ABSTRACT

Background. Silica (Si) is an essential nutrient for primary producers and the molar ratio of Si relative to nitrogen (N) and phosphorous (P) is relevant in the eutrophication process of aquatic ecosystems. Despite the importance of Si, its biogeochemistry in aquatic environments is still poorly understood compared to the amount of knowledge acquired on N and P. Recently, the Si cycle has been described as composed of a continental and an oceanic sub-cycles, which are connected through the hydrographic network. This complex environmental system is nowadays severely altered by human activity.

Lack of knowledge and aims. The aim of this research was to analyze how processes in the hydrographic network interact with the transport and accumulation of Si, N and P. The hypotheses were that (1) alteration of the hydrological characteristics of an aquatic ecosystem, both in terms of reduced frequency of water mixing in lakes or water flow in rivers, changes Si retention and that (2) both benthic and planktonic primary producers can play an important role as Si filters and temporary Si sinks. Two environment were studied in this thesis: a meromictic lake and the riverbed of three rivers that either undergo flow reduction or run dry in summer.

Main results. Lake Iseo was a net Si and P sink and retained 75% of the total Si and 79% of total P loadings. N:Si and N:P molar ratios resulted higher in outflowing than in inflowing waters, with an excess of N respect to Si and P in the emissary river. Si retention was mainly regulated by sedimentation of particulate forms that were in part recycled back to the water column, but were retained in the monimolimnion. Submerged aquatic vegetation (SAV) and microphytobenthos (MPB) were a Si source and a N and P sink with the Si efflux from SAV nearly three times as much as in MPB patches. These findings corroborate the hypothesis that SAV mediates the Si transport from pore water to the water column. Conversely, epilithic macro- and microalgae communities were a DSi sink and a N and P source.

In river sediments, the exposure to air and the subsequent drying interfered with Si biogeochemistry and dry sediment maintained a relatively constant Si concentration. Labile P and N concentrations followed a similar pattern to that of Si but the degree of change was different determining a higher accumulation in sediment of labile inorganic P and N, relative to Si. After dry periods, the sediment rewetting and resuspension had the potential to release to the water a fraction of the Si accumulated during the dry period. As a result, the ratio of released nutrients suggests that the Si fraction is more mobile compared to N and P.

Conclusions. Lentic and lotic ecosystems are not only links that connect terrestrial and marine ecosystems acting as pipes, but they behave as biogeochemical regulators not only of the amount and of timing of Si delivery, but also of its stoichiometry relative to N and P. Both lakes and

hydrological intermittency can modify water flow and, consequently, they are important factors in regulating nutrient pathways and stoichiometry. They directly influence transport processes and indirectly shape the activity of primary producers and microbial communities, and the chemical and physical characteristics of the environment where primary production, decomposition and ultimately mineralization take place.

The chapter of this thesis are based on:

- Chapter 2 entitled "*Silica and Nutrient Loadings and Stoichiometry in a Meromictic Lake (Lake Iseo, Italy)*" is structured in preparation of the submission to Biogeochemistry journal;

- Chapter 3 entitled "*Silica Storage, Fluxes, and Nutrient Stoichiometry in Different Benthic Primary Producer Communities in the Littoral Zone of a Deep Subalpine Lake (Lake Iseo, Italy)*" has been published in Water 2019, 11, 2140;

- Chapter 4 entitled "*Speciation and Stoichiometry of Silica, Nitrogen and Phosphorus in Riverbed Sediments in Relation to Hydrological Variability*" is structured in preparation of the submission to Hydrobiologia journal.