

Perchlorate in the United States. Analysis of Relative Source Contributions to the Food Chain

PURNENDU K. DASGUPTA,^{*,†}
JASON V. DYKE,[†] ANDREA B. KIRK,[†] AND
W. ANDREW JACKSON[‡]

Department of Chemistry and Biochemistry, Texas Tech University, Lubbock, Texas 79409-1061, and Water Resources Center, Texas Tech University, Lubbock, Texas 79409-1023

Perchlorate has been considered by some a potential threat to human health, especially to developing infants and children because it may inhibit iodide uptake by the sodium iodide symporter (NIS) of the thyroid. In the United States, during the last several decades, environmental perchlorate has had three recognized sources stemming from (a) its use as an oxidizer (including in rocket propellants), (b) its presence in Chilean nitrate fertilizer (CNF), and (c) natural production. An analysis of the relative source strengths and how they may influence entry into the food chain has not been conducted. Averaged over the last ~60 years, we estimate that the source strengths have been (a) 10.6, (b) 0.75, and (c) 0.13–0.64 Gg/y for the United States as a whole. Of this, while (b) and (c) represent actual dispersed amounts, the figure in (a) is the amount of perchlorate produced and only a fraction (*f*) of it has been dispersed and often in a more localized fashion. In addition, dispersal of (b) has taken place only over agricultural land. Considering that the total land area in the United States is 5.5× the arable land area, in terms of incorporation into the food chain, the figure cited in (b) has a proportionately greater impact. Most estimates of *f* will thus suggest that over the considered period, the contribution of CNF to incorporation of perchlorate in the food chain has likely been comparable to oxidizer perchlorate, with natural production being a lesser source. Fireworks presently constitute a potentially important source of increasing importance but a quantitative impact cannot yet be assessed.

Introduction

Iodine adequacy is critical to ensure the production of sufficient thyroid hormones, which play a key role in fetal and neonatal neurodevelopment (1, 2). Based on urinary iodine excretion, iodine intake in the United States has fallen markedly since the 1970s although it is still believed to be adequate (3). Although results show that the downslide has stopped at least for now (4, 5), recent studies also show that there are segments of the U.S. population, e.g., women of childbearing age, who may be at particular risk of iodine deficiency (6). A recent study of 100 pregnant women in

Boston found 49% to have an iodine intake below the recommended daily allowance (RDA): 9% had urinary iodine below 50 µg/L, while 150 µg/L would be the expected value for an individual consuming the RDA (7).

It is in this context that one should appreciate the widespread concern, especially in the United States, about the environmental occurrence of perchlorate. Although dubbed “rocket fuel” in the popular press (solid fuel rockets used for launching space vehicles or armaments commonly consist of ammonium perchlorate (AP), aluminum, and a binder (8)), perchlorate also has a natural origin. Given sufficient quantities, the origin can probably be determined on the basis of isotopic analysis (9), but it is a tall order to do so at the trace concentrations at which perchlorate occurs in environmental or biological samples. With some rare exceptions where the source is obvious (e.g., a natural source is necessarily indicated for paleowaters), it cannot generally be ascertained whether the perchlorate in a particular environmental or biological sample is anthropogenic or natural in origin.

The invisible health risks of perchlorate vs the huge potential costs of cleanup have generated intense debate in the United States; this has perhaps become one of the most highly politicized technical debates of the decade (10, 11). Although a National Academy of Sciences panel (12) has provided a reference safe dose for perchlorate, a general consensus on what constitutes a safe dose for infants, children, or other more sensitive segments of the population will likely continue to be debated for some time to come (13–19). Unfortunately, it is often forgotten in the perchlorate debate that the key issue is iodine nutrition. If iodine nutrition is poor, even heroic efforts to reduce perchlorate intake may result in little benefits. In the absence of specified levels of iodine intake, specifying the safety threshold of any iodide transport inhibitor may thus be a daunting task. Whether or not a safe dose of perchlorate is universally accepted, it is physiologically irrelevant as to how much of one's perchlorate intake originates from anthropogenic vs natural sources. As the arsenic crisis in Asia (20) must serve to remind us, being *all natural* does not make it safe.

Perchlorate Use and Production in the United States

Oxidizer Use. A concise summary of total perchlorate production/use in the U.S. is not readily available. As Mendiratta et al. (21) pointed out, perchlorate (especially AP) had been considered a strategic chemical in the U.S. and actual production figures are neither easily available nor likely to be of verifiable accuracy, as the total production figures may be translatable by cognoscenti into the number of missile delivery rockets in production/recycling.

When perchlorate undergoes its intended use as an oxidizer, the conversion of perchlorate to chloride is essentially quantitative. For example, the solid rocket boosters of the space shuttle are typically regarded as the single largest user of AP. We analyzed space shuttle plume samples from the STS-114 launch on July 26, 2005 and found greatly elevated chloride but no clear presence of excess perchlorate over the background. Silva has shown that when fully burnt during regular use, only ~0.05% of the perchlorate present in a road safety flare survives (22). In a rocket propellant, intense high temperatures are sustained and consumption should be even more complete. Dispersal of perchlorate intended for oxidizer use therefore occurs not so much from use but rather when the intended use is not properly carried out. This would be true from rocket propellant to highway flares, and “dispersal”

* Corresponding author present address: Department of Chemistry and Biochemistry, The University of Texas at Arlington, Arlington, TX 76019-0065; phone: (817) 272-3171; fax: (817) 272-3808; e-mail: dasgupta@uta.edu.

† Department of Chemistry and Biochemistry.

‡ Water Resources Center.

includes manufacturing waste to “fuel replacement”. Optimum rocket propellant performance is dependent on particle size, mixing homogeneity, packing density, nature of binder, etc. Once loaded into a rocket, the rocket propellant mixture has a limited life and goes “flat” over time (23) and has to be replaced. Recovery and reuse of perchlorate has not been considered cost-effective. High-pressure jets of water were typically used to wash out the propellant, creating large volumes of perchlorate-contaminated wastewater. Such pollution is of a very high level but is also relatively localized. There are at least 25 states that have sites where perchlorate contaminated effluents have been discharged from Department of Defense (DoD) operated facilities into sewage systems or natural waters (24). In other instances, inadvertent dispersal from manufacturing plants into major water bodies has created low levels of widespread contamination (25).

Perchlorate produced in the United States has been almost exclusively for oxidizer use. In 1998, the U.S.EPA estimated that since the 1950s over 8.7×10^8 lbs (3.95×10^8 kg) were made in the U.S.; some of this was also exported (26), for example, to be used in European space exploration efforts (27). In context, these figures probably represent the weight of the commodity (i.e., ammonium perchlorate, not just perchlorate) that was produced. The perchlorate contents of NaClO_4 and NH_4ClO_4 are not markedly different (81.2 and 84.6% ClO_4 , respectively). Assuming a weighted average of 84% perchlorate (ClO_4), this translates to a total production of $\geq 3.3 \times 10^8$ kg, and an average production rate of 7.1×10^6 kg/y over 1951–1997. However, other sources provide different information.

According to the California Senate Office of Research, the DoD and the National Aeronautical and Space Administration (NASA) signed a 7-year contract with Western Electrochemical Company (WECCO, Cedar City, UT) to purchase 2×10^7 pounds of AP a year (23; however, the relevant web reference cited therein is no longer accessible). It also states that DoD/aerospace use accounted for ~90% of U.S. consumption. One can thus estimate the annual use rate of perchlorate at 8.5×10^6 kg/y, consistent with that inferred from ref 26. (While such corroboration may enhance one’s faith in these numbers, perhaps one should still maintain a skeptical attitude. Reference 23 also states “...perchlorate ion consists of four atoms of chlorine and one atom of oxygen...”).

Another source, a web-available reference work on the toxicological profile of perchlorates, states that “publicly available information indicates NASA and DoD contracted for 40 million pounds of ammonium perchlorate annually in the late 1980s/early 1990s” (28); this is exactly double the figure quoted in ref 23.

We will rely herein on the U.S. Government Accounting Office (GAO), often believed to be the most reliable source, to be the arbiter. A document (29) from the GAO sheds light on the matter. In 1988, 90% of the free world’s AP was produced by Pacific Engineering and Production Company (PEPCON) and Kerr-McGee (KMG). Both plants were located near Henderson, NV; the electrochemical production of perchlorate is aided by lower cost hydroelectric power from the neighboring Hoover Dam. Ammonium perchlorate is not only an oxidizer, it is also an explosive. On May 4, 1988, an explosion destroyed the PEPCON plant (30). The GAO was appointed to look into safety issues as well as the nature and consequences of the production shortfall that might occur. According to the GAO, at the time of the explosion, the annual production capacities of the PEPCON and KMG plants were, respectively, 4.0×10^7 and 3.6×10^7 lbs AP; and the plants were operating at 68% capacity. This amounts to a total perchlorate production rate of 2.0×10^7 kg/y. Over the 1989–1994 period, the GAO projected an annual AP need of 5.9 – 6.78×10^7 lb/y, averaging a perchlorate need of 2.4×10^7 kg/y.

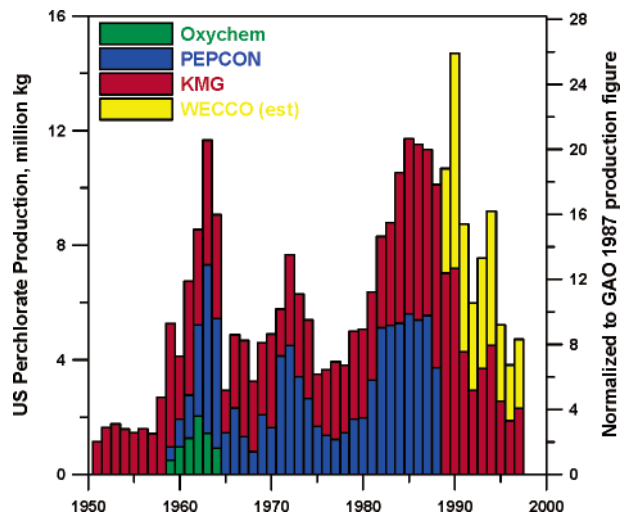


FIGURE 1. Perchlorate Production in the United States. Data on Oxychem, PEPCON, and Kerr-McGee are from EPA archives. The WECCO production is estimated from methods described in text. The left ordinate is EPA data. The right ordinate corresponds to all figures normalized to the 1987 production values quoted by the GAO. The observant student of history will observe herein shadows of the Korean War, the Vietnam War, the Space Race, the Cold War and the first Gulf War.

The U.S.EPA has listed production by three plants: Oxychem LLC (Columbia, MS, 1959–1964), the Kerr-McGee Corp. (KMG, 1951–1997), and the PEPCON plant (1959–1988). After the May 1988 explosion of the PEPCON plant, it was rebuilt 200 miles away in Cedar City, UT under the name Western Electrochemical Company which started production in July 1989. The production data of the WECCO plant are regarded confidential and have not been disclosed. However, estimates can be made from historical production of the PEPCON plant and the manner in which it was rebuilt as the WECCO plant; details of the latter appear in an analysis by Linke (31). In supplementary Table S1 (Supporting Information), based on the data in the U.S.EPA archives (32–34), the production figures for Oxychem (the data for 1964 were estimated as best as possible from the information available), PEPCON, and KMG are tabulated in a spreadsheet form. In computing total perchlorate production from the available data, we have taken into account differences in the forms of the perchlorate produced (ammonium, sodium, potassium, magnesium, etc.). Before the PEPCON explosion occurred, the production ratio of PEPCON to the KMG plant averaged 1.04 over the previous 5 years (1983–1987). In calculating total U.S. production, we assume that the WECCO plant maintained the same ratio to the KMG plant production (except in 1989 when it operated for half the year and therefore only half that production was assumed). The resulting data are shown in Figure 1. It will be noted that as previously mentioned there is a discrepancy between the GAO production figures and this tabulation, with the GAO production figures being $\sim 1.76\times$ higher. The right ordinate scale in Figure 1 corresponds to the entire data set being normalized by this factor, based on a total production figure of 2.0×10^7 kg perchlorate in 1987 as stated by the GAO. The total production in the years 1951–1997 on this basis amounts to 5×10^9 kg, with an average annual production rate of $\sim 1.06 \times 10^7$ kg/y.

Fertilizer Use. Chilean nitrate (CN) has been imported into the United States for over a century. Wines (35), in his acclaimed monograph on fertilizers, states that until a change in political conditions and the development of the “Shanks Process” in the 1880s, CN was too expensive for farmers to use as fertilizer. The first statistics of CN import to the United States are available for 1909–1918 (36) and 1925–1929 (37);

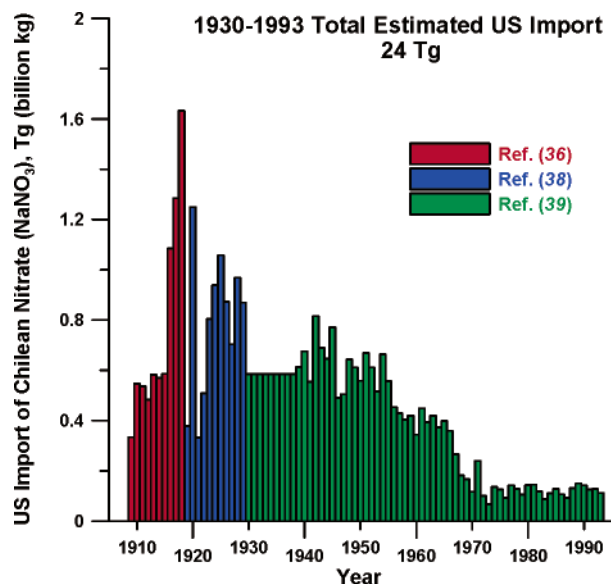


FIGURE 2. Sodium nitrate amounts imported to the United States. Data are from refs 36–39.

these data are shown in Figure 2. Some 49–70% of the imported CN during this early period was used as fertilizer (CNF), averaging ~65% for the first 30 years of the 20th century (38). As large-scale industrial production of fixed nitrogen compounds became more prevalent, non-fertilizer uses as well as U.S. import of CN declined dramatically. We were unable to get information on how much CN has been imported into the United States from the manufacturer (SQM) or the Fertilizer Institute. Previously the U.S.EPA was unable to elicit a meaningful response from the CNF manufacturer on a similar question, or in regard to the perchlorate content of CNF (52). There are, however, alternate reliable sources of such data. Detailed statistics on the amount of imported CN have been maintained by the U.S. Bureau of Mines for 1930–1993 (39; note that from 1969 onward, the mineral imported is listed as NaNO₃ and not specifically as Chilean Nitrate). As may be seen in Figure 2, the consumption during this later period peaked in the 1940s and has steadily declined since 1960, reaching a more or less stable level of $\sim 1.5 \times 10^8$ kg/y NaNO₃ in the early 1990s.

Whereas perchlorate made for oxidizer use is entirely anthropogenic, we would refer to perchlorate dispersed from CNF use as seminatural. Although the material is undoubtedly natural, it is dispersed because of deliberate human use. The presence of perchlorate in naturally occurring Chilean saltpeter was reported by Beckurts (40) as early as 1886. Early studies by Sjollem showed great variation of perchlorate content of CN, ranging from 0 to 6.8% in the same lot; subsequent studies by Maschhaupt showed a maximum perchlorate content of 1.5% (1% in a refined product) (41). More recently, the data for 1932–1967 from the two largest production plants in Chile have been examined. Over this 35-year period, the ores contained about 30% soluble salts and averaged 6.3% nitrate and 0.03% perchlorate. (42, 43). Relative to nitrate, the perchlorate content is thus ~0.5%; some reports suggest a perchlorate content as high as 3.6% (44). The perchlorate content of CNF has certainly varied over the years. In the wake of concern about the presence of perchlorate in CNF, new processing methods have reportedly reduced the perchlorate content of CNF to $\leq 0.01\%$. Urbansky et al. (45) reported a perchlorate content of 0.15–0.18% in CNF for samples bought just prior to the time their manuscript was submitted in 2000. Even earlier, the degree of refinement may have been less and perchlorate content higher. We thus conservatively estimate an average per-

chlorate content of 0.2% over the life of CNF usage in the United States. Over the 1930–1993 period, we estimate the total CNF import to be 2.4×10^{10} kg at an average annual rate of 3.8×10^8 kg/y, corresponding to a perchlorate source strength of 7.5×10^5 kg/y.

We have not considered in this analysis perchlorate content of any fertilizers other than CNF. According to Urbansky et al. (46), other fertilizers are not a significant perchlorate source. Although there was an initial report (44) of perchlorate in non-CNF fertilizers, many of these samples were reported upon reanalysis to contain no perchlorate or much less perchlorate than originally reported (47). There is consensus that some lots of non-CNF fertilizers did contain perchlorate (48, 49); during the review of this manuscript one anonymous reviewer suggested that surplus AP may have been occasionally used as a nitrogen source. However, there is consensus also (47, 48) that such occurrence is rare and may have even been a singular event.

Natural Perchlorate. We have previously demonstrated widespread occurrence of perchlorate in present-day precipitation, shown formation of perchlorate upon passage of NaCl aerosol through simulated lightning or after exposure of chloride to ozone, and shown that in southern high plains (SHP) groundwater perchlorate concentrations best correlate with those of iodate, known to be of atmospheric origin (50). Ongoing analysis of precipitation samples from a number of National Atmospheric Deposition Program sites have indicated wet-only perchlorate concentrations from < 5 ng/L (limit of detection) to 105 ng/L with a mean value of 15 ng/L. Bulk deposition values measured are higher, with maximum values measured ranging up to 250 ng/L (51). Similar ongoing analysis of perchlorate and chloride accumulations throughout the Holocene in the unsaturated zone in the Southwest United States suggests that the perchlorate concentration in precipitation was *at least* 10 ng/L (52; such an analysis ignores any decay of perchlorate in the groundwater over the accumulation period and, as such, the quoted concentration in deposition is really the minimum concentration). Based on their analysis of North-Central New Mexico groundwater that is up to 28,000 years old, Plummer et al. (53) suggest that the concentration in bulk atmospheric deposition was 93 ± 5 ng/L through the Holocene.

While there is some variation in annual rainfall in the United States from year to year, for our purposes it is sufficient to use one typical recent year. Table S3 (Supporting Information) lists rainfall recorded at individual recording stations in the continental United States in 2004 (54), the corresponding averages, land areas of individual states, and the corresponding rainfall values in km³. The area-weighted average rainfall for all the states is thus computed to be 84 cm. We assume that precipitation is the primary vector of atmospheric perchlorate to the soil. With a total area of 7.7×10^6 km², an area-weighted average rainfall of 84 cm and a perchlorate bulk deposition concentration of 100 ng/L amounts to an annual source strength of 6.4×10^5 kg/y. If we assume that at the low end, the perchlorate concentration in rainfall has been 20 ng/L, this annual source strength will be 1.3×10^5 kg/y.

Other Sources. Road safety flares, fireworks, and electrolytic chlorine products (ECP) have been considered as alternate sources of perchlorate contamination in the environment (55). In the first two cases, perchlorate (generally KClO₄) is an important ingredient in the product, whereas in ECP chemicals perchlorate has unintended presence at low levels.

Road safety flares are typically composed of (by weight) 75% Sr(NO₃)₂, and $< 10\%$ each of KClO₄, sulfur, and a binder (56). Not all road safety incendiary/colored smoke

products use perchlorate as an ingredient (57). If a typical flare contains 9 times more nitrate than perchlorate (22) and the flare is 75% by weight $\text{Sr}(\text{NO}_3)_2$, it would follow that a typical flare contains 6.5% by weight perchlorate. The annual use of road flares in Santa Clara County, CA is stated to be 4×10^4 kg/y (22), amounting to a perchlorate content usage of 2.6×10^3 kg/y. If flare use was proportional to the total population (the U.S. population is 176 times that of Santa Clara County), this would amount to 4.6×10^5 kg/y. Accidents and the need for road flares are not linearly related to population but are expected to be much greater in high traffic areas. Based on total flare sales, average cost of a flare, and 3.6 g perchlorate content per flare, a maximum perchlorate content of 1.4×10^5 kg/y from road flares has been estimated (55), this is $\sim 1.4\%$ of the production of total oxidizer perchlorate. Undoubtedly in certain localities, improperly disposed partially burnt or unburned road safety flares may make a significant contribution (58). However, unlike the case of propellant charges, flares are not deliberately disposed of without use. Overall the impact of this source must be insignificant compared to propellant component oxidizer disposal.

Firework use statistics in the United States are available from the American Pyrotechnics Association for 1976–2005 (59). These data are graphically presented in the Supporting Information and also indicate that over this 30-year period fireworks consumption has been rising exponentially (fireworks consumed in $\text{Tg/y} = \exp(0.0732\text{year} - 149)$, $r^2 = 0.98$) and, from this, the average consumption over the last 30 years can be estimated to be 4.5×10^7 kg/y. If we take more of the past years into consideration, this number will decrease significantly; on the other hand, at presently increasing consumption rates, this number has become very large in recent years. Fireworks vary greatly in their type and their composition and perchlorate content. The anatomy of a display firework is complex (see www.pbs.org/wgbh/nova/fireworks/anat_flash.html for a dissection). Some components can contain up to 70% AP or KClO_4 , and there are fireworks that contain no perchlorate or very little perchlorate (60, 61). Presently available information does not allow us to determine the total amount of perchlorate present in fireworks consumed in the U.S. and how much of that enters the environment in an unburned or partially burned state. Because of the paucity of information, we cannot consider the impact of fireworks quantitatively at this time. However, the fact that U.S. consumption of fireworks is exponentially rising and that such displays are often carried out in the vicinity of large water bodies strongly suggest a potential for significant contamination that must be quantitatively assessed in the future.

Hypochlorite and chlorate are two ECP chemicals that are known to contain perchlorate. Hypochlorite is used in water disinfection as well as a pesticide/disinfectant for produce. Data on exact content of perchlorate in hypochlorite samples are scarce. Our own data on perchlorate content of 5% and 10% hypochlorite solutions indicate that freshly bought products contain low levels of perchlorate (~ 10 $\mu\text{g/L}$) and levels increase on aging to low mg/L levels (2–3 mg/L in 6 months for an initially 5% solution), with the 10% solution forming perchlorate at more than twice the rate of the 5% solution. Since these solutions are rarely stored for prolonged periods before use because of intrinsic instability, we do not deem hypochlorite as a major contributor to perchlorate contamination. Under certain conditions, perchlorate formation from hypochlorite is greatly accelerated; this will be discussed elsewhere.

Presently the consumption of sodium chlorate in the United States is $\sim 10^9$ kg/y (55). Data on the perchlorate content of chlorate are again not available. It has been stated to be as high as 0.05% in some cases but this comes from a

patent that claims improvements in reduction of perchlorate content of chlorate (62). Our analysis of admittedly few randomly bought samples of technical/defoliant grade NaClO_3 indicates a perchlorate content less than 0.005%. Even if we assume a 0.01% perchlorate content, the source strength would be 10^5 kg/y. The majority of this chlorate is used as oxidizer and undergoes thermal decomposition and we do not therefore consider this as a very significant source, except again in specific locations. If a more extensive investigation indicates a substantially greater perchlorate content, especially of defoliant grade chlorate, this issue may need to be reevaluated.

Comparison of Source Contributions

If natural sources are solely represented by atmospheric deposition, the degree of perchlorate incorporation in crops or forage from this source will indeed be proportional to the estimated source strength. Even though the natural source strength is the lowest, if perchlorate is indestructible and accumulates naturally, then over geologic time, the natural source will dominate. Although some soil accumulation may occur in an arid region, there are several arguments against general occurrence of such a scenario. Except in arid lands, atmospherically deposited perchlorate, even if stable, is not likely to remain in the plant-accessible topsoil. In arid lands it is unlikely that crops will be grown without the assistance of artificial irrigation, if grown at all. If artificial irrigation is used, atmospherically deposited perchlorate will be washed down and may not remain in the topsoil; however, it may be washed to the aquifer and recirculated to be taken up by a crop. A variety of plants take up perchlorate. Whether or not intrinsically within their own system or symbiotically mediated by bacteria, perchlorate may be substantially reduced by such plants (63–68). Many bacteria can reduce perchlorate (69–73). There is overwhelming evidence that perchlorate is indeed degraded in soils and sediments (74–76) and even in the digestive system of ruminant animals (77). Globally, over 1.2×10^6 km² is devoted to growing rice by the flooded soil cultivation technique, engendering conditions under which anaerobic methanogenic bacteria thrive (78). Although reduction of perchlorate has not yet been tested under such conditions, it is highly likely that some bacterially mediated degradation will occur. If there are operative removal mechanisms for perchlorate that are significant, input rates rather than cumulative amounts over geologic time scales will clearly be more important. However, this may not apply to all situations, for example in places where perchlorate has been allowed to accumulate over long periods in the vadose zone and then artificial irrigation is started using groundwater that then washes the accumulated perchlorate back into the aquifer to be recirculated for irrigation. The natural input rate of 0.13–0.64 Gg/year is therefore considered to be a good metric for incorporation of natural perchlorate into crops except in places where once arid lands are being artificially irrigated with groundwater.

The contribution of CNF to perchlorate in the food chain, although much reduced at the moment compared to yesteryears, may have a greater impact than the annual dispersal rate. Whereas the rain input figures quoted pertain across all lands, the fertilizer input is meaningful only to agricultural land. In the United States, arable land is $\sim 18\%$ of the total land area (79); actual fertilized agricultural land area in use must be smaller still. The fertilizer source strength should thus be accordingly adjusted. We hasten to add that the agricultural bounty and the economic prosperity of the United States is to a large measure dependent on the use of fertilizers and CNF has not played any major role in fertilizer use for decades. Moreover, any dispersal of perchlorate that has taken place through CNF can hardly be called callous or deliberate. Nevertheless, the fact remains that there are few

ways to introduce a chemical into the food chain which will be more efficient than using fertilizer as a vector. In some cases there are clear indications that CNF use over the years may in fact be the primary contributor to perchlorate contamination (80). The average input rate of CNF perchlorate at 0.75 Gg/y over the last several decades translates to 4.2 Gg/y when adjusted for land area for fertilizer application.

At the present time, we cannot take into account the impact of fireworks. However, this is a source that may not be negligible. More broadly, while localized contribution of oxidizer perchlorate is easy to assess in specific situations (there are numerous instances where perchlorate contamination has been traced to defense-related use), its overall contribution is much more difficult to estimate because there are no extant studies that provide a clear indication on how much of the perchlorate manufactured for such purposes has actually been used for intended purposes and how much has been otherwise disposed of. Also, a very substantial amount of the perchlorate made has neither been used nor disposed of, and presently awaits proper disposal (23). If only 5% of the average production rate of 10.6 Gg/y over the last several years may have been improperly disposed of, it will be comparable to the estimated natural input rate. Not perhaps on a localized scenario but on a nationwide basis, an order of magnitude greater fraction (40%) of oxidizer perchlorate would had to have been disposed of to equal CNF impact on crops. Note that if the GAO figures on the production of AP are inaccurate, this will result in a downward revision of the oxidizer perchlorate value. We conclude that while there might be many specific localized exceptions, most reasonable estimates of the disposal fraction of oxidizer perchlorate, not including fireworks, would suggest that CNF perchlorate may have had an impact on perchlorate incorporation at least comparable to oxidizer contributions over the past several decades, with natural contributions being significantly less, except in presently irrigated once-arid lands.

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Supporting Information Available

Additional information as noted in text. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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