Correspondence

Comment on “Perchlorate Identification in Fertilizers” and the Subsequent Addition/Correction

SIR: Perchlorate (ClO$_4^-$) contamination has been reported in several fertilizer materials (1, 2) and not just in mined Chile saltpeter, where it is a well-known natural impurity (3). To survey fertilizers for perchlorate, two analytical techniques have been applied to 45 products that span agricultural, horticultural, and retail markets, including several lots for some (see Supporting Information for details). On the basis of the results presented here, it appears that fertilizers are not significant contributors to perchlorate in the environment.

Standard reference materials were purchased from the National Institute of Standards and Technology. Sealed fertilizer packages were obtained from stores in the vicinities of Pittsburgh, PA; Cincinnati, OH; Knoxville, TN; Batesville, IN; and West Harrison, IN. Bulk agricultural fertilizers were sampled from distributors in Cincinnati, OH, and Greensburg, IN; random samples (~1 kg) were collected. Bulldog Soda sodium nitrate was provided by Prof. W. P. Robarge, Department of Soil Science, North Carolina State University, Durham, NC. KMag (langbeinite) was provided by Prof. E. C. Johnson, Department of Chemistry, University of Wisconsin—Stevens Point, Stevens Point, WI. Overnight shippers were used to transfer items between ORNL and EPA. Package seals were broken only by EPA or ORNL staff.

Product samples were combined with water at a ratio of 10 g dL$^{-1}$ (~10% w/w) and dissolved or levigated in a blender for 2–4 min (using 10–100 g of product). Insoluble materials were leached (post-levigation) by soaking for 24–48 h with intermittent shaking. The aqueous phase was filtered through glass fiber and 0.45-µm cellulose acetate. No measurable analyte loss was observed in standard solutions subjected to such filtration. ESI-MS analysis (4) was adapted as follows. The filtrate was first diluted 10% w/v. A 100-µL aliquot of the dilution was combined with 1.00 mL of 0.20 M C$_{10}$H$_{21}$NMe$_3^-$ and 5.00 mL of methyl isobutyl ketone and diluted to 100 mL in a volumetric flask. Duplicates were run with spikes of 0, 10, and 20 ng mL$^{-1}$ ClO$_4^-$ to allow the data to be analyzed by the method of standard additions. The flasks were stoppered and vigorously shaken; phases separated after 10–30 min. The MIBK extracts were drawn off and kept at ~−15 °C other than during instrumental analysis. For IC analysis, the filtrates were diluted until a 100 ng mL$^{-1}$ spike could be recovered 100 ± 7% (100 µL loop, AG11/AS11 columns, ED40 detector) adapted from Jackson et al. (5).

Perchlorate was detected only in sodium nitrate derived from Chilean caliche (1.2–1.8 mg g$^{-1}$). None of the other materials showed perchlorate above the detection limits, but recovery of fortifications was satisfactory by IC. Detection limits for ESI-MS and IC are below 100 (0.01%) and 50 µg g$^{-1}$ (0.005%), respectively, based on dilution and other factors. At present, perchlorate has been confirmed in only two raw materials, with Chilean sodium nitrate being the well-known source. The U.S. Geological Survey and Air Force Research Laboratories report sporadic detection of perchlorate in sylvite (KCl) (6), and the USGS is pursuing further study.

Modern farming practices use a variety of products, including ammonium nitrate, potassium chloride, and phosphate rock to augment soil nutrients. Some states keep statistics on fertilizer application by N–P–K ratio, but there is usually not a breakdown into individual components. Therefore, even if some fertilizers contain perchlorate, it is difficult to correlate fertilizer consumption and application with exposure risk. For example, the Office of the Indiana State Chemist (OISC) tracks consumption of the top 10 fertilizers semi-annually by N–P–K ratio per county. Some single component formulations are tracked, such as 82–0–0 (NH$_4$) and 46–0–0 (urea). Multiple component formulations are also tracked, but the compounds providing each nutrient are not tracked. The OISC reported that Indiana farmers applied 48–478 tons of urea and 193–347 tons of anhydrous ammonia in 1998 (7), neither of which is contaminated with perchlorate. Fertilizer application to family gardens and lawns is not monitored at all in Indiana, and these products are generally not the same as those used by production farms.

Some of the most common nitrogen sources are ammonia, urea, and ammonium nitrate. More than 99% of these materials are synthesized from atmospheric gases (N$_2$, O$_2$, CO$_2$) or CH$_4$ as opposed to being derived from caliche. Manufacturing processes for these N sources do not use chlorine compounds. These N sources are heavily used for growing corn, wheat, and rice; accordingly, current agricultural production of grain crops is unlikely to be implicated in the polluting of natural waters with perchlorate. At present, there is insufficient information on uptake of perchlorate by food plants to reasonably assess exposure via ingested produce. While there may be a niche for Chile saltpeter in some crops and thus localized perchlorate-tainted runoff, our results suggest that there is minimal cause for concern over water pollution from fertilizers currently used in either agricultural states or backyard gardens. Prior to the Haber process, natural saltpeters were staples in American farming, and so regions that have a history of applying these products should be prepared to monitor for and possibly encounter perchlorate. However, natural saltpeters now constitute ~0.14% of annual U.S. fertilizer consumption. For instance, much of the nitrogen used in the Corn Belt is in the form of urea or ammonia.

There is a consensus that certain lots of some products did in fact contain perchlorate when originally sampled and reported (1), but that phenomenon appears to have constituted a sporadic—if not singular—event rather than reflecting a recurring problem. In fact, 17 additional products analyzed by the same investigators contained no detectable perchlorate (2). Nevertheless, this EPA laboratory is coordinating a more comprehensive survey of fertilizers and raw materials, which aims to resolve the issue completely.

Acknowledgments

We appreciate Kova Fertilizer Inc. and CF Industries Inc. permitting us to sample their products on-site. We thank W. P. Robarge, E. C. Johnson, E. J. Urbansky, and C. A. Urbansky for assistance in sample procurement. We acknowledge OISC’s M. Hancock and P. F. Kane, who provided information for this report. Mention of specific products and/or manufacturers should not be construed as endorsement by the U.S. Government. ORNL is managed by University of Tennessee—Battelle LLC for the U.S. Department of Energy.

Supporting Information Available

Four tables showing detailed information on the 45 products

Literature Cited

(6) Harvey, G. J.; Tsui, D. T.; Eldridge, J. E.; Orris, G. J. 20th Annual Meeting Abstract Book; Society of Environmental and Toxicological Chemists; Abstract PHA015; p 277.

Edward T. Urbansky,* Matthew L. Magnuson, and Catherine A. Kelty
United States Environmental Protection Agency
National Risk Management Research Laboratory
Water Supply and Water Resources Division
Cincinnati, Ohio 45268

Baohua Gu‡ and Gilbert M. Brown‡
Oak Ridge National Laboratory
Environmental Sciences Division and
Chemical and Analytical Sciences Division
Oak Ridge, Tennessee 37831

ES0011515

* Corresponding author phone: (513)569-7655; fax: (513)569-7658; e-mail: Urbansky.Edward@EPA.gov.
‡ Environmental Sciences Division.
‡ Chemical and Analytical Sciences Division.