Accepted Manuscript

Research papers

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PII: S0022-1694(17)30207-X
DOI: http://dx.doi.org/10.1016/j.jhydrol.2017.03.061
Reference: HYDROL 21918

To appear in: Journal of Hydrology

Received Date: 14 July 2016
Revised Date: 24 March 2017
Accepted Date: 27 March 2017

Please cite this article as: Valdes-Abellan, J., Jimenez-Martinez, J., Candela, L., Jacques, D., Kohfahl, C., Tamoh, K., Reactive transport modelling to infer changes in soil hydraulic properties induced by non-conventional water irrigation, Journal of Hydrology (2017), doi: http://dx.doi.org/10.1016/j.jhydrol.2017.03.061

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Reactive transport modelling to infer changes in soil hydraulic properties induced by non-conventional water irrigation

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ABSTRACT

The use of non-conventional water (e.g., treated wastewater, desalinated water) for different purposes is increasing in many water scarce regions of the world. Its use for irrigation may have potential drawbacks, because of mineral dissolution/precipitation processes, such as changes in soil physical and hydraulic properties (e.g., porosity, permeability), modifying infiltration and aquifer recharge processes or blocking root growth. Prediction of soil and groundwater impacts is essential for achieving sustainable agricultural practices. A numerical model to solve unsaturated water flow and non-isothermal multicomponent reactive transport has been modified implementing the spatio-temporal evolution of soil physical and hydraulic properties. A long-term process simulation (30 years) of agricultural irrigation with desalinated water, based on a calibrated/validated 1D numerical model in a semi-arid region, is presented. Different scenarios conditioning reactive transport (i.e., rainwater irrigation, lack of gypsum in the soil profile, and lower partial pressure of CO₂ (pCO₂)) have also been considered. Results show that although boundary conditions and mineral soil composition highly influence the reactive processes, dissolution/precipitation of carbonate species is triggered mainly by pCO₂, closely related to plant roots. Calcite
dissolution occurs in the root zone, precipitation takes place under it and at the soil surface, which will lead a root growth blockage and a direct soil evaporation decrease, respectively. For the studied soil, a gypsum dissolution up to 40 cm depth is expected at long-term, with a general increase of porosity and hydraulic conductivity.

Keywords
Soil; non-conventional water; reactive transport; physical properties; hydraulic properties.
1. INTRODUCTION

Irrigation with non-conventional or low-quality water (treated wastewater, TWW; desalinated water, DW) in arid and semi-arid regions, where water scarcity forces farmers to consider alternative sources, is becoming an increasingly widespread practise in agricultural management to achieve food security (MedWSD Working Group, 2007; Qadir et al., 2007; Tal, 2006). TWW is one of the first non-conventional water resources to be used for irrigation since wastewater treatment is compulsory in the vast majority of developed countries. More recently, use of desalinated water has increased in some developed countries, forced by the high demand of fresh water. Desalinated water cost is affordable for some uses (e.g., drinking water), but still remains costly for agricultural uses (Martínez Beltrán and Koo-Oshima, 2004). A normal practise to re-mineralise DW and to increase the final water volume is to mix DW with the original saline water (Valdes-Abellan et al., 2013) to thus, lower the cost.

Impacts on soil properties from using non-conventional water for irrigation have been widely studied in recent years. Some studies have focused on vadose zone impacts from TWW-based irrigation (Assouline and Narkis, 2013; Lahav et al., 2010; Xu et al., 2010). Reduction in hydraulic conductivity close to the soil surface, along with low salt leaching and built-up salinity in the soil profile have been observed. Clogging processes, similar to those observed from artificial recharge, have also been reported (Bouwer, 2002; Sani et al., 2013). Soil impact studies from highly mineralised water have been addressed mainly by soil columns under laboratory conditions (Lado and Ben-Hur, 2010), while only few detailed studies at field scale, including soil improvement research (e.g., Reading et al., 2012a), have been carried out (e.g., Costa, 1999; Minhas et al., 1994). Most research has established a relationship between water quality in terms of sodium adsorption rates (SAR) and electrical conductivity (EC) and
hydraulic conductivity changes. As far as we know, long-term impact studies on soil from irrigation with intermediate water qualities are lacking. Finally, irrigation with wastewater or desalinated water often introduces inorganic, organic or biological contaminants, which lead to soil degradation and so their consequences are of great environmental concern (Valdes-Abellan et al., 2013).

Modelling variable-saturated flow and reactive transport is an efficient tool to assess the long-term impacts on soil caused by wastewater and saline water application. Modelling approaches have focused on salinity evolution in soil (Kanzari et al., 2012), impact on crop yields (Phogat et al., 2010; Ramos et al., 2011), and a few on soil hydraulic properties (Assouline and Narkis, 2011; Reading et al., 2012b). Most previous research works have focused on possible impacts with a limited type of processes, and did not consider precipitation/dissolution processes, heat flux or changes in soil physical and hydraulic properties. For accurate and reliable model prediction, it is necessary to consider all the processes involved in coupling unsaturated flow, non-isothermal multicomponent reactive transport, and transient soil physical and hydraulic properties (Šimůnek et al., 2006; Wissmeier and Barry, 2009; Steefel et al., 2015).

The main objective of this research is to assess possible long-term changes in soil physical and hydraulic properties from the use of non-conventional water for irrigation. The HP1 code (Jacques et al., 2006; Jacques et al., 2008) to simulate unsaturated water flow and non-isothermal multicomponent reactive transport has been adapted to include the spatio-temporal evolution of soil physical and hydraulic properties as a result of the minerals dissolution/precipitation. It includes porosity, soil hydraulic conductivity and alpha parameter (inverse of air entry value) from the van Genuchten model. A long-term prediction (30 years) of flow and reactive transport processes in the vadose zone of a grass plot irrigated with desalinated water (slight saline) is presented herein. For that
purpose, 3 years of field data, along with a calibrated/validated flow, solute and heat transport model have been used for the long-term predictions. Alternative scenarios as rainwater irrigation, lack of gypsum in the soil profile, and lower partial pressure of CO$_2$ ($p$CO$_2$) than measured in the soil are also considered. This work also aims at assessing possible impacts on vegetation, i.e., root growth blockage, and to shed light on the agricultural management options.

2. NUMERICAL MODELLING

Unsaturated water flow, mass and heat transport are simulated with the HYDRUS-1D code (Šimůnek et al., 2009). The HP1 code (Jacques et al., 2008) for solving non-isothermal multicomponent reactive transport is applied. HP1 couples HYDRUS-1D with the hydrogeochemical code PHREEQC (Parkhurst and Appelo, 2013). This research uses a non-released beta version of HP1, which includes in the modelling process the spatio-temporal variability of soil physical and hydraulic properties (Figure 1).

2.1. Water flow

Unsaturated water flow is modelled according to Richards’ equation (Richards, 1931):

$$\frac{\partial \theta}{\partial t} = \frac{\partial}{\partial z} \left( K(\theta) \left( \frac{\partial h}{\partial z} + 1 \right) \right) - S$$  \hspace{1cm} (1)

where $\theta$ is volumetric water content [L$^3$·L$^{-3}$]; $t$ time [T]; $z$ the vertical space dimension [L]; $K(\theta)$ unsaturated hydraulic conductivity function of soil [L·T$^{-1}$]; $h$ soil pressure head [L]; and $S$ a sink term that represents water uptake by plants [L$^3$·L$^{-3}$·T$^{-1}$]. The soil
hydraulic properties are defined by van Genuchten-Mualem constitutive relationships (Mualem, 1976, van Genuchten, 1980):

\[
\theta(h) = \begin{cases} 
\theta_r + \left( \theta_{s,upd} - \theta_r \right) \left[ 1 + \alpha_{upd} h^\theta \right]^{-\frac{1}{\theta \alpha}} & \text{if } h < 0 \\
\theta_{s,upd} & \text{if } h \geq 0 
\end{cases}
\]  
\tag{2}

\[K(h) = K_{upd} S_e \left\{ 1 - \left[ 1 - S_e^{\alpha(n-1)} \right]^{-\frac{1}{\theta \alpha}} \right\}^2
\]  
\tag{3}

where \( S_e \) is effective saturation:

\[S_e = \frac{\theta(h) - \theta_r}{\theta_{s,upd} - \theta_r}
\]  
\tag{4}

and \( \theta_{s,upd} \) the modified saturated water content [L\(^3\)·L\(^{-3}\)]; \( \theta_r \) the residual water content [L\(^3\)·L\(^{-3}\)]; \( K_{upd} \) new saturated hydraulic conductivity [L·T\(^{-1}\)]; and \( \alpha_{upd} \) [L\(^{-1}\)], \( n \) [-], and \( l \) [-] the empirical coefficients that determine the shape of the hydraulic functions, being \( \alpha \) updated in each computational time step. In order to avoid over-parametrisation, \( l = 0.5 \) is commonly assumed, based on Mualem (1976).

### 2.2. Heat transport

Heat transport modelling is performed after taking into account the different equilibrium constants of the mineral phases and soil temperature. The governing heat transport equation is:

\[
\frac{\partial C_p(\theta) T}{\partial t} = \frac{\partial}{\partial x} \left( \lambda(\theta) \frac{\partial T}{\partial x} \right) - C_v \frac{\partial q T}{\partial x} - C_s S T
\]  
\tag{5}

where the new parameters are: \( T \) temperature of soil [K, T]; \( C_v \) and \( C_p \) volumetric heat capacity of the liquid phase and the porous medium (de Vries, 1963), respectively [J·m\(^{-3}\)·K\(^{-1}\), M·L\(^2\)·T\(^{-2}\)]; \( \lambda(\theta) \) apparent thermal conductivity of soil [J·s\(^{-1}\)·m\(^{-1}\)·K\(^{-1}\), M·L·T\(^{-3}\)·K\(^{-1}\)]; \( q \) volumetric water flux density [L·T\(^{-1}\)], and the rest of parameters are previously
defined. The three terms on the right represent heat transfer by conduction, heat transport by water, and energy uptake by plant roots associated with root water uptake, respectively.

The apparent thermal conductivity combines the thermal conductivity \( \lambda_0(\theta) \) of the porous medium (solids plus water) with flow-induced macrodispersivity (de Marsily, 1986):

\[
\lambda(\theta) = \lambda_0(\theta) + \beta_i C_{ri} |q|
\]

(6)

where \( \beta_i \) is thermal dispersivity [L]. The volumetric heat capacity of liquid phase incorporates the thermal conductivity notation after the rearrangement of the thermal dispersivity length units (Chung and Horton, 1987):

\[
\lambda_n(\theta) = \omega_1 + \omega_2 \theta + \omega_3 \theta^{0.5}
\]

(7)

where \( \omega_1, \omega_2, \) and \( \omega_3 \) are empirical parameters [M·L·T\(^{-3}\)·K\(^{-1}\)].

2.3. Multicomponent reactive transport

The advection-dispersion equation, with the additional reactive term to take into account geochemical processes, is used to solve transport:

\[
\frac{d(\rho C_i)}{dt} = \frac{\partial}{\partial z} \left( \theta D_i \frac{\partial C_i}{\partial z} \right) - \frac{\partial (q_i C_i)}{\partial z} - S_{C,i} C_i + R_i;
\]

\[
\frac{d(\rho s_i)}{dt} = -R_i
\]

(8)

where \( \rho \) is bulk density of the porous media [M·L\(^{-3}\)]; \( s \) solute \( i \) concentration in the solid phase [M·M\(^{-1}\)]; \( C_i \) aqueous concentration of element \( i \) [M·L\(^{-3}\)]; \( D \) dispersion coefficient of element \( i \) in the liquid phase [L\(^2\)·T\(^{-1}\)]; \( C_{ri} \) concentration of element \( i \) of the sink term [M·L\(^{-3}\)]; \( R_i \) is a source/sink term of element \( i \) due to heterogeneous geochemical reactions [M·L\(^{-3}\)·T\(^{-1}\)].
The dispersion coefficient in the liquid phase, $D$, represents the combined effects of dispersion and molecular diffusion:

$$ D = \eta \frac{|q|}{\theta} + D_m \tau $$

(9)

where $\eta$ is dispersivity [L]; $D_m$ temperature-dependent ions diffusion coefficient [L$^{-2}$·T$^{-1}$]; $\tau$ tortuosity (dimensionless), calculated as $\tau = \theta^{\alpha / 3} / \theta_s^2$ (Millington and Quirk, 1961).

Reactive solute transport, as defined, involved a number of interrelated processes and dependent parameters depending on the state of the system. The effect of temperature on the diffusion coefficients and equilibrium constants, i.e., the non-isothermal character, is also considered (Appelo and Postma, 2005; Parkhurst and Appelo, 2013).

2.4. Soil properties changes

HP1 allows changes of flow and transport parameters induced by changes in the geochemical state variables (e.g., Jacques et al., 2011; Xie et al., 2015; Francisca and Glatstein, 2010). In this research, and as main new implementation in this well-known numerical tool, variation of porosity in soil media is estimated after each geochemical computational step by considering the balance between the amount of precipitated and dissolved minerals. The hydraulic conductivity and van Genuchten alfa parameter scaling factors, $\alpha_{\text{GM}}$ [-] and $\alpha_{\text{K}}$ [-], respectively, at each location in the soil profile are computed according to Wissmeier and Barry (2009, 2010). Note that porosity is assumed to be the saturated volumetric water content, $\phi \approx \theta_s$. Therefore, the scaling factors are as follow:

$$ \alpha_{\text{GM}} = \left( \frac{\theta_s' + \theta_s}{\theta_s' + \theta_s} \right)^{1/3} $$

(10)
\[
\alpha_{K1} = \left( \frac{\theta_r - \theta_s}{\theta_r - \theta_w} \right)^{8/3}
\] (11)

where * denotes the new values after mineral reactions.

On the other hand, water salinity and temperature are used to estimate the potential changes in water density (Eq. 12) and dynamic viscosity (Eq. 13), and their influence on the hydraulic conductivity as consequence. They are respectively as (e.g., Sharqawy et al., 2010):

\[
\rho_w = \left( a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4 \right) + \left( b_1 + b_2 T s_s + b_3 T^2 s_s + b_4 T^3 s_s + b_5 T^4 s_s \right)
\] (12)

where \( a_1 = 9.999 \cdot 10^2 \); \( a_2 = 2.034 \cdot 10^{-2} \); \( a_3 = -6.162 \cdot 10^{-3} \); \( a_4 = 2.261 \cdot 10^{-5} \); \( a_5 = -4.657 \cdot 10^{-8} \); \( b_1 = 8.020 \cdot 10^2 \); \( b_2 = -2.001 \); \( b_3 = 1.677 \cdot 10^2 \); \( b_4 = -3.060 \cdot 10^{-5} \); \( b_5 = -1.613 \cdot 10^{-5} \); \( T \) is temperature [Celsius]; and \( s_s \) salinity [kg·kg\(^{-1}\)], and

\[
\mu_w = \mu \left( 1 + A s_s + B s_s^2 \right)
\] (13)

where \( \mu = 4.2844 \cdot 10^{-5} + [0.157 \cdot (T+64.993)^2 - 91.296] \); \( A = 1.541 + 1.998 \cdot 10^{-2} \cdot T - 9.52 \cdot 10^{-5} \cdot T \); and \( B = 7.974 - 7.561 \cdot 10^{-2} \cdot T + 4.724 \cdot 10^{-4} \cdot T^2 \). The scaling factor for hydraulic conductivity is obtained through the relation between hydraulic conductivity and intrinsic permeability of the porous media

\[
\alpha_{K2} = \frac{\rho_w^{\alpha_{GM}} \mu_w^{\alpha_{GM}}}{\rho_w \mu_w}
\] (14)

where * denotes the new values after mineral reactions.

Therefore, the updated van Genuchten alpha parameter and saturated hydraulic conductivity (in Eqs. 2 and 3) are as:

\[
\alpha_{upd} = \alpha_0 \cdot \alpha_{GM}
\] (15)

\[
K_{upd} = K_0 \cdot \alpha_{K1} \cdot \alpha_{K2}
\] (16)
where subscript 0 denotes the initial values, and the subscript upd denotes the new values at each node of the modelled soil profile.

With the new calculated values of van Genuchten alpha parameter and saturated hydraulic conductivity, Hydrus 1D solves in a coupled way water flow, solute and heat transport (Šimůnek et al., 2009). Subsequently, the PHREEQC code is called and all potential hydrogeochemical reactions taking place in the soil media, including fluid-fluid and fluid-solid reactions, are computed. In the next step, once the dissolved and precipitated species are known, porosity is recalculated at each depth. Similarly, soil water density and viscosity data are updated according to geochemical speciation and heat transport results. The updated values of porosity distribution along depth (assumed equal to the saturated water content) and soil water density and viscosity are used to compute the changes in the soil hydraulic properties, including van Genuchten alpha parameter and saturated hydraulic conductivity, prior to the next time step (Figure 1).

3. FIELD SITE AND EXPERIMENT

3.1. Experimental site

The field experiment was conducted on an experimental plot set up in Alicante (SE Spain). The area is characterised by a semi-arid Mediterranean climate with dry hot summers and mild winters: 18°C mean annual temperature and a precipitation rate of 330 mm yr⁻¹. Rainfall takes place mainly in spring and autumn, when intense rainfall events occur. The mean annual reference evapotranspiration, \( ET_0 \), according to Penman-Monteith (Allen et al., 1998) accounted for \(~1278\) mm.

The experimental plot (9 x 5 m²) is cultivated with a mixture of turf grass species (St. Agustine grass, \textit{Stenotaphrum secundatum}, and ray grass, \textit{Lolium perenne}) to mimic landscape management. It is irrigated with desalinated water by micro-sprinklers (from
summer 2011 to present time), with a mean annual value of 1550 mm (Valdes-Abellan et al., 2013). The monitoring of the volumetric soil water content and soil temperature has been done by sensors at depths of 20, 40, 60, 90 and 120 cm. Temperature of the top soil surface has been also monitored by a sensor located at 1 cm depth, in order to establish the upper boundary condition. The soil pressure head has been controlled only at depths of 20 and 60 cm. A detailed description of the experimental plot and installed devices can be found in Valdes-Abellan et al. (2015).

3.2. Characterization of the soil properties

Physical and hydraulic soil properties have been determined from disturbed and undisturbed soil cores taken at different depths. The laboratory determinations included: soil bulk density according to (Grossman and Reinsch, 2002), porosity (Flint and Flint, 2002), particle size distribution (Gee and Or, 2002), saturated and residual volumetric water content, saturated hydraulic conductivity (Reynolds and Elrick, 2002) and soil water retention curves, SWRC (Dane and Hopmans, 2002).

The chemical properties of soil media have been determined from disturbed samples. The soil chemical composition and soil mineralogy have been obtained by X-Ray fluorescence, XRFS (Abderrahim et al., 2011; Brindley and Brown, 1980) and X-Ray diffractometry (Jones, 1991), respectively. Cation exchange capacity, $CEC$, has been determined according to Sumner et al. (1996), while organic carbon, $OM$, based on Nelson and Sommers (1996).

3.3. Irrigation water quality

Irrigation is carried out with a mix of desalinated water (DW) from an inland brackish aquifer (Prats and Chillón Arias, 2001; Prats et al., 1997) and the groundwater
that is pumped directly from the aquifer (see Supplementary Material). The desalination process includes a post-treatment stage with Ca(OH)$_2$ addition to meet Spanish Ca$^{2+}$ and HCO$_3^-$ concentration requirements (Royal Decree 1138/1990). Mixing brackish groundwater and DW is quite variable, with the fraction of raw groundwater ranging between 5% and 22% in winter and summer, respectively (Valdes-Abellan et al., 2013).

Irrigation water sampling has been carried out monthly. Chemical determinations, including major ions and physicochemical parameters, have been done following standards procedures, while in situ determinations have been carried out with a multiparameter recording device, which includes pH, temperature, redox potential [$Eh$] and electrical conductivity.

The saturation index, $SI$, for the relevant minerals and ionic species has been calculated after considering atmospheric conditions (i.e., $pCO_2$ equalled $10^{-3.5}$ atm) with the PHREEQC-3.1.7 code (Parkhurst and Appelo, 2013), based on minteq.v4.dat as the thermodynamic database (Ball and Nordstrom, 1991).

4. MODEL APPLICATION

4.1. Main scenario

A 140 cm deep soil profile and three soil layers have been defined according to the soil characterisation results of the experimental plot (Table 1 and Figure 2). The horizontal uniformity (i.e., homogeneous and isotropic) observed across the experimental plot allows to consider a one-dimensional model. A 30 years numerical simulation with HP1 has been performed to predict the geochemically-induced (mineral kinetics) long-term changes in soil physical and hydraulic properties.

A calibrated/validated water flow model from soil water content and pressure head observations along three years is used as initial soil parameterization (Table 1)
Atmospheric boundary condition (potential evapotranspiration, water input and root water uptake) are considered, while free drainage is assumed as the lower boundary condition since water table is far below the domain. Root depth is considered constant, 6 cm, while for potential evapotranspiration $ET_p$, according to Penman-Monteith, 10 cm height is considered for the cultivated grass species on the plot. Root water stress was modelled by the modified Feddes model (Wesseling and Brandyk, 1985; Feddes et al., 1978). The original Feddes model considers a maximum water uptake between $h_2$ and $h_3$, zero water uptake when soil pressure head is below and above two boundary levels, $h_4$ and $h_1$, respectively, and linear transitions between these domains. A double value of $h_3$ depending on the potential water uptake is considered in the modified Feddes model (Wesseling and Brandyk, 1985) (Figure 3). The values adopted for the current crop (grass) are: $h_1=-10$ cm; $h_2=-25$ cm; $h_{3.1}=-240$ cm; $h_{3.2}=-360$ cm; and $h_4=-8000$ cm. And the threshold values of evaporation to trigger $h_{3.1}$ or $h_{3.2}$ values are 1 mm day$^{-1}$ and 5 mm day$^{-1}$ (i.e., if $ET_p > 5$ mm day$^{-1}$, then $h_{3.2}$ is used, while if $ET_p < 1$ mm day$^{-1}$, then $h_{3.1}$ is used).

Soil thermal properties (Table 2) have been obtained from a calibrated heat transport model, and by inverse method, for the period 1 September 2011-30 Abril 2013. The measured and simulated temperature results, at different depths for the calibration period, are included in the Supplementary Material.

For the multicomponent reactive transport, dissolution and precipitation of five mineral species are considered: dolomite, calcite, aragonite, anhydrite, and gypsum (molar volumes, http://database.iam.ac.ru/mincryst/, listed in Table 3). The initial soil content (moles) of these mineral species have been derived from the mineralogical determinations. Initial equilibrium of calcite and gypsum in the soil water is considered; $p_{CO_2}$ in soil is set at $10^{-1.5}$ atm in the root zone and at $10^{-3}$ atm below it (Appelo and
Postma, 2005) after considering that biological activity diminished below this depth (Figure 2). The rainfall presents low mineralisation, and it is considered in equilibrium with $p\text{CO}_2 = 10^{-3.5}$ atm. The dispersivity values for the different soil layers of the model have been obtained by inverse modelling of a tracer test, as described in Valdes-Abellan et al. (2014) (Table 1).

The data (precipitation, irrigation and evapotranspiration, as well as temporal and intensity distribution) collected along the Sep-11 Aug-14 period are used to generate the 30 year time future scenario data set. For this exercise, global change effects as derived from the ICCP panel are not taken into consideration, although a rise in both temperature and the intensity of extreme rainfall events in the study area are expected (Candela et al., 2009).

**4.2. Considered scenarios of environmental conditions**

Three different scenarios to assess soil media response to changes in the boundary and initial conditions compared to the reference scenario are studied. Proposed scenarios include representative and probable environmental conditions and agricultural practices: i) *rain-fed irrigation*, with input only from precipitation, while changes in the initial conditions are not considered; ii) *lack of gypsum in the soil profile*, in order to highlight the importance of gypsum in the processes, given its molar volume; iii) a *lower $p\text{CO}_2$ ($p\text{CO}_2$ of $10^{-2.5}$ atm) in the root zone* than the reference scenario initial value; to carry out a sensitivity analysis of this parameter and, given the key role that $p\text{CO}_2$ (atmospherically and biologically controlled) plays in calcite precipitation and dissolution. In bare and no-tillage soils, $p\text{CO}_2$ can be generally lower than $10^{-1.5}$ atm (e.g., Lee, 1997; Loisy et al., 2003).
5. RESULTS AND DISCUSSION

5.1. Soil and water composition: chemical indices

Calcite is the most abundant mineral followed by quartz (Table 4) in the three defined soil layers; both minerals accounted for 85.3%, 90.5% and 90.4% composition for layer 1, 2 and 3, respectively. Compared with the other layers, layer 1 exhibits higher SiO$_2$ content and lower CaO content. Presence of clay minerals is practically negligible, except layer 1 where Illite content accounts for 9.7%. Gypsum is not present in layer 1, but in layers 2 and 3. The three layers have low CEC and OM contents, being slightly higher in layer 1 than in layers 2 and 3 (Table 4).

Table 5 summarises the monthly-analysed chemical composition and physico-chemical parameters of irrigation water. The chemical balance error was always lower than 1.9%. It shows a monthly variation of the applied water, with sodium-chloride-sulphate facies at a neutral pH. The chemical indices (i.e., Hardness, TAC, SAR) are also computed. SI shows that irrigation water is subsaturated for most of the possible mineral phases within the existing pH range. Yet under atmospheric conditions, almost saturated or even oversaturated conditions (i.e., $SI > 0$) prevail for the most relevant mineral species: aragonite, calcite, dolomite, anhydrite and gypsum. The $SI$ variation along a year for these minerals is shown in Figure 4. Note the increased $SI$ of Ca- and Mg-carbonate during the summer season, which indicates that mineral precipitation may occur. From the chemical indicators SAR and EC, there is a medium risk of alkalinisation for most of the water samples, while the risk of salinization is high (or even very high) in all the analysed samples (see Supplementary Material).

5.2. Main scenario: reactive transport and long-term impacts
The transport regime is characterized by two dimensionless numbers. The Péclet number, which compares the relative importance of advective and diffusive effects during transport. Here, computing it as $\text{Pe} = (v/D_m)\Delta z$ (e.g., El-Kadi and Ge, 1993), where $v$ is the mean water velocity [L·T$^{-1}$] ($v=q/\theta$), and $\Delta z$ the spatial discretization [L]. 1 cm in this case. The Damkohler number, which compares the mean travel time to the time required to reach the equilibrium, $\text{Da} = \Delta z(\theta/q)/(C_{eq,i}/R_i)$, (e.g., Maher and Chamberlain, 2014), where $C_{eq,i}$ is the thermodynamic limit (i.e., the maximum concentration) [M·L$^{-3}$], and $R_i$ is the reaction rate of element $i$ [M·L$^{-3}$·T$^{-1}$]. The average $\text{Pe}$ is smaller than 1, and the $\text{Da}$ for the two main mineral species involved (i.e., calcite and gypsum) is similar to 1. Based on these two criteria, we assume that the geochemical equilibrium is reached between the old resident water, new input water and soil minerals.

Figure 5a and 5b, spatio-temporal plots, show predicted mass change content (mol) in the soil profile with time for calcite and gypsum, respectively, compared to the initial values. For better illustration/readability and understanding of the most relevant processes, the soil profile of Figure 2 is zoomed to 60 cm depth, and not 140 cm depth completed with the numerical simulations. Dolomite, aragonite and anhydrite have not been considered in the evaluation of the soil physical and hydraulic properties changes, since their dynamic of precipitation/dissolution is negligible.

As expected, calcite dissolution/precipitation dynamic is strongly influenced by $p\text{CO}_2$. On the soil surface, at a depth between 0 and 2 cm, precipitation of calcite is expected, leading to a carbonate crust formation. Similar results have been reported by Gran et al. (2011) and Nachshon et al. (2011a, b). Simulation indicates that calcite dissolution will occurs in the root zone, where a maximum $p\text{CO}_2$ of $10^{-1.5}$ atm is adopted considering existing biological activity (Figure 2). Irrigation water, saturated in
calcite under atmospheric conditions (Table 5 and Figure 4) and subsaturated in the root zone (between 2-6 cm), will dissolve calcite from soil. The mixture of these two different waters, which are both saturated for calcite, but with a different $pCO_2$, will lead to a water composition that is subsaturated for this mineral (Appelo and Postma, 2005). Below the root zone, between 6 and 10 cm depth, the lower $pCO_2$ will induce calcite precipitation (Figure 5a).

Soil gypsum content presents a more regular geochemical behaviour than calcite. The input water, subsaturated in this mineral facies, will imply the continuous dissolution of the available gypsum in the soil profile (Figure 5b). Gypsum will be completely dissolved by the input water from top to bottom of the soil profile. The horizontal bands are the result of different initial gypsum content in each soil layer defined.

Simulation shows that two main processes control the saturated hydraulic conductivity patterns (Figure 5c): first, soil water salinity cyclical process and, specially, temperature changes as observed from the vertical bands (seasonal-annual variation of temperature) (Eq. 11); second, calcite and gypsum dissolution/precipitation (Eq. 14). The spatio-temporal evolution of the porosity, temperature, water salinity, density and dynamic viscosity, all of them affecting the hydraulic conductivity, are included in the Supplementary Material. Figure 5d shows the spatio-temporal evolution of the alpha parameter (inversely correlated with air entry into soil matrix) from the van Genuchten model. It is intimately related to changes in porosity (see Supplementary Material), in this case $\theta_s$, according to Eq. 10. The updating of $K_s$, $\theta_s$ and $\alpha$ implies new pressure-saturation curves every time step and depth.

The expected calcite crust formation on the soil surface will mean an upper hydraulic conductivity barrier, with a subsequent reduction of infiltration and direct
evaporation. Between 2 and 6 cm depth, porosity changes are consequence exclusively of calcite dissolution since the X-ray mineralogy determinations indicate no gypsum in the top layer (Table 4). Therefore, hydraulic conductivity-scaling factor shows an increase at this depth interval (Figure 5c). Below the root zone (6-20 cm), gypsum dissolution and calcite precipitation will take place. The effect of gypsum dissolution on porosity (molar volume double than calcite, Table 3) is greater than calcite precipitation. As a result, porosity will increase and also the saturated hydraulic conductivity, so no root growth blockage is expected despite the calcite precipitation below roots. After 30 years of simulation and at higher depths than 20 cm, the expected calcite changes are lower. $pCO_2$ changes are very important in the upper part of the soil profile, due to atmospheric and root zone influence. Below the root zone, $CO_2$ concentration tends to stabilize, but also soil water content and saturation indexes of the considered minerals. In other words, in the upper part of the soil profile there is a non-steady state (i.e., non-equilibrium), while below the action of the evaporation and roots, the soil reaches a quasi-steady state (i.e., quasi-equilibrium). At long-term and below 20 cm, only gypsum dissolution will be important. Less significant changes are detected at around 40 cm depth, although slow gypsum dissolution is expected to continue for longer times and greater depths.

5.3. Scenarios of environmental conditions

Rain-fed irrigation

Figure 6 summarises simulation results after considering that irrigation is not applied. As the water input by rainfall is much lower than in the irrigation scenario, all the geochemical processes (dissolution/precipitation) (Figure 6a and 6b), and impacts on soil physical (porosity) and hydraulic (conductivity) properties, became less
significant. The only observed changes correspond to annual and seasonal temperature impact on the $K_s$ (Figure 6c), while it is null for $\alpha$ (Figure 6d). Calcite crust on the soil surface did not build up, highlighting the role of the desalinated water application as a leading factor of soil physical and hydraulic properties changes. Therefore, no affection to infiltration, direct evaporation or root growth are expected, while vegetation death is highly probable due to the semi-arid conditions.

**Absence of gypsum in the soil profile**

According to the reference scenario results, gypsum dissolution plays an important role in $\theta_s$ and $K_s$ changes, even when considering low initial concentration in the soil profile (gypsum is not present in layer 1, and it is below 7% in layer 2 and under 3% in layer 3).

In a gypsum-free soil profile, calcite will precipitate in the soil surface, as a crust, while it will dissolve within the first few centimetres below the crust; aragonite will also precipitate at this depth (Figure 7a). The lack of gypsum in the soil profile impairs its dissolution although the infiltrating water is subsaturated in it (Figure 7b). Compared with the reference scenario: $\theta_s$ will be reduced due to calcite precipitation and will not be counterbalanced with gypsum dissolution; and $K_s$ will mainly decrease along the soil profile except in the root zone (Figure 7c).

The development of a less permeable layer below the root zone (between 6 and 20 cm depth, approximately), with a scaling factor of 0.5 for $K_s$ and 0.8 for the $\alpha$ parameter of van Genuchten model (Figure 7c and 7d), will imply the root growth blockage at long-term.

**Lower $pCO_2$ in the root zone**

The obtained results are similar to the reference scenario, although processes such as precipitation/dissolution of calcite are of less magnitude (Figure 8a). The maximum calcite precipitation in the soil surface and below the roots is expected to be reduced
from 5 to 3 moles, while calcite dissolution in the root zone from 5 to 2 moles with respect to the reference scenario. Gypsum dynamics is virtually independent of $pCO_2$ and almost will follow the reference scenario pattern, i.e., all the gypsum available in the soil profile will be gradually dissolved (Figure 8b). The changes in the $K_s$ and $\alpha$ (Figure 8c and 8b) are also similar to the reference scenario. Therefore, no necessarily a reduction of $pCO_2$ or aeration of the system will imply significant changes in the soil physical and hydraulic properties with respect to the reference scenario.

6. CONCLUSIONS

Assessment of impacts on soil properties by non-conventional water irrigation is an increasing concern problem. Understanding and integrating all the involved processes, and quantifying the expected impacts can be achieved through numerical process-based modelling. However, the use as starting point of field data, both from soil and boundary conditions, can reduce considerably the associated uncertainty.

This work presents a numerical model that combines water flow, heat and non-isothermal multicomponent reactive transport, along with a self-proposed computation of the spatio-temporal variability in the soil physical and hydraulic properties. The application of this numerical model to evaluate the long-term (i.e., 30 years) impacts on soil from the irrigation with non-conventional water (i.e., desalinated water) in a semi-arid region reveals its potential as a predictive tool. For the particular soil and boundary conditions studied, two aspects stand out: i) the key role played by the partial pressure of CO$_2$ (atmospherically and biologically controlled), which triggers the precipitation of calcite on the surface and just below the root zone, and the dissolution in between, and ii) the gypsum dissolution in the soil profile, counterbalancing the calcite precipitation. As main expected long-term impacts, for gypsum-bearing soils, as in our case, porosity
and saturated hydraulic conductivity will increase along the profile mainly by gypsum
dissolution (molar volume of gypsum is double than calcite), except on the surface and
below roots due to calcite precipitation. However, this localized calcite precipitation
will reduce the direct soil evaporation and could imply the root growth blockage.

Other probable scenarios, beside the reference case, considering different initial
and boundary conditions have also been proposed based on their interest for the region.
The different scenarios results have demonstrated the importance of individual
components: i) the rain-fed scenario (i.e., no irrigation) shows that the use of low
quality irrigation water (desalinated water, subsaturated in gypsum) will trigger most of
the reactions; ii) in the gypsum-free soil profile scenario, a carbonate crust formation on
the surface and below the root zone is expected to occur, with a potential reduction by a
factor 2 and 0.2 of the saturated hydraulic conductivity and the alpha parameter of van
Genuchten model, respectively, since the porosity reduction by calcite precipitation is
not counterbalanced by gypsum dissolution; and iii) a lower partial pressure of CO₂
scenario shows an expected reduction in the calcite precipitation on the surface and
below the roots, while changes in the soil physical and hydraulic properties are expected
to be similar to the reference case, since gypsum dissolution is the main control on
them.

Although results and conclusions depend on specific local conditions, including
soil mineralogy, irrigation water quality and climate, among others, obtained results can
contribute to improve understanding of processes in similar regions. Note that such a
modelling approach forms a basis for studying climate change effects either through the
methodology of climatic analogues (Leterme et al., 2012) or the generation of climate
change scenarios (Candela et al., 2009); the evaluation in detail of the relative
importance of climate change in the studied processes needs to be addressed in further investigations.

ACKNOWLEDGEMENTS

This study forms part of the CGL2010-22168-C03/BTE and CGL2013-48802-C3-3-R projects, financed by the Spanish Ministry of Economy and Competitiveness, and of the GRE15-19 project financed by the University of Alicante. Gratitude is also expressed to Dr. Iñaki Vadillo from the University of Malaga; the IMDEA-AGUA and Dr. Ignasi Queralt from the IDAEA-CSIC.

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Figure 4. Temporal evolution of the saturation index $SI$ of irrigation water.

Figure 5. Space-time plots of expected changes in (a) calcite content (mols), (b) gypsum content (mols), (c) the $K_s$ scaling factor, $\alpha_k$, and (d) the alpha of van Genuchten model scaling factor, $\alpha_{GM}$, for the reference scenario.

Figure 6. Space-time plots of expected changes in (a) calcite content (mols), (b) gypsum content (mols), (c) the $K_s$ scaling factor, $\alpha_k$, and (d) the alpha of van Genuchten model scaling factor, $\alpha_{GM}$, for the rain-fed scenario.

Figure 7. Space-time plots of expected changes in (a) calcite content (mols), (b) gypsum content (mols), (c) the $K_s$ scaling factor, $\alpha_k$, and (d) the alpha of van Genuchten model scaling factor, $\alpha_{GM}$, for the gypsum-free soil profile scenario.
Figure 8. Space-time plots of expected changes in (a) calcite content (mols), (b) gypsum content (mols), (c) the $K_s$ scaling factor, $\alpha_{k1}/\alpha_{k2}$, and (d) the alpha of van Genuchten model scaling factor, $\alpha_{GM}$, for the lower partial pressure of CO$_2$ ($p$CO$_2$) in the root zone scenario.

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**REFERENCES**


Water flow, heat and solute transport

Hydrus1D

Geochemical reactions

PHREEQC

Change in soil hydraulic properties

\[ a_{GM} = \left( \frac{\theta' + \theta_r}{\theta + \theta_r} \right)^{1/3} \]

\[ a_k = \frac{\theta' (\theta' + \theta_r)^{2/3}}{\theta_r (\theta + \theta_r)} \cdot \rho_w \cdot \mu_r \cdot \rho_w \cdot \mu_w \]

New porosity, \( \phi \approx \theta_r \)

Dissolved/precipitated moles

New water density, \( \rho_w \)

New dynamic viscosity, \( \mu_r \)

Soil water salinity and temperature
Layer 1, clay loam:
Calcite  9.3 mol/100 cm³ soil
Gypsum  0.0 mol/100 cm³ soil

Layer 2, sandy loam:
Calcite  12.5 mol/100 cm³ soil
Gypsum  0.7 mol/100 cm³ soil

Layer 3, loam:
Calcite  12.9 mol/100 cm³ soil
Gypsum  0.5 mol/100 cm³ soil
Soil water pressure head, h (cm)
Table 1. Summary of the soil physical, hydraulic and transport properties.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Depth (m)</th>
<th>Sand/Silt/Clay (%)</th>
<th>Texture</th>
<th>Bulk density, ρ (g cm(^{-3}))</th>
<th>Porosity (%)</th>
<th>Particle density (g cm(^{-3}))</th>
<th>θ(_s) (cm(^3) cm(^{-3}))</th>
<th>θ(_r) (cm(^3) cm(^{-3}))</th>
<th>α (cm(^{-1}))</th>
<th>n (-)</th>
<th>K(_s) (cm day(^{-1}))</th>
<th>Dispersivity, η (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0-0.05</td>
<td>36.2/29.6/34.2</td>
<td>Clay loam</td>
<td>1.38</td>
<td>47</td>
<td>2.65</td>
<td>0.48</td>
<td>1.90</td>
<td>5.11·10(^{-3})</td>
<td>1.48</td>
<td>5.9</td>
<td>2.44</td>
</tr>
<tr>
<td>2</td>
<td>0.05-0.39</td>
<td>59.1/34.8/6.0</td>
<td>Sandy loam</td>
<td>1.5</td>
<td>41</td>
<td>2.53</td>
<td>0.39</td>
<td>1.42</td>
<td>2.47·10(^{-2})</td>
<td>1.42</td>
<td>50</td>
<td>14.99</td>
</tr>
<tr>
<td>3</td>
<td>0.39-1.40</td>
<td>45.4/47.1/7.5</td>
<td>Loam</td>
<td>1.42</td>
<td>44</td>
<td>2.54</td>
<td>0.41</td>
<td>1.66·10(^{-2})</td>
<td>1.66·10(^{-2})</td>
<td>1.83</td>
<td>60.9</td>
<td></td>
</tr>
</tbody>
</table>


Table 2. Soil thermal properties of the three defined soil layers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Longitudinal thermal dispersivity, β(_t) [cm]</th>
<th>(b_1) [W m(^{-3}) K(^{-1})]</th>
<th>(b_2) [W m(^{-3}) K(^{-1})]</th>
<th>(b_3) [W m(^{-3}) K(^{-1})]</th>
<th>Volumetric heat capacity of the solid phase, C(_s) [J m(^{-3}) K(^{-1})]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>-0.197</td>
<td>-0.962</td>
<td>2.521</td>
<td>2.013·10(^6)</td>
</tr>
<tr>
<td>2</td>
<td>1</td>
<td>0.206</td>
<td>0.393</td>
<td>1.534</td>
<td>1.648·10(^6)</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>0.281</td>
<td>0.451</td>
<td>1.534</td>
<td>2.251·10(^6)</td>
</tr>
</tbody>
</table>

Table 3. Solid mineral phases, chemical reactions, molar volume and molar mass of the solid mineral phases considered.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Reaction</th>
<th>Molar volume (cm(^3) mol(^{-1}))</th>
<th>Molar mass (g mol(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dolomite</td>
<td>(CaMg(CO(_3))_2 = Ca^{2+} + Mg^{2+} + 2CO_3^{2-})</td>
<td>64.12</td>
<td>184.34</td>
</tr>
<tr>
<td>Calcite</td>
<td>(CaCO_3 = Ca^{2+} + CO_3^{2-})</td>
<td>36.93</td>
<td>100.06</td>
</tr>
<tr>
<td>Aragonite</td>
<td>(CaCO_3 = Ca^{2+} + CO_3^{2-})</td>
<td>34.17</td>
<td>100.06</td>
</tr>
<tr>
<td>Anhydrite</td>
<td>(CaSO_4 = Ca^{2+} + SO_4^{2-})</td>
<td>46.00</td>
<td>154.09</td>
</tr>
<tr>
<td>Gypsum</td>
<td>(CaSO_4 \cdot 2H_2O = Ca^{2+} + SO_4^{2-} + 2H_2O)</td>
<td>74.56</td>
<td>172.08</td>
</tr>
</tbody>
</table>
### Table 4. Oxide states components of the solid phase and mineralogy for the three defined layers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>1</th>
<th>2</th>
<th>3</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Calcination loss (% of weight)</strong></td>
<td>40.90</td>
<td>38.33</td>
<td>35.97</td>
</tr>
<tr>
<td><strong>Oxide states components of the solid phase, X-Ray fluorescence (% of weight)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>6.43</td>
<td>1.73</td>
<td>2.98</td>
</tr>
<tr>
<td>CaO</td>
<td>27.15</td>
<td>46.00</td>
<td>45.67</td>
</tr>
<tr>
<td>Cl</td>
<td>0.10</td>
<td>0.09</td>
<td>0.05</td>
</tr>
<tr>
<td>Fe&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt;</td>
<td>1.84</td>
<td>0.48</td>
<td>0.76</td>
</tr>
<tr>
<td>K&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>1.45</td>
<td>0.31</td>
<td>0.48</td>
</tr>
<tr>
<td>MgO</td>
<td>2.53</td>
<td>2.06</td>
<td>1.99</td>
</tr>
<tr>
<td>MnO</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Na&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>0.40</td>
<td>0.20</td>
<td>0.18</td>
</tr>
<tr>
<td>P&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt;</td>
<td>0.10</td>
<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>SO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>0.17</td>
<td>2.94</td>
<td>0.95</td>
</tr>
<tr>
<td>SiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>18.65</td>
<td>7.71</td>
<td>10.82</td>
</tr>
<tr>
<td>TiO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>0.26</td>
<td>0.02</td>
<td>0.06</td>
</tr>
<tr>
<td><strong>Components of the solid phase, X-Ray fluorescence (ppm)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba</td>
<td>0.00</td>
<td>6.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Br</td>
<td>11.50</td>
<td>16.75</td>
<td>12.00</td>
</tr>
<tr>
<td>Cu</td>
<td>12.00</td>
<td>17.25</td>
<td>11.00</td>
</tr>
<tr>
<td>Ni</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>Pb</td>
<td>26.50</td>
<td>26.00</td>
<td>20.33</td>
</tr>
<tr>
<td>Rb</td>
<td>51.50</td>
<td>18.75</td>
<td>24.33</td>
</tr>
<tr>
<td>Sr</td>
<td>482.00</td>
<td>1193.25</td>
<td>1193.67</td>
</tr>
<tr>
<td>Zn</td>
<td>37.50</td>
<td>19.75</td>
<td>15.33</td>
</tr>
<tr>
<td>Zr</td>
<td>100.50</td>
<td>39.00</td>
<td>87.00</td>
</tr>
<tr>
<td><strong>Soil mineralogy reported by X-Ray diffractometry (% of the solid mineral phase)</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Calcite</td>
<td>67.2</td>
<td>80.2</td>
<td>83.1</td>
</tr>
<tr>
<td>Quartz</td>
<td>18.1</td>
<td>10.6</td>
<td>7.2</td>
</tr>
<tr>
<td>Gypsum</td>
<td>0</td>
<td>9.2</td>
<td>4.1</td>
</tr>
<tr>
<td>Illite</td>
<td>9.7</td>
<td>0</td>
<td>2.9</td>
</tr>
<tr>
<td>Dolomite</td>
<td>5</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Albite</td>
<td>0</td>
<td>0</td>
<td>1.2</td>
</tr>
<tr>
<td>Orthoclase</td>
<td>0</td>
<td>0</td>
<td>1.6</td>
</tr>
<tr>
<td><strong>Cation exchange capacity and organic matter content</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CEC (meq·100g&lt;sup&gt;-1&lt;/sup&gt;)</td>
<td>12.4</td>
<td>4.7</td>
<td>5.8</td>
</tr>
<tr>
<td>OM (% C of dry soil weight)</td>
<td>0.8</td>
<td>0.21</td>
<td>0.12</td>
</tr>
<tr>
<td>OM (% oxidable OM)</td>
<td>1.38</td>
<td>0.36</td>
<td>0.22</td>
</tr>
</tbody>
</table>

### Table 5. Physico-chemical characteristics and major ion contents for irrigation water during the 2011-2012 period.

<table>
<thead>
<tr>
<th></th>
<th>Jan</th>
<th>Feb</th>
<th>Mar</th>
<th>Apr</th>
<th>May</th>
<th>Jun</th>
<th>Jul</th>
<th>Aug</th>
<th>Sept</th>
<th>Oct</th>
<th>Nov</th>
<th>Dec</th>
<th>**</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>pH</strong></td>
<td>7.90</td>
<td>7.95</td>
<td>8.10</td>
<td>7.80</td>
<td>7.90</td>
<td>8.11</td>
<td>8.28</td>
<td>8.60</td>
<td>8.30</td>
<td>7.70</td>
<td>7.70</td>
<td>7.10</td>
<td>7.9 (0.4)</td>
</tr>
<tr>
<td></td>
<td>12.0</td>
<td>11.3</td>
<td>16.2</td>
<td>21.7</td>
<td>24.9</td>
<td>30.3</td>
<td>23.8</td>
<td>17.9</td>
<td>10.1</td>
<td>15.9</td>
<td>9.4</td>
<td></td>
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<td>----------</td>
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<td></td>
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<tr>
<td>T (°C)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Eh (mV)</td>
<td>219.8</td>
<td>189.8</td>
<td>209.7</td>
<td>158.4</td>
<td>189.2</td>
<td>349.3</td>
<td>164.8</td>
<td>148.5</td>
<td>161.2</td>
<td>220.4</td>
<td>221.1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>EC (µS cm⁻¹)</td>
<td>2090</td>
<td>1755</td>
<td>1677</td>
<td>2070</td>
<td>2160</td>
<td>1822</td>
<td>1890</td>
<td>1277</td>
<td>1707</td>
<td>1809</td>
<td>1132</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Hardness (mg CaCO₃ L⁻¹)</td>
<td>396.5</td>
<td>327.3</td>
<td>303.9</td>
<td>368.6</td>
<td>434.7</td>
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- : not available
** : average (standard deviation)
Highlights of the research paper entitled “Reactive transport modelling to infer changes in soil hydraulic properties induced by non-conventional water irrigation”:

- Non-isothermal multicomponent reactive transport with spatio-temporal variability of soil physical and hydraulic properties
- Long-term impacts of non-conventional water irrigation on soil
- Root zone control on partial pressure of CO$_2$ and precipitation/dissolution of calcite
- User-friendly numerical tool for water management, irrigation strategies and water policy makers.