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Chemical weathering rates and CO_2 consumption in the Savuto basin (Sila Massif, Italy) inferred from riverine water chemistry

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Abstract. The aim of this work was to estimate the silicates (SWR) and carbonates (CWR) weathering rates as well as the CO_2 consumption in the Savuto basin (Sila Massif, Southern Italy), studying the riverine water chemistry. Six sampling sites were investigated. Starting from the rain composition, atmospheric and anthropogenic inputs were subtracted to total dissolved load allowing the estimation of the SWR and CWR. The obtained weathering rates are: (i) SWR= 9.6 t/km^{2}a and (ii) CWR= 12.8 t/km^2. Moreover, an indirect estimation of CO_2 moles consumed was performed based on the reaction stoichiometry for both silicate ($CO_{2\ sil}$) and carbonate ($CO_{2\ carb}$) weathering processes. The results show that the consumption of $CO_{2\ sil}$ is equal to 2.2x10^5 mol/Km^2 a, whereas the consumption of $CO_{2\ carb}$ is equal to 3.5x10^5 mol/Km^2 a.

Keywords: Chemical weathering; CO_2 consumption; riverine water chemistry.

1. Introduction

Chemical composition of river waters is the result of several contributes like atmospheric input, anthropogenic input and chemical weathering of different rocks. Carbonates and silicates weathering require atmospheric and soil CO_2 to occur, becoming a short- and long-term sink to CO_2. In this regard, the knowledge of the dissolved load transported by rivers allows an evaluation of weathering rates and an indirect estimation of the atmospheric CO_2 consumed by weathering (Donnini et al., 2016). On this basis, the weathering rates as well as the CO_2 consumption in the Savuto basin (Sila Massif, Southern Italy) were estimated via the riverine water chemistry.

The Savuto river originates in the Sila massif at 1250 m a.s.l, it flows southwest for 48 km and meets the Tyrrhenian Sea at the Gulf of Saint Eufemia. The total drainage area of the river is 413 km^2. From geological point of view, the Savuto basin is mostly made up of Paleozoic metamorphic rocks, mainly phyllites and schists and subordinately gneiss, with local plutonic intrusions; less frequent are ophiolite-bearing schists, phyllite and carbonate of Mesozoic age, and sedimentary terrains (Miocene-Holocene) (Figure 1).

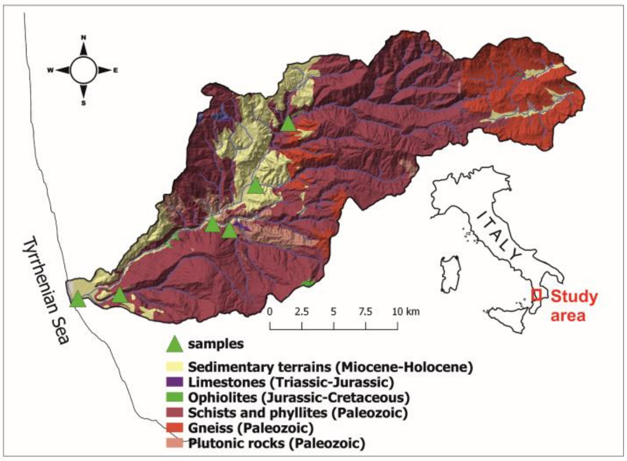

Figure 1. Simplified lithological map of the Savuto basin and samples location.

2. Materials and methods

2.1. Field work and laboratory analysis

Riverine water chemistry was investigated measuring in the field instable parameters such as pH, Eh, temperature, alkalinity and specific electrical conductivity via portable instruments. In the field, the flow rates were also measured. A total of six samples were collected. Each sample was filtered in situ through a 0.45 μm pore-size membrane filter and stored in clean polyetilene bottles. The dissolved SiO_2 was determined via colorimetric method using a portable spectrophotometer, whereas the concentrations of major ions (Ca^{2+}, Mg^{2+}, Na^+, K^+,Cl^-, SO_4^{2-}, F^-, NO_3^-, and PO_4^{3-}) were obtained in laboratory by HPLC.

2.2. *Calculation methods*

Starting from local rain composition, atmospheric and anthropogenic inputs were subtracted to total dissolved load allowing the estimation of silicate (SWR) and carbonate (CWR) weathering rates (Li et al., 2016; Liu et al., 2013; Gurumurthy et al., 2012). Based on these results, an indirect estimation of CO_2 moles consumed was performed stating from reaction stoichiometry for silicate ($CO_{2\ sil}$) and carbonate ($CO_{2\ carb}$) weathering processes, respectively (Wu et al., 2013). Here below are reported the used equations.

***Atmospheric input** (Liu et al., 2013)*

$X\,(Ca, Mg, Na, K, Cl, SO4, F)_{atm} = (Cl_{min} * (X/Cl)_{rain})$

***Anthropogenic input** (Liu et al. 2013)*

$X_{anthr} = NO_3 + PO_4^{+}\ Cl^* + Na^*$

$Cl^* = Cl_{min}$ after atmospheric correction

Na^* = Mass balance $\qquad Cl^* = Na^*$

***Silicate Input** (Gurumurthy et al, 2012)*

$X_{sil} = Ca_{sil} + Mg_{sil} + Na_{sil} + K_{sil}$

$Ca_{\ sil} = Na_{\ sil}\ x\ (Ca/Na)_{\ rock}{}^*$

$Mg_{\ sil} = Na\ sil\ x\ (Mg/Na)_{rock}\ {}^*$

$Na_{\ sil}$ = Na after atmospheric and anthropogenic correction

$K_{\ sil}$ = K after atmospheric correction

* $(Ca/Na)_{\ rock}$ and $(Mg/Na)_{rock}$ were calculated based on local rocks analysis.

Carbonatic Input

$X_{carb} = Ca_{carb} + Mg_{carb}$

***Silicatic weathering rate (SWR)** (Wu et al., 2013; Gurumurthy et al., 2012)*

$SWR = Q/A * \Sigma\,(Na + K + Mg + Ca)_{sil} + SiO_2)$

*Q= flow rate**;** A= basin area*

***Carbonatic weathering rate (CWR)** (Wu et al., 2013; Gurumurthy et al., 2012)*

$CWR = Q/A * \Sigma\,(Ca + Mg)_{\ carb}$

Q= flow rate; A= basin area

***$CO_{2\ sil}$ consumption** (Wu et al., 2013)*

$[CO_2]_{sil} = (2Ca_{sil} + 2Mg_{sil} + Na_{sil} + K_{sil}) * Q/A$

Albite

$2NaAlSi_3O_8 + 2CO_2 + 11H_2O \rightarrow$

$Al_2Si_2O_5(OH)_4 + 2HCO_3^{-} + 2\ Na^{+} + 4H_4SiO_4$

Anorthite

$CaAl_2Si_2O_8 + 2CO_2 + 3H_2O \rightarrow Al_2Si_2O_5(OH)_4 + 2HCO_3^{-} + Ca^{2+}$

***$CO_{2\ carb}$ consumption** (Wu et al., 2013)*

$[CO_2]_{carb} = (Ca_{carb} + Mg_{carb}) * Q/A$

Calcite

$CaCO_3 + CO_2 + H_2O \rightarrow Ca_2^{+} + 2HCO_3^{-}$

3. Results and conclusions

The results showed that the silicate input prevails in the samples Sav_01 and Sav_02, whereas the carbonate input prevails in the samples Sav_03, Sav_04, Sav_05 and Sav_06. Generally, the dissolved load of the rivers in the study area is dominated by the carbonate input which accounts for about 39% of the whole basin, followed by silicate (28%), atmospheric (18%). and anthropogenic inputs (14%) (Figure 2). The silicate and carbonate imprint to the riverine water chemistry depends of (i) the different minerals dissolution rates (carbonate > silicate), (ii) the main lithotypes outcropping into the studied area and their extension and (iii) the water-rock interaction time.

Although the silicate rocks cover most of the basin area (Figure 1), the CWR is higher than SWR. It should be noted that carbonate weathering includes the carbonate rocks s.s., the carbonate cements in sedimentary rocks and the carbonate minerals (dolomite and calcite) which could be present as veins or as widespread crystals in silicate rocks (Apollaro et al 2009; White et al., 2005).

The obtained weathering rates are the following: (i) SWR= 9.6 t/km^2a and (ii) CWR= 12.8 t/km^2.

Based on these values, an indirect estimation of CO_2 moles consumed was performed for silicate ($CO_{2\ sil}$) and carbonate ($CO_{2\ carb}$) (Wu et al., 2013*)*. The results showed that the consumption of $CO_{2\ sil}$ is equal to $2.2\ x10^5$ mol/Km^2 a, whereas the consumption of $CO_{2\ carb}$ is equal to $3.5x10^5$ mol/Km^2 a.

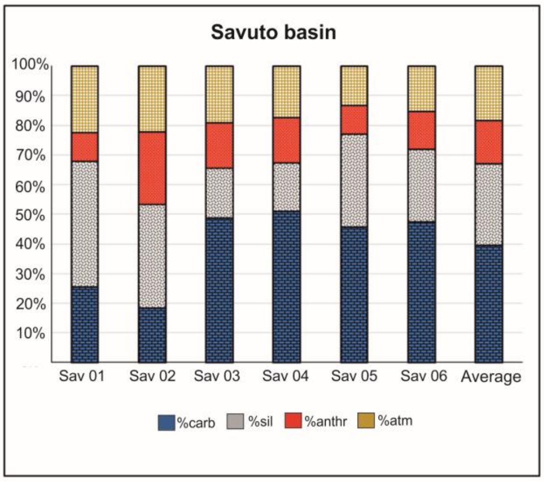

Figure 2. Results of the relative contributions (%) of different sources in each sample.

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