Comments on “Determination of total arsenic using a
novel Zn-ferrite binding gel for DGT techniques:
Application to the redox speciation of arsenic in river
sediments” by Gorny et al.

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Gorny et al. recently described a new diffusive gradients in thin films (DGT) technique, which utilizes a binding gel layer containing zinc ferrite, for the measurement of total arsenic in natural waters [1]. The major justification for a new metal oxide binding layer for arsenic are the assumptions that the sodium hydroxide eluent, required for the Metsorb and zirconium oxide binding layers, introduced analytical challenges at low concentrations, and that ferrihydrite does not perform well in seawater. None of these assumptions are strongly justified by the authors or supported by the literature, nor are they supported by the results of this study. The comparison of the point of zero charge for various metal oxide binding agents used in DGT is interesting and worthwhile, but would have been more convincing if zirconium oxide was included. The validity of the assumptions made by Gorny et al., several factual errors, and limitations with the discussion require highlighting.

The authors note in their introduction that “Metsorb HMRP 50 and ZrO binding gels are not well adapted to arsenic determination at low concentration due to some inherent analytical problems induced by the elution step with NaOH eluent.” Presumably the authors are referring to the ionization suppression that can occur when analyzing solutions containing high concentrations of easily ionizable elements like sodium, which tends to suppress the ionization of arsenic due to its relatively high first ionization potential. In fact, all eluent solutions require a dilution prior to analysis by ICP-MS, typically at least 10-fold, so that the sample matrix is suitable and there is sufficient volume for analysis. The analysis of a diluted eluent from a Metsorb DGT sampler, containing 2% HNO₃ and 0.1 mol L⁻¹ NaOH, is not problematic with modern ICP-MS instruments, which can be easily tuned to have a robust plasma (i.e. low CeO:Ce ratios) that suffer negligible ionization suppression. Previous users of DGT methods with Metsorb or ZrO binding gels, which have required elution with sodium hydroxide, have reported reproducible results and excellent detection limits [2-6].

The evaluation of the newly described zinc ferrite DGT technique was done using experimental conditions that have not been previously used by researchers in the field of DGT method development. The authors used 0.1 mol L^{-1} boric acid as a buffer to maintain pH in the range of 7.5 – 9. This approach has never been used in the testing of DGT performance – other researchers have simply adjusted the pH of unbuffered solutions using dilute acid or base, or have used a very low buffer concentration (e.g. $0.005 \text{ mol L}^{-1} \text{ NaHCO}_3$) [7]. Such a high concentration of boric acid in the experimental solutions is not representative of any environmental conditions that DGT samplers are likely to be deployed in, and the effect of this matrix on the performance of different DGT binding layers is unknown.

An essential step in the validation of a new DGT method is its deployment in solutions that represent the complex matrices likely to be encountered in field deployments. This is often done using solutions of synthetic freshwater or seawater, or even collected natural waters [3, 5, 7-11]. In solutions that were prepared to test the zinc ferrite DGT technique under conditions representative of seawater, Gorny et al. used solutions containing 0.1 mol L^{-1} boric acid and either $20 \text{ g L}^{-1} \text{ NaCl}$ or $2 \text{ g L}^{-1} \text{ Na}_2\text{SO}_4$. These conditions are unrepresentative of the ionic composition of seawater, which contains numerous other constituents and approximately 1000-fold less boric acid. Gorny and co-workers tested zinc ferrite, ferrihydrite, and Metsorb DGT samplers in these experimental solutions and found poor performance of Metsorb DGT ($C_{\text{DGT}}:C_{\text{SOLN}} < 0.30$). As a result, they concluded that Metsorb DGT was not suitable for measuring arsenic in seawater. This is in direct disagreement with numerous prior studies that have demonstrated excellent performance of Metsorb DGT for measuring arsenic in seawater (Table 1). The use of unrepresentative experimental conditions (i.e. 1000-fold higher boric acid concentration than natural seawater) casts doubt over the conclusions made by Gorny et al.

Table 1. Summary of the performance of Metsorb DGT for measuring arsenic in seawater

Experimental conditions	Deployment time	$C_{DGT}:C_{SOLN}$	Ref
100 $\mu\text{g L}^{-1}$ As(III) or As(V) in natural seawater	72 h	0.85 – 1.07	[3]
15 $\mu\text{g L}^{-1}$ As(V) in synthetic seawater	92 h	0.90	[10]
37.5 $\mu\text{g L}^{-1}$ As(V) in natural seawater	72 h	0.90 – 1.00	[12]

Finally, Gorny and coworkers evaluated the performance of the zinc ferrite DGT method, and the existing ferrihydrite and Metsorb DGT methods, for the measurement of arsenic in sediment porewaters. Sediment profiling DGT samplers (with a rectangular exposure window of 17 x 150 mm) were deployed in collected sediment cores, and after removal were sliced at 10 mm intervals to obtain a one-dimensional profile of arsenic concentration with depth. They found good agreement between As(V) concentrations measured by the zinc ferrite and ferrihydrite DGT samplers, with differences of < 10%. However, the concentrations measured by Metsorb DGT were consistently higher than those measured by either of the other two methods. If the Metsorb DGT was performing poorly, as suggested by Gorny and co-workers, it would be expected to provide an underestimate of arsenic concentrations, not an overestimate. The flux of analyte into a DGT sampler is controlled by the passive diffusion of the analyte through the diffusive layer, a polyacrylamide hydrogel in this case. Therefore, it is simply not feasible that the Metsorb binding layer increased the diffusive flux of arsenic from the porewater and overestimated the porewater concentration. It seems much more likely that the Metsorb DGT is providing a more accurate measurement of the porewater arsenic, while the ferrihydrite and zinc ferrite DGT methods are underestimating the concentration (by over 50% in some cases). One possibility is that the effective capacity of the ferrihydrite and zinc ferrite binding layers is being reached under these deployment conditions, leading to a decreased flux of arsenic into the samplers and thus a lower mass accumulated during the deployment. Previous work [3, 13] has shown ferrihydrite to be more susceptible than Metsorb to interference from bicarbonate, an anion present in high concentrations in

sediment porewaters due to respiration of organic matter, which can occupy binding sites and thus reduce the binding capacity for the analyte of interest. Another possibility is that the reducing nature of the deployment matrix is causing reductive dissolution of the iron(III)-based binding agents, leading to losses of adsorbed arsenic from the zinc ferrite and ferrihydrite DGT samplers. Potential mechanisms for this include the direct reduction of Fe(III) by iron reducing bacteria, or the chemical reduction of Fe(III) by Mn(II) and/or dissolved sulfide produced as metabolic end-products of manganese and sulfate reduction. Unfortunately, none of these possibilities are discussed by Gorny and co-workers.

Future research should focus on resolving the inconsistencies between the findings of Gorny et al., and the prior research published in this field. In particular, the testing of zinc ferrite DGT should be repeated in more realistic matrices, such as synthetic or natural freshwater and seawater. The effect of anoxic conditions on the stability of iron(III)-based binding agents such as zinc ferrite and ferrihydrite should also be evaluated, to determine if their reductive dissolution causes poor DGT performance in sediment porewaters.

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