Man made water cycles: Isotope tracing of desalinated seawater through water supply, sewage and groundwater

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Non-conventional water resources like desalinated water and treated sewage play today a key role in the water balance of many developed countries in arid and semi-arid regions. The worldwide capacity of desalination is expected to double within ten years to reach 62 Mm^3/d in 2015 [1]. This massive arrival of "man-made" fresh water in the water cycle is expected to change geochemical and isotope characteristics of surface and groundwater. A pilot study in 2008 [2] has shown the highly specific isotope signatures of reverse osmosis (RO) desalinated seawater. Our current study presents isotope data (B, $H+O_{H2O}$, $S+O_{SO4}$) on the largest system of soil-aquifer treatment (SAT) in the Middle East - the Shafdan site, Israel - where 130 Mm^3/Y of treated wastewater from the greater Tel Aviv region are infiltrated through ponds into the sandy Mediterranean Coastal Aquifer, recovered and then transported 70 km further to the South for unrestricted irrigation in the Negev desert. In Sept. 2010 and Feb. 2011, we analysed treated wastewater before infiltration, together with groundwaters at different distances from the infiltration ponds, as well as samples from the Tel Aviv drinking water supply and the product waters from two RO desalination plants. B isotopes of sewage show a siginficant shift from 1994 with a $\delta^{11}B$ of +9.7 ±2.8‰ *vs.* NBS951 [3] to 2010-11 with + 40.4 ±0.7‰ (n=5). This shift is explained with (1) a change in legislation lowering considerably the perborate contents in washing powders (1999-2008) and (2) the massive arrival of desalinated seawater in the drinking water supply ($\delta^{11}B$ of 53±3‰, [2]) since 2007. The breakthrough of this new boron signature has not yet been observed in the aquifer, not even for the wells closest to the infiltration ponds and no significant shift was observed between the two campaigns. This can be due to temporary sorption on clays leading to an important delay of B with respect to water [4] inducing a highly non-conservative behaviour. δ^2H and $\delta^{18}O_{H2O}$ in wastewater and groundwater can be quantitatively explained by the different components of regional water supply, including the new desalination permeate. $\delta^{34}S$ and $\delta^{18}O$ of sulphates in wastewater, observed in the vicinity of the infiltration pond, are very different from desalinated seawater, the latter very depleted in SO_4^{2-}, as sewage sulphate is dominated by other sources. This study reveals the usefulness of multi-isotope tracing for elucidating the mixing components and pathways of water and solutes in a nearly completely artificial regional water cycle.

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NO_2^--induced abiotic redox processes during microbial NO_3^--dependent Fe(II) oxidation

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Anaerobic, neutrophilic nitrate-reducing Fe(II)-oxidizing bacteria are found in many anoxic environments and were suggested to play an important role in nitrogen and iron cycling. In this study we conducted batch experiments with the mixotrophic, nitrate-reducing, iron(II)-oxidizing *Acidovorax* sp. strain BoFeN1 isolated from anoxic littoral sediments [1]. This strain produces nitrite in the low mM range as an intermediate during denitrification. Nitrite has long been identified as a strong oxidant for Fe(II) particularly under acidic pH conditions [2] but also at neutral pH in the presence of minerals and heavy metal ions that function as catalysts [3,4]. This raises the question whether the oxidation of ferrous iron is indeed enzymatically catalyzed or whether to a large extent it is just a chemical reaction as a consequence of microbial nitrite formation during acetate oxidation. A key problem occurring during investigation of these processes is the quantification of Fe(II) oxidation over time in the presence of nitrite that forms during denitrification. The acidification of the samples with HCl during dissolution of the iron mineral phases followed by the widely used spectrophotometric ferrozine assay leads to a rapid, abiotic oxidation of Fe(II) by even small amounts of nitrite. This abiotic Fe(II) oxidation in turn leads to underestimated and thus incorrect values and therefore to an overestimation of oxidation rates. To obtain correct Fe(II) data we used a revised Fe extraction protocol and added 40 mM sulfamic acid to our samples. Sulfamic acid reacts with the nitrite and prevents abiotic Fe(II) oxidation by nitrite. With this revised analytical procedure we observed a much slower Fe(II) oxidation rate with BoFeN1 (3.4 mM/day) than previously published (6 mM/day) [5]. We also quantified abiogenic oxidation of ferrous iron by mM concentrations of nitrite added to sterile culture medium at neutral pH and found rapid Fe(II) oxidation suggesting that the abiotic oxidation of Fe(II) by nitrite produced during heterotrophic denitrification contributes significantly to overall Fe(II) oxidation rates observed. Additionally, we grew strain BoFeN1 at different temperatures and found that at lower temperatures nitrite accumulated to a higher extent than in cultures growing at room temperature. This suggests that abiotic nitrite-dependent Fe(II) oxidation is even more important in low-temperature environments such as lake sediments. In summary, our experiments demonstrate the importance of nitrite formation during heterotrophic nitrate reduction in mixotrophic nitrate-reducing, Fe(II)-oxidizing cultures. The ability of nitrite to oxidize ferrous iron in the presence of biogenic Fe(III) minerals also at neutral pH raises the question if the importance of the biological process was overestimated until now. Accurate measurements of Fe(II) concentrations over time with the described revised Fe extraction method are necessary to reevaluate the Fe(II) oxidation rates of known Fe(II)-oxidizing strains. This may allow to better understand the role of abiotic Fe(II) oxidation by nitrite in these systems.

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