

Quantification of Diffuse Carbon Dioxide Earth Degassing from Central Apennine (Italy): The Carbon Mass Balance in Regional Aquifers Approach

Carlo Cardellini (geochem@unipg.it)¹, Giovanni Chiodini (chiod@ischia.osve.unina.it)²,
Francesco Frondini (geochem@unipg.it)¹, Stefano Giaquinto (geochem@unipg.it)¹,
Franco Parello (parello@unipa.it)³ & Luca Peruzzi (geochem@unipg.it)¹

¹ Dipartimento di Scienze della Terra, Università di Perugia, Piazza Università, Perugia, 06100, Italy

² Osservatorio Vesuviano, via Diocleziano 328, 80124 Napoli, Italy

³ Dipartimento di Chimica e Fisica della Terra, via Archirafi 36, 90123 Palermo, Italy

Central Italy is characterised by an anomalous flux of deeply derived CO₂. In the western Peri-tyrrhenian sector of Central Italy, CO₂ degassing occurs mainly from focused emissions (vents and strong diffuse degassing) and thermal springs, whereas in the eastern Apennine area deep CO₂ is dissolved in "cold" groundwater of regional aquifers hosted by Mesozoic carbonate-evaporite formations. The different hydro-geological features of the two areas, control the degassing stiles: (i) in the Peri-tyrrhenian area, where terrigenous units with low permeability, overlie the compressional permeable structures made up of Mesozoic carbonate units, the gas accumulate in the buried reservoirs from where is expelled generating gas emission at the surface. This model which occasionally has been directly observed by deep drillings (i.e. at Torre Alfina), explain the general coincidence between CO₂ anomalies and local positive anomalies of the gravimetric field; (ii) in the eastern area, where the carbonatic Apennine belt hosts big regional aquifer, most or part of the deeply-generated gas are dissolved by groundwater because the relatively high solubility of CO₂ in water.

Influx of deep CO₂ into twelve carbonate aquifers (12500km²) of the Central Apennine have been computed through the mass-balance of inorganic carbon, that couples groundwater geochemistry with isotopic and hydro-geological data (Chiodini et al., 2000). The mass-balance calculations have been made according to equations proposed by Wigley et al. (1978) for the evolution of TDIC and ¹³C compositions in natural water systems where multiple sources and sinks are present, assuming the absence of carbon sinks before the groundwater discharge. The effect on calculations of "no-sinks assumption" have been investigated through the theoretical modelling of the process. The errors resulted negligible over the range of TDIC and PCO₂ values of groundwater samples of this study.

Mass-balance calculations allowed us to estimate that 6.5x10¹⁰ mol y⁻¹ of inorganic carbon are dissolved in the studied aquifers. Approximately 23% of this amount derives from biological sources active during the infiltration of the recharge waters, 36% comes from carbonate dissolution, while 41% is representative of deep carbon sources characterised by a

common isotopic signature ($\delta^{13}\text{C} = -3\text{‰}$) compatible with the carbon isotopic composition of a CO₂ deriving from a crustally contaminated mantle or with a mantle CO₂ enriched in ¹³C during crustal storage processes (Chiodini et al., 1999; 2000). The calculated deep CO₂ influx rate ranges from 10⁻² to 10⁷ mol y⁻¹ km⁻², increasing regionally from east to west in the study area.

Basing on carbon mass-balance results and on the qualitative and quantitative evidences of CO₂ degassing in the volcanic and geothermal area of the Peri-tyrrhenian sector a total flux of deeply derived CO₂ of 1-3 x 10¹¹ mol y⁻¹ have been estimated from an area of about 45000 km² contained between the Tyrrhenian coast line and the Apennine chain. This value is comparable with the CO₂ discharged by some of the larger CO₂ producing volcanoes and is about 5-10% of the estimated magmatic CO₂ discharged globally to the atmosphere by active volcanoes (1-4 x 10¹² mol y⁻¹; Williams et al., 1992; Allard, 1992). Our estimates for diffuse degassing of CO₂ in Central Italy suggest that rates of global inorganic CO₂ emission from the earth may be greatly underestimated. Regional aquifers located in areas of high CO₂ fluxes can dissolve, transport and release to the atmosphere large quantities of deeply-derived CO₂ and the quantity of CO₂ involved in this process, affecting most of the tectonically active areas of the world as suggested by the world distribution of CO₂ rich groundwater (Barnes et al., 1978), is probably of the same order of magnitude, or larger, than the quantity directly emitted from active volcanoes.

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