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Letter to the editor re: Datta et al., 2006

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In a recent publication, Datta et al. (2006) present the results of a study conducted to assess the speciation and in vitro bioavailability (or bioaccessibility) of arsenic in soil. In this study, two soil types were spiked with dimethylarsinic acid (DMA) and were incubated for one year in a static test system. Soil arsenic was then extracted and speciated, and the results were used to develop estimates of bioaccessibility and potential cancer risk. Unfortunately, the analyses presented in the article contain a number of errors and unfounded conclusions. As a result, in its present form, the publication cannot be considered as a complete or reliable analysis. This letter briefly summarizes the shortcomings of the article and provides suggestions for correcting the errors included in the analyses. Similar issues have been observed in other articles published by this research group (*e.g.*, Sarkar et al., 2005, 2006) and the errors in these analyses should also be corrected.

1. Concerns regarding the design of the geochemistry studies

The approach used to assess the speciation and bioaccessibility of arsenic in the test soils has a number of significant limitations that raise questions regarding the implications of the observed results. The most serious concern with the geochemistry approach is that the information presented in the article does not show that DMA was converted into inorganic arsenic in the test system or that such a conversion would occur in the gastrointestinal tract; nevertheless, the researchers suggested that such a conversion was potentially occurring. This discordance between the researchers' conclusions and the reported results is particularly important because such a conclusion is contradicted by available information from human and animal studies regarding arsenic metabolism and disposition (*e.g.*, Buchet et al., 1981; Marafante et al., 1987; Hughes and Kenyon, 1998). This issue is discussed in more detail in the section of this letter entitled "Unfounded Statements Regarding Arsenic Biotransformation."

To assess the speciation and bioaccessibility of the arsenic present in the tested soil samples, the authors performed a sequential extraction that yielded arsenic associated with different fractions of the test soils; however, the specific identities of the arsenic species present in each soil fraction were not explicitly determined by the authors. Moreover, the sequential extraction methodology studies cited by the authors to support their approach do not differentiate arsenic species from one another. Instead, the specific "forms" of arsenic are defined only by features of the methods used.[1] As a result, the authors' conclusion that inorganic arsenic was generated from DMA is not based on direct measurement of specific arsenic compounds, but only on the relative apportionment of "total arsenic"[2] among the various test fractions at different times during the experiment.

Specifically, the authors reached this conclusion based on their observation that a larger portion of the total arsenic detected in extracts was present in the extractants representing the operationally-defined "iron- and aluminum-bound phase" and the "calcium- and magnesium-bound phase" in the sampling events conducted in Months 4 and 12 than in the sampling event that occurred immediately after DMA addition. The validity of this conclusion is unsupported, because no evidence is

[1] The specific procedures used by Datta et al. and the implications of the observed results are unclear because the extraction procedures used in the sources cited to support their extraction approach vary significantly (i.e., Lum and Edgar, 1983; Chunguo, 1984; Chunguo and Zihui, 1988).

[2] Total arsenic includes all measured arsenic regardless of the specific form or compound.

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provided to demonstrate that the form of arsenic measured in the extractants was not DMA. DMA can bind strongly to soil (*e.g.*, Wauchope, 1975); therefore, the proportions of total arsenic found in each extractant are just as likely to have changed due to slow equilibration between soluble DMA and soil-bound DMA as to transformation to other forms of arsenic. As a result, the conclusions of this study regarding the transformation of DMA are not supported by the data generated in the study.

In addition, the authors failed to conduct a mass balance analysis to compare the amount of arsenic present in the test soils with the amounts extracted by the test procedures. Without such an analysis, scientifically supported conclusions cannot be drawn regarding the quantity and significance of the arsenic removed with each extraction fraction. For example, the authors did not report the percentage of the added arsenic that was recovered at any of the testing time periods. Instead, they present only the percent of the recovered arsenic in each of the operationally-defined phases. As a result, the percentages for these phases always add up to 100%. Without knowing the recovery of the arsenic, one cannot draw reliable conclusions regarding the distribution of arsenic in soil.

Finally, the authors reported the results only for the soil to which the lowest arsenic concentration was added (i.e., 45 mg/kg), and for which the results are most likely to have been significantly influenced by the background levels of arsenic in the soil (i.e., 15 mg/kg) and by strong binding. Questions regarding the potential contributions of the native soil arsenic to the observed results should have been avoided by including a control sample of unamended soil in the test methodology.

2. Errors in risk assessment calculations

The publication includes calculations of the "excess cancer risk" associated with various arsenic concentrations in the test soils evaluated in the geochemistry studies. The authors are correct in noting that bioaccessibility and bioavailability information should be included when calculating risk estimates; however, the actual risk calculations presented in the article contain numerous errors and omissions, resulting in incorrect risk estimates. These errors include the following:

- *Omission of standard risk assessment components*: The calculation omits numerous essential standard components of basic cancer risk assessment equations including body weight, exposure frequency and duration, and averaging time. The omission of body weight is particularly critical because it not only yields incorrect quantitative risk estimates but also results in incorrect (and non-corresponding) units in the calculations presented in the article.[3]
- *Incorrect use of bioaccessibility estimates*: To estimate the bioavailable amount of arsenic corresponding to the various test soils, the calculation directly multiplies applied arsenic concentrations by the bioaccessibility estimates expressed as percents (see, *e.g.*, Table 4 of the article). In fact, bioaccessibility estimates reflect the fraction of the total amount of arsenic that is accessible. Thus, the correct calculation should multiply the original total arsenic concentration by the fractional form of the bioaccessibility estimate to yield the bioaccessible arsenic concentration. For example, in the first line of Table 4, the arsenic concentration (AsCS) of 45 mg/kg should be multiplied by 0.807 (not 80.7) to yield the bioaccessible arsenic concentration at the 4-month test time.

These errors yield quantitative risk estimates that are approximately 4 orders of magnitude greater than estimates derived using corrected approaches.[4] In particular, simply using the bioaccessibility estimates correctly would reduce the risk estimates by a factor of 100, while including the body weight in the calculations presented in the article would reduce the risk estimates by approximately another 1–2 orders of magnitude.[5]

[3] As presented in the first equation of Section 2.4 of the article, the chronic daily intake (CDI) has units of mg (of arsenic)/day, as obtained by multiplying the arsenic concentration in soil (AsCS, in units of mg of arsenic per kg of soil) by a daily soil ingestion rate (in units of kg of soil per day). In the second equation in Section 2.4, the CDI is stated to have units of mg/kg/day; however, no intermediate step is provided to yield these new units. The missing (and necessary) step to reconcile the units is to divide the CDI from the first equation by an assumed body weight in kg to yield a dose in the correct units for use with the cancer slope factor.

[4] Other less substantial errors in the risk calculations include misstatement of the units for the carcinogenic slope factor, i.e., the correct units are $(mg/kg/day)^{-1}$, i.e., the risk per unit of intake, not mg/kg/day as stated in the article. Although it does not change the quantitative toxicity values used in the risk calculations, it should also be noted that the IRIS database is available on-line (at: http://www.epa.gov/iris) and thus, a substantially more recent citation than that provided in the article is available.

[5] The specific quantitative impact of including body weight in the calculations depends on the specific exposure scenario examined in the risk calculations. Typical body weight assumptions range from 15 kg for young children to 70 kg for adults (US EPA, 1997).