Keeping Track of our Arsenic Intake: A Possible Citizen-Science Project

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Background

It has been known for well over 100 years that our food, beverages and drinking water all contain low concentrations of arsenic. But it is only relatively recently that the details of possible health hazards are emerging. The large number of arsenic compounds that are found in the environment may be classified as (a) naturally occurring, (b) deliberately introduced, and (c) accidentally introduced. Biological processes in both the aquatic and terrestrial environments transform these arsenic compounds, and both the products and reactants are transported around the surface of the planet, so it is inevitable that they get into food and water. We have known since the late 1980's that the forms of arsenic that occur in fish and other seafood, in relatively high concentrations, are not harmful at all. In other foods, only four compounds are found: the two inorganic compounds, arsenite and arsenate, and two methylated derivatives of arsenate known as monomethyl and dimethyl arsenic (MMA and DMA). The trimethylated compounds are known but are not found in food and drink, and the tetramethyl compounds are the harmless ones found in fish. The inorganic compounds are considered to be non-threshold, class 1 carcinogens (i.e. they definitely cause cancer in humans, and there is no dose that does not produce a response). Less is known about the toxicity of MMA and DMA, which at the moment are considered to be of intermediate toxicity but non-cancer-causing in humans.

It is only in the last 15 years or so that any details about the nature and amounts of the different arsenic compounds in foods other than fish have been reported. Although the data is really very limited at this stage, there is convincing evidence that rice contains much higher concentrations of both inorganic arsenic and DMA than does any other foodstuff..Modeling studies of how much arsenic we ingest from our food and drink based on these rather limited data support the notion that many of us (in both the USA and Europe) are exposed to inorganic arsenic through the consumption of rice and rice products at doses that exceed what is considered acceptable. As there is no dose that does not produce an increased risk of getting cancer, what is acceptable is defined in terms of the associated risk. In the USA, relevant government agencies think that the acceptable risk threshold is one in ten thousand; in Europe, the risk threshold is one in a hundred. Scientists in the USA have also calculated the value for the dose that corresponds to the 1 in 10,000 risk to be 0.027 micrograms of arsenic per kilogram of body weight per day. This translates, for a 160-lb adult to about 2 micrograms (μg) of arsenic per day.

The November 2012 issue of *Consumer Reports* contained the results of the analysis of 65 rice and rice-based products, just under half of which were rice (both brown and white). Concentrations of (a) the total arsenic, (b) the sum of the two inorganic arsenic compounds and (c) the sum of DMA and MMA were reported for 3 or 4 lots of the same product. The highest values found (all in rice grown in the USA) were about 900, 200 and 850 micrograms per kilogram (kg) of rice, respectively. If the arsenic ingested from a typical 45-gram serving of rice is not to exceed 2 μg, the concentration of inorganic arsenic should not exceed 44 μg per kg. Of the just under 100 analyses of rice reported, only 6 values were below this threshold, and so not surprisingly, as most of us ingest arsenic from sources other than rice, *Consumer Reports* recommends that adults restrict their rice intake to 2 servings per week.

It is going to be some time (maybe quite a long time) before bags of rice come with the inorganic arsenic concentration printed on the label, and as we have very little idea of how concentrations are changing over time, I am proposing that "citizen scientists" could contribute data for such a study as well as keep an eye on how much arsenic they were eating *if* there was a way to measure the inorganic arsenic content of rice that could be carried out in the kitchen (or, for those households with school-age children, in a school lab).

Chemical Measurement.

The determination of the arsenic species in rice is within the capabilities of modern analytical chemistry. After thorough mixing of grains and grinding to a flour, most expert laboratories will prepare a solution of the arsenic-containing compounds by extraction in a sealed vessel in a scientific microwave oven followed by centrifugation. A small portion of the extract is then injected into a high performance liquid chromatography apparatus. The separated compounds are washed sequentially off the chromatography column into a plasma-source mass spectrometer acting as an element-specific detector. The detection capability of such as method is between 1 and 10 μg of arsenic per kg of rice for each of the four arsenic compounds that might be found in rice (namely, the two inorganic compounds together with MMA and DMA).

Arsenic Article Continued…..

Clearly, a different approach is needed for a method performed in the kitchen. My hypothesis is that such measurements *are* possible by suitable adaptation of the home/field test-kits designed to measure arsenic in drinking water. A number of companies make such test-kits, and most are based on the Gutzeit modification of the Marsh test. The version of this that we use in our research, made by the Hach company, requires a 50 milliliter (mL) sample volume, and can detect down to 10 µg of inorganic arsenic per liter of solution, (the current US EPA maximum limit for arsenic in drinking water.) That is, the test can detect a mass as low as 500 nanograms of arsenic.

Arsenic compounds in rice can be extracted with hot water, but working directly with grains has proved difficult, a considerable fraction of the solution (and hence the extracted arsenic) is absorbed by the partially cooked rice. However, it is not difficult to grind a known mass of rice to a flour, this may help to overcome the problem of limited transfer of arsenic compounds into the solution. The next stages of the analysis are not so easy. A considerable amount of starch is also extracted and this interferes with the reaction between the arsenic and the zinc. It does not suppress it completely, but it renders the color chart provided by the Hach Company inaccurate. I have a number of ideas for overcoming these problems, and the on-going development of the method forms the basis for projects for undergraduates, working both in the arsenic-project (See STEM Ed. Inst. Newsletter 2008) and in independent study in my group. One modification we made a few years ago replaces naked-eye detection with digital image analysis with the help of the AnalyzingDigitalImages software developed by John Pickle and used in the STEM DIGITAL program.

Citizen Scientists

I was awarded a small grant by the American Chemical Society for a pilot program providing a public lecture-demonstration on the UMass Amherst Campus in December 2011 followed by distribution of test-kits to interested members of the audience, together with instructions for how to measure the arsenic content of rice in their kitchens. Participants could work through the calculations themselves or could send back a photograph of the exposed test strips placed next to the printed color chart that was included in the package. Just over 30 volunteers were recruited of whom 5 sent back results, all of which were positive in the sense that measurable colors were obtained on the test strips. But it was clear that the procedure needed further development.

Following this program, I wrote proposals to the National Science Foundation for funds to support its further development. In addition to refining the extraction procedure, dealing with the starch interference and calibration accuracy, it is necessary to demonstrate that when the results of the analyses are compared with those of the same materials obtained by the scientific laboratory procedure described above, there are no significant differences.
Unfortunately, the relevant directorate at NSF did not find this work sufficiently compelling and two proposals were rejected. In the meantime, I have further preliminary data from participants in (a) the STEM Digital summer workshops in summer 2012 and 2013, (b) STEM Ed Saturday seminars in March 2011 and 2013, (c) a summer college experience for high school students in 2012, and (d) the participants in the course NATSCI 697J (STEM DIGITAL) for members of the Science Ed. Online Masters program. All have found that it is possible to detect arsenic in rice by a "kitchen-based" method. In addition, two groups in the arsenic project and two participants in the UMass College of Natural Sciences First-Year Research Experience during the fall semester of 2013 and a group of high-school students at Four Rivers Charter School in Greenfield are exploring how to improve the performance of the test. In particular they will look at the effects of time and temperature on the basic arsine-generation reaction.

Other Challenges

There is considerable parallel activity in the analytical chemistry research community in response to calls for the introduction of regulations on the concentrations of arsenic compounds in foods and beverages. Any arsenic-in-food regulation has to be underpinned by the availability of reliable chemical measurements. The reported capability of laboratories around the world to measure the inorganic arsenic content of rice are worrying: only about half of the participants in a recent proficiency test run by a European agency obtained what the organizers called "satisfactory" results. Results of the analyses of different lots of the same rice by one laboratory show much greater variability than would be expected if the only source of variation was the random fluctuations in the response of the instruments. My students have shown very recently that this might be due to sampling errors, as we have found that (a) concentrations of arsenic in individual grains can vary by as much as a factor of 2000, and (b) rice may contain just a few percent of "super grains," containing up to 5000 µg of arsenic per kg, compared with the more usually encountered concentrations of 10 – 100 µg of arsenic per kg of rice. This has serious implications for the procedure by which a sample is taken from a bag.

Can I help?

The project is at a really interesting stage, and I would be very receptive to offers of help. I have almost no financial resources (and so one way to help is to identify potential funding agencies to which I can apply). To get involved with the experiments, you need access to a kitchen or a lab with the necessary equipment to grind and "cook" rice, and you need a digital camera. You also need at least one EZ arsenic test kit from the Hach Company, which costs about $50 and provides two reaction vessels and reagents for 100 tests. To discuss participation in the project, send me an e-mail at Tyson@chem.umass.edu.