

## Response to Comment on “Release of Arsenic to the Environment from CCA-Treated Wood. 2. Leaching and Speciation during Disposal”

In their comments, Bessinger et al. of Exponent, Inc. (1) consistently suggest that our approach overestimates leaching rates and by no means suggest that the leaching rates are underestimated. We believe that their underlying assumptions are questionable and that leaching rates may in fact increase if their assumptions are in error. Below are specific examples.

Bessinger et al. (1) suggest that leaching rates were overestimated due to the absence of soil within the C&D lysimeters. That leaching rates would decrease with the inclusion of soil is debatable since there is considerable literature that supports an increase in arsenic mobility from soils containing organic and mineral components (2). Given this information it is possible that the inclusion of soil within the lysimeters could also increase leaching rates.

Bessinger et al. state that the assumption of a constant leaching rate overestimates arsenic leaching. First, we should point out that anything other than a constant leaching rate would require speculation about the chemistry and infiltration rates occurring over time within the landfill. Furthermore, the C&D scenario showed no decline in leaching rate throughout the study (Figure 2 in ref 4 showed a relatively constant slope) and thus provided no basis upon which to render an assumption other than a constant leaching rate.

Bessinger et al. imply that the non-weathered wood fraction in the lysimeters was too high resulting in greater arsenic leaching rates. The assumption that non-weathered wood leaches more than weathered wood is questionable, as weathered wood has been shown to release more arsenic, particularly after long periods of time (5). If weathered wood leaches more arsenic than non-weathered wood, we believe that Bessinger et al.'s primary assumption is in error and one can argue the opposite with respect to leaching rates.

Comments made by Bessinger et al. regarding arsenic speciation are misleading. First, the Nico et al. (6, 7) papers cited focused on arsenic and chromium speciation in solid phases using XAS. Arsenic speciation information reported in Khan et al. (4) was for leachates, i.e., aqueous forms. It is inappropriate to validate results obtained from one technique for one matrix using data gained from other matrices. Additionally, Nico et al. (7) found free arsenate ions to be the dominant solution-phase arsenic form and state that “once in solution, arsenic no longer complexes with Cr or Fe”. Nico et al. (7) use our previous results (5) to support their findings. Second, Bessinger et al. incorrectly claims that we introduced uncertainty by using chemical methods incapable of distinguishing between As(V) species and that we reported only total As(V) concentrations. The technique we used, HPLC-ICP-MS, is currently the most widely used analytical method for determining arsenic species in aquatic environments and closer inspection of Figures 2, 3, and 4 in our paper (4) shows the results for all four arsenic species and the total.

In their discussion of arsenic mobility below the landfill, Bessinger et al. contradicted their own arguments. In one case, they suggest an inconsistency between the speciation of arsenic from the lysimeters (primarily as As(V)) and those observed in groundwater wells (As(III)) near C&D landfills, which represents a failure to recognize that arsenic speciation can change within the subsurface. In another case, Bessinger et al. argue that arsenic would precipitate as orpiment ( $\text{As}_2\text{S}_3$ ), although recent studies (8) show arsenic–sulfur complexes to play a key role in arsenic mobility and toxicity in sulfate-reducing environments. The observation that sulfate-reducing conditions may increase arsenic mobility thus refutes Bessinger et al.'s assumption that arsenic will be immobilized in the subsurface as a precipitant.

In summary, the underlying assumptions made by Bessinger et al. are baseless and their argument that the lysimeter study overestimates arsenic leaching is unjustifiable. Bessinger et al. make inappropriate comparisons between Nico et al. and our article (4). Moreover, Bessinger et al. failed to recognize habitual changes in arsenic speciation and its effects on arsenic mobility in the subsurface, specifically under reducing conditions below landfill (3). Of particular concern is the lack of recognition by Bessinger et al. to the vast quantities of arsenic associated with the use and disposal of treated wood. As acknowledged in their comment and as observed in our data, about 10% of the landfills in Florida are currently experiencing elevated arsenic in their groundwater wells. These impacts are surprising given the time needed for arsenic to leach from the wood, travel through the aquifer, and ultimately be detected at groundwater-monitoring wells; a leaching process that can take tens to hundreds of years and which suggest greater arsenic impacts for the future. The large quantities of arsenic associated with CCA-treated wood and the potential for arsenic-containing leachate to migrate should be accounted for in the management of this material.

### Literature Cited

- (1) Bessinger, B.; Redding, B.; Lowney, Y. Comment on “Release of arsenic to the environment from CCA-treated wood. 2. Leaching and speciation during disposal. *Environ. Sci. Technol.* **2007**, *41*, 364–365.
- (2) Bauer, M.; Blodau, C. Mobilization of arsenic by dissolved organic matter from iron oxides, soils, and sediments. *Sci. Total Environ.* **2006**, *354*, 179–190.
- (3) Keimowitz, A. R.; Simpson, H. J.; Stute, M.; Data, S.; Chillrud, S. N.; Ross, J.; Tsang, M. Naturally occurring arsenic: Mobilization at a landfill in Maine and implications for remediation. *Appl. Geochem.* **2005**, *20*, 1985–2002.
- (4) Khan, B. I.; Jambeck, J.; Solo-Gabriele, H. M.; Townsend, T. G.; Cai, Y. Release of arsenic to the environment from CCA-Treated Wood. 2. Leaching and speciation during disposal. *Environ. Sci. Technol.* **2006**, *40*, 994–999.
- (5) Khan, B.; Solo-Gabriele, H. M.; Dubey, B. K.; Townsend, T.; Cai, Y. Arsenic speciation of solvent-extracted leachate from new and weathered CCA-treated wood. *Environ. Sci. Technol.* **2004**, *38*, 4527–4534.
- (6) Nico, P. S.; Fendorf, S. E.; Lowney, Y. W.; Holm, S. T.; Ruby, M. V. Chemical structure of arsenic and chromium in CCA-treated wood: Implications of environmental weathering. *Environ. Sci. Technol.* **2004**, *38*, 5253–5260.

- (7) Nico, P. S.; Ruby, M. V.; Lowney, Y. W.; Holm, S. T. Chemical speciation and bioaccessibility of arsenic and chromium in chromated copper arsenate-treated wood and soils. *Environ. Sci. Technol.* **2006**, *40*, 402–408.
- (8) Stauder, S.; Raue, B.; Sacher, F. Thioarsenate in sulfidic waters. *Environ. Sci. Technol.* **2005**, *39*, 5933–5939.

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