



# Comparison and evaluation of laboratory performance on a method for the determination of perchlorate in fertilizers†‡

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This report details the interlaboratory validation of a method for the determination of perchlorate in fertilizers. In this method (EPA/600/R-01/026), a solid sample of fertilizer is ground. Subsequently, the ground material is either leached with deionized water to dissolve any perchlorate salt in the case of minimally soluble fertilizers (e.g. supertriplephosphate or timed-release products), or simply dissolved in the case of highly soluble fertilizers (e.g. urea, NaNO<sub>3</sub> or KCl). The resulting aqueous solution is then subjected to ion chromatography with suppressed conductivity detection. Four laboratories applied the method to field samples of 48 different products (commodity chemicals) and to seven quality control samples prepared by the Environmental Protection Agency (EPA). Additional tests were conducted by three other laboratories on specific materials. Recovery (81–111%) was demonstrated on spikes of known concentration, and a preliminary assured reporting level was determined for each fertilizer matrix by each laboratory. Injection-to-injection precision was satisfactory: generally less than 15% difference, and always less than 25%. All of the laboratories used Dionex IonPac AG16 guard and AS16 separation columns with NaOH or KOH as eluent. Detection was by suppressed conductivity. The method was shown to be sufficiently robust for the screening of fertilizers for perchlorate, but performance was low on a mixture of siliceous minerals (kaolinite and bentonite). Both laboratory performance and method performance are validated.

## 1 Aim of investigation

Perchlorate was discovered and confirmed in Californian water supplies in 1997,<sup>1,2</sup> and the Environmental Protection Agency (EPA) placed perchlorate on the Drinking Water Contaminant Candidate List in 1998.<sup>3,4</sup> Subsequently, it has been found in other US states, but current data show minimal occurrence nationwide.<sup>5</sup> Instead, contaminated sites appear to be confined geographically and linked to identifiable point sources, such as military installations and manufacturing sites.<sup>5,6</sup> While perchlorate is known to affect thyroid function at sufficient concentrations,<sup>7</sup> the EPA has not established any enforceable health standards or regulations for perchlorate in drinking water or other media. However, some states have set limits independently. Concern over perchlorate in fertilizers began in 1999 when an EPA laboratory found perchlorate in several products.<sup>8–10</sup> While some studies corroborated occurrence in fertilizers, others did not.<sup>9,11–15</sup> However, it is important to point out that each study tested different products. In addition, the methods of analysis varied among investigators. Nonetheless, many investigations relied on ion chromatography for at least some of their data.<sup>8–12,16,17</sup>

Our objective in this paper is to describe the validation of a method employed by the EPA to assess perchlorate occurrence in fertilizers used in the USA on large-scale agricultural production farms, lawns, vegetable gardens and other venues.

This work builds on the findings of a previous investigation conducted by the US Air Force Research Laboratories (AFRL).<sup>16</sup> The analytical chemistry of perchlorate has been reviewed elsewhere.<sup>18</sup> While many techniques have been used to determine perchlorate, the method<sup>19</sup> used in this investigation has been adapted from EPA Method 314.0†,<sup>20</sup> which was developed for the analysis of drinking water samples, and is based on ion chromatography.

## 2 Experimental

### 2.1 Design

The study was composed of two distinct phases. Phase 1 was designed to evaluate laboratory performance and to assess the robustness of the ion chromatographic portion of the method. Robustness was framed in terms of two sets of criteria. First, the method was to be clear, easy to follow and minimally laborious or tedious. Second, it was to give satisfactory results when conducted by an experienced chemist. Participant laboratories were required to use ion chromatography, but were permitted to choose columns and operating conditions on their own, within certain restrictions. Phase 1 test samples included a wide variety of fertilizer matrices. Phase 1 was largely intended to evaluate the ability of each laboratory to measure perchlorate in the presence of a high ionic strength and/or high solute concentration matrix. Therefore, many liquid samples of known perchlorate concentration were included. This ensured that each laboratory was working with the same solution at the start, and eliminated the leaching/dissolution step as a source of error for interlaboratory comparison of ion chromatography

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results. Phase 1 was conducted in such a manner that laboratories did not know the identities of the samples, even with regard to their general composition, and the EPA did not know the identities of the laboratories when analyzing the data. An intermediary at the Office of Indiana State Chemist (OISC) was designated to assign numbers to laboratories and to eliminate any direct communication between the laboratories and EPA that might bias our perceptions.

In Phase 2, bulk samples of materials were collected, homogenized and sent to the participating laboratories. All of the Phase 2 materials were solids. Consequently, Phase 2 allowed an evaluation of the leaching/dissolution (and other pretreatment) steps, distinct from the ion chromatography analyses of the solutions, and an assessment of the variation attributable to the leaching and/or dissolution steps among participant analytical laboratories. Phase 2 also included a set of quality control standards that were not identified to the laboratories as distinct from real-world samples. In Phase 2, laboratories were permitted to communicate directly with the EPA regarding specific samples or methods; however, laboratory data were initially identified only with the code number assigned by the OISC. Only after the data had been tabulated and examined were the laboratories linked with their data. For both phases, data were sent to the EPA laboratory in Cincinnati for evaluation and analysis.

## 2.2 Selection of participant laboratories

Participation was open to any US laboratory that agreed to abide by the project rules. Principally, the rules were as follows: (i) laboratories would not be compensated financially or by

other means for their participation; (ii) strict confidentiality would be maintained; laboratories would be permitted to contact only the authors or a designated intermediary at the OISC; (iii) all data, chromatograms, notebooks and records would be available to the EPA for examination; (iv) copies of chromatograms would be furnished to the EPA; (v) data would be supplied in a specified format; (vi) the EPA would have unlimited use of the data and results; (vii) the EPA would determine the validity of any measurement or practice; (viii) laboratories would be required to demonstrate proficiency to the EPA's satisfaction; (ix) the EPA would determine when and how data and results would be released or cleared for use; (x) laboratories would allocate sufficient resources to meet the project timetable.

The following laboratories requested to participate in the process and were accepted: California Department of Food and Agriculture (CDFA), Dionex Corporation, American Pacific Corporation (AMPAC), North Carolina State University Department of Soil Science (NCSU), Montgomery Watson Laboratories (MWL) and IMC-Phosphates Environmental Laboratory.

## 2.3 Phase 1: evaluation of participant laboratories and method robustness

**2.3.1 Preparation of performance evaluation standards.** A set of performance evaluation materials was prepared by the EPA laboratory in Cincinnati. The identities of the Phase 1 materials are given in Table 1. These materials spanned commodity chemicals, water-soluble plant foods and granulated/pelletized lawn fertilizers. All of the raw materials were either ACS

**Table 1** Standard materials prepared by the EPA for use in Phase 1

No.	Form <sup>a</sup>	Composition <sup>b</sup>
1	S	Agricultural grade granulated triplesuperphosphate [mostly Ca(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub> ·H <sub>2</sub> O]
2	S	Bentonite + kaolinite (50% w/w) + 990 µg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> )
3	S	Agricultural (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub>
4	L	Agricultural grade NH <sub>4</sub> NO <sub>3</sub> + 620 µg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> )
5	S	Agricultural grade NH <sub>4</sub> NO <sub>3</sub> + 310 µg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> )
6	S	Duplicate of No. 5
7	S	ACS reagent urea + 530 µg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> )
8	S	ACS reagent urea
9	S	Agricultural grade KCl (0-0-60)
10	S	Duplicate of No. 9
11	L	ACS reagents: urea, K <sub>2</sub> SO <sub>4</sub> , NaCl, (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> , KNO <sub>3</sub> + xylene cyanole FF <sup>c</sup>
12	L	Duplicate of No. 11
13	L	No. 11 + 170 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> )
14	L	No. 11 + 170 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (NH <sub>4</sub> <sup>+</sup> )
15	S	Vigoro lawn winterizer, 22-3-14
16	S	Scotts lawn winterizer, 22-3-14
17	S	Duplicate of No. 16
18	S	No. 16 + 1.4 mg g <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup>
19	L	Agricultural grade (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> ; ACS reagents: urea, KCl, NaNO <sub>3</sub> , MgSO <sub>4</sub> , bentonite, CoCl <sub>2</sub> ·6H <sub>2</sub> O, NiCl <sub>2</sub> ·6H <sub>2</sub> O <sup>d</sup>
20	L	No. 19 + 82 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> )
21	L	No. 19 + 82 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (K <sup>+</sup> )
22	L	No. 19 + 82 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (NH <sub>4</sub> <sup>+</sup> )
23	L	No. 19 + 82 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (NBu <sub>4</sub> <sup>+</sup> )
24	L	No. 19 + 82 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (NOct <sub>4</sub> <sup>+</sup> ) + ~0.5% w/w SDS <sup>e</sup>
25	L	Deionized water + 6.2 ng mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> + trace FD&C Blue No. 1
26	L	Cincinnati tap water + 34 ng mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> )
27	L	Cincinnati tap water + 1.34 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (Na <sup>+</sup> )
28	L	Peter's water-soluble plant food, 20-20-20
29	L	Miracle Gro tomato food, 18-18-21
30	L	ACS reagent (NH <sub>4</sub> ) <sub>2</sub> HPO <sub>4</sub> + 12 µg mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (NH <sub>4</sub> <sup>+</sup> )
31	L	ACS reagent KCl + 74 ng mL <sup>-1</sup> ClO <sub>4</sub> <sup>-</sup> (K <sup>+</sup> )

<sup>a</sup>Form of the material: S, a dry, powdered *solid*; or L, an aqueous *liquid* solution. All of the liquid samples were made by leaching or dissolving the solid in deionized water at a ratio of 10 g dL<sup>-1</sup> (*i.e.* ~10% w/w). <sup>b</sup>Cations of the perchlorate salts used to fortify these materials are identified in parentheses. All of the major components were either ACS reagent grade or agricultural grade and verified to be perchlorate-free (within the limits of experimental error) by the EPA. <sup>c</sup>Ingredients for No. 11: 100 g each (NH<sub>2</sub>)<sub>2</sub>CO, K<sub>2</sub>SO<sub>4</sub>, (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub> and KNO<sub>3</sub>, 50 g NaCl, <0.1 g xylene cyanole FF. <sup>d</sup>Ingredients for No. 19: 118 g agricultural grade (NH<sub>4</sub>)<sub>2</sub>HPO<sub>4</sub>, ACS reagents: 118 g (NH<sub>2</sub>)<sub>2</sub>CO, 71 g KCl, 47 g NaNO<sub>3</sub>, 24 g MgSO<sub>4</sub>, 24 g bentonite, 16 mg CoCl<sub>2</sub>·6H<sub>2</sub>O, 16 mg NiCl<sub>2</sub>·6H<sub>2</sub>O. <sup>e</sup>SDS = sodium dodecylsulfate, CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>OSO<sub>3</sub>Na, an anionic surfactant. SDS was added to aid in the dispersion of the tetraoctylammonium perchlorate, which resisted dissolution despite vigorous blending and agitation.

reagent grade or verified to be perchlorate-free (within the limits of experimental error) by the EPA. A combination of solid and liquid (aqueous) samples was sent to each laboratory under tamper-evident custody seal.

Solid samples were ground using a kitchen blender. Approximately 200 g of material can be satisfactorily ground while ensuring adequate mixing. To obtain enough of each material, multiple ground portions were placed into jars and mixed by several repetitions each of stirring, shaking and rotating (both by rolling the jar and end-over-end mixing). While our original intent was to use a ball mill, we found that considerable caking of the material occurred after 5–10 min of operation, regardless of the composition or size of the grinding media. This appears to be primarily due to the hygroscopic (and sometimes even deliquescent) nature of some of the compounds. Many prilled fertilizers are coated or dusted with additives (processing aids/anti-caking agents) to keep them free-flowing. Participant laboratories were sent pre-weighed portions ( $4.00 \pm 0.05$  g) of solid materials in high-density polyethylene (HDPE) or polypropylene (PP) bottles.

All of the liquid samples were made by leaching or dissolving the solid in deionized water at a ratio of  $10 \text{ g dL}^{-1}$  ( $=0.1 \text{ g mL}^{-1}$ ); the choice of unit reflects the convenience of relating to mass per cent since  $10 \text{ g dL}^{-1} \approx 10\% \text{ w/w}$ . While some samples dissolve completely and form a homogeneous solution, others do not and require additional attention. Some water-soluble plant foods contain small amounts of silicate minerals (e.g. sand), calcium sulfate, calcium carbonate or other gritty particles that do not dissolve readily, if at all. For example, agricultural grade granular triplesuperphosphate contains a considerable fraction of insoluble matter. Timed-release or controlled-release fertilizers are often coated with methylene-urea polymers that hydrolyze slowly, but the pellets can be crushed (with a mortar and pestle) or cut (in a blender) to expose the soluble inner components to the aqueous phase; polymer shells remain behind and are filtered off. Lastly, lawn and garden products (normally called specialty products by the fertilizer industry) are usually formulated with fillers which serve as diluents to prevent overapplication by the consumer. Some fillers are insoluble minerals that readily settle out, while others form finely divided suspensions that are resistant to settling. When necessary, the liquids were filtered to remove observable sediment or suspended particulate matter. Filtration was through a bed of at least 2 cm of glass fiber and  $0.45 \mu\text{m}$  cellulose acetate membranes. When the insoluble matter settled sufficiently such that a liquid sample could be decanted without transfer of the particulates, the liquid was not filtered. When some prilled agricultural grade urea or sodium nitrate products were dissolved, a froth or foam formed at the surface. This phenomenon appears to be linked with the processing aids used to prevent clumping as neither compound exhibits surfactant properties; foaming is not observed with reagent grade chemicals. Furthermore, animal feed grade urea (which we had tested previously) does not exhibit this property. Whenever froth or foam was observed in liquid standards, it was confined to the neck of a volumetric flask, suctioned off and discarded (it was not subjected to any type of analysis). Liquid samples were subsequently decanted into LDPE or PP containers and sent to the participant laboratories.

**2.3.2 Fortification procedure.** Initially, it was not clear what method should be used to fortify solid materials. There are several principles that should ideally be adhered to in the production of a standard material: (i) the analyte should be distributed as homogeneously as possible; (ii) the amount of analyte in a mass of sample (*i.e.* its concentration) should be accurately and precisely known; (iii) the form of the analyte should be similar to that associated with materials known to contain the analyte; specifically, the cation of the salt should be matched, *e.g.*  $\text{KClO}_4$  should be used to spike  $\text{KNO}_3$ ; (iv) the

spiking procedure should not alter the matrix. In practice, it is essentially impossible to achieve all of these for a perchlorate-in-fertilizer standard, in part because so little is known about the nature of previously reported perchlorate contamination. Therefore, the choice of fortification approach requires striking some semblance of balance among these various needs, either by varying the approach to achieve one objective specifically, or by ranking the objectives and then picking an approach that meets those of higher priority.

Several approaches were used here. In the case of Nos. 4, 5 and 6, the solids were spiked with analyte by directly pipetting a methanolic solution of sodium perchlorate into the pre-weighed 4.0 g portion. The methanol was then permitted to evaporate. While this does not uniformly distribute the analyte throughout the material, it does ensure that a precise and accurate amount of analyte is delivered to the sample.

An additional concern is the homogeneous distribution of the analyte throughout the matrix. For Nos. 11 and 19, tracers were added to permit an assessment of the mixing process. A dye, xylene cyanole FF, was added to No. 11, while two transition metal chloride salts were added to No. 19. As the components were mixed, the colored dye and/or metal salts became indistinguishable from the bulk material and served as an indicator of homogeneity. The procedure for the addition of tracers was as follows. Small amounts of dye or metal salts were combined with approximately 10 g of one of the major components and triturated by mortar and pestle. This mixture was then added to the blender in small portions with periods of blending in between additions. Although we relied on eyesight alone to assess the adequacy of trituration and mixing, it would have been possible to use spectrometric methods for a more rigorous test.

In the case of liquid samples, ensuring homogeneity was simpler due to the nature of an aqueous solution, and special efforts were not required. Because our primary objective in Phase I was to evaluate the laboratories' ion chromatography capabilities, a large number of liquid solutions were used to eliminate the fortification procedure as a source of error.

**2.3.3 Method.** In the case of solid samples, participant laboratories were instructed to consume the entire sample by adding 40.0 mL of high purity (polished), deionized water ( $\rho \geq 18 \text{ M}\Omega \text{ cm}$ ) directly to the bottle. Soluble materials were to be dissolved and used without further treatment; however, laboratories were permitted to suction off froth or remove grit by filtration or centrifugation. If they chose to filter a sample, laboratories were required to show that a  $10 \text{ ng mL}^{-1}$  perchlorate standard (in deionized water) was unaffected by the filtration. Duplicate analyses of each solution and satisfactory recovery of a spike were required. The method<sup>19</sup> itself has been published separately, and further details will not be repeated here. A few procedural points are worth mentioning since they refer to matters that were unspecified in the method and left to the individual laboratories' discretion. Some of the laboratories used electric mechanical shakers while others used manual shaking during the leaching/dissolution steps. Strong base eluents (NaOH or KOH) were used at concentrations of 0.050 M, 0.060 M, 0.065 M or 0.10 M. Some laboratories used a Dionex (Sunnyvale, CA, USA) EG40 eluent generator, and some laboratories included an ATC-1 anion trap column on the eluent supply line. Flow rates were  $1.0\text{--}1.2 \text{ mL min}^{-1}$ . Dionex IC systems with IonPac AG16/AS16 columns were used by all. Detection was by suppressed conductivity with ASRS Ultra suppressors at 300 mA (in external water mode); most laboratories used ED40 electrochemical detectors. Some laboratories filtered some samples ( $0.22 \mu\text{m}$  or  $0.45 \mu\text{m}$  nominal pore size), especially those prepared at higher solid-to-water ratios; the more dilute samples (*e.g.* 1/2000 dilution or more) did not necessarily require filtration. Dionex vials use filter caps, and this was the extent of filtration at some of the laboratories.

## 2.4 Phase 2: evaluation of full method using real-world samples

**2.4.1 Selection, collection and processing of materials.** In Phase 2, laboratories were required to execute the full method for all materials, beginning with a finely ground solid. The materials represented current major suppliers and/or manufacturers. Materials were gathered from several geographic locations to account for variation that is locality-dependent since commodity chemical usage is often dictated by transportation costs. Both raw materials (*i.e.* single commodity chemicals) and multiple-component products were included; however, more effort was focused on the commodity chemicals. There are at least three good reasons for this. First, raw materials should contain higher concentrations than formulated products (*i.e.* blending dilutes the analyte). Second, analyses of single components are likely to suffer from less severe matrix effects. Third, multiple-component products are generally made from these very same raw materials which are the ingredients purchased by companies that formulate specialty fertilizers. To better evaluate the ruggedness of the method and its susceptibility to various matrix elements, Phase 2 materials included common, potential anionic interferences, *e.g.* sulfate, chloride, phosphate and nitrate. Phase 2 materials are listed in Table 2.

Whenever possible, bulk samples were procured under the supervision of state government agents authorized by their agencies and recognized by the Association of American Plant Food Control Officials (AAPFCO) for the collection of fertilizers. In addition to manuals and/or methods from the AAPFCO,<sup>21</sup> the Association of Official Analytical Chemists<sup>22,23</sup> and The Fertilizer Institute (TFI),<sup>24</sup> written instructions were issued to each inspector/collector outlining the specific protocol to be used. These instructions were in addition to and complementary to the standard sampling practices. In a few cases, state inspectors were unavailable, and knowledgeable practitioners from industry were permitted to collect the bulk samples. Sampling was conducted at the actual production site whenever possible to eliminate potential for contamination by other materials. Repeated samplings using a Missouri D tube collector were transferred to zipper-seal low-density polyethylene bags and tagged with identifying information, including manufacturer/supplier, location, time/date, name of collector and chemical composition.

The collected samples were sent under custody seal to the International Fertilizer Development Center (IFDC) in Muscle Shoals, AL, USA. The IFDC riffled the samples and divided them into smaller portions. The individual portions were then ground, packaged, numbered and sent under custody seal to participant laboratories. Additional portions were sent to two EPA laboratories and to AFRL for archiving. Each laboratory or archive sample was assigned a unique numerical code by the IFDC so that comparison and identification were rendered impossible without the key.

**2.4.2 Quality control and performance evaluation.** A series of quality control samples was prepared for Phase 2 by the Environmental Protection Agency, Office of Research and Development, National Risk Management Research Laboratory, Water Supply and Water Resources Division (EPA-ORD-NRMRL-WSWRD) and sent to the IFDC for distribution to the participating laboratories. The composition of these is given in Table 2, along with the identifications of the real-world samples. These samples were created by grinding materials in a kitchen blender. Perchlorate salts were added to small amounts of solid, and continually ground. The container sides were scraped down and this was followed by additional grinding. The process was repeated several times.

Each laboratory submitted its results to the EPA for evaluation and tabulation. Laboratories were required to

submit chromatograms for the sample solutions and fortifications they made to demonstrate acceptable recovery in the matrix. Laboratories were also required to submit proof of the goodness of their calibrations, instrument performance, detection limit and sensitivity.

## 3 Results and discussion

### 3.1 Phase 1

Using perchlorate standards prepared from deionized water, the participant laboratories were able to generate linear calibration functions with  $R^2 > 0.99$  and slopes with a relative standard error of less than 2% as shown in Table 3. While two laboratories obtained  $y$  intercepts statistically indistinct from zero, four did not. In addition, scatter in the data could make the standard error in the  $y$  intercept sufficiently large so that the  $y$  intercept would be indistinct from zero, but the fit would still be poor, especially for lower concentrations. Accordingly, the performance criteria are defined to require that the  $y$  intercept be less than 70% of the average peak area for the 5.0 ng mL<sup>-1</sup> standard and less than 40% of the average peak area for the 5.0 ng mL<sup>-1</sup> standard. In addition, the standard error in the  $y$  intercept is constrained to be less than 40% of the average peak area for the 10 ng mL<sup>-1</sup> standard, and less than 3.5% of the average peak area for the 100 ng mL<sup>-1</sup> standard. In those cases in which the  $y$  intercept  $b$  was not smaller than its standard error  $\epsilon_b$ , it was no greater than 40% of the value of the error, so that  $1 - |b/\epsilon_b| < 0.40$ , and this can be established as a performance criterion.

Satisfactory instrument performance was demonstrated by injecting a 50 ng mL<sup>-1</sup> continuing calibration check standard after every 10 to 15 samples. Recovery on fortifications was within the limits of 80–120%, and reproducibility on duplicate injections was generally within 15%.

Laboratories were required to demonstrate their ability to detect perchlorate in fertilizers. Some laboratories failed to adequately test simple aqueous samples with analyte concentrations in the parts-per-billion range, and were cautioned not to dilute samples initially. For example, materials 25, 26 and 27 posed problems. No. 25 was intentionally colored to give it the appearance of a solution made by dissolving a water-soluble plant food. Several laboratories overdiluted Nos. 25 and 26 due to inadequate screening, and were therefore unable to detect perchlorate. In Phase 1, the matrix was not identified to the laboratories. This made the procedure more difficult and time-consuming. For this reason, major chemical constituents were identified for the laboratories in Phase 2. The greatest source of error was computational, especially with regard to dilution factors and unit conversions. This was evident from the examination of the chromatograms and comparison with the calibration data. To minimize these errors, the reporting requirements and directions of the method were modified to require that calculations be shown and each dilution step or unit conversion be carefully documented. Due to the minor and identifiable nature of the errors, all of the laboratories were approved to participate in Phase 2.

Although the recovery of perchlorate was generally invariant to the means of fortification, a few points are worth noting. No. 24, which was spiked with tetraoctylammonium perchlorate, had extremely poor recovery, around 10%. Tetra-butylammonium perchlorate resisted dissolution during the preparation of standards, but gave acceptable results upon analysis, with recoveries similar to the sodium, potassium and ammonium salts. No laboratory was able to reliably detect perchlorate in No. 2, which contained bentonite and kaolinite. Apparently, these silicates confound the method. Fortunately, the concentration of siliceous minerals is low in most fertilizers. Somewhat surprising, none of the laboratories found perchlorate in No. 7 (perchlorate-tainted ACS reagent urea);

**Table 2** Fertilizers and related materials used in Phase 2

No.	Composition	Manufacturer/supplier
1	Lawn fertilizer, 22-3-14	Scotts Company, Marysville, OH
2	Ammonium monohydrogen phosphate (DAP <sup>a</sup> )	IMC-Agrico
3	Urea	Potash Corporation of Saskatchewan
4	Potassium chloride (MOP <sup>b</sup> )	Potash Corporation of Saskatchewan
5	Iron oxide	Sims Agriculture
6	Limestone	Millersville Lime
7	Potassium magnesium sulfate (Sul-Po-Mag <sup>c</sup> )	IMC-Kalium, Carlsbad, NM
8	Potassium chloride (MOP <sup>b</sup> )	Mississippi Potash, Carlsbad, NM
9	Osmocote 18-6-12	Scotts, Marysville, OH
10	Miracle Gro lawn fertilizer, 36-6-6	Scotts, Port Washington, NY
11	Miracle Gro plant food, 20-20-20	Scotts, Port Washington, NY
12	Langbeinite, mechanical mining	IMC-Kalium, Carlsbad, NM
13	Langbeinite, drill and blast	IMC-Kalium, Carlsbad, NM
14	Potassium magnesium sulfate (Sul-Po-Mag <sup>c</sup> )	IMC-Kalium, Carlsbad, NM
15	Limestone	Chemical Lime, Salinas, CA
16	Ammonium sulfate	Simplot, Pocatello, ID
17	Urea	Unocal <sup>d</sup>
18	Ammonium sulfate	Dakota Gasification, Bismarck, ND
19	Ammonium monohydrogen phosphate (DAP <sup>a</sup> )	IMC-Agrico
20	Potassium magnesium sulfate (Sul-Po-Mag <sup>c</sup> )	IMC-Kalium
21	Potassium sulfate	IMC-Kalium
22	Ammonium sulfate	Dutch State Mines (DSM)
23	Ammonium dihydrogen phosphate (MAP <sup>a</sup> )	IMC-Agrico
24	Iron oxide	Fritt Industries, Ozark, AL
25	Limestone	E.R. Jahna, Lake Wales, FL
26	Urea	Unocal <sup>d</sup>
27	Clay	Ag Sorb
28	Potassium chloride	Potash Corporation of Saskatchewan
29	Urea	CF Industries, Donaldsonville, LA
30	Ammonium nitrate	LaRoche, Atlanta, GA
31	Ammonium monohydrogen phosphate (DAP <sup>a</sup> )	Agrium, Soda Springs, ID
32	Ammonium dihydrogen phosphate (MAP <sup>a</sup> )	Agrium, Soda Springs, ID
33	Potassium sodium nitrate	SQM, Chile
34	Ammonium nitrate	Mississippi Chemical, Yazoo City, MS
35	Potassium nitrate	SQM, Chile
36	Sodium nitrate	SQM, Chile
37	Ammonium nitrate	Mississippi Chemical, Yazoo City, MS
38	Granular triplesuperphosphate (calcium phosphates)	Cargill, Riverview, FL
39	Ammonium dihydrogen phosphate (MAP <sup>a</sup> )	Simplot, Pocatello, ID
40	Ammonium monohydrogen phosphate (DAP <sup>a</sup> )	Simplot, Pocatello, ID
41	Limestone	Georgia Marble
42	Potassium nitrate	Sociedad Química y Minera, Chile
43	Plant food, 10-10-10	SSC, Statesville, NC
44	Clay	Oil Dry Co., Ripley, MS
45	Potassium magnesium sulfate	IMC-Kalium, Carlsbad, NM
46	Potassium nitrate	Vicksburg Chemical Co., Vicksburg, MS
47	Ammonium monohydrogen phosphate (DAP <sup>a</sup> )	Potash Corporation of Saskatchewan, Aurora, NC
48	Granular triplesuperphosphate (calcium phosphates)	IMC-Agrico, Mulberry, FL
<i>Quality control samples prepared by EPA-ORD-NRMRL-WSWRD (all solids)</i>		
49	Potassium chloride + 6.8 mg ClO <sub>4</sub> <sup>-</sup> g <sup>-1</sup>	J.T. Baker (Phillipsburg, NJ) ACS reagent KCl and KClO <sub>4</sub>
50	Peter's water-soluble plant food, 20-20-20 + 6.2 mg ClO <sub>4</sub> <sup>-</sup> g <sup>-1</sup>	Scotts (Marysville, OH) + GFS (Columbus, OH) ACS reagent NaClO <sub>4</sub>
51	Granular triplesuperphosphate + 2.7 mg ClO <sub>4</sub> <sup>-</sup> g <sup>-1</sup>	A.H. Hoffman (Lancaster, PA) + GFS ACS reagent NaClO <sub>4</sub>
52	Urea + 1.8 mg ClO <sub>4</sub> <sup>-</sup> g <sup>-1</sup>	D.W. Dickey & Son (Lisbon, OH) + Aldrich (Milwaukee, WI) ACS reagent NH <sub>4</sub> ClO <sub>4</sub>
53	Potassium chloride (no analyte added)	CF Industries (Cincinnati, OH) + A.H. Hoffman
54	Ammonium nitrate (no analyte added)	Cargill (Shelbyville, KY)
55	Chilean sodium nitrate (Chile salt peter) <sup>e</sup>	A.H. Hoffman (mfd. by Sociedad Química y Minera)

<sup>a</sup>DAP=diammonium phosphate, MAP=monoammonium phosphate. <sup>b</sup>MOP=muriate of potash. <sup>c</sup>Sul-Po-Mag=sulfate of potash/magnesia. <sup>d</sup>Unocal is now owned by Agrium. <sup>e</sup>This material had previously been found to contain 1.7 mg ClO<sub>4</sub><sup>-</sup> g<sup>-1</sup> by EPA; no perchlorate salts were added to increase this value.

however, this appeared to be a dilution problem. Lastly, the scatter in No. 31, which contained tainted ACS reagent KCl, was rather substantial, with reported concentrations ranging from undetectable to 1.6 times the true value. Based on the problems reported to us, it was clear that a lack of knowledge about the matrix (which often led to overdilution), combined with the time constraints of the schedule, made accurate analysis very hard for some materials. As a result, the timetable was readjusted following the review of the Phase 1 results. In many respects, Phase 1 was a learning process for the laboratories and for us. By the end of the process, it was obvious that trace analyses of fertilizers are more involved than typical drinking water analyses for which Method 314.0<sup>†</sup> was

designed, and require considerably more expertise, experience, patience and time to do well.

### 3.2 Phase 2

Of the real-world samples, perchlorate was detectable only in materials derived from Chilean caliche. Five of the seven quality control standards also contained perchlorate. Table 4 shows the positive results obtained by the laboratories that elected to participate in Phase 2. All of the samples were tested by NCSU, CDFA, IMC and AMPAC; not all of the samples were tested by Dionex, EPA-Athens or MWL. Only one laboratory reported a concentration above the preliminary

**Table 3** Calibration results for six laboratories using chromatographic peak area ( $y$ ) as a linear function of perchlorate concentration ( $x$ , expressed in  $\text{ng mL}^{-1}$ ):  $y = mx + b$

	EPA	CDFA	AMPAC	Dionex	MWL <sup>c</sup>	NCSU
$b$	-13807	-1561	-2027	-2612	-2403	-1697
$\epsilon_b^a$	10126	2854	7376	2048	2045	1447
$\epsilon_b/b$ (%) <sup>a</sup>	-73.34	-182.78	-363.95	-78.39	-85.10	-85.26
$1 -  b/\epsilon_b $	0.3635	n/a	n/a	0.2757	0.1751	0.1729
$m$	4679.9	1408.4	2108.9	1336.6	1381.3	998.2
$\epsilon_m^b$	54.41	11.86	34.13	8.51	25.88	6.89
$\epsilon_m/m$ (%) <sup>b</sup>	1.16	0.84	1.62	0.64	1.87	0.69
$R^2$	0.99919	0.99929	0.99765	0.99960	0.99895	0.99962
$b/A_5$ ppb (%)	70.5	22.8	17.9	45.8	49.7 <sup>c</sup>	19.1
$b/A_{10}$ ppb (%)	32.6	11.6	11.0	21.9	20.3	39.3
$\epsilon_b/A_{10}$ ppb (%)	23.9	21.1	39.9	17.2	17.3	16.3
$\epsilon_b/A_{100}$ ppb (%)	2.27	2.15	3.39	1.60	1.49	1.51

<sup>a</sup> $\epsilon_b$ =standard error in  $b$ ,  $\epsilon_b/b$ =relative standard error in  $b$ . <sup>b</sup> $\epsilon_m$ =standard error in  $m$ ,  $\epsilon_m/m$ =relative standard error in  $m$ . <sup>c</sup>MWL used a 4.0  $\text{ng mL}^{-1}$  standard rather than a 5.0  $\text{ng mL}^{-1}$  standard, and so that peak area was used to compute the ratio instead.

assured reporting level (*vide infra*) that was inconsistent with the data from the other laboratories. In that case, the laboratory was directed to repeat the analyses of several materials, including that with the suspect value. In addition, a portion of material was taken from the archives and sent to that laboratory for testing. Results obtained for the archived material and the repeat analysis for the laboratory sample were consistent with the other laboratories' results, and the original datum was discarded as erroneous.

Perchlorate was satisfactorily quantified in the quality control samples by all of the laboratories. The results from the positive hits for Phase 2 are shown in Table 4. Samples of Nos. 5, 23, 40 and 42 were analyzed independently by MWL and by EPA-Athens. Perchlorate was detectable only in No. 42; MWL found  $2675 \mu\text{g g}^{-1}$ , while EPA-Athens found  $2845 \mu\text{g g}^{-1}$ . These values are consistent with the results reported by the other laboratories. Recoveries of fortifications ranged from 81% to 111%, regardless of the specific increase in concentration resulting from spiking. The increases in concentration,  $\Delta[\text{ClO}_4^-]$ , and the recoveries are reported in Table 5. All laboratories demonstrated satisfactory performance in this regard. On the other hand, there is a negative bias in the ion chromatography results for the quality control samples (Nos. 49–52, 55), with the measured concentrations falling below the concentrations calculated from known masses of components. That notwithstanding, it seems premature to conclude that there is a determinate error associated with the measurement based on one data set. Regardless, the relative deviation remained below 20%, which is satisfactory for our purposes.

Precision can be assessed using the analyses of Phase 2 No. 33, which was sent to each laboratory in unidentified duplicate portions. The difference between average measurements (No. 33a vs. 33b) ranged from a minimum of 0.3% to a maximum of 14%. Relative to the average computed by pooling all the data (five values for 33a and five for 33b), individual laboratories varied from -4.3% to +3.2%. The pooled average was  $3973 \mu\text{g g}^{-1}$ , with a pooled estimated standard deviation of  $200 \mu\text{g g}^{-1}$ , or 5% RSD. Other data sets randomly selected from the submitted materials showed similar statistics. Inter-laboratory agreement was high, as shown by the range of RSDs in Table 4: 4–11%. Certainly, as a screening tool for ascertaining whether a material contains perchlorate, the method is suitably accurate and precise. For such an objective, it suffices to achieve 1–2 significant digits in the concentration value. The method is capable of less than 10% RSD if a suitable number of samples is run. Accuracy is largely dependent on the quality of the calibration and the appropriate choice of dilution factor, and can be improved by narrowing the domain used for calibration and experimenting with various dilutions to obtain the best chromatograms.

Rather than a minimum reporting level (MRL) or method detection limit (MDL), which are the standard approaches to detection limits used in EPA methods, we have defined a new quantity, the *assured reporting level* (ARL). The ARL is a matrix-specific limit of detection (expressed as an analyte: fertilizer mass ratio) based on the recovery of a fortification (spike) of analyte, and is determined by diluting the matrix until the spike is satisfactorily recovered. Both the MRL and MDL are defined in Method 314.0 $\ddagger$ . In part, we wanted to

**Table 4** Perchlorate concentrations ( $\mu\text{g g}^{-1}$ ) exceeding the preliminary assured reporting level for Phase 2 materials (Table 2) as reported by participating laboratories<sup>a</sup>

No.	True	CDFA <sup>b</sup>	NCSU <sup>b</sup>	AMPAC <sup>b</sup>	IMC <sup>b</sup>	Dionex	Average	ESD <sup>b</sup>	ESDM <sup>b</sup>	RSD (%) <sup>b</sup>
33 <sup>c</sup>	—	3700	4020	4200	4066	3860	3969	193	86	5
33 <sup>c</sup>	—	3925	4270	3700	4136	3850	3976	227	102	6
35	—	2624	2380	2100	2288	2240	2326	195	87	8
36	—	1860	1950	1800	2054	1920	1917	96	43	5
42 <sup>d</sup>	—	2424	2542	2050	2455	2340	2362	189	84	8
49	6800	5720	5960	6200	6377	6140	6079	250	112	4
50	6200	5730	5190	5100	5737	5430	5437	296	132	5
51	2700	2540	2700	2080	2376	2300	2399	236	105	10
52	1800	1540	1790	1430	1511	1810	1616	173	77	11
55	1700 <sup>e</sup>	1550	1580	1440	1680	1700	1590	105	47	7

<sup>a</sup>Each laboratory's concentration is based on an average of values from at least two injections. Sample loops were 1000  $\mu\text{L}$  in volume, except for Dionex, which used a 500  $\mu\text{L}$  loop. <sup>b</sup>CDFA=California Department of Food and Agriculture; NCSU=North Carolina State University Department of Soil Science; IMC=IMC Phosphates Environmental Laboratory; ESD=estimated standard deviation for the sample space; ESDM=estimated standard deviation of the mean; RSD=relative standard deviation=ESD/average. <sup>c</sup>Since the duplicates of No. 33 were the same solid, it is possible to compute statistics for all 10 reported values: average= $3973 \mu\text{g g}^{-1}$ ; ESD= $199 \mu\text{g g}^{-1}$ ; ESDM= $63 \mu\text{g g}^{-1}$ . <sup>d</sup>No. 42 was also analyzed by EPA-Athens ( $2845 \mu\text{g g}^{-1}$ ) and MWL ( $2675 \mu\text{g g}^{-1}$ ). When these two results are combined with those above, the average becomes  $2476 \mu\text{g g}^{-1}$ , with an ESD of  $253 \mu\text{g g}^{-1}$ , and an ESDM of  $96 \mu\text{g g}^{-1}$ . <sup>e</sup>The 'true' value for No. 55 is based on the analyses conducted by EPA-Cincinnati of 55 separate solutions (plus duplicate injections) as well as separate confirmation by complexation ESI-MS.

**Table 5** Tested fortifications (spikes) and recoveries for dilutions of 10 g dL<sup>-1</sup> solutions of Phase 2 materials

No.	CDFA			NCSU			AMPAC			IMC			Dionex		
	Spike/ ng mL <sup>-1</sup>	Recov (%)	Diln <sup>a</sup>	Spike/ ng mL <sup>-1</sup>	Recov (%)	Diln <sup>a</sup>	Spike/ ng mL <sup>-1</sup>	Recov (%)	Diln <sup>a</sup>	Spike/ ng mL <sup>-1</sup>	Recov (%)	Diln <sup>a</sup>	Spike/ ng mL <sup>-1</sup>	Recov (%)	Diln <sup>a</sup>
1	10	98	100	10	101	100	10	93	10	200	85	10			
2	10	102	50	50	98	500	10	90	100	200	100	100	10	107	100
3	10	107	25	50	93	100	10	103	50	200	102	50			
4	10	109.5	50	10	93	100	10	97	10	200	98	100	10	103	100
5	10	98	10	10	87	100	10	97	10	200	89	10			
6	10	104	5	10	98	100	10	93	1	200	100	100			
7	10	93	500	50	85	100	10	106	10	200	103	100	10	95.9	100
8	10	108	10	30	96.5	100	10	93	10	200	87.5	10	10	101	100
9	10	104	100	50	101	500	10	103	100	200	96.5	100	10	97.7	100
10	10	99	50	50	101	500	10	93	1000	200	97	10			
11	10	101	500	50	95	500	10	109	100	200	99	100	10	96.5	100
12	10	100	50	10	88	100	10	91	10	200	104	100			
13	10	92	50	50	89	100	10	92	50	200	80.5	10			
14	10	96	50	50	88	100	20	90	50	200	88	10			
15	10	105	5	10	96	100	10	91	5	200	117	10	10	108	100
16	10	106	25	50	86.5	100	10	95	50	200	99	50	10	106	100
17	10	90	25	10	96	100	10	108	2	200	93	10			
18	10	106	25	50	94	100	10	97	50	200	97.5	100			
19	10	93	100	50	97	500	10	107	10000	200	97	50	10	110	100
20	10	101	500	50	88	100	10	106	10	200	102	100			
21	10	95	50	50	91	100	10	96	50	200	103	100			
22	10	107	10	50	81.5	100	10	95	50	200	85	10			
23	10	98	200	50	99	500	50	92	50	200	95	100	10	106	100
24	10	107	10	10	84	100	10	106	10	200	103	100			
25	10	97	5	10	96	100	10	99	1	200	93	10			
26	10	96	25	10	97	100	10	106	10	200	102.5	100			
27	10	92	2	10	92	100	10	93	50	200	107	10			
28	10	102	25	30	94	100	10	94	10	200	98.5	100			
29	10	105	25	10	95	100	10	91	10	200	105	50	10	110	100
30	10	100	5	10	95	100	10	101	20	57	96.5	10			
31 <sup>b</sup>	10	100	100	50	95	500	10	91	50	200	98	100			
31 <sup>b</sup>	10	95	500	50	97	500	10	94	50	200	88	100			
32	10	97	250	50	97	500	10	93	1000	400	98	100	10	103	100
33 <sup>b</sup>	50	90	4000	100	100	5000	20	95	10000	57	98	5000	100	102	5000
33 <sup>b</sup>	50	102	5000	50	107.5	5000	20	103	10000	57	97	5000	100	101	5000
34 <sup>b</sup>	10	100	5	50	81	100	20	106	10	57	93.5	100			
34 <sup>b</sup>	10	102	5	10	97	100	10	102	50	200	85	10	10	102	100
35	10	109	4000	100	98	2000	30	104	5000	57	98.5	2000	100	106	2000
36	10	107	2000	100	98	2000	20	105	5000	57	98	2000	100	103	2000
37	10	94	5	10	99	100	10	102	10	57	91.2	10			
38	10	95	1000	50	108	500	10	100	1000	200	88	50	10	98.1	1000
39	10	101	500	50	95	500	10	92	100	200	103	1000			
40	10	94	200	50	98	500	10	93	50	200	101	100	10	110	1000
41	10	93	5	10	98	100	10	103	1	200	97	10	10	98.7	100
42	50	108	4000	100	99	2000	30	98	5000	57	97	2000	100	105	2000
43	10	96	100	50	93	100	10	109	100	200	88.5	10			
44	10	94	2	10	91	100	10	93	10	200	88.5	10			
45	10	91	50	10	91	100	10	102	50	200	109	50			
46	8	104	25	10	94.5	100	10	105	5	200	101	50			
47	10	103	250	50	99	500	10	92	100	200	81	10	10	100	100
48 <sup>b</sup>	10	110	1000	50	99	500	20	102	100	200	91	100	10	95.8	1000
48 <sup>b</sup>	10	92.5	500	50	105	500	10	103	1000	200	94	100	10	105	1000
49	50	104	10000	100	97	5000	50	95	10000	20	101	5000	50	95.2	10000
50	40	95	5000	100	109	5000	50	93	10000	57	98.5	5000	40	99.4	10000
51	100	93	4000	100	111	2000	60	105	2000	20	98	2000	20	105	10000
52	50	105	2000	100	97.5	2000	50	91	1000	20	100	1000	20	102	10000
53	10	102	10	10	92.5	100	10	91	10	200	94	10			
54	10	101	5	10	100	100	10	109	10	200	110	10			
55	50	103	2000	100	100	2000	50	94	1000	57	96	1000	100	102	2000

<sup>a</sup>Dilution factor refers to subsequent dilution of a stock solution prepared by leaching or dissolving the material at 10 g dL<sup>-1</sup> (~10% w/w). The dilution factor is 1/*f* where *f* is the number reported in the table. <sup>b</sup>Samples 31, 33, 34 and 48 were supplied to the laboratories as blind duplicates.

distinguish the ARL from the MDL and the MRL, which are both defined in Method 314.0, and to avoid the confusion that might result from using the same terms to refer to a detection limit for a solid material.

We have specified a new term because the ARL is different from both the MRL and MDL and reflects a parameter for the starting *solid* rather than an aqueous solution, even though it is the solution that is subjected to ion chromatography. Like the

MDL, the ARL is the smallest analyte concentration that can be measured and is distinguishable from the noise. Unlike the MDL, the ARL is matrix-specific and is not based on instrument performance using a well-defined and generally well-behaved material (*e.g.* deionized water). Unlike the MRL, the ARL does not arbitrarily set a value to be tested, such as the lowest calibration standard. Furthermore, there are no calibration standards based on the solid in this method. The

ARL represents a matrix-specific limit of detection because it is based on a process of reducing matrix effects by dilution. In addition, the ARL is broader in definition than the MRL because it can be determined for materials that contain a large concentration of analyte. In its customary usage, the MRL would not be assessed for such materials.

The procedure for determining the ARL is described in detail in the method, but several key points are worth mentioning here. In the case of sample in which the analyte is undetectable, the ARL is determined using the successful recovery of a 10.0 ng mL<sup>-1</sup> spike. In practice, a dilution is chosen for which the spike is likely to be recovered. If the recovery is in fact satisfactory, the concentration is raised by factors of 10 until the spike cannot be satisfactorily recovered (<80%). Subsequently, volumetric dilutions of 90%, 80%, etc. are spiked until the recovery is again satisfactory. Based on the dilution of the matrix, the ARL is determined. For those materials in which the analyte is detected at a high concentration, the initial spike is set to 20% of the concentration of the analyte. If the spike is not recovered, successive 10% v/v dilutions are used until the spike is recoverable. Once such a concentration has been found, the previous concentration is diluted volumetrically to 90%, 80%, etc. as before. The lowest dilution factor which still allows satisfactory recovery (*i.e.* where the matrix is most concentrated) is used to compute the ARL. When the material contains a high concentration of the analyte, the ARL found in this way is only an estimation of the true value. Since it is not possible to remove the analyte from the matrix so as to test the matrix independently, or to duplicate the matrix using reagent chemicals, this represents a practical limitation. Due to the procedure as well as normal variation, it is likely that laboratories will report different ARLs for the same material. If the process is truncated prematurely, the quantity is less well-known and termed a preliminary assured reporting level (pARL). The pARLs calculated from the fortification and dilution data are reported in Table 6.

### 3.3 Limitations

This method should be regarded as a screening tool. While effective at ruling out perchlorate contamination within the limits of experimental error and current technology, it does not definitively identify or quantify perchlorate in a specific product. Because it relies on a chromatographic retention time for identification, any positive finds should be subjected to other means for confirmation, preferably spectrometric methods, such as attenuated total reflection-Fourier transform IR (ATR-FTIR)<sup>25</sup> or Raman spectrometry,<sup>26</sup> complexation electro-spray ionization mass spectrometry (cESI-MS),<sup>10</sup> electro-spray ionization high field asymmetric-waveform ion mobility spectrometry (ESI-FAIMS)<sup>27,28</sup> or ESI-MS-MS.<sup>29</sup> While perchlorate has been reported in sylvite (a naturally occurring mineral form of KCl),<sup>30</sup> only one natural source of perchlorate in fertilizer has been continually verified by multiple investigations using multiple techniques over decades of work: specifically, caliche ores that are rich in sodium nitrate and found in South America, especially in the Chilean desert.<sup>11,31,32</sup> Accordingly, positive results that either are for products not derived from caliche or fall outside established concentration ranges should be regarded as suspect until confirmed by other techniques.

This method was designed for and tested on fertilizers, which tend to form solutions of high ionic strength. This method was not tested on minerals, soils or other sorbents; consequently, it should not be applied to other media without careful investigation. It is generally accepted that perchlorate adsorbs to soil particles through outer-sphere complexes, where the ions engage in simple electrovalent bonds and serve to balance electric charge on the surface.<sup>33,34</sup> Such adsorption is often influenced by pH due to protonation of mineral oxo moieties

**Table 6** Preliminary assured reporting levels (expressed in µg g<sup>-1</sup>) for Phase 2 materials

No.	CDFA	NCSU	AMPAC	IMC	Dionex	Average	ESD
1	10	10	1	20		10	7
2	5	250	10	200	10	95	107
3	2.5	50	5	100		39	40
4	5	10	1	200	10	45	77
5	1	10	1	20		8	8
6	0.5	10	0.1	200		53	85
7	50	50	1	200	10	62	72
8	1	30	1	20	10	12	11
9	10	250	10	200	10	96	107
10	5	250	100	20		94	97
11	50	250	10	200	10	104	101
12	5	10	1	200		54	84
13	5	50	5	20		20	18
14	5	50	10	20		21	17
15	0.5	10	0.5	20	10	8	7
16	2.5	50	5	100	10	34	37
17	2.5	10	0.2	20		8	8
18	2.5	50	5	200		64	81
19	10	250	1000	100	10	274	373
20	50	50	1	200		75	75
21	5	50	5	200		65	80
22	1	50	5	20		19	19
23	20	250	25	200	10	101	103
24	1	10	1	200		53	85
25	0.5	10	0.1	20		8	8
26	2.5	10	1	200		53	85
27	0.2	10	5	20		9	7
28	2.5	30	1	200		58	83
29	2.5	10	1	100	10	25	38
30	0.5	10	2	5.7		5	4
31	10	250	5	200		116	110
31	50	250	5	200		126	102
32	25	250	100	400	10	157	148
33	2000	5000	2000	2850	5000	3370	1367
33	2500	2500	2000	2850	5000	2970	1051
34	0.5	50	2	57		27	26
34	0.5	10	5	20	10	9	6
35	400	2000	1500	1140	2000	1408	600
36	200	2000	1000	1140	2000	1268	678
37	0.5	10	1	5.7		4	4
38	100	250	100	100	100	130	60
39	50	250	10	2000		578	826
40	20	250	5	200	100	115	97
41	0.5	10	0.1	20	10	8	7
42	2000	2000	1500	1140	2000	1728	352
43	10	50	10	20		23	16
44	0.2	10	1	20		8	8
45	5	10	5	100		30	40
46	2	10	0.5	100		28	42
47	25	250	10	20	10	63	94
48	100	250	20	200	100	134	81
48	50	250	100	200	100	140	73
49	5000	5000	5000	1000	5000	4200	1600
50	2000	5000	5000	2850	4000	3770	1188
51	4000	2000	1200	400	2000	1920	1197
52	1000	2000	500	200	2000	1140	747
53	1	10	1	20		8	8
54	0.5	10	1	20		8	8
55	1000	2000	500	570	2000	1214	664

(and thus associated variable-charge soils), as is the case with goethite [ $\alpha$ -Fe(O)OH]<sup>35,36</sup> or alumina ( $\gamma$ -Al<sub>2</sub>O<sub>3</sub>).<sup>37</sup> Similar outer-sphere behavior has been observed when perchlorate salts have been used to vary ionic strength or to provide a competitor to probe the adsorption of another anion.<sup>38-41</sup> In fact, perchlorate salts are often used as indifferent electrolytes, where they are added to adjust ionic strength and to provide non-complexing species for diffuse ion swarms. The available data suggest that perchlorate sorption on soils and many other media should be weak and may be undetectable at moderate ionic strength ( $\mu > 0.05$  M) in an ionic medium (salt solution) typical of fertilizer solutions (*i.e.* rich in HPO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup> or Cl<sup>-</sup>). Nevertheless, weak ionic bonding does not imply that

deionized water leaching is sufficient to release any sorbed ions. In the case of variable-charge soils or protonated mineral surfaces, a perchlorate-saturated medium (as might be found in highly contaminated sites) may be resistant to releasing its load unless displacement (substitution) by a preferred anion occurs (e.g.  $\text{PO}_4^{3-}$ ,  $\text{SiO}_3^{2-}$ ,  $\text{F}^-$ ,  $\text{OH}^-$  or even  $\text{Cl}^-$ ). Likewise, low ionic strength media may have too few competing anions and thus may show unselective adsorption. In addition, surface modification of a medium may complicate sorption, as in the case of surfactant-modified zeolites or minerals.<sup>42-44</sup> Accordingly, merely fortifying a medium with an aqueous perchlorate solution and fully recovering the spike in a leachate does not guarantee that the perchlorate concentration has been accurately measured. Prudence dictates a considerable level of characterization and validation.

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