September 11, 2010

To: Dr. Gerald Bowes

From: Prof. Dr. W. Shotyk

Re: REVIEW of DRAFT Public Health Goal for Hexavalent Chromium in Drinking Water (dated August 2009)

Dear Dr. Bowes,

I have read all of the information you have provided, including the guidelines for the review process, the comments by reviewers of the pre-release draft, and of course the DRAFT Public Health Goal (PHG) report itself. In addition, I have read some of the most recent studies of Cr in groundwater, to help put my own data (included here) in perspective, including redox state speciation and Cr stable isotope studies.

In general, the PHG report is excellent and I have no significant criticisms. However, I have some minor, general comments which are made below, and a few specific remarks about the PHG of 0.06 parts per billion of Cr in drinking water; these comments are based on my experience measuring Cr in natural freshwaters, including groundwaters and surface waters. The report clearly indicates that the PHG is not a mandatory requirement and is not developed as a target level for cleanup of contaminated waters. However, I have added my data for your information, only so that the PHG can be viewed from the perspective of natural abundance data obtained using "clean lab: methods and procedures.

Although I am not a toxicologist, my impression is that the authors have carefully reviewed the relevant, available literature, and critically discussed the most important findings, including the reduction of Cr(VI) to Cr(III) in the stomach, and its toxicological relevance. Shortcomings of individual studies are clearly indicated, for example the strengths and weaknesses of the studies of hexavalent chromium bioassays (in Table 1). The mechanisms of hexavalent chromium toxicity, to the extent it is understood, are also outlined.

In some cases, the authors seem to have gone "above and beyond" e.g. in the case of the survey of the percent of the population taking ant-acid stomach medications and the significance this might have for the reduction of Cr(VI), or in the case of mining and critically re-evaluating the data available for Cr contamination in the City of Jinzhou.

My <u>minor comments</u> are as follows:
The units employed for concentration are inconsistent, sometimes on the same page, including mg/L, mg/kg, and ppm (parts per million); this probably reflects the concentration units employed in the original publications and is a general problem in reviewing scientific literature, not something unique to this report. If the authors are reluctant to convert the original units to a single set of internally consistent concentration

units, which is completely understandable, in the very least please include a Table (e.g. in the Appendix) listing the units used.

Also, given the number of abbreviations used throughout the report, a Table summarizing and defining these would also be helpful.

On p.21 it is indicated that “trivalent chromium is an essential mineral”, but “element” would be more appropriate than “mineral”. A “mineral” is clearly defined in the earth sciences literature.

The occurrences of CrO_3 (there are at least two) should be replaced by Cr_2O_3.

My major comment is regarding the absolute value of the PHG itself (ie regarding the value of 0.06 parts per billion of hexavalent chromium in drinking water). As noted by one of the reviewers of the pre-release draft, this concentration may be low relative to the abundance of total dissolved chromium in some natural freshwaters.

Again, the report clearly indicates that the PHG is not a mandatory requirement and is not developed as a target level for cleanup of contaminated waters. Rather, the PHG is based upon the relevant toxicological data for hexavalent chromium. I understand this, and my remarks below do not in any way call into question the PHG for of 0.06 parts per billion of hexavalent chromium, nor the procedure employed to determine this value, as described in this report. Rather the comments below are meant simply to help put this value into a geochemical perspective.

In Attachment 1 of the documentation provided, we learn that the Department of Public Health considers the PHG, along with cost and feasibility in deciding on the regulatory level known as Maximum Contaminant Level (MCL); my additional comments are written with both the PHG and MCL in mind. Again, my results are intended only to be able to view these values from the perspective of the abundance of total dissolved Cr in selected natural waters.

In Appendix A (given below), I have included concentrations of total dissolved Cr in selected surface waters and groundwaters, as well as snow, tap water, and bottled waters. These data, some published and some unpublished, are from my own metal-free clean lab at the Institute of Earth Sciences, University of Heidelberg, Heidelberg, Germany. All measurements were performed using sector-field ICP-MS (lower limit of detection 0.015 parts per trillion [ie 15 pg/L, or parts per quadrillion]). Analytical details including a description of sub-boiling distillation of nitric acid used for cleaning and sample acidification, as well as the kinds of containers employed and the cleaning procedures used, are given in the publications listed in Appendix A.

First, please note that the concentrations reported in Appendix A are far lower than the concentrations for total Cr typically being reported for natural freshwaters. However, the data reported here are, in some cases, three orders of magnitude lower than the Cr concentrations reported by government agencies for the same regions of Ontario, Canada, simply because these agencies do not employ the “clean lab” methods we used (which were developed for polar snow and ice).

Second, the data presented for surface waters and groundwaters only represent my own data from intensive studies of many samples taken from only one lake watershed, and only one region of artesian springs. In other words, the data has very limited geographic significance.

Third, the data refer to total concentrations of Cr in the groundwaters and snow, and “dissolved” (< 0.45 microns) in the case of the surface waters (Kawagama Lake). The groundwaters are all anoxic (based on our measurements of redox potential), so the very low concentrations of Cr reported should be almost exclusively Cr (III). The surface waters are oxygenated, so the Cr should be exclusively Cr (VI).

Fourth, please note that the data for bottled waters represent 132 brands from 28 countries. Thus, the median Cr concentration (82 parts per trillion) can be taken as being representative of bottled waters generally.

Given these remarks, it is clear from the data in Appendix A the PHG value (60 parts per trillion) is about an order of magnitude greater than the concentrations of total Cr in the groundwaters of Springwater and Tiny Townships. These anoxic groundwaters have a pH of 8 and are generally in equilibrium with calcium carbonate.

However, the PHG value (60 parts per trillion) is below the values we have found for contemporary snow in southern Ontario (an important source of water to our streams and lakes) and generally below the values for total dissolved Cr in the streams and lakes of the Kawagama Lake watershed from rural Ontario (ca. 3 h driving N of Toronto).

Finally, the PHG value (60 parts per trillion) is significantly below the value I have found (200 ppt) for tap water from the city of London, ONT.

Again, except for the bottled water data, the data presented in Appendix A has very limited spatial or temporal validity - it is based on a very limited number of measurements I have undertaken. Despite this caveat, all of the data shown in Appendix A, and presented in the publications listed there, were obtained using the clean lab methods and procedures we developed (and published) for polar snow and ice. Thus, although the data may not be very representative in geographic terms, it is certainly accurate.

While one of the reviewers of the pre-release draft has indicated that the PHG value (60 parts per trillion) may be low relative to the abundance of total dissolved chromium in some natural freshwaters, that reviewer was referring to the published data obtained using “traditional” or “conventional” methods of measurement. When comparing my own data with published data, the order of magnitude differences in concentrations which are typically seen, probably reflects, in many if not most cases, differences in analytical methods and procedures.

Having said that, the PHG value presented here is low, relative to surface water and tap water, even when those samples are collected, handled, and measured using clean lab methods.

Again, I have no question about how the authors of this report arrived at the PHG value of 0.06 parts per billion hexavalent chromium. I simply wish to indicate that this concentration may be low, relative to the abundance of Cr in natural freshwaters, even when the natural waters are tested using “clean lab” methods.

One final, personal remark about Cr and contact dermatitis. On p. 58 it is indicated that “virtually no response is detected at concentrations below 4 to 5 ppm”. I am allergic to Cr and can no longer wear leather in direct contact with my skin. My skin reacted quickly (within a few hours) to a stainless steel watch bracelet; this is itself was remarkable in that the rate of corrosion of the stainless steel bracelet must have been very low. The bracelet was subsequently coated by the manufacturer with gold followed by rhodium, but again my skin reacted within a few hours. A second bracelet was coated with titanium using phase vapour deposition, but again my skin reacted within a few hours. Finally the manufacturer developed a bracelet of titanium and rubber, and only then did the allergic reaction cease. As a scientist suffering from an allergy to Cr, I was amazed to see how sensitive skin could be. I have no data about Cr release rates from these materials, only these observations, but it is difficult to imagine parts per million levels of Cr being released from a stainless steel watch bracelet coated with either Au/Rh or Ti.

APPENDIX A
Concentrations of total Cr in selected water samples (parts per trillion [ng/L])

Please note that all measurements described here were performed using the “clean lab” methods developed for polar snow and ice and employing sector field icp-ms. Information about the analytical methods can be found in the following publications:

Krachler, M., Zheng, J., Fisher, D.A. and Shotyk, W. (2005) Analytical procedures for improved trace element detection limits in polar ice from Arctic Canada using ICP-SMS. *Analytica Chimica Acta* 530:291-298.

Krachler, M., Zheng, J., Fisher, D.A. and Shotyk, W. (2004) Novel calibration procedure for improving trace element determinations in ice and water samples using ICP-SMS. *Journal of Analytical Atomic Spectrometry* 19:1017-1019.

1. Groundwater, two artesian springs, collected from galvanized steel pipes, Cr concentration range 5 to 8 ppt (Springwater Township, Simcoe County, ONT). These data are found in the following publication:

Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S. and Zheng, J. (2010) Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water. *Journal of Environmental Monitoring* 12:208-217.

2. Groundwater, artesians springs, stainless steel or acid-washed high density polyethylene, Cr concentration range 1 to 8 ppt (dedicated groundwater research wells, Springwater Township, Simcoe County, ONT); unpublished data

3. Snow, southern Ontario, four sampling locations, Cr. concentration range ca. 100 to 150 ppt. These data are found in the following publication:

Shotyk, W., Krachler, M., Aeschbach-Hertig, W., Hillier, S. and Zheng, J. (2010) Trace elements in recent groundwater of an artesian flow system and comparison with snow: enrichments, depletions, and chemical evolution of the water. *Journal of Environmental Monitoring* 12:208-217.

4. Surface water, Kawagama Lake surface water, Cr concentration range 50 to 300 ppt. While the Cr concentration data are unpublished, the Pb concentration data and a description of the site can be found in the following publication:

Shotyk, W. and Krachler, M. (2010) The isotopic evolution of atmospheric Pb in central Ontario since AD 1800, and its impacts on the soils, waters, and sediments of a forested watershed, Kawagama Lake. *Geochimica et Cosmochimica Acta* 74:1963-1981.

5. Tap water, London, ONT (from a single household, water having been running for 1 h), Cr concentration 200 ppt, unpublished data

6. RO water (same household in London ONT), Cr concentration 30 ppt, unpublished data

7. Bottled water, international survey of 132 brands from 28 countries, 6 ppt to 1720 ppt, median 82 ppt

Krachler, M. and Shotyk, W. (2008) Trace and ultratrace metals in bottled waters: survey of sources worldwide and comparison with refillable metal bottles. *Science of the Total Environment* 407:1089-1096.

The great challenges in measuring the abundance of trace metals in natural freshwaters are briefly noted in the following editorial

Shotyk, W. and Krachler, M. (2010) Determination of trace element concentrations in natural freshwaters: how low is "low", and how low do we have to go? *Journal of Environmental Monitoring* 11:1747 - 1753, DOI: 10.1039/b917090c.