Supplementary Material

# Appendix A

**Carbon mass balance**

Following the methods developed by Chiodini et al. (2004; 2020) is possible to deconvolve the Total Dissolved Inorganic Carbon of groundwater (TDIC) into distinct carbon pools. The external carbon contribution, Cext, (i.e., the carbon not deriving from aquifer rocks dissolution) and its isotopic composition δ13Cext can be calculated for each sample by following carbon mass balance equations:

TDIC= Cext + Ccarb (A.1)

δ13Cext × Cext + ​ δ13Ccarb × Ccarb = δ13CTDIC × TDIC (A.2)

where Ccarb is the carbon deriving by the dissolution of carbonate rocks of the aquifer and δ13Ccarb is its isotopic composition.

To compute Cext and δ13Cext from eqs. A.1 and A.2, TDIC and δ13CTDIC are analytically determined while δ13Ccarb is assumed to be constant and equal to the average δ13C of numerous samples of carbonate rocks from southern Appennines investigated aquifers (+1.8‰; Chiodini et al., 2020 and references therein). The term Ccarb is computed as (Ca + Mg) − SO4, considering the dissolution of carbonate minerals (i.e., calcite and dolomite) and the possible presence of gypsum/anhydrite, for those samples (Table S1) from carbonate aquifers located on the Calabria-Basilicata regions (Apollaro et al., 2020, 2012).

For the samples of other springs of Basilicata region located in correspondence of terrains of the ophiolite-bearing Ligurian Complex tectono-stratigraphic unit where crustal and ultramafic rocks as Gneiss and Serpentinite are dominant (Dichicco et al., 2019; Sansone et al., 2011) the term Ccarb was computed considering only the Ca concentration. In fact, Margiotta et al. (2014) studied the interaction between these waters and the surrounding rocks defining with R-mode factor analysis the relationships between trace elements, Ca, Mg, and HCO3 present in the waters. The results of this study showed a correlation between Ca and HCO3, but not between Mg and HCO3, demonstrating that only Ca comes from the dissolution of carbonate compounds. To compute δ13Cext for these samples we assume a δ13Ccarb equal to -0.6‰, i.e the average δ13C of different calcite veins from the Serpentinite rocks belonging to the Frido Unit in the Pollino Massif (i.e. the area where the springs are located; Rizzo et al., 2020).

For other samples located at the base of the mountain chain of Catena Costiera, Sila massif and Aspromonte where metamorphic lithologies are dominant (Table S1; Tursi et al., 2021, Apollaro et al. 2019, 2009; Vespasiano et al., 2021), the Ccarb term was not considered because no significant carbonate dissolution should occur considering that the silicate rock hosting the aquifers should be carbonate free (Barry et al., 2021).

Moreover, comparing dolomite saturation index (SIdol) with calcite saturation index (SIcalc) all samples for which is possible to define Ccarb are in equilibrium with calcite and dolomite (-0.1≤SI≤0.1). Other samples show SI<-0.1 (i.e., undersaturated) with only two samples (Cotr.PC and An) with SI>0.1 (i.e oversaturated) (Figure S1 and Table S1). We need to clarify that the elements (Ca, Mg, HCO3) needed for calcite and dolomite precipitation in aquifers hosts in non-carbonate lithologies could come from the dissolution, by CO2 and H2SO4, of silicate minerals, as shown, for example, by the following reactions (Ulloa-Cedamanos et al., 2021):

2NaAlSi3O8 (s) (Albite) + 2CO2 (g) + 11H2O(l) → Al2Si2O5(OH)4 (Kaolinite) + 2Na+(aq) + 2HCO3-(aq) + 4H4SiO4 (aq)

2KAlSi3O8 (s) (Orthoclase)+2CO2 (g)+6H2O(l) → Al2Si4O10(OH)2 (montmorillonite)+2K+(aq) + 2HCO3-(aq) + 2H4SiO4 (aq)

CaAl2Si2O8(s) (Anorthite) + 2CO2(g) + 2H2O(l) → Al2Si2O5(OH)4 (Kaolinite) + Ca2+(aq) + 2HCO3-(aq)

Ca2-xMgx(SiO3)2 (s) (Ca-Mg silicate)+ 2H2SO4 + 2H2O(l)→ (2-x)Ca2+(aq) + xMg2+(aq) + 2SO42- + 2H4SiO4(aq)

In Figure S2 a and b the major ions ratios, as HCO3/Na, Ca/Na and Mg/Na have been used to define possible correlations between the elements in water and their origin from the host rocks. In fact, these ratios in water can reflect the elemental ratios in different local bedrock and solubility of corresponding elements during chemical weathering (Liu & Han, 2020). Cold water significantly approaches to a carbonate end-member, suggesting that carbonate weathering is dominant. Thermal samples show lower elemental ratios, even than a silicate end member (see Liu & Han, 2020), indicating weathering processes dominant on silicate rocks. In this case, the lowest values can be due to different processes such as Halite dissolution and the effect of carbonate dissolution is negligible (<0.05%).

These evidences demonstrate that Ccarb contribution cannot be accounted for thermal water, and it should not weight on the total carbon balance. This allow us to approximate that all the C present in thermal waters come from external sources (i.e., Cdeep and Cinf) and we can write:

TDIC = Cext

δ13CTDIC = δ13Cext

Hence Cext can be divided into two different contributions: i) Cinf, i.e., carbon from biogenic source in soil and atmospheric CO2 and ii) Cdeep, i.e., carbon from deep (mantle/crustal) source.

The Cinf, Cdeep and the relative isotopic compositions, δ13Cinf and δ13Cdeep are computed by considering the following carbon balance:

Cinf  + ​Cdeep = Cext (A.3)

δ13Cinf × Cinf   + ​δ13Cdeep × Cdeep = δ13Cext × Cext (A.4)

To solve this system of two equations and four unknown variables we use the binary plot δ13Cext versus 1/Cext where mixtures among different sources show a linear trend (Figure S3).

In detail, (i) the isotopic compositions of soil-derived CO2 (δ13Cinf = -22‰) is considered unique and derived from δ13Cext average value of the infiltrating water samples; (ii) Cinf is determined for different group of samples at the interception of the mixing lines (black lines) connecting a defined deep end-member (1/Cext=0 and δ13Cdeep= 0.3 mean value for metamorphic CO2; Dai et al., 1996; Hunt, 1996; Clark and Fritz, 1997; Evans et al., 2008) with the infiltrating water line computed at δ13C= -22‰ (green line). This computation gives different Cinf values from 0.55 to 3.5 mmol/l with an average of 1.5 mmol/l; iii) the carbon concentration from deeply derived CO2 (Cdeep) of each sample is given by inserting the computed Cinf in Eq. A.3. We would like to clarify that carbon budget estimates represent a maximum value due to the assumptions made to estimate Cext. If indeed there has been appreciable carbonate dissolution for all samples, our estimates would be an overestimation.

**Carbon Flux**

The specific flux of deep sourced CO2 (FCdeep in mol yr-1 km-2) was calculated for each spring by following equation:

FCdeep=Cdeep∙(Q/S) (A.5)

where Cdeep is deep sourced CO2 expressed in mol∙kg-1, Q is the spring flow rate in m3∙yr-1 and S is the spring catchment area in km2.

Table S2 report for each spring the needed data to calculate the deep carbon flux. For thermal water in the northern part of the region it was possible to calculate for each spring the specific flows (hydrogeological data from Allocca et al., 2007 and De Vita et al., 2018). For all the other thermal springs distributed throughout the Calabrian territory, the existing hydrogeological data do not allow an equally precise calculation to be made. The only available data for these samples are the areas of the aquifers to which the single spring belong (http://www.ildistrettoidrograficodellappenninomeridionale.it). The total water discharge of these aquifers is not known and therefore it was not possible to calculate the extent of the hydrogeological basin for each spring and consequently the carbon fluxes. However, in order to have a minimum value, the deep carbon fluxes for each spring were calculated considering the total area of ​​belonging aquifer. In this case for the springs belonging to the same aquifer, the Cdeep contributions were added together and divided by the total area of ​​the aquifer. The flow values (FCdeep) ​​for these springs could therefore be an underestimation of those actually present in the area.