## Eutrophication-threatened aquatic ecosystems: sediment biogeochemical processes towards nutrients control

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Eutrophication of surface water bodies results mainly from anthropogenic activities occurring in their watersheds. Nutrient loads from intensive fertilization and livestock are a major problem, particularly during intense precipitation, due to the transport of nutrients through the watershed lotic system into downstream water bodies (Martins et al., 2008). Nowadays, eutrophication is also due to internal inputs of phosphorus (P), as is the case of Azoreans lakes (Ribeiro et al., 2008). Sediments are sites of intense microbial activity fostered by the presence of several organic and inorganic electron donors and acceptors that can be metabolised either under oxic or anaerobic conditions (Martins et al., 2010). Nevertheless, little attention has been paid to the sediment microbial community. In that regard, the present work aims to characterize the sediment microbial community, as well as the geochemical profiles towards the control of nutrients flux between sediments and water column. This work was carried out using as a study model, the volcanic lakes Verde, Azul, Fogo and Furnas (Azores, Portugal).

Geochemical profiles from lake Verde sediments presented high organic matter - OM (20  $\pm$  2 %), total phosphorus - TP (2.10  $\pm$  0.08 mgP/gDW), total nitrogen - TN (1.31  $\pm$  0.50 mgN/gDW), and total iron - TFe (8.06  $\pm$  0.13 mgFe/gDW) concentrations in the uppermost sediment layer (1 cm), and decreasing concentrations with sediment depth. Profiles from lake Azul (OM ~12  $\pm$  1 %, TP ~0.77  $\pm$  0.02 mgP/gDW, TN ~0.14  $\pm$  0.08 mgN/gDW and TFe ~3.78  $\pm$  0.26 mgFe/gDW) and lake Furnas (OM ~10  $\pm$  1 %, TP ~0.81  $\pm$  0.05 mgP/gDW, TN ~0.23  $\pm$  0.12 mgN/gDW and TFe ~4.52  $\pm$  0.31 mgFe/gDW) were quite homogeneous in depth. The distribution of phosphorus fractions in the different sediment layers was fairly homogeneous and the highest amounts of P (71 %) were bounded to metal oxides (25 %) and incorporated into biomass and detritus (46 %).

Besides, dominant members of the sediment bacterial community, investigated by denaturing gradient gel electrophoresis and cloning of the bacterial 16S rRNA gene fragment, were mostly affiliated to Proteobacteria (Alpha-, Delta-, and Gamma-

## Oral sessions



subclasses), Bacteroidetes/Chlorobi group, Chloroflexi, Cyanobacteria, Actinobacteria and Gemmatimonadetes phyla, and to Candidate divisions OP1 and OP11. Subsequently, bacterial type densities, determined by quantitative PCR, presented an almost homogeneous distribution of bacteria in the first 10 cm of sediment depth. Denitrifying bacteria - DNB dominated the sediment from lakes Verde (0.5 %) and Fogo (8.6 %), while in lakes Azul and Furnas were the nitrite oxidizing bacteria - NOB (10.7 %) and ammonium oxidizing bacteria - AOB (5.7 %), respectively. Globally, nitrifying bacteria (AOB + NOB) accounted for the highest densities (0.9 % to 13.3 %), followed by DNB (0.5 to 8.6 %), iron-reducing bacteria (0.1 % to 1.4 %), and phosphorus-accumulating organisms - PAO (less than 0.3 %). The amount of total bacteria and PAO in the sediments seemed to depend on the trophic state of the lakes being higher in the eutrophic lake Verde than in the oligomesotroohic lake Fogo.

Factorial experiments with homogenized sediments, carried out to assess the activity of bacteria involved in N, P and Fe cycling, suggested that bacteria performing nitrification/denitrification, iron reduction and, biological phosphorus uptake/release were active in the sediments. With these testes, it was also possible to relate the activity of DNB with the release of P from sediments. As a potential bioremediation strategy to prevent P release from sediments, the electrochemical activity of the bacterial community inhabiting lake Furnas sediments was assessed by cyclic voltammetry and a benthic microbial fuel cell (BMFC) was operated. Cyclic voltammograms showed the occurrence of oxidation–reduction reactions, suggesting that sediment bacteria were electroactive under tested conditions. The BMFC operated with lake Furnas sediments presented a low power density (1 mW/m2) indicating that further work is required to optimize its power generation.

Finally, the calibrated mathematical model for lake Verde water quality proved to be effective to support the decision making processes in aquatic restoration programs. Modelling results showed that water quality in lake Verde tends to deteriorate unless a strong policy of environmental protection is adopted: annual average values of 34  $\mu g/L$  total P and 2.0 mg/L of phytoplankton biomass can be reached in a 10 years horizon. Prospective scenarios showed that a reduction of P load into lake Verde to half of the actual value will improve water quality: an average concentration of total P of 26  $\mu g/L$  and phytoplankton biomass of 1.4 mg/L could be reached in a 10 years horizon. The reduction of both internal P loads from sediments and external P load into the lake Verde will lead to significant improvements in water quality.

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