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# Geochemical Methods to Assess Agriculture Sustainability

*Trolard Fabienne, Kaniewski David and Bourrié Guilhem*

## Abstract

Facing global changes and the challenge of food security, scientists are being questioned by decision-makers and stakeholders on the sustainability of agro-systems. The main difficulty in dealing with this question is to obtain enough data over long periods of time. Monitoring slow drifts and weak noises is needed to forecast tipping points that can jeopardize the present steady state. High-resolution datations by radiocarbon coupled with detailed palynological determinations in sediments, historical archives on yields and crop quality, and high-frequency field in situ measurements give information on climatic changes from multi-secular to seasonal and hourly time scales. In the long term, climatic forcing dominates agriculture performance, at that time only organic agriculture, with oscillations between prosperity and misery driven by climate and intermediated by civilization flourishing and collapsing; in the medium term, in modern agriculture, irrigation provides a provisional buffering effect on yield and crop quality despite present warming; in the short term, either under non-fertilized forested ecosystem or intensive rice cropping, the same patterns are evidenced and point to the importance of soil microflora shifting from aerobiosis to anaerobiosis. In all cases, geochemistry offers appropriate tools to decipher the climate-soil-agriculture complex interplay.

**Keywords:** geochemistry, sustainability, agro-systems, isotopes, in situ monitoring

## 1. Introduction

In the world, agriculture developed in the last 10,000 years, and most plant and animal species of interest to humans have been domesticated since. Today's agriculture still relies almost exclusively on these same species, and a large part of economy is based upon the production and trade of only less than 10% of these domesticated plant and animal species [1].

Facing global changes and the challenge of food security, scientists are being questioned by decision-makers and stakeholders in the territories on the sustainability of agro-systems. Valuable information on this topic and recommendations can be derived from the study of practices and processes related to agriculture over time.

All farming systems implemented since 10,000 years on the Earth are still present today. But is it reasonable to consider that the most efficient systems in terms of productivity can be the most sustainable? How can we approach and explore the notion of sustainability in agriculture? In current agricultural practices, is it possible to distinguish between those that could be considered sustainable and those that would not be? Sustainability means maintenance of steady-state conditions over long periods. The main difficulty in dealing with these questions is to obtain

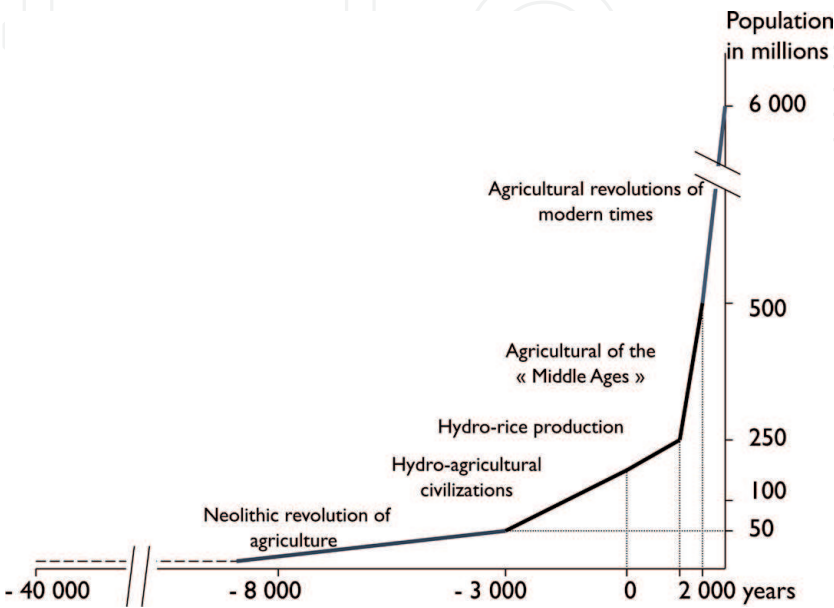
enough data over long periods of time. The ability to detect slow drifts and weak noises is needed to forecast tipping points that can eventually modify or jeopardize the present steady state.

In the present chapter, geochemical data are processed to gain this information. In fact, the interest of geochemistry is to produce scalar-type information that obeys the universal laws of chemistry, whatever the place and time in the Earth's surface conditions. It offers remarkably robust concepts and models that are valid for several orders of magnitude on space and/or time scales (e.g., from nanometer to megameter and from picosecond to millennium). Thus, we have used it in the study of different agro-systems and exploring long-time (up to 1000 years), medium-time (around 60 years), and short-time (1 hour to 3–4 months) phenomena.

## 2. Short historical evolution of agriculture

Agriculture appeared almost concomitantly in the Middle East, particularly in the Euphrates Valley, in Central America, and in Asia. With the global warming ending the last quaternary ice age, agriculture spread to Europe, West Africa and South America, and then North America and Oceania. From a historical perspective, we can observe (**Figure 1**), firstly, that the development of agrarian systems is directly linked to the growth of human population and, secondly, that each positive inflection of the curve corresponds to significant improvements and innovations in agricultural practices.

During the evolution of agricultural practices, we distinguish a first period from less than –10,000 years to 1850, called organic agriculture, in which progresses rested mainly on the improvement of the use of internal energy of the agriculture system. It thus starts with manual farming where only the farmer's labor force counts. Then the lightly hitched agriculture appears in which the animal force is introduced but with animals not specifically dedicated to work in the fields (soil tillage) and, finally, the heavily hitched agriculture, with animals selected for their physical strength, in which the farmers could maintain them during winter, because they became able to stock a stable surplus of fodder grown during the summer season. In the middle of the nineteenth century, with organic farming, a farmer could work a maximum of 5 ha with a yield remaining below 50 quintals per hectare.



**Figure 1.**  
*The development of agrarian systems is linked to the growth of the human population (from [1]).*

The second period, called mineral agriculture, runs from 1860 to today. It is marked by the increased use of energy external to the agriculture system, with the steam engine for the heavily hitched agriculture of the end of the nineteenth century and especially with oil that allowed the development of mechanization, irrigation, and production of fertilizers and xenobiotics and with genetic improvement. Thus, for the most efficient farming systems in the world, a farmer is able to work more than 150 ha and to produce over 20,000 quintals per year. In the present world, however, all types of agriculture still coexist.

### 3. Investigations of the period from 4500 years BP to today

To illustrate the long-time investigations, the period from 4500 years to today has been explored by the help of radiocarbon dating and palynological determinations.

#### 3.1 Materials and methods

For isotopic and palynological characterizations, soil and/or sediment cores were drilled and sampled as continuously as possible. One core was drilled on the delta of Mirna River (Gulf of Venice) in coastal Croatia continuously at 720 cm depth [2].

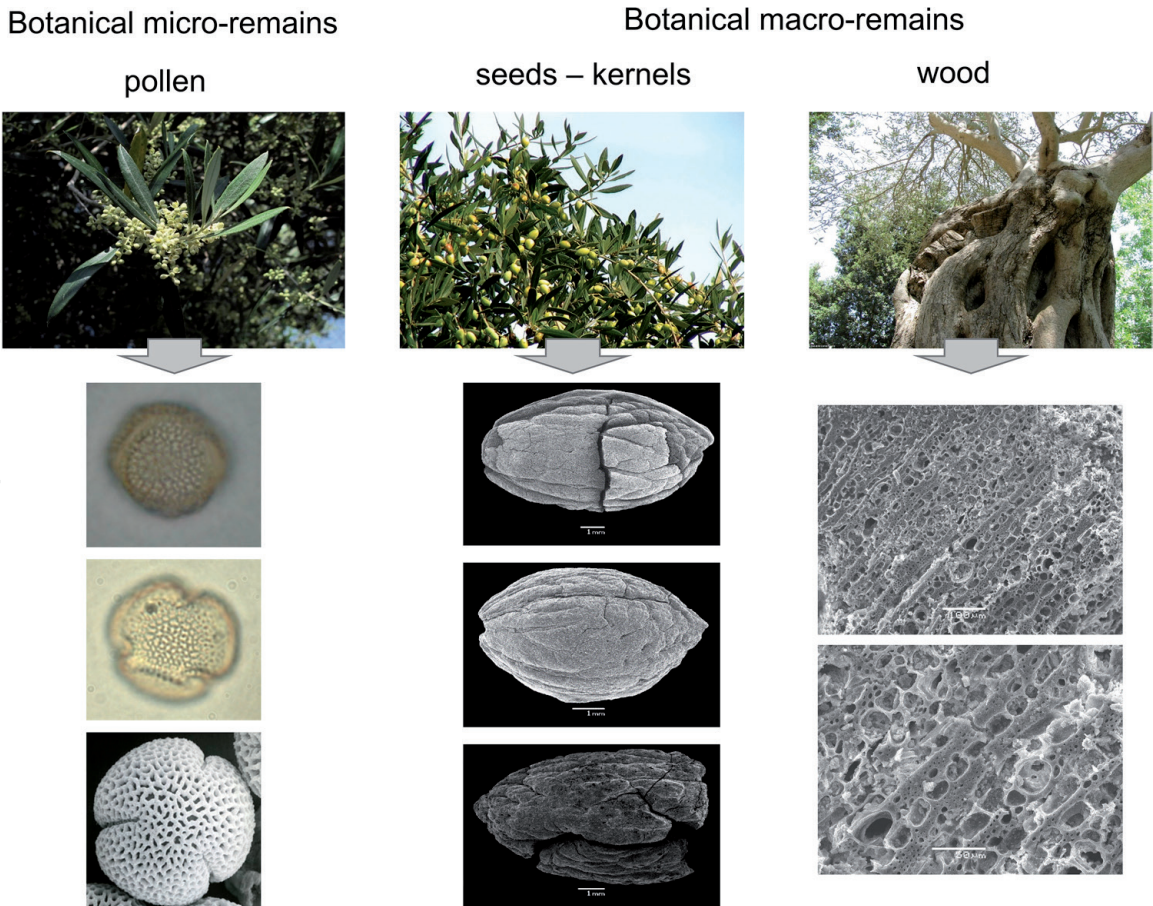
The chronology of the core is based on accelerator mass spectrometry  $^{14}\text{C}$  dating of short-lived terrestrial samples (seeds and small leaves). No botanical macro-remains were found in the middle core, but the use of marine shells (involving the radiocarbon-dating reservoir effect) and bulk samples (involving potential contaminants) was strictly avoided in order to minimize chronological biases in the age-depth model. Dated samples were calibrated (1 sigma ( $\sigma$ ) and 2 $\sigma$  calibrations, respectively, 68 and 95% confidence interval) using CALIB REV 7.0.4 [3]. The average chronological resolution for the core stratigraphy is 7 years per  $\text{cm}^{-1}$  (1.43 mm per year $^{-1}$ ). **Figure 2** shows some examples of micro-botanical remains like pollen and macro-botanical remains like seeds, kernels, and wood pieces.

#### 3.2 Results and discussion

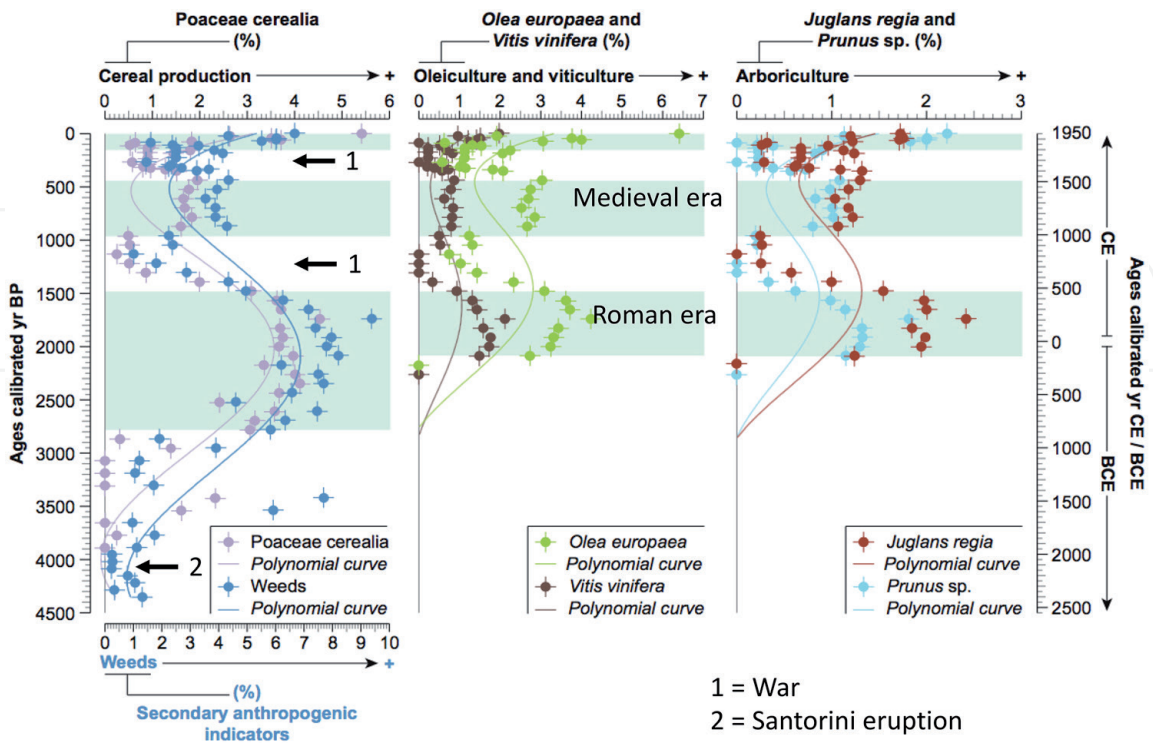
Since the rise of agriculturally based societies in the Mediterranean, and concomitant population growth in coastal areas, humans have gradually generated irreversible impacts on natural biotic resources. The introduction of agricultural practices and human-induced fires in northern Istria is dated to 5000 BP [4]. The cultivated species were mostly cereals (*Secale*, *Hordeum*, *Avena*, and *Triticum*), the same genus found in the Mirna region (**Figure 3**). The succession of agropastoral activities can be determined here, with cereals (about 3000 years BP), olive growing, viticulture, and orchards (about 2000 years BP) (**Figure 3**). Optima appear in Medieval and Roman eras.

The periodicity of agropastoral activities was investigated using a wavelet analysis, highlighting the long-term trends versus storm surges with a 950-year period [2]. This suggests that low storm activity and enhanced freshwater inputs in the delta have favored arboriculture and agriculture. Conversely, periods of higher storm surges, which generated the intrusion of saline water into the freshwater-fed plains and into the groundwater table, led to severe agricultural losses. The comparison of the two signals, fitted to a 950-year filter, shows that, at a millennial time scale, anthropogenic activities and storminess are in antiphase [2]. In addition, we can observe that the most prosperous periods of agropastoral activities correspond to the optima of the Roman civilization and the Medieval era. The abandonment of

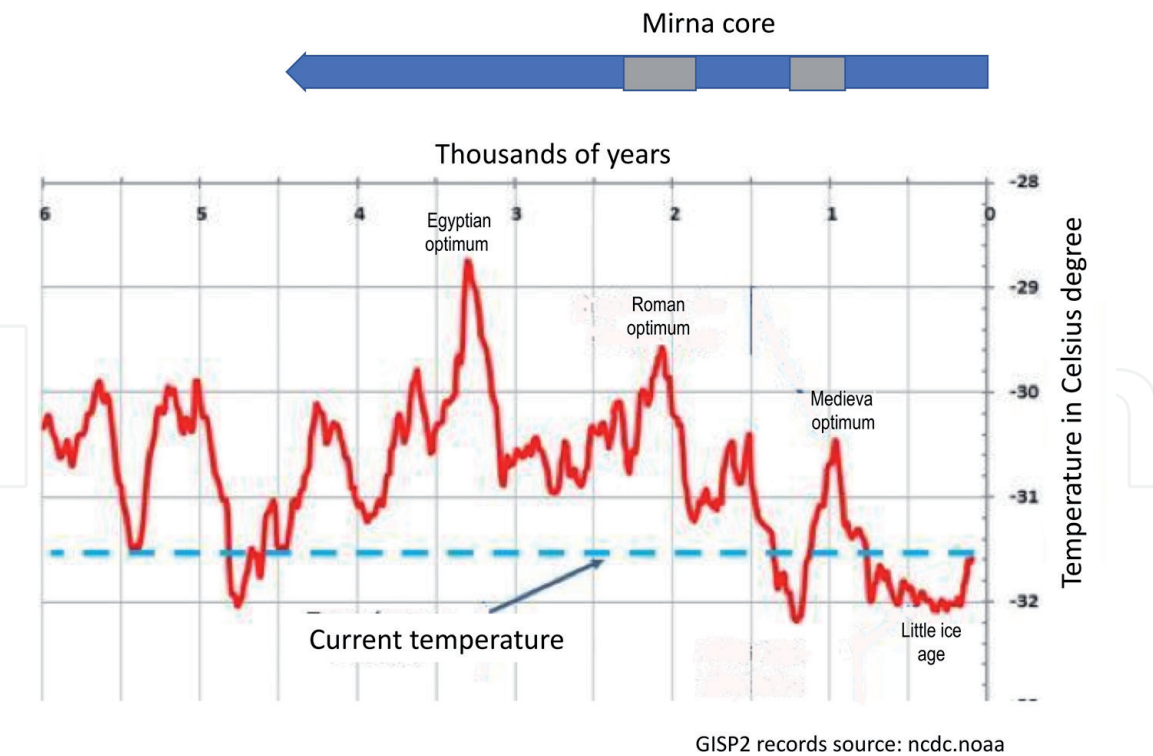




**Figure 2.**  
Examples of botanical micro- and macro-remains observed by optical microscopy or by scanning electronic microscopy.



**Figure 3.**  
Reconstruction of agropastoral activities from Mirna region during 4500 years with the help of isotopic  $^{14}\text{C}$  datation and palynological determinations (modified from [2]).



**Figure 4.**  
*Position of intensive paleo-agropastoral activities (in gray) from Mirna core placed on the 6000 years BP temperature variation reconstructed from ice cores drilled in Central Greenland. For the detail of datation of Mirna's core, see Figure 3.*

all agricultural activities around 1650 years BC can be ascribed to the consequences of the major volcanic eruption of Santorini. The ends of the prosperous periods can be related to the invasions of the northern peoples (the so-called Dark Ages) and war periods. A maximum is indeed observed at 3500 BP, followed by a minimum at 3200 BP. This latter minimum can be ascribed to the collapse of Bronze Age civilization near 1177 BC = 3127 BP [5].

By comparison with the curve of temperature over 6000 years BP building up from ice cores drilled in the center of Greenland, the results show that the agropastoral optima of Mirna's core correspond also to thermal optima (Figure 4).

#### 4. Investigations of medium-time period (60 years) in intensive agriculture

For the medium-time investigations, the consequences of intensive agriculture of the last 60 years have been studied in the irrigated grasslands in Crau's area (hay production with COP label) in southeast of France.

##### 4.1 Materials and methods

The Crau's area covers up to 600 km<sup>2</sup> at the south of Alpilles mountains. A part of the territory is occupied by a natural semiarid steppe, named "coussoul," and, in another part, by irrigated grasslands and orchards. Thanks to Adam de Craponne, a sixteenth-century engineer, a first irrigation canal was built up, and the irrigation network extended until the nineteenth century. The network supports the production of the Crau hay with a protected designation of origin, which is exported all over the world to feed racehorses, the Sisteron lamb, and the Arles Merinos sheep, which are

produced with a label of geographical indication of origin. Irrigated grassland production is regulated by three cuts of hay (i.e., cut 1, cut 2, and cut 3) and sheep grazing in the field during the winter. The gravity irrigation with water of Durance river secures the renewal, up to 70%, of the groundwaters in the aquifer, which supply the water consumption of 280,000 inhabitants and industrial activities of Marseille harbor.

A database concerning hay's mineral content, dry matter, and climate dynamics was statistically analyzed [6].

In addition, the geochemical variations of water composition during its pathway from irrigation channel till the phreatic aquifer were recorded and modeled. For modeling with PHREEQC software [7], we have defined a priori the processes, which can impact water chemistry, such as evaporation, dissolution, precipitation, and exchange with the plant [8].

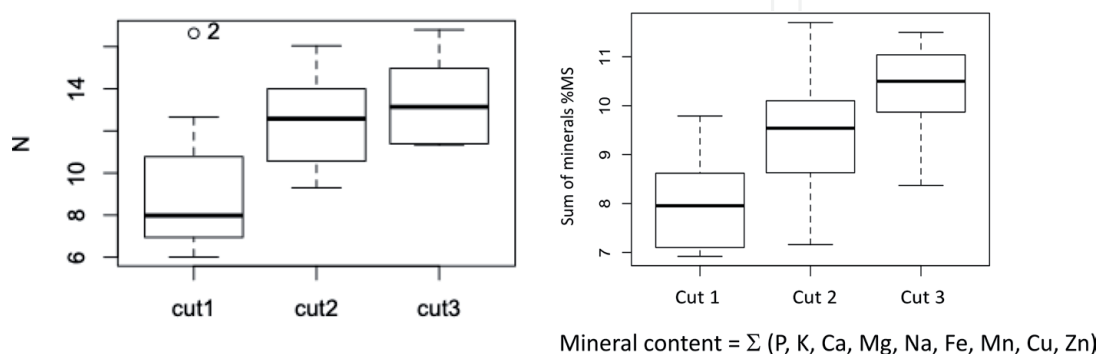
## 4.2 Results and discussion

Nitrogen and phosphorus contents in hay increase from cut 1 to cut 3, whereas the potassium decreases significantly in cut 3. These results are explained by seasonal changes in the floristic composition of the hay [9]. But globally the total inorganic content in Crau hay increases over time from cut 1 to cut 3, and this order has remained constant since 1960 (**Figure 5**).

Statistically, these results show a steady state of the production, which has been maintained, both in quantity and quality despite an average temperature increase of 1.9°C since 1960 [10].

For each chemical element measured in the waters, a model of fluxes is built up [6]. Activities and saturation indexes ( $SI = \log Q - \log K$ ) were computed by using PHREEQC [7], using phreeqc.dat database: activity coefficients were computed with Debye-Hückel extended law, as ionic strength is small enough (*ca.* 0.01 M). The reaction of reduction of nitrate into ammonium was removed from the database as it is biologically mediated, and N(III) and N(V) were considered as distinct elements separated by a kinetic barrier.

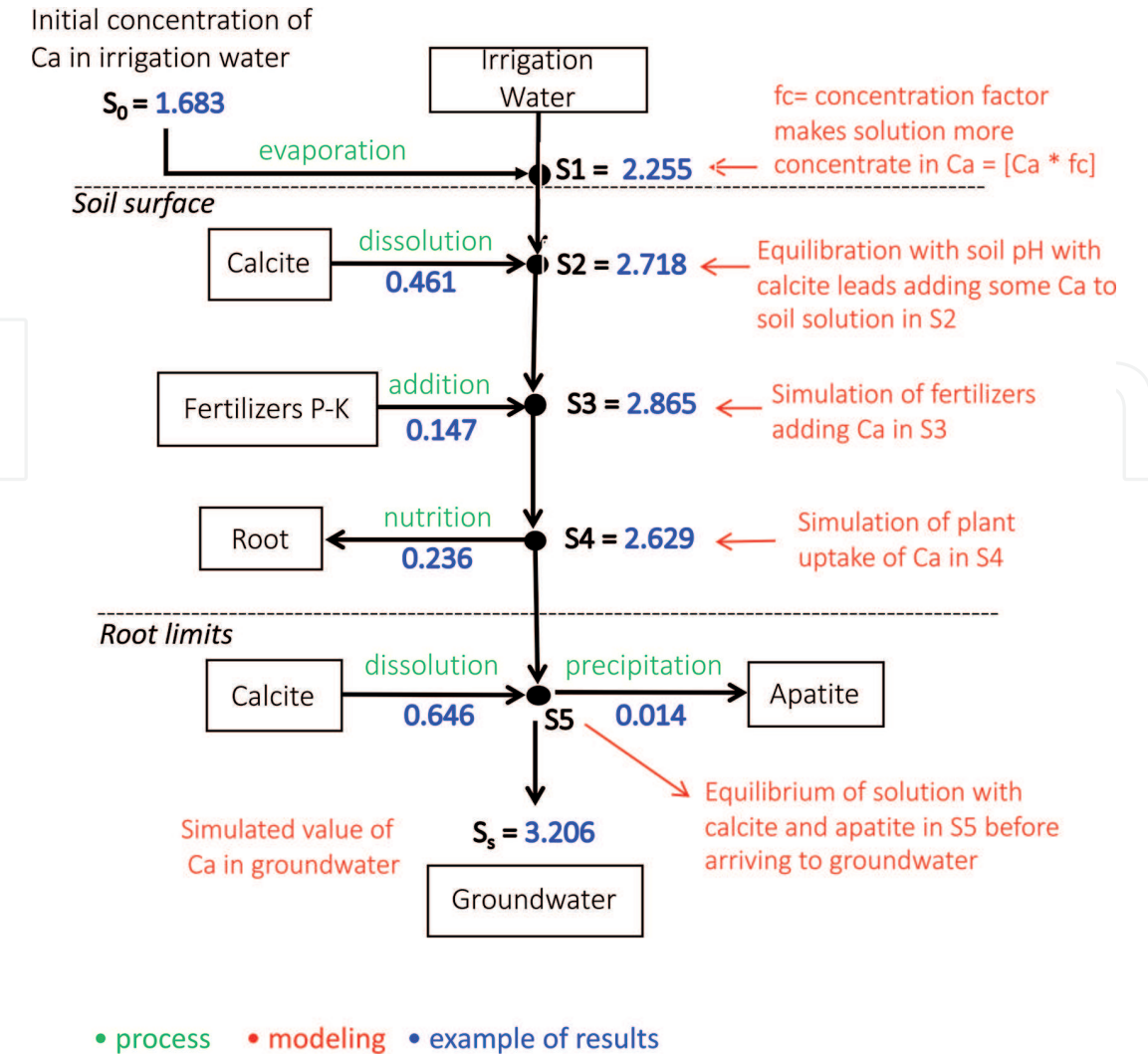
On **Figure 6a** models for calcium are presented. At each step, where chemistry of water changes, the soil solution is computed. The time step is 2–3 months corresponding to the duration of hay growth for one cut. Thus, between solution S1 and S2, the evaporation of the water induced a loss of water and a concentration of the elements. Then, from S2 to S3, the  $p\text{CO}_2$  (partial pressure of  $\text{CO}_2$ ) of the soil, which is 30–100 times larger than in the outer atmosphere, results in acidification of solution and calcite dissolution. From S3 to S4, the model



**Figure 5.**

Nitrogen and total inorganic element contents in hay as function of the cut (from [9]). The mineral content of the hay is defined, per unit of dry matter expressed in percentage, by the sum of the content of the following elements: phosphorus, potassium, calcium, magnesium, sodium, iron, manganese, copper, and zinc.





**Figure 6.**  
 (a) The pathway of calculation of fluxes of Ca during soil solution changes from surface irrigation water to groundwater; (b) for the 4 years of monitoring of water in Crau's area, comparison between measured and computed values of Na, Ca, Mg, C, K, S, and Cl for each cut (from [6]).

simulated the fertilizer impact on the soil solution. Inorganic fertilizers (P, K) consist of gypsum  $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ , calcium dihydrogenphosphate  $\text{Ca}(\text{H}_2\text{PO}_4) \cdot 2\text{H}_2\text{O}$ , arcanite  $\text{K}_2\text{SO}_4$ , and sylvite  $\text{KCl}$ . The last three minerals were introduced in the database, with their thermodynamic properties [7C]. Dissolution of fertilizers was simulated by PHREEQC as the dissolution of a mixture of the above minerals. From S4 to S5, the model simulated the element uptake by plants. P absorption by plants was simulated as the removal of calcium phosphate from the solution, S absorption by plants as the removal of gypsum, and calcium being absorbed in excess to the sum of P and S, the remaining Ca absorption was simulated as a CaO removal from the solution; Na, K, and Mg absorption by plants were simulated respectively as the removal of  $\text{Na}_2\text{O}$ ,  $\text{K}_2\text{O}$ , and  $\text{MgO}$  from the solution. Removal of elements by plant is computed by PHREEQC as a dissolution with negative coefficients, in the same way as evaporation is computed with a negative coefficient for water. To avoid transient negative concentrations, fertilizer dissolution was simulated before absorption by plants. In point S5, the soil solution is reequilibrated with the minerals of the aquifer.

The fluxes have been computed for the three cuts per year during 4 years of monitoring the water quality both in irrigation network and in groundwater (Figure 6b). All simulations are computed at the average temperature of



groundwater. With a  $R^2$  larger than 0.96, regardless of the year or the cut, or the chemical element, the proposed model simulates very well the transformation of irrigation water into groundwater, describing for these 4 years a steady state.

Thus, our findings suggest that irrigation, both with the water inputs and quality of water, have played a key role for the sustainability of hay production till 60 years.

## **5. Investigations of short time in agro- and ecosystems**

The short time (1 hour intervals) of processes in agro- and ecosystems were recorded by in situ monitoring both of solid and water in a forested hydromorphic soil and in a paddy field. In both systems, the geochemistry of iron is marked by strong interactions between the solid minerals and the soil solution when oxidoreduction phenomena occurred [11, 12].

### **5.1 Materials and methods**

With the progress of in situ instruments and sensors developed for spatial research and Mars exploration, a miniaturized Mössbauer spectrometer, Mimos II, was built up [13, 14]. The signal emitted by the source of the spectrometer is recorded using reflection-based geometry, which is not influenced by the thickness of the sample, unlike conventional transmission geometry [15]. Mimos II was placed in a tube, in the soil. Mössbauer spectra were recorded in a nondestructive way through windows at different depths till 1.20 m depth. Periodically the instrument is moved back to fixed positions that allow us to monitor the changes of iron mineralogy as a function of time [15].

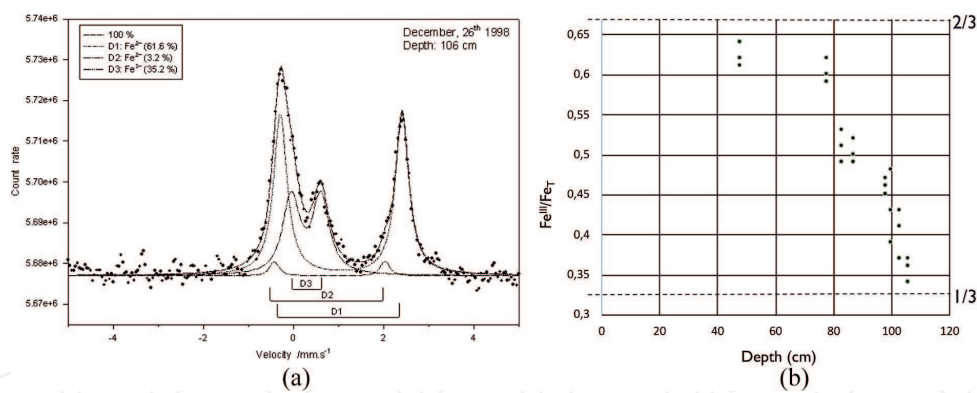
The progress of in situ instrumentation also concerns the monitoring of water quality thanks to progress in the oceanographic research. Such a probe was used to monitor soil water in Brittany in the Fougères forest and in Camargue paddy field. The pH, redox potential, temperature, and electrical conductivity were hourly measured, and data were stored in the probe and collected every fortnight.

### **5.2 Results and discussion**

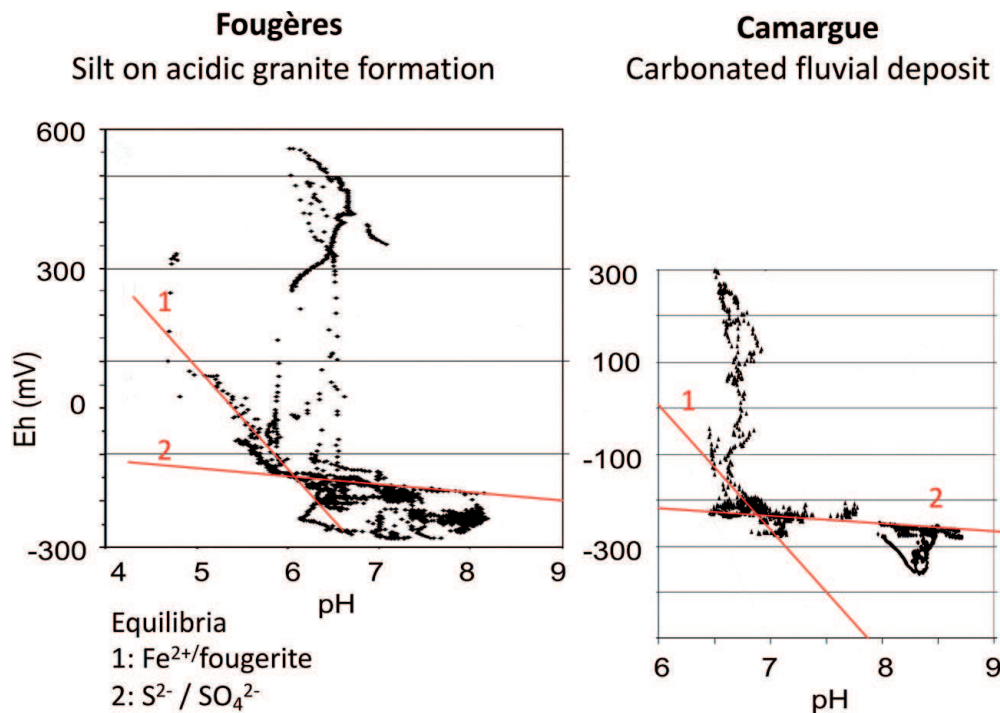
**Figure 7a** shows a typical Mössbauer spectrum obtained in the forested area, characterizing the fougérite mineral, which is a mixed hydroxide of Fe(II) and Fe(III) from green rust family [16, 17]. The points are the measures recorded by the instrument, and the lines are obtained by fitting Lorentzian functions to the signal. Thus the spectrum shows two doublets D1 and D2 characterizing the crystal environment of Fe(II) and one doublet D3 characterizing the crystal environment of Fe(III) in the mineral structure.

About 30 spectra were obtained during one hydrological year (i.e., between October 1998 and September 1999), and the variations of the ratio of Fe(III) to total iron are reported as a function of depth (**Figure 7b**). At a given depth, it changes in time, with fluctuations of the water table and anaerobiosis/aerobiosis conditions. When in reductive conditions, the signal of fougérite appears in less than 1 week [15].

Both at Fougères and in Camargue, plots of Eh-pH diagrams (**Figure 8**) show fast and large variations in short time in a quasi-identical range of variations, though soils are largely different, i.e., acidic in Brittany and carbonated in



**Figure 7.**  
(a) Example of Mössbauer spectrum obtained in situ with Mimos II instrument; (b) variation of the  $Fe^{III}/Fe_{total}$  ratio of iron minerals as function of depth and time (from [15]).



**Figure 8.**  
Eh-pH variations in soil solution at Fougères and in Camargue recorded in situ with an oceanic probe. Each point is the average of sequence of 20 measurements recorded during 1 mn every hour.

Camargue. The observed measures both at Fougères and in Camargue show large variations covering the whole domain of existence of aqueous Fe(II) and Fe(III) oxides. The rH values calculated according to the following equation:

$$rH = Eh/0.029 + 2 \text{ pH} \tag{1}$$

vary in between 4 and 14.4 at Fougères and in between 4 and 5.5 during the irrigation period in the Camargue. These values are much smaller than 20, which is the upper limit admitted for reducing media [18]. The “loops” of fast evolution, in a few hours, toward oxidizing conditions (i.e., Eh up to 100 mV) with small variations of pH are explained by the infiltration of oxygen-rich rainwater and then a return to the redox state of the initial steady state.

The representation of the thermodynamic equilibria of Fe<sup>2+</sup>/fougerite and of S<sup>2-</sup>/SO<sub>4</sub><sup>2-</sup> is given by curve 1 and curve 2, respectively. The geochemical modeling shows that the principal controls of the water quality are exerted by Fe<sup>2+</sup> versus

green rust fougérite, when reduction is moderate, and sulfide versus sulfate equilibria, when reduction is high.

## 6. Conclusions

Agriculture evolving from organic to mineral farming since 10,000 years has greatly increased its performance and has capacity to feed humanity. Geochemistry combined with other disciplines, such as palynology, bioclimatology, mineralogy, etc., offers cutting edge methods to investigate both long-time, medium-time, and short-time processes in agro- and ecosystems.

The long-term investigations show that soils and sediments have recorded agropastoral activities and thus paleo-agriculture can be studied. The combination of global climatic events (temperature deduced from ice cores), storm activities, and relative sea level movements led to socioeconomic destabilization of the local society and impacted the sustainability of agriculture in these remote times. This has led to a renewal of historical studies, integrating the above cited disciplines and others, especially genomics with DNA analyses and identification of mutations, anthropology, and archeology. Emblematic events in the history of mankind were recently revisited: late Bronze Age collapse of civilization mentioned above [5], shedding light on the mysterious invasions of the “Peoples of the Sea,” and very recently the fall of the Roman Empire [19]: here too, e.g., isotope geochemistry ( $^{10}\text{Be}$ ) was used to reconstruct variations of solar irradiance. According to this study [19], climatic changes combined with apparition of three successive pandemics (first pest due to *Yersinia*, under emperor Justinian) are facilitated by commercial routes connecting tropical regions in Africa to the Mediterranean, from the Caspian Sea to Scotland. Eventually, economic (including monetary), political troubles, and migrations of peoples from Asian steppes to the West due to climatic change led to wars and the ultimate collapse of the Roman Empire. It appears then that multidisciplinary studies nowadays extensively use geochemistry not only to precise datation but to reconstruct climatic changes and migration routes.

In the present concern about climate change, it is important to stress that it is multifactorial and such studies necessitate decades of cooperation. They point too to the factors that increase the resilience of societies toward external forcings and help to detect tipping points and to build scenarios that can be integrated in decision support systems [20].

Medium-term investigations, particularly for agro-systems, are difficult to perform because data are scarce: the time step for an agronomist or a farmer is most often the cultural year. The medium-term investigations of the grasslands in Crau area show that Crau's irrigation network has built up the soils in Crau by silt depositions since the sixteenth century. Since 60 years, the hay quality remains constant. Water quality remains constant along the year and contributes directly to the plant nutrition. This irrigated agro-system has mitigated until today the temperature increase, around 2°C, observed in this area.

In situ instrumentation and sensors allow us to address dynamics at two scales that escape to classical agronomic analysis: slow drifts and high-frequency events (pulses). In particular the continuous monitoring of master variables of soil solution can record these events and help us to understand the dynamics of agro-systems and their evolution in the long term.

This kind of information is needed to manage the sustainability of agro-systems because the soil is a nonrenewable capital at human scale.

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