

Redox conditions in infiltration basins of a large scale soil aquifer treatment (SAT) of effluent

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Soil Aquifer Treatment (SAT) is considered to be an efficient and reliable effluent tertiary treatment system, in which the vadose zone and the aquifer serve as mechanical, geochemical and biological filters. In the SAT system of the Shafdan reclamation plant, Israel, large volumes of secondary effluent (about 130 million m³ annually) are recharged into the Costal Plain Aquifer and are recovered for irrigation after residence time of a few months in the aquifer.

A severe degradation of the reclaimed water quality occurs due to a sharp increase of the Mn concentrations. This enrichment is the result of sedimentary Mn-oxides reduction under suboxic conditions within the aquifer. Such conditions prevail in the aquifer due to the intensive organic matter oxidation and nitrification that take place in the upper part of the vadose zone and consume the dissolved oxygen from the recharged effluent [1].

The present work focuses on the redox reactions that occur in the infiltration basins as well as in the upper few meters below the basins, and aims to determine their sensitivity to different conditions, such as sunlight, temperature and recharge regime.

The preliminary results point to diurnal changes in the intensity of different redox reactions in the basins which have a significant impact on the redox conditions of the infiltrating effluents. The dissolved oxygen (DO) increases during the day to over-saturation values and decreases during night to under-saturation due to net photosynthesis and respiration, respectively. Unlike the DO, the dissolved organic carbon (DOC) in the effluents is quite stable during the 24-hour period. Moreover, the DOC concentrations in the water in the upper one meter of the vadose zone are higher than those in the basin. This implies that significant part of DOC oxidation takes place downward in the vadose zone. A combination of nitrogen mass balance and isotopic composition of oxygen and nitrogen in nitrates point to nitrogen removal by both NH₃ volatilization and denitrification.

[1] Oren *et al.* (2007) *Environ. Sci. Technol.* **41**: 766-772.

An electrochemical approach to determine the redox properties of iron-bearing clay minerals

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Clay minerals often contain redox-active structural iron (Fe) that can participate in electron transfer reactions with several environmental constituents, including bacteria, biological nutrients, and pollutants. Despite significant work, the electron accepting/donating capacities and Fe²⁺/Fe³⁺ reduction potential(s) remain difficult to access due to the lack of reactivity between clay minerals and electrodes.

In the current study, we have overcome this challenge by using organic electron transfer mediator compounds that rapidly react with both the clay mineral and the working electrode. Our approach uses chronocoulometry, where a fixed potential is applied (E) to the working electrode in a solution containing the mediator. The current (I) is then monitored after the addition of a known amount of clay mineral to quantify the number of electrons transferred. Electrochemical studies were complemented by batch experiments, where a solution of mediator at a set potential (E) is spiked with an aliquot of smectite and the change in potential is measured over time.

For these experiments, we have used an Fe-rich model clay mineral (ferruginous smectite, SWa-1). Highly reducing ($E = -0.64$ V, SHE) and highly oxidizing ($E = +0.61$ V, SHE) potentials led to the complete reduction and oxidation of the structural Fe of the smectite, respectively. At intermediate potentials, the Fe²⁺/Fe³⁺ ratio has been measured as a function of E , pH, and the reduction/re-oxidation cycles of the smectite. We find that the redox properties of structural Fe cannot be described by a single standard reduction potential (E°); instead, the properties can be explained by either capacitor-like behavior or a distribution of local structures of octahedrally bound Fe with distinct E° values. Additionally, the reduction/re-oxidation cycles of the smectite appears to strongly influence the Fe(II)/Fe(III) versus E relationship and the electron accepting/donating capabilities during Fe reduction and oxidation. The outcome of our study will help to address the biogeochemical implications of Fe redox reaction involving clay minerals.