

## Comment on "Trace Metal Levels in Uncontaminated Groundwater of a Coastal Watershed: Importance of Colloidal Forms"

Sañudo-Wilhelmy et al. (1) document very clearly the levels of trace metals and organic carbon in filtered groundwater from eastern Long Island. They point out correctly that the levels of these metals and organic carbon are as low as found in the open ocean, necessitating the same precautions against sample contamination that have been adopted by the ocean sciences community.

These authors also point out the importance of considering the colloid fraction in the understanding of the fate and mobility of metals in groundwater. Many other studies have also suggested that colloids facilitate transport of metals, radionuclides, and organic pollutants in groundwater (2, 3). It is in regards to the groundwater sampling and the separation of colloids using cross-flow filtration (CFF) that we raise important issues not considered by these authors.

CFF is used to assess in-situ size distributions. Under ideal conditions

$$C_{\text{filtrate}} = C_{\text{colloidal}} + C_{\text{permeate}} \quad (1)$$

where  $C_{\text{filtrate}}$  is the concentration in the filtrate (filtrate passing through a 0.45- $\mu\text{m}$  pore-sized filter in this study),  $C_{\text{colloidal}}$  is the concentration retained by the CFF membrane (a 1-kDa cutoff is used here), and  $C_{\text{permeate}}$  is the concentration in the solution that passes through the CFF membrane. CFF is a procedure that can introduce both positive (contamination) and negative (sorption losses) biases, such that in practice

$$C_{\text{filtrate}} = C_{\text{colloidal}} + C_{\text{permeate}} + C_{\text{blank}} - C_{\text{loss}} \quad (2)$$

where  $C_{\text{blank}}$  is the apparent CFF blank and  $C_{\text{loss}}$  represents all losses to the CFF system, both chemical and physical.

The first-order assumption is that sample introduced to the CFF system represents ambient conditions in the groundwater, and in this regard the use of low-flow groundwater purging/pumping methods is essential (4) as addressed by Sañudo-Wilhelmy and colleagues (1). Since sampling of groundwater can involve collecting waters undersaturated with respect to oxygen and thus low redox conditions, a second issue is redox control. Redox-sensitive metals, such as Mn and Fe, are soluble under more reducing conditions. Exposure of reduced waters to the atmosphere can cause oxidation of these elements and formation of insoluble forms that can scavenge dissolved trace metals on to colloidal and particulate iron and manganese oxides (5, 6).

We have found systematic changes in Fe CFF mass balance/recovery as a result of exposing reducing groundwater from Cape Cod to air. After exposure for 24 h, Fe losses were up to 82% as compared to a <1% loss then CFF is conducted under a  $\text{N}_2$  atmosphere throughout sampling and processing for redox control (7). In addition, we find that coprecipitated elements such as phosphorus show markedly higher loss (up to 94%) and higher percent colloidal distributions following the oxidation of Fe in the same experiments.

In Sañudo-Wilhelmy et al.'s study (1), samples were collected in trace metal clean containers, but there was no redox control during the >3-h field sampling interval and for periods up to 24 h prior to CFF in the lab. We cannot

determine if these effects in Long Island groundwater ( $\text{O}_2$  ~40–60% saturation; SI wells, June 1999 in the Supporting Information of ref 1) would be as severe as observed in our study, but without redox control, we cannot be assured that the sample introduced to the CFF represents the in-situ conditions. The delay of CFF processing could result in both size and redox speciation changes. In a recent study of colloidal Pu at the SRS, we have found much lower colloidal partitioning of Pu in groundwater relative to earlier studies (8). We attribute at least part of this difference to the use of a new groundwater CFF procedure conducted immediately on site and under  $\text{N}_2$  conditions to minimize redox changes in our groundwater samples.

The second assumption behind CFF methods is that the membrane retention characteristics are well-known for a particular set of CFF conditions. Effective cutoffs can vary using the same CFF system under differing conditions of concentration, flow, pressure, and recirculation design (9) and vary even more widely between different manufacturers CFF membranes (10). We have even found variations as large as 50–93% in the retention characteristics of the same CFF membrane used here but purchased several years apart (ref 11 and unpublished data, this lab), indicating possible changes in manufacturing protocols of this particular membrane. Tests of each CFF membrane using standards of known molecular weight and under the same CFF conditions as in the field are needed, and the results of such calibrations together with run conditions should be reported with every CFF study (9). The lack of such supporting data in Sañudo-Wilhelmy et al. (1) does not mean that their CFF system did not perform; however, it makes comparison to other studies using different CFF protocols, such as discussed in their Figures 2 and 3, unreliable.

Equation 2 reduces to eq 1 when  $C_{\text{blank}}$  and  $C_{\text{loss}}$  are low, i.e., when a mass balance can be achieved between the measured  $C_{\text{filtrate}}$  and the two size classes that are separated. Sañudo-Wilhelmy et al. (1) show a mass balance after CFF processing of 40–140% for the trace metals and 80–120% for organic carbon. CFF blanks can arise either from contamination from the CFF system itself or from cross-contamination between samples. While Sañudo-Wilhelmy et al. (1) run proper acid-cleaning and Milli-Q rinsing steps between samples, they do not report measured metal or organic C concentrations in the Milli-Q fractions that would allow us to assess this blank. Also, the Shelter Island groundwater dissolved organic carbon concentrations are 6.5–41  $\mu\text{M}$ . The lower values of several micromolar are typical of DOC Milli-Q/instrumental blanks. Thus, it is impossible to rule out contamination artifacts without further study as they did not evaluate  $C_{\text{blank}}$ .

Sañudo-Wilhelmy et al. (1) did evaluate  $C_{\text{loss}}$  on selected samples by analyzing the acid-rinse solutions. The inclusion of the measured  $C_{\text{loss}}$  improves the mass balance greatly; however, a large  $C_{\text{loss}}$  greatly complicates interpretation of CFF data. If, as is done here,  $C_{\text{blank}}$  is assumed to be zero and  $C_{\text{loss}}$  is assumed to arise solely by sorption or losses of colloids to the CFF system, then adding this fraction to the colloid concentration results in a significantly larger apparent colloidal distributions since  $C_{\text{colloidal}}^* = C_{\text{colloidal}} + C_{\text{loss}}$ . In many of the samples in this paper,  $C_{\text{loss}}$  is 40–60% of the total, while  $C_{\text{colloidal}}$  as determined directly by CFF is only 20–30%, thus reporting  $C_{\text{colloidal}}^*$  increases apparent colloid distributions by factors of 2 or more. These authors gain confidence in this approach by the fact that the difference between  $C_{\text{filtrate}}$

–  $C_{\text{permeate}} = C_{\text{colloidal}}$  “by difference” is similar to  $C_{\text{colloidal}}^*$ , which mathematically must be the case (see eq 2). They use this difference approach rather than the colloids retained by the CFF to arrive at groundwater colloid abundances in many well samples. We take issue with this approach as there is no a priori reason that trace metals in the permeate would be less inclined to be lost to system surfaces via sorptive processes. They also present no data from their CFF system to suggest that the metals released by acid-rinsing represent colloidal losses only.

In conclusion, while we laud the effort to apply trace metal clean procedures to groundwater studies, we are less confident in the colloid results of this study. The lack of a mass balance is a clear warning sign that results cannot be considered reliable beyond the total error in the mass balance. While a mass balance of better than 10–20% cannot always be achieved because of the limitations of our analytical and sampling methods, larger losses such as reported here should be avoided. In particular, sorbed pools should not be attributed to any particular size fraction. Recent controlled experiments to minimize losses by balancing cross membrane pressure and recirculation rate are to be encouraged (9) as well as the careful testing of different membrane designs that exhibit lower sportive losses. We urge a cautious interpretation of any results that suggest colloid-facilitated transport using groundwater data that do not take account of the crucial issues related to groundwater sampling and CFF applications discussed here.

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