# Multi-isotope composition of freshwater sources for the southern North and Baltic Sea

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## ABSTRACT

We measured the stable hydrogen ($\delta^2H$) and oxygen ($\delta^{18}O$, $\delta^{17}O$) stable isotope composition of different fresh water sources for the coastal southern North and Baltic Sea (precipitation, river waters, fresh water inlets, coastal beach springs, fresh waters in and emerging from coastal marine sediments (SGD)) at sites in Germany, Poland and the Netherlands. Results are compared to the GNIP LMWL at Cuxhaven and the GMWL. The stable isotope results are complemented by the analysis of major and trace elements and nutrients in river and SGD samples to add information about ground water developments and mixing processes.

## INTRODUCTION

The hydrological cycle is reflected by specific water isotope signatures found in precipitation, surface, and ground waters (e.g., Dansgaard, 1964; Craig & Gordon, 1965; Gat, 1996). Since fresh waters of different generation and ages may enter the coastal areas it is expected that they carry characteristic stable isotope signatures. Information about the specific composition of different fresh water sources allows for a use in mixing models for the origin of coastal waters and the deduction of benthic-pelagic coupling. Traditionally, investigations focused on the abundance of the isotopes H-1, H-2, O-16, and O-18 (e.g., Gat, 1996; Röpert et al., 2012). With the development of new analytical methods, also the O-17 isotope came into the focus of interest (e.g., Angert et al., 2004; Luz & Barkan, 2010).
We investigated the multi-isotope composition of different sources for fresh waters at sites with relevance for the southern coastal North and Baltic Sea areas (precipitation, rivers, fresh water inlets, coastal beach springs, fresh waters in and emerging from coastal marine sediments (SGD)). The composition of winter precipitation (rain, snow) at locations in Northern Germany (Warnemünde, Oldenburg (Oldb.), Lüneburg) and the Netherlands (Texel Island) was analyzed to derive local meteoric water lines in order to compare the measurements with the GNIP station in Cuxhaven (NW-Germany) and the GMWL. Precipitation in the towns of Oldenburg and Lüneburg is of relevance, since it may reach the North Sea coast-line via the Hunte/Weser and Ilmenau/Elbe systems, respectively. Selected precipitation events were resolved in enhanced time resolution. Stable isotope results for river and SGD (submarine groundwater discharge) samples were further complemented by on-site measurements (temperature, pH, salinity) and selected hydrogeochemical analyses (main and trace elements, nutrients, dissolved carbonate system).

## MATERIALS AND METHODS

Water samples from fresh water inlets, and coastal sediments were taken as described earlier (Beck et al., 2011; Kotwicki et al., 2014; Winde et al., 2014). Water aliquots were immediately filtered (0.45 µm membrane filters) for further analyses by ICP-OES (Thermo iCAP 6300 DuoThermo Fisher Scientific) and a QuAAtro nutrient analyzer (SEAL Analytical). Precipitation sampling was carried out using a Hellmann-type rain gauge (NE of the town Lüneburg) or otherwise with open plastic sampling devices. At the Lüneburg site, the amount of fallen rain (volume per area of surface) was additionally quantified on a regular daily base. Stable isotope measurements (H-1, H-2, O-16, O-17, O-18) were conducted by means of a CRDS system (Picarro L2140-i) giving results in the conventional δ-notation versus the V-SMOW standard. The international standards VSMOW, SLAP, and GISP, besides in-house standards, were used to scale the isotope measurements.

## RESULTS AND DISCUSSIONS

### *Precipitation.*

Short-term sampling of winter precipitation on the Dutch island Texel followed a non-amount-weighted correlation equation of $\delta^2H = 7.5 * \delta^{18}O + 6.5$ ($n = 19$; $r^2 = 0.99$), close to the LMWL at the German coastal town Cuxhaven ($\delta^2H = 7.8 * \delta^{18}O + 5.2$; Röper et al., 2012).

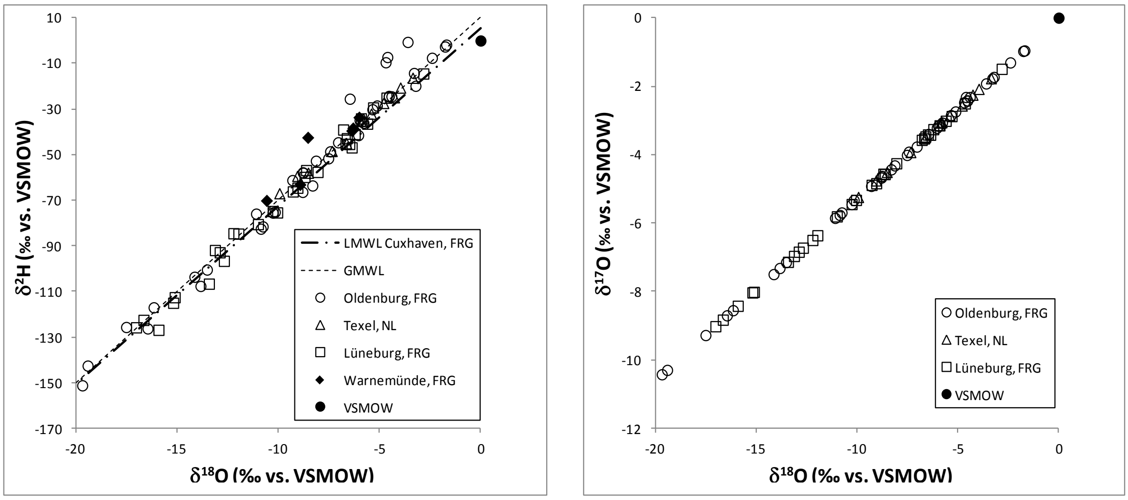


**Figure 1. $\delta^{18}O$ - $\delta^2H$, and $\delta^{18}O$ - $\delta^{17}O$ co-variations in winter precipitation (December 2013 - March 2014). LMWL at Cuxhaven from Röper et al. (2012).**

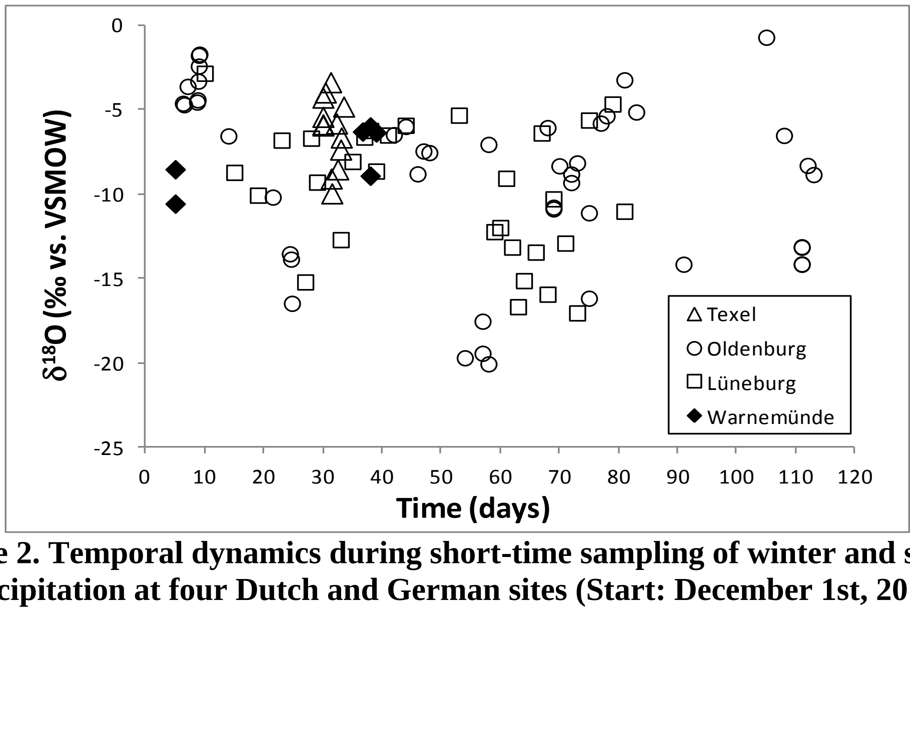


**Figure 2. Temporal dynamics during short-time sampling of winter and spring precipitation at four Dutch and German sites (Start: December 1st, 2013).**

The short-term sampling based LMWL at the Site Lüneburg ($\delta^2H = 8.2 * \delta^{18}O + 10.8$; n = 30; $r^2 = 0.99$; December 2013 to March 2014) falls close to the GMWL. Results for the Site Warnemünde ($\delta^2H = 7.4 * \delta^{18}O + 9.6$; n = 6; $r^2 = 0.84$) and Site Oldenburg ($\delta^2H = 8.5 * \delta^{18}O + 16.5$ (n = 39; $r^2 = 0.98$) demonstrate differences (Figures 1 and 2), that are caused by meteorological characteristics, like different water sources, temperature regimes, and precipitation amounts. Sites of SGD, fresh water beach springs, and coastal low-salinity pore waters were investigated at the North Sea (Janssand - backbarrier tidal area of Spiekeroog Island; northern beach of Texel Island) and the Baltic Sea (Meschendorf, Puck Bay). For a more detailed understanding, more prolonged time series with an amount-weighted evaluation are required, that are currently in progress.

***Rivers, submarine groundwater discharge, beach springs & coastal low-salinity pore waters.***

Samples from rivers draining into the North Sea (Elbe) and the Baltic Sea (Schwentine, Warnow) fall close to the LMWL established at Cuxhaven (Röper et al., 2012). The deep pore waters from a long drill core recovered on the Janssand, a sand flat in the backbarrier tidal area of Spiekeroog Island (Beck et al., 2010), are positioned on a mixing line between modern North Sea water and fresh waters positioned close to the modern LMWL at Cuxhaven. Fresh waters escaping on beaches of Texel Island are positioned on a mixing line between the LMWL and North Sea water (Figure 3).

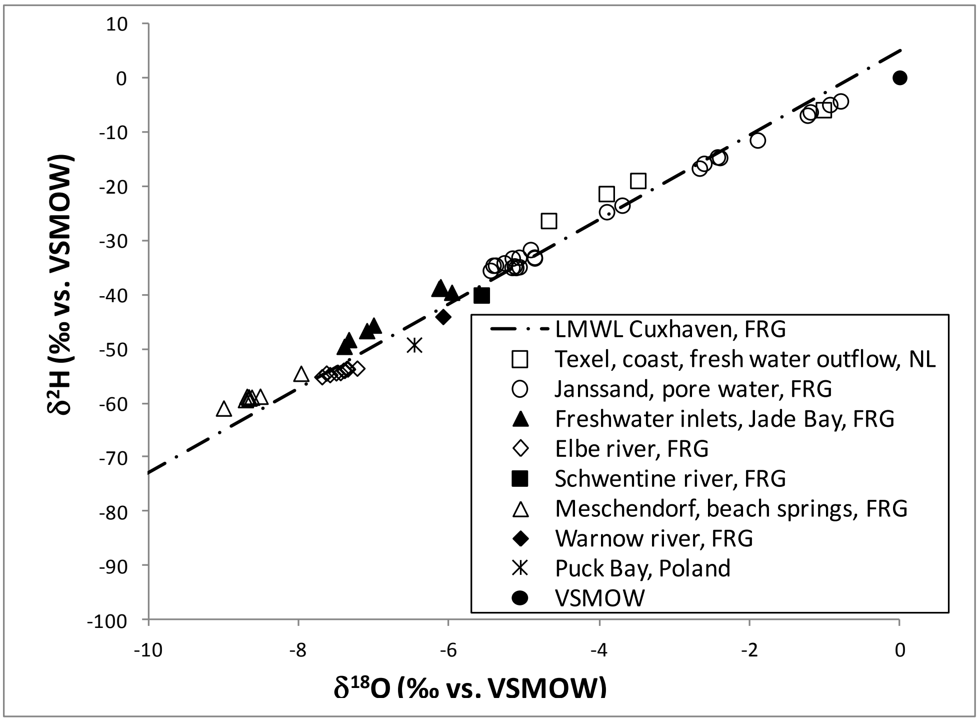


**Figure 3. Stable oxygen and hydrogen isotope composition of different fresh water sources (rivers, fresh water springs at the shore line, pore waters from a long sediment core recovered from the Janssand in the backbarrier tidal area of Spiekeroog (Beck et al., 2010)) for the North Sea: Janssand, Elbe, Texel, Jade Bay, and the Baltic Sea: Meschendorf, Schwentine, Warnow. The sample of Puck Bay is a mixture between SGD ($\delta^{18}O \approx -10.3‰$, $\delta^2H \approx -76‰$; Vogler et al., unpublished) and Baltic Sea water.**

Seasonal studies on different scales and more river and SGD sites are required to further develop quantitative balances for the impact of different fresh waters on the coastal regions of the North and Baltic Sea. Major and trace elements, including nutrients, of SGD samples further allow for the application of mixing models with more saline bottom waters and reflect the pathways of ground water evolution.

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