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Commentary

Perchlorate levels in samples of sodium nitrate fertilizer derived from Chilean caliche

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"Capsule": *Sodium nitrate fertilizer, made from refined caliche, also contains perchlorate — a potential environmental contaminant.*

Abstract

Paleogeochemical deposits in northern Chile are a rich source of naturally occurring sodium nitrate (Chile saltpeter). These ores are mined to isolate $NaNO_3$ (16–0–0) for use as fertilizer. Coincidentally, these very same deposits are a natural source of perchlorate anion (ClO_4^-). At sufficiently high concentrations, perchlorate interferes with iodide uptake in the thyroid gland and has been used medicinally for this purpose. In 1997, perchlorate contamination was discovered in a number of US water supplies, including Lake Mead and the Colorado River. Subsequently, the Environmental Protection Agency added this species to the Contaminant Candidate List for drinking water and will begin assessing occurrence via the Unregulated Contaminants Monitoring Rule in 2001. Effective risk assessment requires characterizing possible sources, including fertilizer. Samples were analyzed by ion chromatography and confirmed by complexation electrospray ionization mass spectrometry. Within a lot, distribution of perchlorate is nearly homogeneous, presumably due to the manufacturing process. Two different lots we analyzed differed by 15%, containing an average of either 1.5 or 1.8 mg g^{-1}. Inadequate sample size can lead to incorrect estimations; 100-g samples gave sufficiently consistent and reproducible results. At present, information on natural attenuation, plant uptake, use/application, and dilution is too limited to evaluate the significance of these findings, and further research is needed in these areas. Published by Elsevier Science Ltd.

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1. Introduction

Among its natural resources, Chile possesses caliche ores rich in sodium nitrate ($NaNO_3$). The caliche is mined and leached to obtain the sodium nitrate, which is further refined and prilled to produce a commercial fertilizer. This product is made by Sociedad Química y Minera S.A. (SQM), which mines and refines caliche at facilities in María Elena and Pedro de Valdivia in northern Chile. SQM markets its products in the USA under the name Bulldog Soda through its North American subsidiary, Chilean Nitrate Corporation (CNC, 1999). Annually, ~75,000 short tons of Chilean nitrate products are imported into the USA (Renner, 1999b). Sodium nitrate (N–P–K ratio: 16–0–0) is known by several synonyms, e.g. nitratine, soda niter, and nitrate of soda. CNC markets the product to growers of tobacco, citrus fruits, cotton, and some vegetable crops, particularly emphasizing that the products are low in chloride content (CNC, 1999). Conversations with county agricultural extension agents and fertilizer distributors suggest that usage of this product can be highly localized in some areas. SQM also sells this product to companies such as Voluntary Purchasing Groups, Inc., or A.H. Hoffman, Inc., who repackage and resell it (to retailers) as Hi-Yield® or Hoffman® nitrate of soda, respectively.

Chile's paleogeochemical sodium nitrate deposits are known to contain naturally occurring perchlorate (ClO_4^-) (Schilt, 1979; Ericksen, 1983). Subsequent to the

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discovery of perchlorate in water supplies in the western United States, including the Colorado River, this ion has come under study by the Environmental Protection Agency (EPA; Urbansky, 1998; Damian and Pontius, 1999; Renner, 1999a) due to possible effects on the thyroid gland (Environmental Protection Agency, 1998; Clark, 2000). As a result of this concern, perchlorate was included on EPA's drinking water Contaminant Candidate List (CCL; Perciasepe, 1998), and was recently added to the Unregulated Contaminants Monitoring Rule (UCMR; Browner, 1999). Attention was focused on perchlorate in fertilizers as a result of a controversial communication by Susarla et al. (1999; cf. Renner 1999b; The Fertilizer Institute, 1999). The potential for groundwater and surface water contamination via agricultural runoff is an obvious concern, and so EPA and other agencies have been analyzing fertilizers to quantitatively determine perchlorate content.

The regulatory fate of perchlorate as a drinking water contaminant is still unknown (Pontius et al., 2000). However, perchlorate contamination in potable water supplies is difficult to treat (Urbansky and Schock, 1999); thus, it is desirable to minimize release as much as possible. It appears that microbes capable of reducing perchlorate are fairly abundant (Logan, 1998; Coates et al., 1999, 2000; Nzengung and Wang, 2000). Nevertheless, there is little information available on natural attenuation, and UCMR data will indicate how widespread perchlorate contamination is in public potable water supplies.

Quantitation of perchlorate by ion chromatography (IC) is likely to dominate the analysis of both drinking water (Jackson et al., 1999, 2000) and fertilizers (Susarla et al., 1999, 2000). For potable water, other techniques are available for determining perchlorate, such as electrospray ionization mass spectrometry (ESI-MS) (Urbansky et al., 1999; Clewell et al., 2000; Magnuson et al., 2000a, b). Capillary electrophoresis and Raman spectrometry have been applied specifically to fertilizers by other investigators (Susarla et al., 1999).

A fair volume of literature is dedicated to sampling fertilizers and similar bulk materials (Benedetti-Pichler, 1956a, b; Lance, 1980; The Fertilizer Institute, 1996; Association of Official Analytical Chemists International, 1997; Jaeger and Nagel, 1997; American Society for Testing and Materials, 1999a, b). Nonetheless, sampling continues to be a source of debate among those of us concerned with qualitatively and quantitatively determining perchlorate in fertilizers. Little is known about the distribution of perchlorate in geologic nitrate deposits; therefore, little can be discerned about the distribution of perchlorate in sodium nitrate fertilizers. This problem is exacerbated in heterogeneous multicomponent formulation fertilizers, such as lawn fertilizers, because we do not know which raw ingredient/s is/are responsible for supplying the perchlorate. At the present time, sodium nitrate derived from Chilean caliche is the only confirmed source of perchlorate.

SQM uses large leaching vats to dissolve the soluble components of the caliche. The leachates are further refined and then prilled. Because an aqueous dissolution step is involved, homogeneous distribution of perchlorate would be expected within the product derived from a batch of ore processed at one time. Even if perchlorate salts are locally concentrated in pockets within the caliche, the refining process should homogenize the material. Our objective was to determine whether the perchlorate was uniformly distributed within bags and lots of material as suggested by the manufacturing process.

2. Materials and methods

2.1. Procurement and custody

Ten 2.27-kg (5.00-lb) bags of nitrate of soda (A.H. Hoffman, Inc., 167 Greenfield Road, Lancaster, PA 17601, USA) were purchased by EPA staff from stores in the greater Cincinnati tristate area. A.H. Hoffman verified that the material we purchased was repackaged SQM Bulldog Soda (communication to the authors). Five bags were purchased from each of two manufacturing lots. Packaging was verifed to be intact prior to opening by EPA. Although the material we purchased is marketed as a horticultural fertilizer, we emphasize that it is a repackaged version of the same Chilean sodium nitrate sold to tobacco growers and other farmers. As we noted earlier, sodium nitrate is not a major agricultural fertilizer, but has become established in some niches.

2.2. Sampling and dissolution

From each bag, five 10.0-g and five 100.0-g samples were removed, representing various regions of the bagged product. The product was not mixed or riffled in any way, nor was it ground. One lot had uniform, well-defined, and well-formed prills, while the other contained particles very heterogeneous in size and shape; there was a mixture of prills, finely ground particles, and hard clumps. Samples were dissolved to give 100 g l^{-1}. The remainder of the bag was weighed and dissolved into deionized water at the same ratio. Prior to analysis, each solution was diluted 10% v/v to produce a solution at 10 g l^{-1}.

2.3. Analysis and confirmation

A 1.000 g ClO$_4^-$ l^{-1} perchlorate solution was prepared by dissolving Aldrich (Milwaukee, WI, USA) ACS reagent grade ammonium perchlorate into deionized

water. This stock solution was serially diluted to produce standards at concentrations of 0 (blank), 1.00, 2.50, 5.00, 7.50, 10.0, 15.0, 20.0, and 25.0 mg l^{-1} and used to generate a linear calibration plot ($R^2 = 0.999$). The lower limit of detection is ~0.5 mg l^{-1}. Samples were analyzed on a Dionex (Sunnyvale, CA, USA) DX-300 ion chromatograph with 4-mm AG11 (guard) and AS11 (analytical separation) columns using a 500 μl sample loop with conductivity detection. The ASRS (suppressor) current was set to 300 mA. Eluent was 0.10 M NaOH(aq) operated isocratically at a flow rate of 1.00 ml min^{-1}. Duplicate injections agreed within 1.2%. After every fifth sample, at least one calibration check standards was run with blanks also run after at least every 10th sample. Fortified samples (17.0 mg l^{-1} spike) were run approximately after every 10th sample; average recovery was 94%.

Confirmatory identification of perchlorate was made as follows. Into a 100-ml volumetric flask, the following were added: a 100 μl aliquot of a 10 g l^{-1} solution, 1.00 ml of 0.20 M $C_{10}H_{21}NMe_3Br$(aq) solution, 99 ml of deionized water, and 5.00 ml pesticide residue analysis grade methyl isobutyl ketone. Flasks were stoppered and shaken. After separation, the MIBK phase was drawn off. MIBK extracts were subjected to ESI-MS. $C_{10}H_{21}NMe_3(Br)(ClO_4)^-$ and $C_{10}H_{21}NMe_3(ClO_4)_2^-$ complexes were identified by m/z ratio as described previously (Magnuson et al., 2000a, b) using a Finnegan-Mat (San Rafael, CA, USA) TSQ 700 quadrupole spectrometer; operating parameters were as described. The lower limit of detection in solution is ~0.5 ng ml^{-1}. One sample from each lot was randomly selected for confirmatory analysis.

3. Results and discussion

It is recommended that samples of at least 100 g be used to ensure local inhomogeneities are avoided. However, as long as several replicates are used, the average value remained nearly constant regardless of sample size. If only one sample is to be analyzed, however, more attention must be paid to sampling the material. It is worth noting that one of the 10.0-g samples contained only 0.82 mg g^{-1} and another only 0.74 mg g^{-1}, about half the average for the bag or the lot in both cases. Otherwise, individual 10.0-g samples varied in perchlorate concentration from a low of 1.39 mg g^{-1} to a high of 1.96 mg g^{-1}. For the bags of fertilizer we tested, this sampling artifact was completely lost if 100-g samples were considered, however.

Because it is easy to dissolve any mass of sodium nitrate, the time and cost associated with dissolution of larger samples are not practical constraints. It should be possible to obtain a suitable composite sample by reducing the material to a uniform size (as by forced sieving) and subsequent riffling. As Jaeger and Nagel (1997) point out, settling occurs based on particle size and not density. Consequently, it is essential that sampled materials be comprised of particles of uniform size and shape.

Regardless of the sample size or lot tested, perchlorate in the solid fertilizer ranged from 0.7 to 2.0 mg g^{-1}, variation of less than a factor of 3. That notwithstanding, there is unquestionably lot-to-lot variability. The first lot had an average perchlorate concentration of 1.5 mg g^{-1}, while the second had an average perchlorate concentration of 1.8 mg g^{-1}, a 15% relative difference. Our original conjecture that the perchlorate should be reasonably uniform in distribution is in fact borne out by the data. Presumably, this is the net effect of combining large amounts of caliche of varying perchlorate content and leaching the soluble materials into an aqueous solution, which is homogeneous by definition. Although some local variation in distribution can be observed, it appears that these products are of nearly constant perchlorate content at the 100-g scale. Consequently, agricultural use of this material might be predicted to give a fairly uniform perchlorate distribution on the soil based on the limited results of this study. However, any extrapolation to agricultural use must be carefully qualified; sweeping generalizations cannot be made. Depending on the acreage, actual farming practices might consume several tons of such material; it is sold by the pallet in 22.7-kg (50-lb) bags. Furthermore, fertilizer from several processing lots may be applied at a specific site.

For the time being, it is probably reasonable to estimate that sodium nitrate fertilizers derived from Chilean caliche contain approximately 0.5–2 mg g^{-1} of perchlorate anion. Because it is possible to quantitate the perchlorate concentration for each manufacturing lot, it is not necessary to use such rough numbers. If the perchlorate content is known for specific fertilizer lots to be applied, this concentration can be used to estimate the total amount of perchlorate available for dissemination to the environment so that *appropriate*, site-specific measures may be taken to protect nearby aquatic ecosystems or potable water sources. It is premature to speculate what measures — if any — might be *appropriate* as the ecological impact of perchlorate is not well known. Moreover, the impact will be influenced by a number of factors, including rainfall and irrigation, dilution, natural attenuation, soil adsorption, and bioavailability — most of which are *not* known in sufficient detail to make meaningful predictions at this time. Ongoing research suggests that perchlorate-reducing microbes can be quickly cultured in the laboratory, which suggests that biodegradative processes might completely metabolize perchlorate to chloride in regions with adequate rainfall, nutrients (lactate, acetate, etc.) and under oxygen- and nitrate-free conditions.

4. Conclusions

We must emphasize that it is premature to take any steps regarding the use of natural Chile saltpeter as a fertilizer. Knowledge of health effects and significant variation in ecosystems preclude any specific recommendations. However, it is our hope that this commentary spurs other researchers to investigate natural attenuation and soil adsorption in a variety of climates and soil types wherever Chilean sodium nitrate is used. Furthermore, it will be necessary to have accurate data on the distribution and application of specific analyzed lots of fertilizer to be used framed within the characteristics of a site-specific watershed or ecosystem. In addition, there is some question as to how much perchlorate can be found in caliche ore. Ideally, these values would be better defined.

5. US government notice

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