Sulfate-oxygen isotope insight into anaerobic methane oxidation in estuarine sediments

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Methane production is driven mostly by microbially mediated methanogenesis. In marine sediments, this naturally produced methane is almost entirely consumed by anaerobic methane oxidation (AOM) coupled to bacterial sulfate reduction (BSR). This coupling between AOM and BSR remains enigmatic. We use the sulfur and oxygen isotope composition of aqueous sulfate ($\delta^{18}O_{SO4}$ and $\delta^{34}S_{SO4}$ respectively) consumed through AOM to further our understanding of this critical microbially-mediated process. We focus on highly stratified estuaries in the coastal area of Israel (the Yarkon and the Qishon). At these sites, sulfate is rapidly consumed and methane concentrations subsequently increase suggesting a coupling between sulfate and methane consumption.

Although the pore fluid geochemistry (e.g. sulfate and dissolved inorganic carbon concentration profiles) are similar at the studied sites, the isotope geochemistry (e.g. the $\delta^{34}S_{SO4}$, $\delta^{18}O_{SO4}$, and $\delta^{13}C_{DIC}$ in the pore fluid and the $\delta^{34}S$ of the sedimentary pyrite) is fundamentally different among the sites. Because the sulfur and oxygen isotopes in pore fluid sulfate are indicative of the relative intracellular fluxes of sulfur intermediates during BSR, we conclude that the isotope geochemistry require that the mechanism of BSR differs among the studied sites and in different sulfate-methane transition zones. We use a model for the various intracellular steps during BSR to explore what may cause these differences. We conclude that the geochemical interpretation of these sites may underrepresent the processes occurring in the subsurface as suggested by the isotope data. This suggests that recycling of sulfur intermediates may be fundamentally different in BSR coupled to AOM than when coupled to standard organic matter oxidation.

Groundwater contamination potential - vulnerability assessment

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Águeda watershed is a sub-catchement of the Douro river (northern Portugal) and it is distributed on both Spanish and Portuguese territories. The main core of this work is the achievement of a methodological tool able to be used for vulnerability assessment in ttransboudary watersheds.

Groundwaters' vulnerability mapping was carried out by two different methodological approches: DRASTIC and DRASTIC Pesticide [1].

DRASTIC is a numerical index derived from ratings and weights assigned to seven parameters – Deep to water, net Recharge, Aquifer media, Soil media, Topography, Impact of the vadose zone and hidraulic Conductivity. The obtained values raises between 23 (not vulnerable) to 230 (highly vulnerable). Drastic Pesticide uses the same parameters with the reassignment of attributes' weights to stress the importance of agricultural activities.

DRASTIC's map for Águeda watershed shows three spatially distributed vulnerability classes: low (102 - 119), moderate (120 - 139) and moderate to high (140 - 154). The low vulnerable zones occupy almost 78% of the all area while the moderate vulnerable zones correspond to 21% of the remaining area. The moderate to high vulnerable zones represents less than 1% of the total area and it is localized in the central part of the Águeda watershed overlapping the tertiary sedimentary aquifer and the mostly populated area.

DRASTIC Pesticide map shows four spatially distributed vulnerability classes: low (120 - 139), low to moderate (140 - 159), moderate to high (160 - 179) and high (180 - 195). The high proportion increases considerably in the central zone of the Águeda watershed representing more than 20% of the land parceling.

Although similar hydrogeological intrinsic characteristics are observed in the central watershed's area obvious differences can be stressed when anthropogenic activities are taken into consideration. Feasibility studies and the development of specific monitoring activities must be addressed in future work.

[1] Aller L, Bennet T, Lehr JH, Petty RJ, Hackett G. 1987. DRASTIC: a standardized system for evaluating ground water pollution potential using hydrogeologic settings. EPA/600/2–87/035, U.S. Environmental Protection Agency, Ada, Oklahoma, 641 pp.

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