Chemical weathering and consumption of atmospheric carbon dioxide in the Alpine region

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A B S T R A C T

To determine the CO_2 consumption due to chemical weathering in the Alps, water samples from the 32 main Alpine rivers were collected and analysed in two periods, spring 2011 and winter 2011/2012. Most of the river waters are characterized by a bicarbonate earth-alkaline composition with some samples showing a clear enrichment in sulphates and other samples showing a slight enrichment in alkaline metals. The amount of total dissolved solids (TDS) ranges between 96 and 551 mg/L. Considering the major ion composition and the Sr isotopic composition of water samples, coherently with the geological setting of the study area, three major reservoirs of dissolved load have been recognized: carbonates, evaporites and silicates. Based on a chemical mass balance, the flux of dissolved solids, and the flux of carbon dioxide consumed by chemical weathering have been computed for each basin and for the entire study area. Results show that the flux of dissolved solids, ranges from 8×10^3 to 411×10^3 kg km^{-2} y^{-1}, with an average value of 127×10^3 kg km^{-2} y^{-1}, while the flux of carbon dioxide consumed by chemical weathering in the short-term (<1 Ma) is 5.03×10^5 mol km^{-2} y^{-1} 1 on average. Since part of the CO_2 is returned to the atmosphere through carbonate precipitation and reverse weathering once river water reaches the ocean, the CO_2 removed from the atmosphere/soil system in the long-term (>1 Ma) is much smaller than the CO_2 consumed in the short-term and according to our calculations amounts to 2.01×10^4 mol km^{-2} y^{-1} on average. This value is almost certainly a minimum estimate of the total amount of CO_2 fixed by weathering on the long-term because in our calculations we assumed that all the alkaline metals deriving from rock weathering in the continents are rapidly involved in the process of reverse weathering in the oceans, while there are still large uncertainties on the magnitude and significance of this process. The values of CO_2 flux consumed by weathering are strongly correlated with runoff while other potential controlling factors show only weak correlations or no correlation. Our estimation of the CO_2 consumed by weathering in the Alpine basins is in the same order of magnitude, but higher than the world average and is consistent with previous estimations made in river basins with similar climatic conditions and similar latitudes.

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1. Introduction

Carbon is continuously cycled among oceans, atmosphere, ecosystems, and geosphere (Holland, 1978; Berner, 2003; Kump et al., 2009). Considering the time scale of the phenomena, longer or shorter than one million years, it is possible to distinguish the "short-term" carbon cycle and the "long-term" carbon cycle. In the "short-term" carbon cycle, carbon is exchanged mainly within the superficial systems (atmosphere, oceans, biota, soil, and anthropogenic CO_2 production). Over the "long-term", carbon is involved in slow exchanges between the solid Earth and the ocean–atmosphere system, and the concentration of

atmospheric carbon dioxide derives primarily from the balance between CO_2 uptake by chemical weathering and CO_2 release by magmatism–metamorphism (Berner et al., 1983; Berner, 1991, 1994; Berner and Kothavala, 2001; Berner, 2004, 2006; Gislason and Oelkers, 2011; Li and Elderfield, 2013).

Chemical weathering is a key process for understanding the global carbon cycle, both on long and short-terms (Brady, 1991; Kump et al., 2000; White, 2003; Kump et al., 2009; Tipper et al., 2006), and chemical weathering rates are complex functions of many factors including dissolution kinetics of minerals (Brantley, 2003), mechanical erosion (Pinet and Souriau, 1988), lithology (Basu, 1981; Amiotte-Suchet and Probst, 1993a; Amiotte-Suchet and Probst, 1993b; Bluth and Kump, 1994), tectonics (Hren et al., 2007; Dixon et al., 2012; Li et al., 2009), biota (Knoll and James, 1987; Schwartzman and Volk, 1989; Drever, 1994; Berner

et al., 2003), climate (Fournier, 1960; Walker et al., 1981; Bluth and Kump, 1994), hydrology (Tardy, 1986; Berner and Berner, 1987; Amiotte-Suchet and Probst, 1993b; Velbel, 1993), and various human activities (Flintrop et al., 1996; Yang et al., 1996).

Solutes produced by chemical weathering on the continents are carried to the oceans by rivers. Therefore, the composition of river water is a good indicator of chemical weathering processes (Mackenzie and Garrels, 1966; Garrels and Mackenzie, 1971; Meybeck, 1987; Tardy, 1986; Probst, 1992; Gaillardet et al., 1999; Viers et al., 2007; Berner and Berner, 2012), and the flux of solutes is an indirect measure of the transfer of carbon from the atmosphere to the terrestrial rocks. In fact, given that carbonate and silicate weathering needs atmospheric and soil CO_2 to occur, the evaluation of the weathering rates, that is the knowledge of the dissolved loads transported from the continents to the oceans, allows for an indirect estimation of the atmospheric CO_2 consumed by weathering. Under this perspective, the study of the elemental fluxes due to present day chemical weathering is necessary to understand the past and to make reliable models about the future trends of the global carbon cycle (Brady, 1991; Millot et al., 2002; Beaulieu et al., 2012).

The study of chemical weathering is based on two complementary approaches, namely (i) small scale studies of river basins characterized by a single lithology (Amiotte-Suchet and Probst, 1993b; Bluth and Kump, 1994; White and Blum, 1995; Gislason et al., 1996; Louvat and Allègre, 1997), and (ii) global scale studies based on data from large rivers (Berner et al., 1983; Meybeck, 1987, 2003; Probst et al., 1994; Amiotte-Suchet, 1995; Amiotte-Suchet and Probst, 1995; Boeglin and Probst, 1998; Gaillardet et al., 1999; Mortatti and Probst, 2003). Small scale studies can give detailed data on the weathering rates of a specific rock type under a given climate, while large scale studies can provide global data, integrating the contributions of large portions of continental crust and different climatic regions.

Gaillardet et al. (1999), using an inverse modelling approach based on the river water chemistry and Sr isotopic composition, calculated the weathering rates and the fluxes of CO_2 consumed by rock weathering for the basins of the 60 largest rivers of the world, computing a world average CO_2 consumption due to chemical weathering of 246 mol km^{-2} y^{-1}. Three of the rivers considered in Gaillardet et al. (1999) drain the Alpine chain (i.e., Rhine, Rhone, and Po) and are characterized by CO_2 consumption rates two to five times higher than the world average. Considering the variability of rocks and soils that characterizes the region, the Alpine chain can be considered a model location to study the present-day atmospheric CO_2 consumption over a large region.

In this work, we present a detailed study of the dissolved loads transported by the 32 main Alpine rivers, in order to (i) estimate the present-day weathering rates and the related atmospheric and soil CO_2 consumption for the entire Alpine region, (ii) compare our results with the data of earlier works, (iii) evaluate the relative importance of carbonate and silicate weathering both on short and long-term global carbon cycle, and (iv) determine the main environmental and geological parameters controlling the weathering rates and the CO_2 consumption in the Alps.

Starting from the chemical composition of river waters, the amount of CO_2 consumed by rock weathering has been modelled using a multidisciplinary approach based on the MEGA geochemical code (Major Element Geochemical Approach — Amiotte-Suchet, 1995; Amiotte-Suchet and Probst, 1995, 1996), a GIS based hydrologic and geologic study, and an isotopic study.

2. Study area

The Alps (south-Central Europe) are a collisional belt generated by the convergence of the African and European plates and the consequent closure of the ocean basin located in the Mediterranean region during Cretaceous to present (Trümphy, 1960; Frisch, 1979; Tricart, 1984; Haas et al., 1995; Stampfly et al., 2001; Dal Piaz et al., 2003).

The Alps are characterized by an arc shape and extend, west to east, from the Gulf of Genova to Wien (Fig. 1). South of Genova, the Alpine range disappears, as it was fragmented during the Late Neogene by the opening of the Tyrrenian basin. Here the Alps are partially continuous to the Apennine chain. To the east, the former connection between the Alpine and Carpathian belts is buried below the Neogene fill of the Wien and Styria (Pannonian) basin. North of Alps is located the Molasse Basin (a Cenozoic foredeep basin) that extends from France to the eastern border of Austria. Other major Cenozoic basins are the Rhône Graben to the west, and the Po Plain to the south.

According to the direction of tectonic transport, the Alps (Fig. 1) may be subdivided into two belts of different size, age, and geological characteristics (Dal Piaz et al., 2003): (1) the Europe-vergent belt, a thick collisional wedge of Cretaceous–Neogene age, consisting of continental and minor oceanic units radially displaced towards the Molasse foredeep and the European foreland, (2) the Southern Alps, a shallower (non-metamorphic) and younger (Neogene) thrust-and-fold belt displaced to the south (Adria-vergent), which developed within the Alpine hinterland of the Adriatic upper plate, far from the oceanic suture. The Periadriatic Line, a major fault system of Oligocene–Neogene age, separates these belts. The various segments of the Periadriatic Line take various names, from west to east, the Canavese, Insubric, Giudicarie, Pusteral and Gaital lines (Dal Piaz et al., 2003; Schmid et al., 2004).

From a hydrological point of view, the Alps contribute significantly to the total discharge of the major European rivers, most of which have their headwaters in the Alps and transport the Alpine waters to lower-lying areas. The Alps are crucial for water accumulation and water supply, and therefore they are often referred to as a natural "water towers" (Viviroli and Weingartner, 2004).

Water resources in the Alps are stored in glaciers (in the Alps, around 5150 glaciers presently cover about 2909 km^2, approximately 1.5% of the total area of the Alps), lakes, groundwater reservoirs, and soils. The Alps represent an enormous natural water reservoir since precipitation in winter is retained as snow and ice. Considerable quantities of water can be accumulated and released through the summer melting of glaciers and snow, thus providing water during the dry season when precipitation and runoff are often least in the lowlands, and demands are highest. Particularly, this becomes effective in the dry months of late summer, when the Alps play a distinct supportive role with regard to overall discharge. This natural storage mechanism benefits many river systems in Europe, including the four major alpine rivers, the Rhine, the Danube, the Po, and the Rhône.

A comparison between the proportion of discharge that can be expected on the basis of the catchment size and the actual discharge measured demonstrates the hydrological significance of the Alps that, with a mean contribution ranging from 26% (Danube) to 53% (Po) of the total discharge, supply up to 2–6 times more water than might be expected on the basis of the catchment size (Weingartner et al., 2007).

Generally the Alpine rivers have a maximum flow rate in July, and a minimum rate in January. This is because the runoff of Alpine catchments is influenced by glacier melt, snow accumulation, and snowmelt (Gurtz et al., 1999; Verbunt et al., 2003).

3. Materials and methods

3.1. Theoretical background

The dissolved load of streams originates from atmospheric input, pollution, evaporite dissolution, and weathering of carbonate and silicate rocks. The application of mass balance calculations allows for the quantification of the different contributions (Bricker and Jones, 2003). The quantification of the carbonate and silicate components of dissolved load is essential for the evaluation of the atmospheric/soil CO_2 consumed by rock weathering. In fact, the weathering reactions of silicate mineral hydrolysis and dissolution of carbonates consume atmospheric/soil carbon dioxide and produce an increase of alkalinity