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## Geochemical modeling of the system "Water-Soil-Plant Case study: Crau south France

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#### Abstract

Global changes (urban spread and climate change) make necessary to integrate data and build indicators that allow stakeholders to predict territories evolution. We propose a model for the water quality evaluation in a « grassland – soil – water » system, taking into account evaporation,  $CO_2$  geochemical role, nutrient uptake by plants and interactions with soil minerals. Crop model and geochemical model are interfaced. Historical data collected since 1960 show the evolution of the chemical composition of hay. Presently, irrigation waters are over-saturated with respect to calcite and under-saturated with respect to gypsum.

Keywords: Geochemical modeling, Global changes, Permanent grassland

### 1. Introduction

In a context of global changes (urban sprawl and climate change), the risks of degradation of natural and agricultural environments are increasing. Climate change may positively or negatively impact the services provided by ecosystems on which our social systems depend (Trolard et al., 2013). And to ensure the resilience of a territory deal with these changes requires from the concepts of limited space, scarce resources (especially soil and water) and integrate information that characterize the spatio-temporal trajectories of ecosystems to test possible development scenarios. Irrigated systems can regulate the local climate, water resources and food security. The proposed model integrates concepts from agronomy, climatology, geochemistry and soil science and is tested on a demo territory: the Crau.

### 2. Study area, material and methods

The Crau is a territory of 600 km<sup>2</sup> limited in the north by the Alpilles, the Rhône in the west, the Mediterranean Sea in the South and the Etang de Berre in the east. The natural landscape is a semi-arid pebbly steppe, the Coussoul, which since the 16th century has been transformed into part (12,500 ha) by gravity irrigation of grasslands with water taken from the Durance River. In addition to providing water to plants, irrigation has also contributed to the thickening of grassland soils by contribution of silt deposit. This agro-hydro-system provides products in high value: hay Crau (Certified Origin Product, COP), lamb from Sisteron (IGP) and Merino of Arles (IGP). The Crau hay is harvested in three sections each year in May, June - July and August - September. In addition, irrigation recharges groundwater for 75% of the 550 million m<sup>3</sup> of the aquifer. This system is now threatened by both urbanization of farmland and decreasing water availability for irrigation, estimated at 30% by

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2030 according to the median scenario. To build the model, it is necessary to consider all of the reaction factors of the system. Thus it is necessary to acquire data on: (1) the chemical composition of irrigation water and groundwater; (2) soil mineralogy; (3) the nature of the fertilizer brought on grassland soils; (4) the quantities of chemicals exported during the various cuts of hay, and (5) the effect of winter grazing of meadows by sheep passage.

The data is the result of sampling field campaigns (irrigation water, botanical composition of hay, mineralogy and chemical composition of soil and fertilizer), or the collection of historical chronicles (hay chemical analysis, groundwater) or simulation of cultural model (STICS, Brisson et al., 1998).

Analyses of irrigation water are carried out every 15 days in 6 points of channels distributed on the territory of the Crau (Canal de Craponne, Congress Canal, Canal of Craponne branch of Istres, Langlade Canal, and Ditch Rageyrol Canal de Craponne (before Arles) Arles branch. The measures in situ are pH, electrical conductivity (EC  $\mu$ S/cm 25°C) and temperature (t °C), and then samples (n=16) were filtered at 0.45  $\mu$ m in the field. The laboratory measurements are alkalinity (meq/l), major anions (F<sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>) by ion chromatography, major cations (K<sup>+</sup>, Ca<sup>2+</sup>, Na<sup>+</sup>, Mg<sup>2+</sup>) by atomic absorption and H<sub>4</sub>SiO<sub>4</sub> by colorimeter. Monitoring of species composition for each cut is made by recognition of species and determination of the weight percentages of the species (fresh weight / dry weight). Analyses of major mineral elements of the main families of plants were performed by ICP using dry residues on the three cuts of 2015. A database of the mineral composition of the hay since 1960 has been built from slips analysis conducted for the Committee of Crau hay. The chemical composition of groundwater analysis is extracted from the ADES database (http://www.ades.eaufrance.fr/) from several points distributed on the groundwater area of the Crau (Fig. 1).



Fig. 1. Selected points of the chemical composition analysis of groundwater in Crau area from ADES database.

Soil samples of meadows and coussouls at the depth 15, 30 and 50 cm in the Crau area is made, analyses are not yet performed. On the other hand, soil data were obtained from scanning the soil map of Arles (Bouteyre and Duclos, 1994) by considering not only the limits of the soil units, but also the precise geographical referencing of soil survey, limits of different horizons and soil analyses (pH, particle size, active limestone, cation-exchange capacity etc.) at each point extracted from the soil map. A priori information of objects and extension of soil properties in different spatial horizons were spatialized on the base of DSI algorithm (Discrete Smooth Interpolation).

Representative samples of fertilizers used in Crau were also collected from the Crau hay Committee. On these samples X-ray patterns and multi-elemental analysis by ICP were made. The fertilizer used on Crau is phosphopotassique which is composed of four soluble minerals: calcium dihydrogen phosphate monohydrate Ca(H<sub>2</sub>PO<sub>4</sub>)<sub>2</sub>.H<sub>2</sub>O, gypsum CaSO<sub>4</sub>.2H<sub>2</sub>O, the arcanite K<sub>2</sub>SO<sub>4</sub> and sylvite KCl.

The construction of the conceptual model is based on the interface between the existing models, a model of culture and a geochemical model. The culture model chosen is the STICS model, which takes into account climate, soil characteristics, and the type of culture. In modeling output, STICS calculates the evapotranspiration of the crop, the amount of water that drains into the deep horizons of the soil and the amount of biomass produced. The geochemical model is chosen PHREEQC (Parkhurst and Appelo, 1999). Calculates the degree of saturation of the solids mineral constituents solutions (calcite, gypsum etc.).

#### 3. Global Change analysis

Global change scenarios were analyzed in Crau area for 2025-2035 as a future period by Olioso et al., 2013 and Trolard et al., 2016. Some of key findings are: (i) temperature has increased since 1980 with a rate of  $0.5^{\circ}$ C each 10 years; this trend continues in the mid-term horizon (*i.e.* 2025-2030); (ii) annual precipitation has not changed significantly since the beginning of the 19<sup>th</sup> century; (iii) reference evapotranspiration *ETo*, computed using the FAO56-PM method has increased in the recent past and will increase significantly in the near future (around 1.5 - 2 mm/year); (iv) irrigated grassland area will decrease by 6 to 11 % in 2030; because of replacement of irrigated grasslands by other land uses, specially urban areas, which jeopardize the sustainability of groundwater and permanent grassland.

#### 4. Results and discussion

The main processes that change the chemical composition of water in the system "irrigation water - meadow - soil - groundwater" are: evaporation, dissolution or departure of CO2, the reactions with the plant, reactions with soil and surface formations through to the water transfer and fertilizer inputs (Fig. 2).

The effect of these processes on a set of partial data has been tested (Bourrié et al., 2013). The proposed conceptual model is based mainly on the interface between STICS and PHREEQC, whose input and output data are detailed in Fig. 3.



Fig. 2. Sequence of processes that change the chemical composition of water through its transfer in soil profile

Fig. 3. Interface between crop model (STICS) and geochemical model (PHREEQC) to simulate the variation of chemical composition of water starting from irrigation water arriving to groundwater in the system "soil – water- plant".

In this model, STICS calculates the biomass produced from the climate data, crop management and the terms of the water balance. This allows to estimate the water concentration factor between evaporation of irrigation water and water that seeps into the surface horizon of the soil. PHREEQC simulation is then used to calculate changes in the quality of the water during its passage into the ground, the amounts of dissolved or precipitated mine rals, the absorption of minerals by plants and dissolution of mineral fertilizers.

In the table 1, results showed that irrigation water is supersaturated with respect to the calcite and significantly under saturated with respect to gypsum. While this index can be positive or negative for groundwater indicating the super-saturation and under-saturation. The decrease of the saturation index in respect to calcite of the groundwater shows that the calcite precipitates in the soil before reaching in the groundwater.

Table 1:Some results of saturation index of irrigation water for Craponne channel and groundwater (point 6) with respect to the calcite and gypsum.

Date	ate Irrigation Water		Groundwater	Water	ndwater
	SI Calcite	SI Gypsum	SI Calcite SI Gypsum	SI Gypsum	SI Gypsum
31/07/2015	0.55	-2.00	0.0513 -1.2231	-2.00	-1.2231
14/08/2015	0.68	-1.81	0.1626 -1.2066	-1.81	-1.2066
28/08/2015	0.65	-1.98	0.0392 -1.2595	-1.98	-1.2595
07/09/2015	0.61	-1.81	-0.0209 -1.2675	-1.81	-1.2675
26/09/2015	0.60	-1.83	-0.0184 -1.3659	-1.83	-1.3659

The X-ray diffraction shows that the fertilizers used in Crau contain four main minerals: calcium phosphate  $Ca(H_2PO4)_2$ . $H_2O$ , gypsum CaSO<sub>4</sub>.2H2O, the arcanite  $K_2SO_4$  and sylvite KCl. It is observed that these fertilizers contain no silicate component.

The floristic composition of Crau hay in the first cut (in May) is dominated by grasses, while the third cut in August is richer in legumes. The analytical study of chronic 1960-2013 of the mineral composition of hay shows, according to statistical tests, the dry matter content remained constant since 1960, the third cut is more mineralized than the second and the first (Fig. 4). It is the same for N and P, but not for K. The results of this historical database analysis were published in Ajaf (Mohammed et al., 2016), which showed the role of irrigation system to maintain the Crau area resilience.



Fig. 4. Average of total mineral content with the standard deviation of hay (permanent grassland in Crau area) for three cuts per year for the period 1960-2013. For all of this period, the sequence of total mineral content is Cut3>Cut2>Cut1.

#### 5. Conclusion

The used irrigation water in Crau area are supersaturated with respect to the calcite and under-saturated with respect to gypsum. This counteracts the natural tendency of soils to acidification in temperate climates. The dry matter content of Crau hay remained substantially constant from 35 years, but the difference in mineral levels between the 3 cuts are stable. This affects the water quality variations in the three cuts, as result the inputs into the groundwater. The model coupled culture model / geochemical model allows to establish these variations. His calibrating opens up the prospect of using it to simulate scenarios of climate change and land use.

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# Assessment of groundwater recharge and the hydraulic relationship between the Quaternary sedimentary aquifers in the Thach That- Dan Phuong locality, Hanoi by isotopes techniques

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### Abstract

The Red River delta is covered by Quaternary sediments with thickness varying from 40 meters inland to 200 meters in the coastal area. Transgression and regression in Quaternary period have led to the formation of aquitards and aquifers which play a significant role for water supply to the population in the whole of the delta and in Hanoi, the capital of Vet Nam. This study aims at to assess the groundwater recharge and the relationship between the Quaternary (Holocene and Pleistocene) aquifers in the Thach That-Dan Phuong locality based on the geological structure of the study region, on the water stable isotopic composition ( $\delta^2$ H,  $\delta^{18}$ O) and on the result of the groundwater dating by the Tritium (<sup>3</sup>H) method. To our understanding, such a kind of study was the first time conducted in Viet Nam.

Keywords: Ground water recharge, Stable isotopes, Ground water dating, Red river delta

### 1. Introduction

The study area is located in Western Hanoi and it includes 3 districts: Thach That, PhucTho and Dan Phuong. In frame work of VietAs project, 5 well fields (Phu Kim, Phung Thuong, Van Coc, K-transect and H-transect) have been drilled along a transect directed from the edge of the mountainous Thach That to the Red River (Dan Phuong) (Fig. 1).



Fig 1. A map of the study area

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