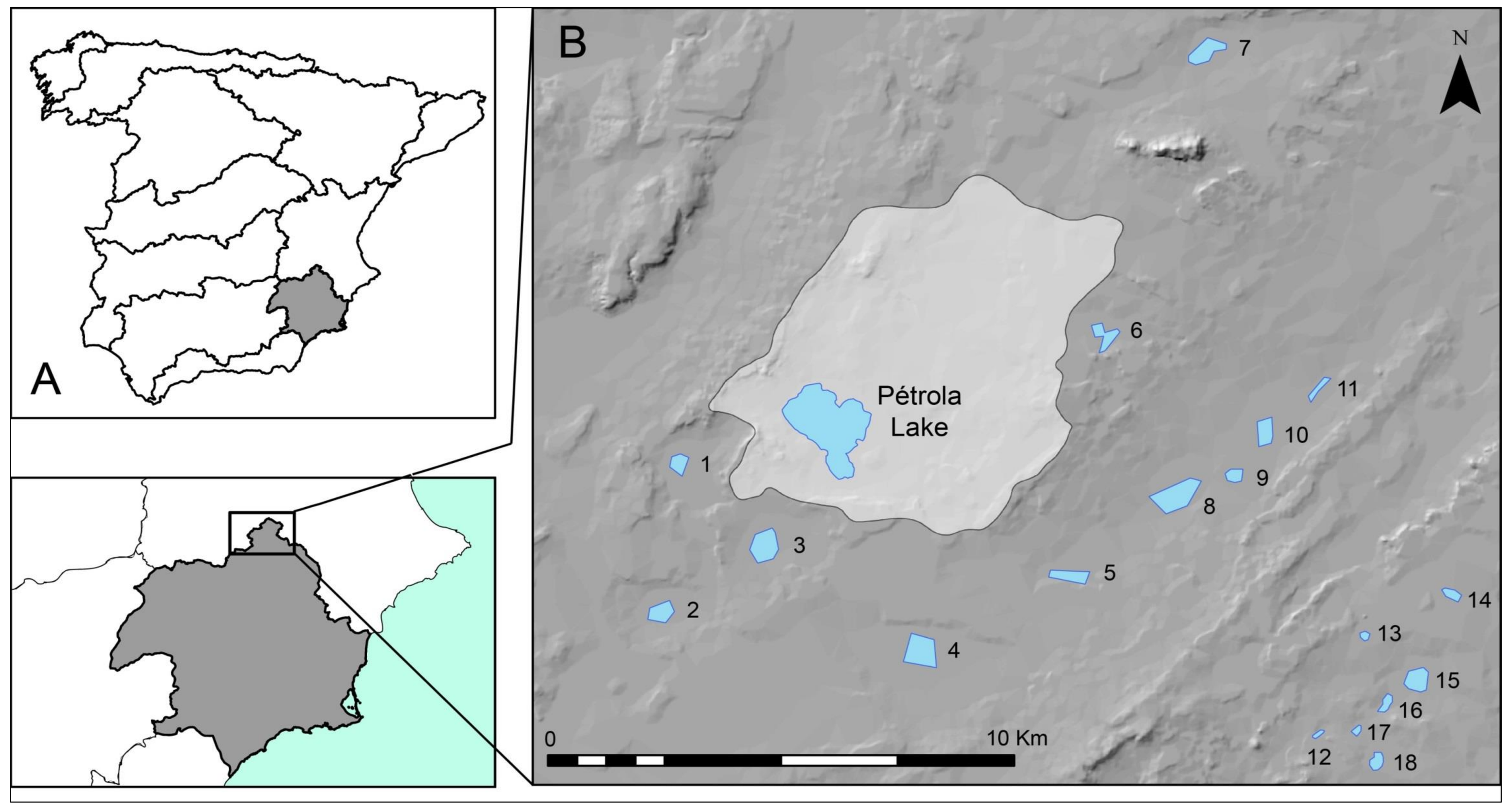

Fig. 1: A) Location of Segura River Basin. B) Pétrola Basin in the saline complex.

Conclusions

- Negative Eh was found in all the treatments at the end of the experiment in the water column.
- Complete attenuation of 3.5 mg of N-NO_3^- was observed in the first 30 h of incubation, coupled with a temporal increase in N-NO_2^- concentration. The NRR (0.03 mmol d^{-1} L^{-1}) was lower than obtained in previous studies under flow-through conditions (1.25 mmol d^{-1} L^{-1}).
- The increase of N-NH_4^+ in the water column appears to be the consequence of dissimilatory nitrate reduction (DNRA) during the first 30 h after spike addiction.
- The increase in alkalinity in the water phase was positively correlated to the increase in DOC demonstrating the importance of DOC as proton-acceptors in this system.
- N-NH_4^+ accumulation in sediment was only found in treatment 3. This suggests the uptake by bacterial communities.
- Further work is necessary to clarify the microbial pathways of NO_3^- attenuation.

Materials and methods

- Incubations using 9 intact organic-rich lake sediment cores (20 cm in thickness) in plexiglas mesocosms (V=12.6 l)
- Treatments: 1) light and oxic conditions; 2) dark and oxic conditions; 3) dark and anoxic conditions (Fig. 2)
- Incubation time: 108 hours (36 h for stabilization)
- Spike addition: 3.50 mg (0.25 mmol) of N-NO_3^-

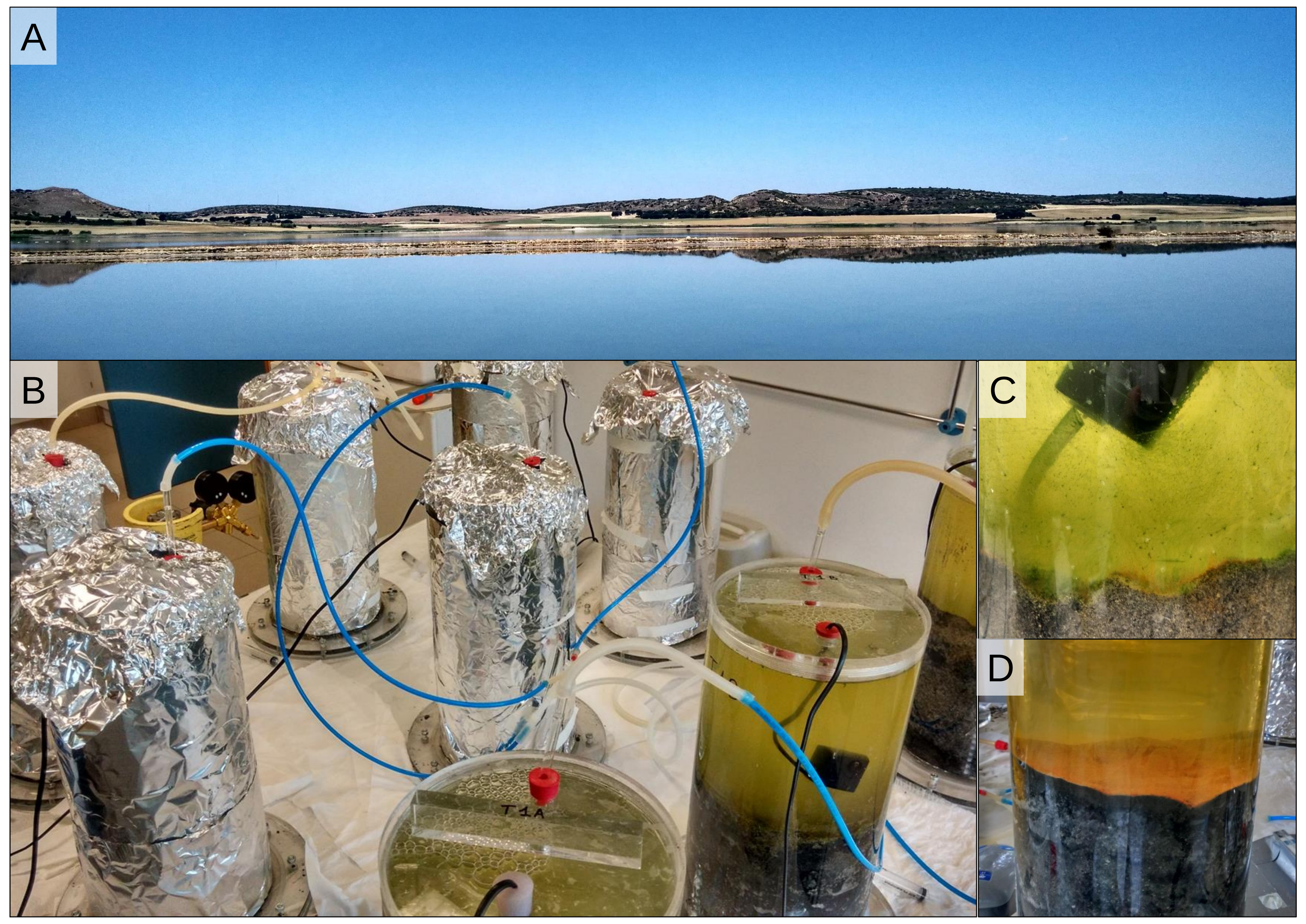

Fig. 2: A) Sample location in Pétrola Lake. B) Set of treatments by triplicates with the incubated sediments. C) Detail of treatment 1 with abundance in cyanobacteria and oxides. D) Detail of treatment 2 with oxides of Fe and Mn at the end of the experiment.

- Temperature (T), pH, electrical conductivity (EC), total dissolved solids (TDS), redox potential (Eh), dissolved oxygen (DO), dissolved nitrogen (DN), dissolved organic carbon (DOC), alkalinity and inorganic N-species in water (n=180) were measured, as well as inorganic N-species in sediment at 5 cm depth (n=12).

	T (°C)	pH	EC (mS/cm)	TDS (g/L)	Eh (mV)	DO (mg/L)
Initial conditions (n=9)	23.0 ± 2.73	8.92 ± 0.37	72.1 ± 6.21	46.5 ± 3.27	136 ± 2.85	6.70 ± 3.96
End: Treatment 1 (n=3)	28.7 ± 1.66	7.89 ± 0.08	75.9 ± 3.90	45.5 ± 3.30	-106 ± 28.1	6.46 ± 0.26
End: Treatment 2 (n=3)	29.4 ± 0.74	7.93 ± 0.13	76.8 ± 0.86	47.1 ± 0.56	-114 ± 41.0	6.40 ± 0.73
End: Treatment 3 (n=3)	32.2 ± 0.45	7.40 ± 0.35	80.9 ± 0.91	50.1 ± 8.80	-371 ± 7.51	0.08 ± 0.02

	DN (mg/L)	DOC (mg/L)	Alkalinity (mg/L)	N-NO_3 (mg/L)	N-NO_2 (mg/L)	N-NH_4 (mg/L)
Initial conditions (n=9)	15.7 ± 2.12	210 ± 40.5	275 ± 46.5	0.10 ± 0.06	BLD	0.72 ± 0.12
End: Treatment 1 (n=3)	15.6 ± 2.40	323 ± 35.2	512 ± 81.9	BLD	BLD	1.94 ± 0.22
End: Treatment 2 (n=3)	18.2 ± 2.16	376 ± 31.6	504 ± 70.0	BLD	BLD	2.45 ± 0.15
End: Treatment 3 (n=3)	17.0 ± 1.12	344 ± 67.9	513 ± 45.9	BLD	BLD	2.78 ± 0.17

Table 1: Mean values of chemical analyses in water for the incubations. BLD: below limit of detection.

	N-NO_3 (mg/kg)	N-NO_2 (mg/kg)	N-NH_4 (mg/kg)
Initial conditions (n=3)	0.24 ± 0.04	0.05 ± 0.07	18.0 ± 5.24
End: Treatment 1 (n=3)	0.96 ± 0.19	BLD	8.38 ± 3.77
End: Treatment 2 (n=3)	0.90 ± 0.34	BLD	11.0 ± 2.50
End: Treatment 3 (n=3)	1.02 ± 0.22	BLD	25.7 ± 3.72

Table 2: Mean values of chemical analyses in sediment for the performed incubations. BLD: below limit of detection.

Results and discussion

Water columns of the three treatments followed a general trend in the physicochemical parameters (Table 1). Slightly lower pH values coupled with strongly lower redox potential values were found at the end of the experiments. The accumulation of DOC, Alkalinity and N-NH_4^+ is remarkable, whereas N-NO_3^- disappeared completely.

In sediments, N-NH_4^+ concentrations decreased in treatments 1 and 2, but significantly increased in the treatment 3 (Table 2). The amount of retained N-NO_3^- increased about four times at the end of the experiment.

Concerning to the Inorganic N-species evolution (Fig. 3), N-NO_3^- disappeared in the first 30 h after the addition of the spike. The calculated NNR was 0.03 mmol d^{-1} L^{-1}. DOC followed a similar pattern to N-NH_4^+.

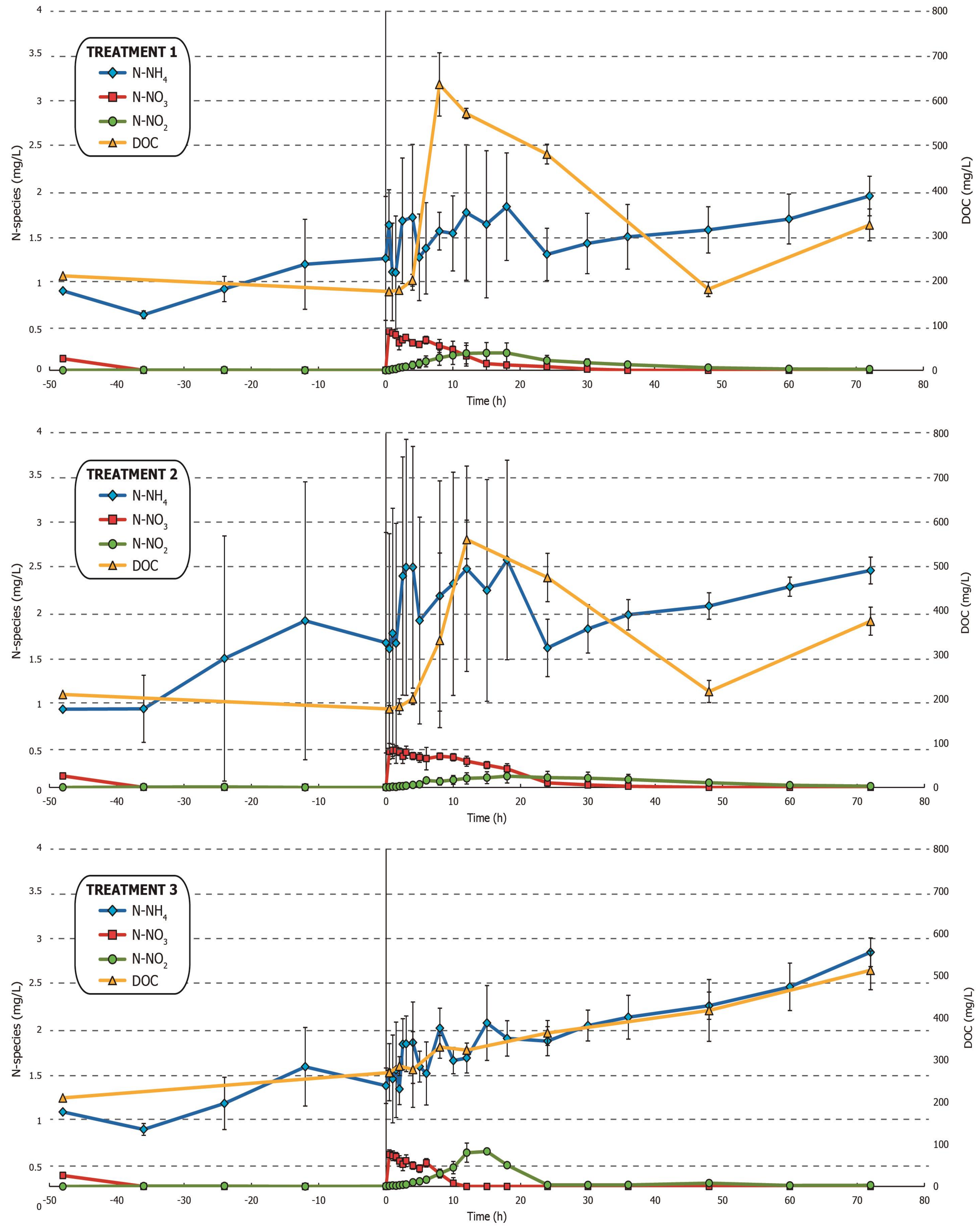

Fig. 3: N-Inorganic species and DOC evolution with time. The negative times indicate the stabilization period. The addition of the N-NO_3^- was performed at 0 h.

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