

## Quantifying air/water exchange using high-resolution time series of dissolved atmospheric Ar, Kr, and N<sub>2</sub> in shallow surface waters

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The rates of gas exchange between the atmosphere and surface waters controls the mass balance and biogeochemical turnover of gases in aquatic systems. The gas exchange rates are variable for different gas species and depend on wind, waves, internal mixing, and other environmental processes. Accurate and site-specific quantification of air/water exchange of different gas species is therefore notoriously challenging, but is crucial to establish robust mass balances of gases in aquatic systems.

We tested a new method that relies on the natural abundance of atmospheric gases to quantify site-specific gas exchange rates as a function of different environmental conditions in shallow water bodies. The heating of the water due to insolation during the day and cooling during the night creates a diurnal variation of the water temperature. The resulting variations of the gas solubilities cause diurnal disequilibria of the air/water gas partitioning, which drives gas exchange fluxes and the corresponding variations of the dissolved-gas concentrations in the water (1).

We used portable membrane-inlet «miniRUEDI» mass spectrometers (2) to obtain high-resolution time series of atmospheric Ar, Kr and N<sub>2</sub> concentrations in the water. This allowed us to close the mass balances and hence to quantify the air/water exchange rates of these gases.

The potential of the method was demonstrated in a controlled experiment using a shallow water-filled tub exposed to diurnal heating and cooling ( $\Delta T = 25$  K) at continuously low wind speeds. The resulting gas exchange velocities ranged from 0.3–0.4 m/d for the different gases with estimated uncertainties of 10-20%. The method was also applied to analyse the gas exchange in a natural lagoon (La Palme, France). The gas exchange rates differed between different sites in the lagoon (approx. 50 m distance) and showed systematic variations with wind speed (up to 20 m/s).

(1): Sanford, WE, Casile, G, Haase, KB. WRR, 2015, 10.1002/2014WR016796

(2) Brennwald, MS, Schmidt, M, Oser, J, and Kipfer, R. ES&T, 2016, 10.1021/acs.est.6b03669