A NOVEL APPROACH FOR ASSESSING EFFECTS OF CLIMATE CHANGE ON VINEYARDS: $\delta^{13}C$ AND $\delta^{15}N$ OF WINE SOLIDS AND $\delta^{13}C$ OF WINE VOLATILES

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In the today's rapidly changing world climate plants are exposed to various abiotic stresses. Grapevine (*Vitis vinifera* L.) is among the most expensive climate-sensitive cultivated crop, which often suffers from water stress due to low rainfall and high evapotranspiration in the cultivation area. In water-stressed grapevines, the photosynthetic yield is low due to a decrease in both leaf area and photosynthetic rate per unit leaf area, causing different physiological and biochemical disorders which affect plant growth, structure and chemistry of the leaf surfaces, grape ripening, soil-nutrient uptake, and also root and stem metabolisms (Koundouras et al. 2006; Pagay et al. 2016). These in turn cause changes in the quantity and composition (content in sugars, organic acids, polyphenols, aroma compounds) of grapes that is generally associated with low wine quality. Therefore, an important current challenge for food/wine chemists working on agriculture/viticulture research is to develop a powerful analytical tool for quantifying how climate changes and water scarcity affect or may affect in the future the plant water status, and thus the quality and quantity of plant food products (e.g., Lund and Bohlmann 2006).

Here we describe a novel approach to reassess water status in vineyards based on compound-specific isotope analysis (CSIA) of wine volatile organic compounds ($\delta^{13}C_{VOC}$) and bulk carbon and nitrogen isotopes of the solid residue ($\delta^{13}C_{SR}$, $\delta^{15}N_{SR}$), along with the C/N atomic ratios. These analyses link gas chromatography/combustion and elemental analysis to isotope ratio mass spectrometry (GC/C/IRMS, EA/IRMS). Water stress in grapevine is assessed by the measurement of the predawn leaf water potential and the stable isotope composition of the berry sugars at harvest or must sugars ($\delta^{13}C_{sugars}$). Field-grown cultivars of Pinot Noir grapevines at the Agroscope research station of Leytron (Valais) were exposed during the growing seasons 2009 to 2014 to controlled soil water availability while maintaining identical the other environmental variables and agriculture techniques. Three soil water statuses were established by 1) drip irrigation (DI) with 9 L water/m^2 per week between flowering and *veraison* (onset of maturity) 2) no irrigation (NI), and 3) no irrigation and plastic-covered soil (NIP) to avoid infiltration of precipitation water.

Wines were produced from grapes harvested during 2009 to 2914 vintages with the same oenological protocol. This permit the assessment of the effects in the biochemistry of grapevines solely induced by changes in the soil water availability. This mimics the more recurrent and prolonged periods of soil water deficiency due to climate changes. For quantitation purposes and standardization of the $\delta^{13}C$ values of the VOCs, the wine samples were spiked with three standard compounds with known concentration and $\delta^{13}C$ values. VOCs were extracted by liquid-liquid extraction and analyzed by GC/MSD, GC/FID, and GC/C/IRMS. $\delta^{13}C$ values were obtained for twenty VOCs among them, fusel alcohols, aldehydes, acids, acetals, esters, lactones, amides, and phenols. The solid residues (SR) were obtained by freeze-drying of wine aliquots and analysed for their C and N content and isotope composition by EA/IRMS.

All the isotopic ratios ($\delta^{13}C_{sugars}$, $\delta^{13}C_{SR}$ and $\delta^{13}C_{VOC}$ in mUr vs. VPDB, and $\delta^{15}N_{SR}$ in mUr vs. Air-N_2) are highly correlated with the field-measured grapevine water status (Figure 1), indicating that the proposed gas chromatography and isotope ratio mass spectrometry approach is a useful tool to assess the changes in the water status of grapevine cultivars in different *terroirs*.

The analytical method was used for the first time to determine the $\delta^{13}C$ and $\delta^{15}N$ values of freeze-dried wine and the concentrations and $\delta^{13}C$ values of wine VOCs, all of which complement the assessment of soil water availability effects on the grapevine. Furthermore, the $\delta^{13}C$ of the volatile compounds help establish (or confirm) their main source(s). Importantly, we also show for first time that the C/N atomic ratios and $\delta^{15}N$ of freeze-dried wines has an unexplored potential for the study of nitrogen dynamics in the soil/grape/wine systems.

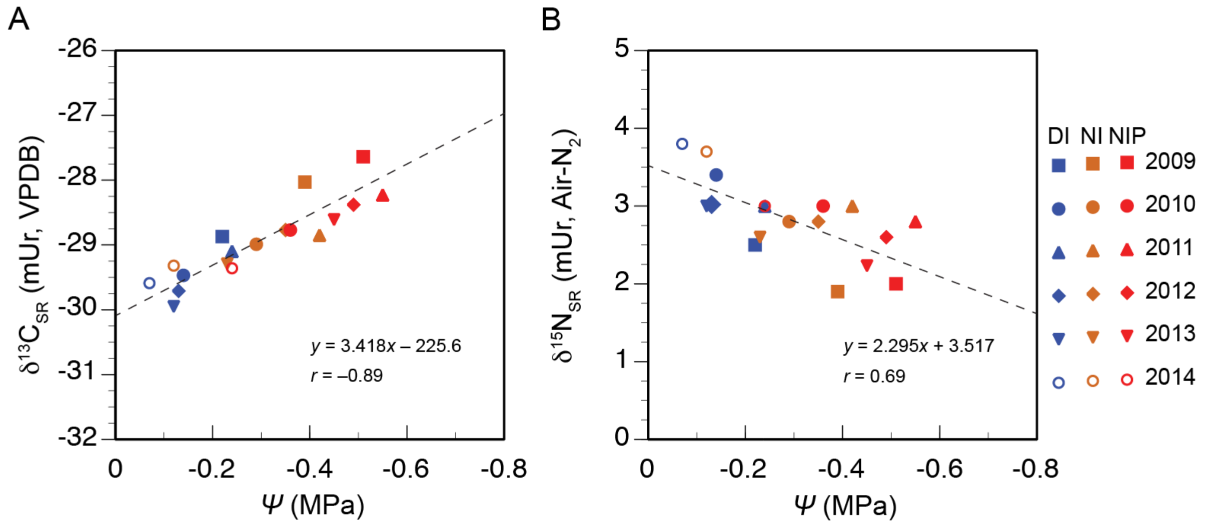

Figure 1 *Carbon (A) and nitrogen (B) isotope composition of freeze-dried Pinot Noir wines from 2009 to 2014 growing seasons and different soil water status. DI = drip irrigation, NI = no irrigation, NIP = no irrigation and plastic covered soil.*

Reference

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