# **EFFECTS OF PLANT GROWTH AND IRRIGATION WATER QUALITY ON REDOX POTENTIAL REGIME AND ELEMENT CONCENTRATIONS OF IRRIGATED SOILS**

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#### Introduction

Oxidation/reduction (redox) potential (ORP) may be considered a "master chemical variable" affecting numerous soil reactions, including oxygen, carbon, nitrogen, manganese, iron, sulfur, chromium, arsenic, selenium and copper. An indirect effect of the redox potential on absorbed elements is also recognized, due to reductive dissolution of manganese and iron oxides for instance.

In a previous experiment we discovered significant redox changes in irrigated soils and we characterized the effects of plant growth and effluent irrigation on the redox regime. The objective of this study is to characterize redox processes in the soil solution under conditions of flooding and decreasing redox potential.

#### Objectives

To study, during flooding, the correlation between continuously measured ORP and concentrations of redox-sensitive constituents in the soil solution.

#### **Experimental Design**

The experiment was conducted in lysimeters that were flooded for time periods varying from 4 to 100 days. The studied parameters included the effects of plant growth (P) vs. bare-soil (C) and effluent (E) vs. fresh water (F) irrigation, giving, in factorial design, the treatments CF, CE, PF and PE. Flooding conditions were achieved by increasing the irrigation frequency, but without preventing drainage. Details of the treatments and of the growing conditions are given in *Table 1* and in *Figure 1*.

Soil-ORP was measured continuously in-situ by permanently installed ORP-Pt electrodes. Soil solution was sampled periodically by suction cups and immediately treated to prevent atmospheric disturbance. Characterization of the extracted solution included measurements of pH, ORP, redox reactant concentrations  $(O_2, NO_3, O_2, O_3)$ Mn, Fe,  $NH_4$  and S) and other major, minor and trace elements.

**Table 1.** Characterization of the tested parameters, the growth conditions and the treatments abbreviations

<b>Tested parameters</b>		Combined
Plant affect	Irrigation solution affect	treatments code
<b>Bare-soil (C):</b> alluvial sandy clayey loam texture soil	<b>Freshwater (F):</b> freshwater with added amounts of N, P and K	CF, CE
<b>Plant (P):</b> Alfalfa ( <i>Medicago</i> sativa L)	<b>Effluent (E):</b> secondarily treated (oxidation ponds) effluent	PF, PE

### **Results and Discussion**

Continuous flooding resulted in a gradual decrease of ORP and NO<sub>3</sub> concentrations and a gradual increase of Mn, Fe and NH<sub>4</sub>. Sulfur reduction was observed on several occasions only in the PE treatments. Rates of these processes were usually higher for the PE treatments, following by PF, CE and CF treatments (Figure 2). pH in all treatments was slightly decreased from  $\sim$ 7.5 to  $\sim$ 7.0 in average.



**Figure 2.** Changes of ORP and concentrations of redox reactants with time after flooding (TaF) in four lysimeters representing the different treatments



greenhouse and schematic

*in-situ* redox measuring system



Probes (ORP /Temp./Tension)

Generally, ORP decreasing resulted in NO<sub>3</sub> decreasing due to denitrification, NH<sub>4</sub> increasing due to the breaking the nitrification process or due to N reduction, and Mn and Fe increasing to reductive dissolution of their solid-phase oxides. Mn and Fe concentrations were limited to  $\sim 0.1$  mM due to their precipitation in the carbonate phase (*Figure 3*).

**NO**3<sup>-2</sup> ⊺

In order to characterize the dynamic of the soil redox processes and to evaluate their relation with the soil-ORP, we define the Equilibrium Index for each reactant i  $(EI_i)$  as follow:

Where the theoretical activity  $a_{eq}$  is governed by a single redox reaction at a given ORP range. The governing reactions that are assumed to control a<sub>eq</sub> are given in *Figure 3*, marked by solid lines.

Changes of EI<sub>i</sub> with time after flooding clearly show that redox processes in the PE treatments were the fastest, followed by PF, CE and finally by CF treatments (see *Figure 4* for the Mn case).

*Figure 4.* Changes in the equilibrium index (EI) of manganese with the time at the different treatments



<u>*Figure 3.*</u> Measured activities of NO<sub>3</sub>, NH<sub>4</sub>, Mn and Fe in the soil solution vs. the total soil redox parameter (pe+pH). Lines for selected reactions are drawn assuming equilibrium conditions for the specific reactions (solid lines represents reactions that are assumed to control  $a_{eq}$ )

$$EI_{i} = \log \frac{a_{i}}{a_{eq}}$$
 (measured activity)  
 $a_{eq}$  (theoretic al activity)



Calculating EI of each element in a specific redox section where they are expected to govern the electrode potential show that none of the redox reactants were in equilibrium during the transition from oxide to reduced conditions (*Figure 5*).



*Figure 5.* Average (±stdev) EI calculated over specific ORP sections where each redox reactant is expected to master the electrode potential (soil-ORP)

Among the tested redox-sensitive reactants Mn was the most indicative for redox variations, reaching equilibrium with MnCO<sub>3</sub> after less than 40 days of flooding (*Figure 4*). Fe reached equilibrium (with FeCO<sub>3</sub>) after less then 60 days.  $NH_4$  concentration tends to equilibrate with its initial concentration in the irrigation solution.  $O_2$ , NO<sub>3</sub> and S did not reach equilibrium with any of their expected phases.

These results show that although changes in soil-ORP are good indication for initiation of various redox reactions, the soil-ORP is not really governed by any of the aforementioned redox reactants, especially at low ORP values. Further study is needed to understand the chemical processes that occur at the micro-environment of the electrode tip, especially under aerated conditions, and their effect on the measured soil-ORP.

#### **Summery and Conclusions**

Flooding of irrigated soils resulted in decrease of soil-ORP and in actuation of various redox reactions.

**Rates of reduction and of redox reactions were** varied among the different treatments and followed the order (from fast to slow): PE > PF > CE > CF.

Changes in concentrations of O<sub>2</sub>, NO<sub>3</sub>, Mn, Fe, NH<sub>4</sub> and  $SO_4$  lag behind the changes in the soil-ORP, approaching equilibrium only under stable reduced conditions.

#### Acknowledgments

This research was supported by Research Grant Award No. IS-3162-99R from BARD, The United States - Israel Binational Agricultural Research and Development Fund and by Research Grant No. 03R-15 from IALC, The International Arid Lands Consortium.

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