

## **Does the Chelex resin in DGT devices really act as a perfect planar sink for metals? Kinetic limitations of DGT measurements**

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Diffusive gradient in thin films (DGT) is a dynamic technique that can measure metal speciation in situ, and has been widely applied to waters, sediments and soils. Like any analytical technique it relies on a number of assumptions, a major one being that the gel-integrated binding phase will bind trace metals irreversibly and near instantaneously. However, the Chelex beads (or another iminodiacetate based resin, SPR-IDA) in a typical DGT device for trace metal measurements is not a perfect planar sink. Multiple resin gel layers were used to enable analysis of different depths of a DGT binding phase. At pH 7, when no fulvic acid was present, metal penetration to the back layer was low and similar for all metals. However, at lower pH up to 42% of an individual metal accumulated by the DGT was in back resin layers. This was most noticeable for Mn at pH 4 and 5, but was also found for Cd and Co at pH 4. These metals have predicted lower affinity for Chelex when compared to other metals. This suggests that binding to Chelex may sometimes be kinetically limited, particularly for Mn. For all metals, more metal was found in back layers when fulvic acid was present. Metal penetration to back layers also increased with decreasing pH. A model was developed to determine the distance that metals may penetrate into DGT resin layers.

## **Production of primary particles at the sea surface that can function as cloud condensation nuclei**

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As the oceans cover the vast majority of Earth's surface, marine clouds are an important contributor to Earth's radiative balance. The formation and microphysics of these clouds depends on the sizes and numbers of aerosol particles present upon which cloud drops can form. In marine environments particles that are directly produced at the sea surface provide the dominant contribution to aerosol mass concentration, but their relative contribution to aerosol number concentration is not well quantified. Knowledge of the size-dependent production flux and its dependence on parameters such as wind speed, is necessary to understand and accurately model cloud formation in the marine atmosphere. Until recently it has been thought that primary aerosol particles produced at the sea surface were not abundant relative to other aerosol particles in the radius range of several tens of nanometers, those sizes thought to be most important for cloud drop formation, but several recent formulations have been presented for the flux of these particles that suggest that they may be produced in large numbers. However, the number of particles that would be produced according to these formulations seems unrealistically high, and failure of many previous investigations to detect particles of these sizes causes concerns as to the extent to which the formulations are applicable to oceanic particle production. Here the production flux of particles with radii at formation less than a few tenths of a micrometer is discussed, with older investigations reviewed and newer formulations examined.