## Geochemistry of fluids in the biochemical methane potential (BMP) estimations through the volumetric approach

**ANTONIO RANDAZZO**<sup>1</sup>, ADELE FOLINO<sup>2</sup>, FRANCO TASSI<sup>3</sup>, FABIO TATÀNO<sup>2</sup> AND SANDRO DE ROSA<sup>4</sup>

<sup>1</sup>Istituto Nazionale Di Geofisica e Vulcanologia, Roma, Italia <sup>2</sup>DiSPeA - Department of Pure and Applied Sciences, Section ChEM - Chemistry, Environment, and Materials, University of Urbino "Carlo Bo", Urbino, Italy

<sup>3</sup>Università degli Studi di Firenze, Dipartimento di Scienze della Terra, Firenze, Italia

<sup>4</sup>ASET S.p.A. public multi-utility group, Fano, Italy

The biochemical methane potential (BMP) is a useful parameter to estimate at lab-scale the bioenergy production through the anaerobic digestion (AD) of organic substrates (biomass and waste). The BMP estimations are pivotal indicators for designing and operating full-scale AD plants. Different labscale approaches for measuring the rate of biomethane production by AD are employed and the volumetric (eudiometric) method is one of the most cost-effective. The labscale eudiometric test is based on the displacement of an alkaline barrier solution for biogas generated by the AD of a selected organic substrate into a closed system (digester). Conventionally, the volume displaced by the biogas in the eudiometer is converted to an equivalent CH4 volume. Geochemical analyses stated that the liquid barrier solution is fully effective in trapping acidic gaseous components like CO2 (generally consisting of about 40% of biogas) but not those components having a solubility in an alkaline solution similar to that of CH<sub>4</sub> such as volatile organic compounds (VOCs) as well as O<sub>2</sub>, Ar, and N<sub>2</sub>. Atmospheric gaseous components are expected to be abundant at the beginning of the AD test because the digester headspace is initially flushed with pure N2 or exposed to air, causing an overestimation of the BMP values. Facing this criticality, the basic eudiometric test was refined by computing the BMP values considering the effective CH<sub>4</sub> contents identified by periodically analysing (and consequently modelling) the main gaseous components in the digester headspace. The complementary determination of 12C/13C values in CO2 and CH4 discriminated the different AD phases and related metabolic pathways, providing information about the evolution of the AD process. Finally, the contextual analysis of the chemical composition of VOCs was pivotal to complete the geochemical characterisation of biogas produced by the AD and evaluate its potential polluting effects. This comprehensive study, as an example of cooperation among environmental engineering, geochemistry, and full-scale management in the waste sector, highlighted how the synergic integration of scientific, technical, and operational disciplines can improve the interpretation of environmental phenomena, proposing unexpected challenges and innovative solutions.