# Effect of irrigation on carbonate dynamics in a calcareous soil using isotopic determinations

*Efecto del regadío en la dinámica de los carbonatos de un suelo calcáreo mediante determinaciones isotópicas*

*Efeito da rega na dinâmica dos carbonatos num solo calcário usando determinações isotópicas*

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**ABSTRACT**

This article evaluates the effect of irrigation on carbonates dynamics in agricultural soils. We studied the proportion and distribution of pedogenic carbonates in different size fractions in a soil with and without irrigation, using the isotopic signature of carbonates C. Irrigation can alter the distribution of soil carbonates and produce a preferential accumulation of pedogenic carbonates (87% to 92% with irrigation for 61% to 74% without irrigation), in the finer fractions.

**RESUMEN**

*Este artículo evalúa el efecto del regadío en la dinámica de los carbonatos en suelos agrícolas. Se ha estudiado la proporción y distribución de carbonatos pedogénicos en las fracciones granulométricas de un suelo en regadío y en secano, usando la firma isotópica de C de los carbonatos. El regadío puede alterar la distribución de los carbonatos del suelo y producir una acumulación preferencial de carbonatos pedogénicos (87% al 92% con riego frente a 61% al 74% sin riego) en las fracciones más finas.*

**RESUMO**

*Este artigo avalia o efeito da rega na dinâmica dos carbonatos em solos agrícolas. A proporção e distribuição dos carbonatos pedogenéticos nas frações granulométricas de solos regados e de sequeiro tem sido estudada, utilizando a assinatura isotópica do C dos carbonatos. A rega pode alterar a distribuição dos carbonatos no solo e uma acumulação preferencial de carbonatos pedogenéticos (87% a 92% com rega versus 61% a 74% sem rega) nas frações mais finas.*

# 1. Introduction

Soil inorganic carbon (SIC) accounts for more than one-third of the total soil C pool (Chevallier et al. 2016). However, the SIC pool and its turnover, and in particular the relationship between carbonate dynamics and soil functioning, has largely been ignored while assessing land-use and farming management practices.

Carbonates in soils, however, are not a closed pool. They can be categorized into primary or lithogenic carbonates and secondary or pedogenic carbonates. The former originate as detritus from limestones or other bedrock-containing carbonates, whereas the latter are formed by dissolution and precipitation of primary carbonates or through dissolution of $CO_2$ into $HCO_3$-, then precipitation with $Ca^{2+}$ or $Mg^{2+}$ from silicate weathering, dust and/or fertilizers (Wang et al. 2015) within the soil profile. In calcareous Mediterranean soils, both types can be present in relatively high proportions in all horizons. However, their relative proportion and their relation to soil functioning has been scarcely studied, partially because distinguishing these two pools can be complicated (Salehi et al. 2004).

The interest in determining the proportion, size-distribution and dynamics of pedogenic carbonates relies on the fact that they can be related to the physical, chemical and biological properties of the soil and, therefore, affect plant growth and soil productivity (Falsone et al. 2010; Virto et al. 2013; Zamanian et al. 2016).

Some soil management factors can affect carbonate dynamics. In particular, irrigation, which directly affects dissolution and precipitation processes, has been seen to be related to a reduction in the concentration of carbonates in the finest soil fractions (de Soto et al. 2017). This effect seems to be site- and management-dependent as other studies such as Zornoza et al. (2016) did not find any important effects of irrigation on SIC in different soils. Indeed, Wu et al. (2008) already reported that the SIC stock showed opposing trends within the top meter of two sites in California following the adoption of irrigation. These contrasting observations indicate that pedogenic carbonates dynamics in semi-arid irrigated soils needs further investigation, taking into account that the total irrigated area in the world is continuously expanding and predicted to cover 60% of all land with irrigation potential in 2050 (Alexandratos and Bruinsma 2012).

The objectives of this work were:

- To verify the hypothesis that irrigation can significantly alter carbonate content in a Mediterranean soil by favouring the occurrence of dissolution and precipitation cycles.
- To investigate the potential consequences of these changes in the accumulation and distribution of pedogenic carbonates resulting from precipitation.

# 2. Materials and Methods

The study was conducted on two plots with the same soil (Xeric Haplocalcid, Soil Survey Staff 2014) under contrasting agricultural managements: one with dryland wheat cropping since at least 50 years and one with a similar management for 50 years and irrigated corn for 7 consecutive years on a plot previously managed in the same way as the one with wheat cropping in Funes (Navarre, Spain).

Soil samples from the tilled layer (0-20 cm), where most biological activity is expected to occur in this soil, were fractionated to obtain the size fractions corresponding to sand, coarse silt, fine silt and clay. Bulk and size-fraction samples were analysed for their total carbonate concentrations and storage (using bulk density) and their isotopic composition of carbonate-C ($\delta^{13}C$).

The isotopic signature of soil carbonates was used to determine the proportion of pedogenic carbonates (*f*), using the simple mix equation proposed by Salomons and Mook (1976):

Eq. (1)
$$ f = \frac{\delta^{13}C_{carbTOT} - \delta^{13}C_{carbPRIM}}{\delta^{13}C_{carbPEDOGEN} - \delta^{13}C_{carbPRIM}} $$

where $\delta^{13}C_{carbTOT}$, $\delta^{13}C_{carbPRIM}$ and $\delta^{13}C_{carbPEDOGEN}$ are the isotopic signature of total, lithogenic and pedogenic carbonates, respectively.

Such a proportion cannot be directly calculated in the bulk samples and also not for any given fraction, because (i) data on $\delta^{13}C_{carbPEDOGEN}$ were not available, as pedogenic carbonates cannot be physically isolated from primary carbonates which impedes the direct measurements of their $\delta^{13}C$, and (ii) $\delta^{13}C_{carbPRIM}$ is unknown and, similarly, lithogenic carbonates cannot be physically isolated from pedogenic carbonates. The determination of theoretical $\delta^{13}C_{carbPEDOGEN}$ values is possible from the isotopic signature of the original soil $CO_2$, assuming that the isotopic composition of respired $CO_2$ is equivalent to that of the soil organic C (Nordt et al. 2000). Therefore, the isotopic signature of pedogenic carbonates would be that of the respired $CO_2$ plus an enrichment factor (4.4‰) due to lower diffusion rates of $^{13}CO_2$ than $^{12}CO_2$ and isotopic discrimination during carbonate precipitation (ca. 12‰, Cerling et al. 1991; Rovira and Vallejo 2008). We considered $\delta^{13}C$ of respired $CO_2$ to correspond to that of total organic C instead of labile fractions in a conservative approach.

As direct determination of $\delta^{13}C$ from lithogenic carbonates was not possible, common values of $\delta^{13}C_{carbPRIM}$ found for lithogenic carbonates (between -2 to 2‰; Ryskov et al. (2000)) were used in a sensitivity analysis in order to investigate the proportion of pedogenic carbonates within this range.

# 3. Results and Discussion

In terms of carbonate storage, those in the bulk and in the sand and clay size-fractions of the irrigated soil were significantly smaller than without irrigation (**Figure 1A**). In terms of carbonate size-distribution and isotopic composition, smaller amounts of carbonates were found with decreasing size fraction. In addition, all the studied size fractions showed more negative values of carbonate $\delta^{13}C$ values in the irrigated than the non-irrigated samples. Within each management system, lower $\delta^{13}C$ values were observed in carbonates with decreasing particle-size (**Figure 1B**). These results can be understood as irrigation significantly decreasing carbonate amounts and changing their size-distribution in the tilled layer in the short-term, likely as a consequence of the modifications in the dissolution and precipitation cycles of carbonates induced by the change in the water regime.

In addition, the calculated proportion of pedogenic carbonate was higher with irrigation, both for bulk soil samples and for all the studied size-factions (**Figures 1C, 1D and 1E**). This suggests that irrigation cannot only be associated to carbonate depletion in the tilled layer, but also to the formation of new pedogenic carbonates in this soil, as previously suggested

by Rovira and Vallejo (2008). This process, if repeated periodically, could be responsible for the observed reduction of δ¹³C of soil carbonates overall in a relatively short period of time.
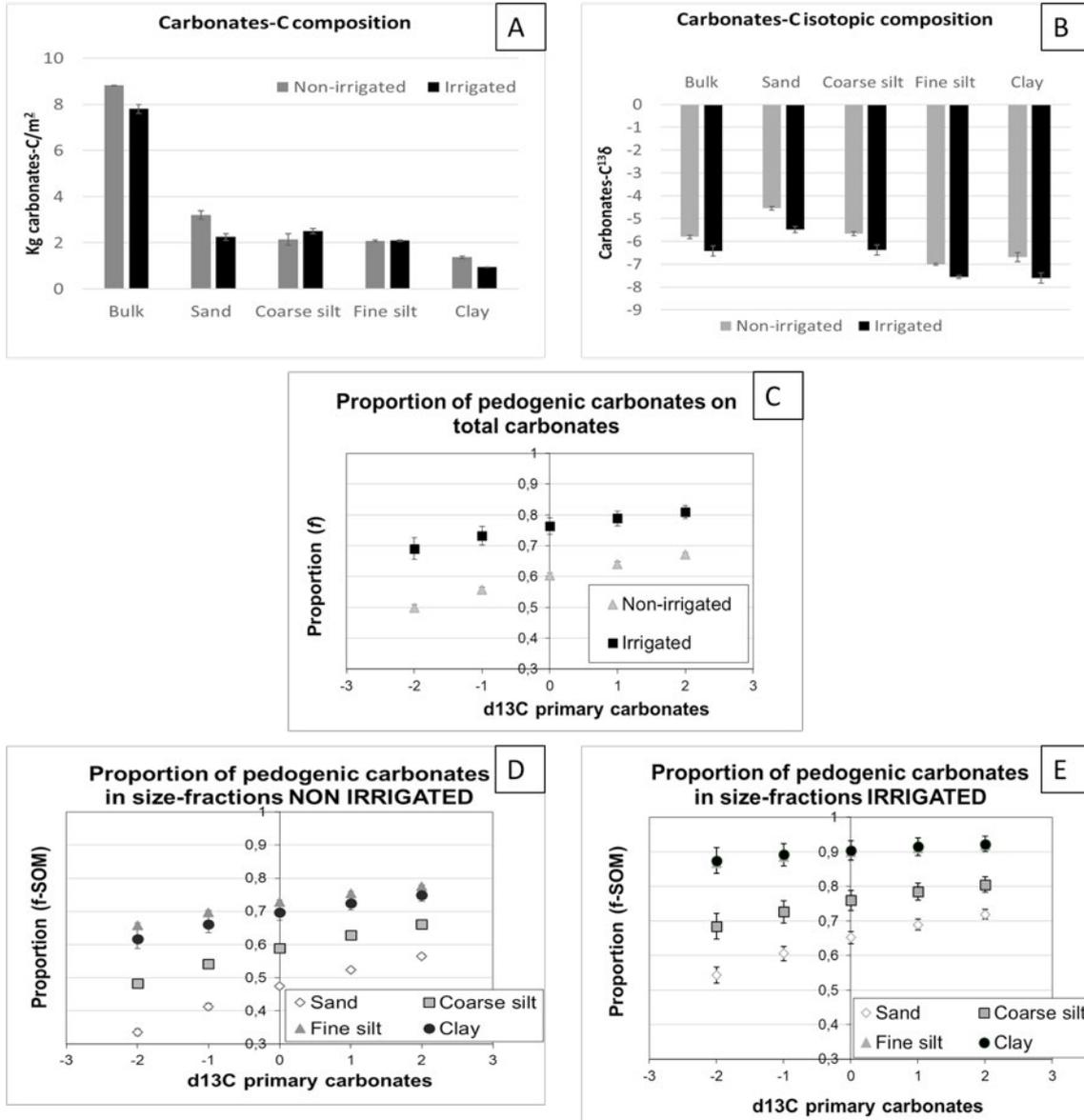


**Figure 1.** Carbonate-C storage and carbonate-C isotopic composition (A and B). Proportion of pedogenic carbonate values for the common range of $δ^{13}C_{carbPRIM}$ values between -2 to 2‰ for total carbonate (C) and particle size-fractions without (D) and with irrigation (E).

In relation to size-fractions, as more pedogenic carbonates were observed in the finest soil fractions (**Figures 1D and 1E**), this can be explained as the expression of a preferential accumulation of pedogenic carbonates in these fractions both with and without irrigation (Magaritz and Amiel 1981), if equivalent previous conditions of the two plots are assumed (Kraimer and Monger 2009). The observed systematical smaller values of δ¹³C in the irrigated samples can in turn only be explained by accelerated carbonate dissolution and re-precipitation since

irrigation was introduced in this soil previously managed for more than 50 years in the same way than the plot still without irrigation. As this accumulation is known to have effects on the porous structure of the soil (Falsone et al. 2010; Virto et al. 2013), as well as in the reactivity of the soil matrix (Zamanian et al. 2016), these results provide evidence that management-induced short-term variations in the soil mineral fraction, which may affect soil functioning, can occur following the implementation of irrigation.

# 4. Conclusions

Carbonates were present in all particle-size classes of the studied soil, with an uneven distribution. The study of their concentration and the estimation of their origin (pedogenic vs. lithogenic) by means of isotopic analyses suggested a depletion of carbonates with size, and a preferential accumulation of pedogenic carbonates in the finest soil fractions.

The introduction of irrigation altered the dissolution and precipitation cycles of soil carbonates. The greater proportion of pedogenic carbonates estimated after seven years of irrigation can be understood as the result of this alteration: pedogenic carbonate formation can be attributed to the precipitation process in the short-term, occurring mainly at the microscale. Because of the known interference of carbonate cycling with soil properties and nutrient availability, the alteration of this cycling from irrigation merits further investigation.

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