

How do soil types affect stable isotope ratios under evaporation: A post corrected evaporation fingerprint of the Cuvelai-Etosa-Basin, Namibia

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Problem: Soil water extractions do not gather the isotopic signature of soil water applied to soils with elevated clay content.

Hypothesis: Soil water stable isotopes are conservative during hydration and dehydration of soils with elevated clay content.

Finding: Spiked experiments indicated that the isotopic signature of soil water is affected by mineral-water interactions. There is a relationship between the surface chemistry of clay minerals and the isotope effect.

$$\delta_{offset} = s * \ln(x) + m$$

Gaj et al., (in revision)

Variable	Description
δ_{offset}	Offset between spike water and extracted soil water
s	Fitted parameter
m	Fitted parameter
X	Chemical compound derived from XRF-analysis of the clay mineral surface

Problem: Mineral-water interactions pose difficulties for the regionalization of soil water stable isotope signatures in catchments with heterogeneous soil types.

Hypothesis: The evaporating front is indicated by the maximum δ -value of the isotope depth profile. The depth the maximum δ -value is not affected by methodical issues.

Finding: The depth of the maximum δ -value is shallower as the calculated depth of the evaporating front. This observation is more pronounced for $\delta^2\text{H}$ values as for $\delta^{18}\text{O}$ values (not shown).

$$\delta(z) = \delta_{res} (\delta_{ef} - \delta_{res} \exp^{-z/z_{ef}})$$

Barnes and Allison, (1988)

Variable	Description
$\delta(z)$	δ -value at depth z
δ_{res}	δ -value of the reservoir (i.e. groundwater)
δ_{ef}	δ -value at the evaporating front
z	Depth
z_{ef}	Depth of the evaporating front

Problem: Observations from isotope depth profiles do not correspond to calculation with van Genuchten parameters.

Hypothesis: Information of isotope depth profiles constrain estimations of van Genuchten parameters.

Finding: The observed depth of the evaporating front from isotope depth profiles does constrain the estimation of van Genuchten parameters of sandy soils. The parameters describing soils with elevated clay content cannot properly constrained.

$$z_{ef} = \frac{1}{\alpha(n-1)} \left(\frac{(2n-1)}{1} \right)^{\frac{2n-1}{n}} \left(\frac{n-1}{n} \right)^{\frac{1-n}{n}}$$

Or and Lehman, (2013)

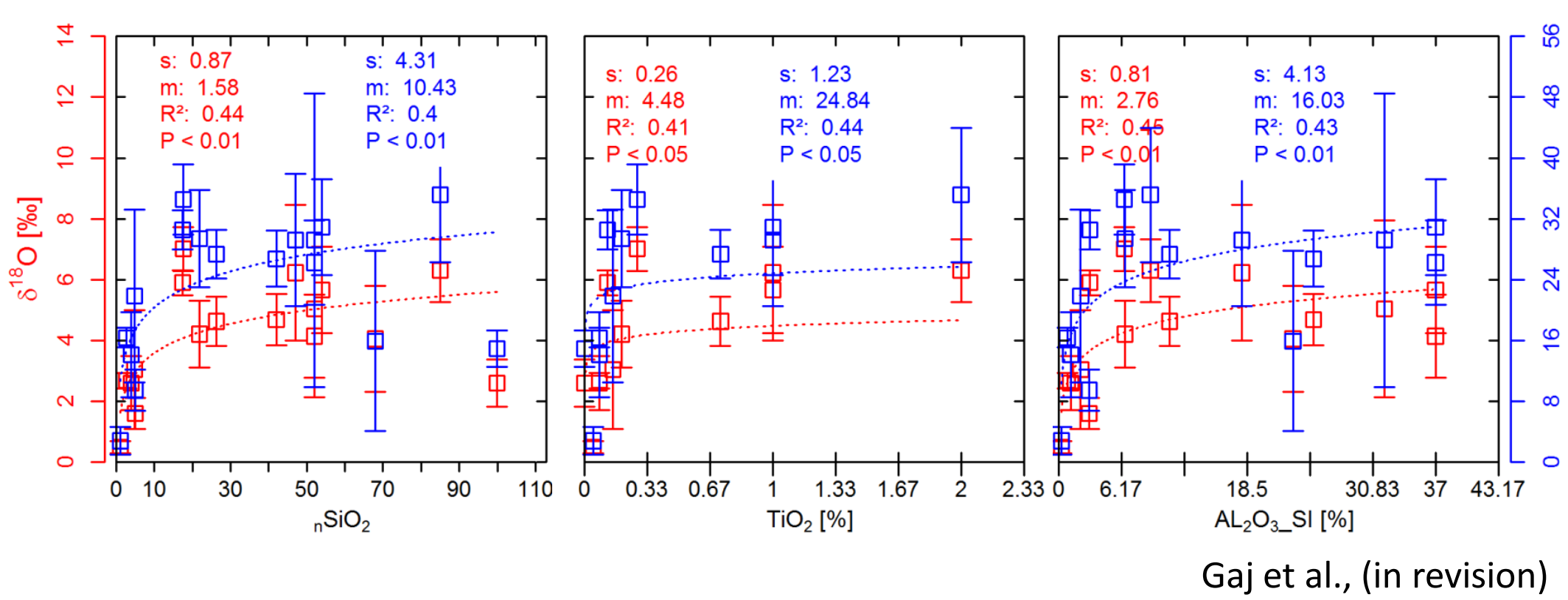
Variable	Description
z	Depth
z_{ef}	Depth of the evaporating front
n	Van Genuchten parameter
α	Van Genuchten parameter

Results and Discussion:

Mineral water interactions are affecting the isotopic composition of bound and free water during hydration and dehydration. The underlying mechanisms are widely unknown and need further investigation.

The determination of the depth and the isotopic signature of the evaporating front is an important factor. It affects calculations using the Craig and Gordon model. The definition of the evaporating front can be different depending on the used approach.

The depth of the evaporating front can be calculated with analytical equations using van Genuchten parameters. The calculated depth do widely not correspond to observation from isotope depth profiles.



Gaj et al., (in revision)

Figure 1: The trueness of the extracted soil water is plotted against the chemical composition determined with the x-ray fluorescence (XRF) analysis. A function of the form $s * \ln(x) + m$ is fitted to the trueness of both $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (dotted line), respectively. The factors s and m are fitted parameters and x is the percentage of the chemical compound. The significants of the regression between modeled and measured data is expressed by R^2 and the p-value. Error bars indicate the analytical error determined from replicate extraction (n=5). Dashed lines for $\delta^{18}\text{O}$ (red) and $\delta^2\text{H}$ (blue) show the analytical error as given by Koeniger et al. (2011).

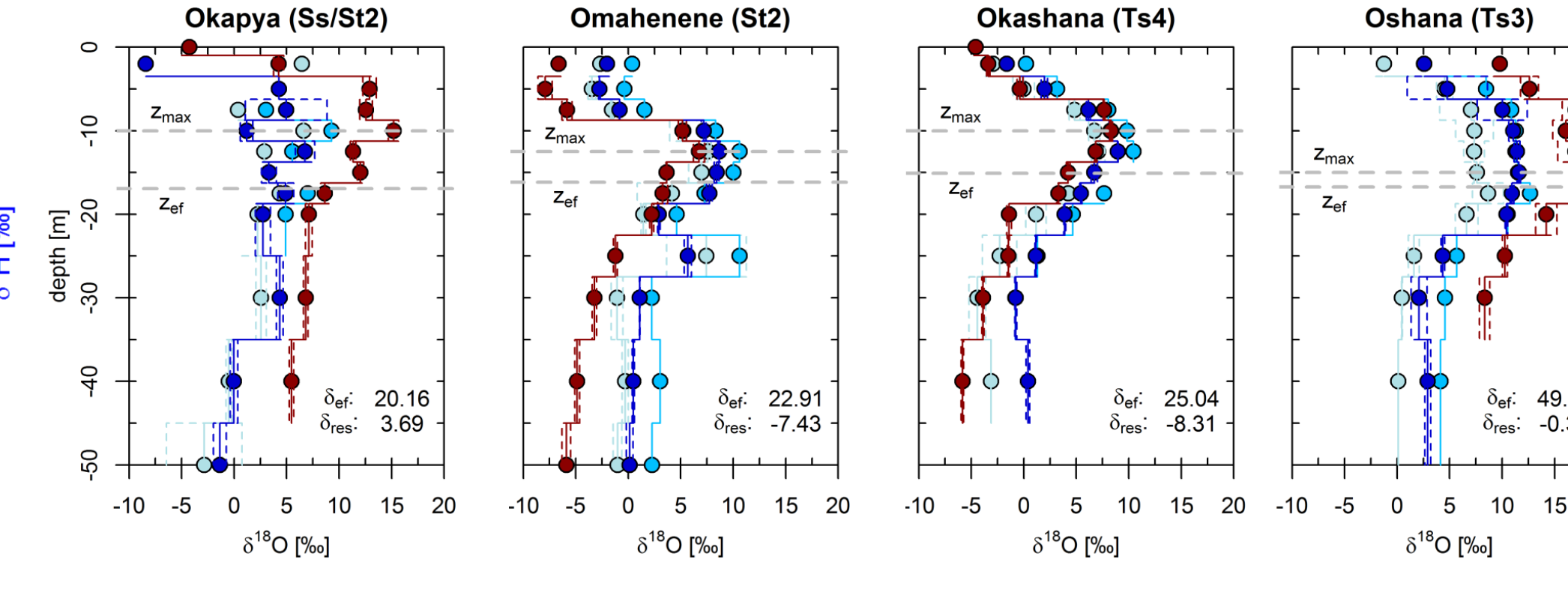


Figure 2: Isotope depth profiles with their corresponding gravimetric water contents (straight lines and dots) and standard deviation (dashed lines) derived of repetitive soil water extraction. Soil water extractions were conducted with 100°C and 200°C extraction temperature. Further isotope values of soil water extractions with 100°C were post corrected using depth profiles of their mineral composition with an approach proposed by Gaj et al. (in revision). Additionally, isotope depth profiles were measured on-site with an in-situ approach (Gaj et al., 2016).

References:

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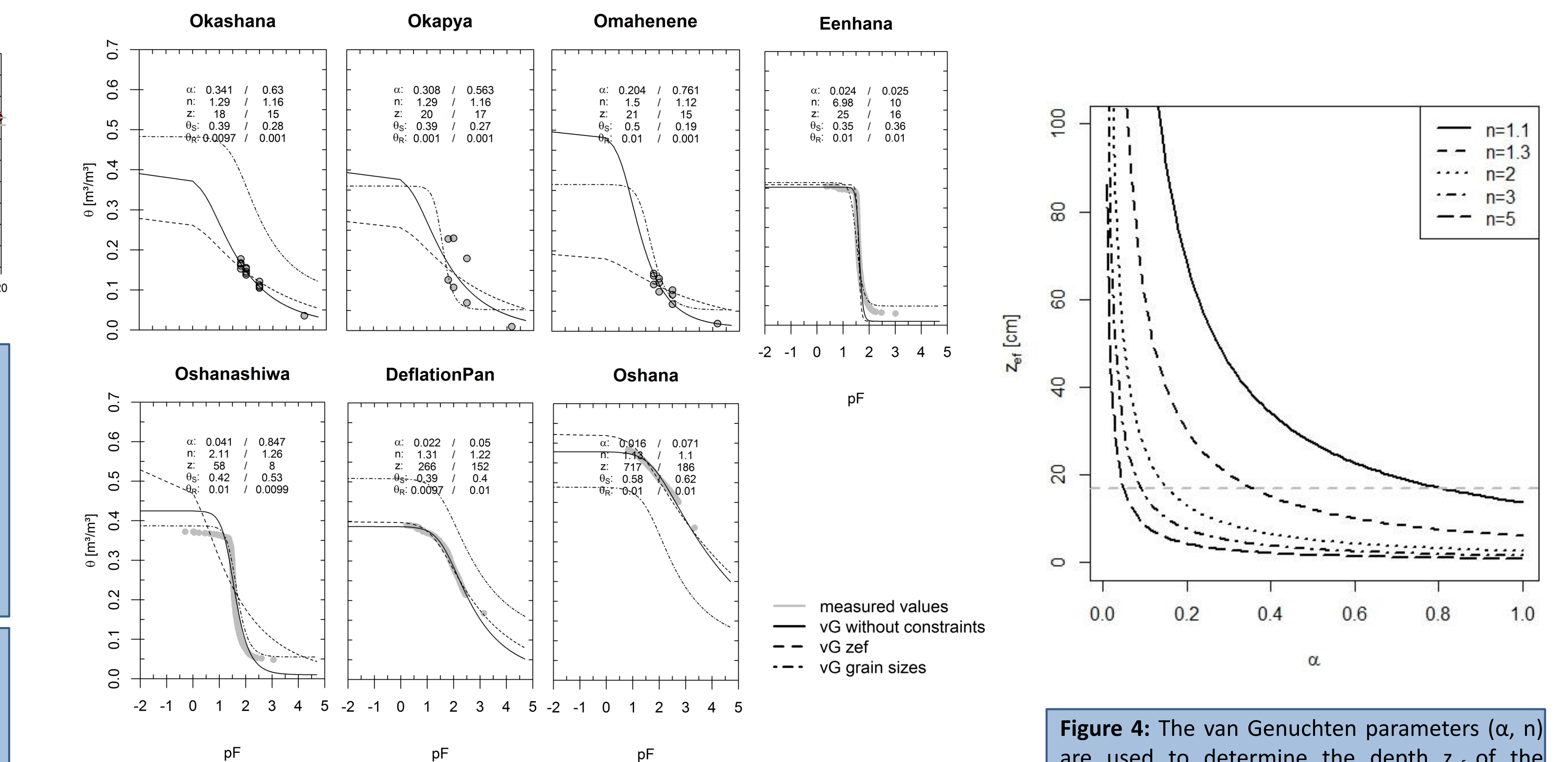


Figure 3: The van Genuchten (vG) parameters (α , n) are determined from the grain size distribution (dotted) and retention data (straight) from laboratory analysis. Additionally, the depth of the evaporating front can be determined with the vG parameters z_{ef} . Therefore the known value of z_{ef} is used to further constrain the estimation of vG parameters (dashed).

Figure 4: The van Genuchten parameters (α , n) are used to determine the depth z_{ef} of the transition from stage I to stage II evaporation. Here z_{ef} is calculated for different values of n and illustrated in dependency of α . The grey line indicates z_{ef} of Okashana.