

## Fertilizer Characterization: Isotopic Data (N, S, O, C, and Sr)

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A detailed isotopic characterization ( $\delta^{15}\text{N}_{\text{Ntotal}}$ ,  $\delta^{15}\text{N}_{\text{NO}_3}$ ,  $\delta^{18}\text{O}_{\text{NO}_3}$ ,  $\delta^{34}\text{S}_{\text{SO}_4}$ ,  $\delta^{18}\text{O}_{\text{SO}_4}$ ,  $\delta^{13}\text{C}_{\text{Ctotal}}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$ ) of 27 commercial fertilizers used in Spain is presented in this paper. Results together with a compilation of fertilizer isotopic published data are used for two purposes: (i) to identify the origin of the primary constituents and raw materials used in fertilizer manufacture and relate these data with their heavy metals and rare earth elements (REE) contents; (ii) to compare the fertilizer isotopic signatures with natural values and other anthropogenic pollutants and evaluate the usefulness of multi-isotopic analyses to trace fertilizer contaminations in future study cases. Isotope data permit us to know, in most cases, the origin of the primary constituents of fertilizers, and the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio distinguishes the origin of the phosphate content—phosphorites or carbonatites—which in turn implies a qualitatively defined and potentially contaminant presence of REE and heavy metals in fertilizers.  $\delta^{15}\text{N}$ ,  $\delta^{34}\text{S}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  have already been used to trace fertilizer contaminations. Their utility can be improved by the coupled use of  $\delta^{15}\text{N}_{\text{NO}_3}$ – $\delta^{18}\text{O}_{\text{NO}_3}$  and  $\delta^{34}\text{S}_{\text{SO}_4}$ – $\delta^{18}\text{O}_{\text{SO}_4}$  to evaluate the fractionation processes that can affect contaminants. Moreover, multi-isotopic analyses, using heavy isotopes, allow us to see beyond the fractionation effects to the fertilizer stable isotope signatures and a better distinction from other anthropogenic contaminants.

### Introduction

Fertilizer consumption in Spain has increased by 20% in the last 15 years, reaching values up to ~2 Mt of nutrients N,  $\text{P}_2\text{O}_5$ , and  $\text{K}_2\text{O}$  in the year 2001 and 6 millions t of fertilizers (1). Consumption in the European Community reached values up to 17 Mt of nutrients in the year 2000, and worldwide consumption in the same year was up to 135 Mt of nutrients (2). At the same time, there is an increasing concern about the use of fertilizers as they are a major source of diffused pollution in agricultural areas: this use results in eutrophication and contamination of surface and groundwaters, accumulation of heavy metals in land and their release to waters, with their potential access in the food chain, etc.

As nitrogen is the nutrient most commonly limiting crop production and applied in the greatest amounts, one of the most important problems is nitrate contamination in surface waters and groundwaters. Ingestion of high nitrate concentrations causes methahemoglobine disease in children and babies, and additionally there is evidence that nitrogenous

compounds formed inside the stomach act as human cancer promoters (3). To deal with these issues, the European Communities have a directive concerning the protection of waters against pollution caused by nitrates from agricultural sources (91/676/EEC). According to this directive, each State Member has to identify its nitrogen vulnerable zones—zones draining into water vulnerable to pollution from nitrogen compounds—and establish codes of good agricultural practices. Also, one of the basic principles of the European Union Treaty, concerning the community policy on the environment, is that “polluter should pay”. According to this principle, as fertilizers are not the only source of these environmental problems and chemical data alone often are not able to discriminate between different sources of pollution, it is necessary to provide new tools to identify and/or quantify the origin of contamination.

Stable isotopes are useful as tracers of agrochemical compounds in the environment. Numerous studies have been carried out using the  $^{15}\text{N}$  and  $^{18}\text{O}$  data of dissolved nitrates in order to discriminate between organic (e.g., human or animal manure) and inorganic (e.g., synthetic fertilizers) nitrogen contaminants in waters (4–7). Nitrate isotopes have also been used to evaluate the fractionation processes in which nitrogen fertilizer compounds are involved (8–11). Sulfur isotopes of dissolved sulfate have been used to estimate the contribution of fertilizers to water pollution (12–14) and soils (15). Regarding strontium isotopes, usually used as tracers of natural water rock interaction, recent papers report the strontium isotopic ratio of fertilizers and use them as tracers of agrochemical pollutants in environmental studies (16–19).

Multi-isotopic studies coupled with chemical data are a powerful tool to trace single and multi-pollutant contaminations and to evaluate in detail the chemical and fractionation processes that occurred. Aravena and Robertson (20) studied the dispersion and degradation of a septic system plume using chemical data together with carbon, sulfur, nitrogen, and oxygen isotopes. Soler et al. (14) distinguished the natural sulfate content in a river system basically from the contribution of urban and/or industrial pollutants by the coupled use of  $\delta^{34}\text{S}$  and  $^{87}\text{Sr}/^{86}\text{Sr}$ . Vitoria et al. (11) characterized the impact of the agricultural activities in groundwaters using chemical and isotope data ( $\delta^{15}\text{N}$ ,  $\delta^{18}\text{O}_{\text{NO}_3}$ ,  $\delta^{34}\text{S}$ ,  $\delta^{13}\text{C}$ ). From these and other studies, one concludes that a thorough characterization of the contamination sources is very important for environmental police to identify the pollutant and evaluate its environmental impact.

The aim of the present study is to give a comprehensive isotopic characterization of 27 synthetic fertilizers, collected from different commercial suppliers from Spain, chemically characterized by Otero et al. (21). Analyses of  $\delta^{15}\text{N}_{\text{Ntotal}}$ ,  $\delta^{13}\text{C}_{\text{Ctotal}}$ ,  $\delta^{15}\text{N}_{\text{NO}_3}$ ,  $\delta^{18}\text{O}_{\text{NO}_3}$ ,  $\delta^{34}\text{S}_{\text{SO}_4}$ ,  $\delta^{18}\text{O}_{\text{SO}_4}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  were carried out to provide a tool for their identification and/or quantification in environmental studies. These isotopic analyses, together with a compilation of previous published isotopic data of fertilizers, were used to identify the origin of fertilizer chemical compounds and to discuss their potential usefulness as tracers of fertilizer contribution to environmental pollution. Otero et al. (21) analyzed the 27 fertilizers elemental concentrations (major, trace, and rare earth elements) to evaluate their entire potential contamination with regards to some actual legislation of countries.

Section 3 of this paper describes the publications that contain other fertilizer isotopic composition data. In section 5, the results of the fertilizers analyzed, together with the literature compilation data, are presented. In section 6, the

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TABLE 1. Isotopic Composition of 27 Fertilizers Used in Spain<sup>a</sup>

fertilizer	whole fertilizer (isotopic composition)		water-soluble (isotopic composition)					
	$\delta^{13}\text{C}_{\text{TOT}}$ (‰)	$\delta^{15}\text{N}_{\text{TOT}}$ (‰)	$\delta^{15}\text{N}_{\text{NO}_3}$ (‰)	$\delta^{18}\text{O}_{\text{NO}_3}$ (‰)	$\delta^{34}\text{S}_{\text{SO}_4}$ (‰)	$\delta^{18}\text{O}_{\text{SO}_4}$ (‰)	$^{87}\text{Sr}/^{86}\text{Sr}$	
Straight								
F1	NH <sub>4</sub> NO <sub>3</sub>	-8.3	-0.7	- <sup>b</sup>	- <sup>b</sup>	8.7	15.0	0.707908 <sup>c</sup>
F2	NH <sub>4</sub> NO <sub>3</sub>	-	2.5	5.6	25.1	0.7	13.4	0.709490
F3	urea	-41.3	-1.1	-	-	-	-	-
F4	NH <sub>4</sub> NO <sub>3</sub> SO <sub>4</sub>	-	1.5	2.0	18.0	8.1	11.9	0.708592 <sup>c</sup>
F5	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-	-0.3	-	-	-1.0	9.5	0.708503 <sup>c</sup>
F6	(NH <sub>4</sub> ) <sub>2</sub> SO <sub>4</sub>	-	0.0	-	-	0.9	10.0	0.708462 <sup>c</sup>
F7	Ca(NO <sub>3</sub> ) <sub>2</sub>	-	3.9	4.5	22.1	-	-	0.703350
F8	K <sub>2</sub> SO <sub>4</sub>	-	-	-	-	7.1	13.5	0.715216
FF NPK								
F9	13-0-46	-23.6	-0.5	-1.0	48.5	3.8	7.7	0.708259
F10	15-5-30	-28.0	0.1	0.3	22.1	1.4	12.8	0.710934
F11	17-6-18	-28.1	0.3	2.0	23.1	-6.5	10.9	0.709365
F12	15-10-15	-30.0	0.3	1.7	24.2	1.1	12.0	0.711350
F13	0-52-34	-	-	-	-	-	-	0.708108
F14	12-61-0	-	-1.1	-	-	-0.2	9.2	0.705038
BT NPK								
F15	10-10-18	-34.3	0.8	-	-	6.8	12.6	0.708206
F16	5-7-10	-23.9	1.8	-	-	6.7	14.6	0.707860 <sup>c</sup>
F17	16-8-12	-29.9	-1.0	-	-	9.0	13.6	0.709359
F18	8-6-20	-25.8	-0.6	1.0	19.2	11.4	11.9	0.708398
F19	12-12-17	-25.1	-0.5	1.1	20.1	1.5	14.6	0.708064
F20	12-12-17	-27.4	0.4	0.8	21.0	5.8	14.0	0.703606
F21	15-15-15	-3.0	-1.7	-1.6	19.8	-	-	0.703400
F22	7-14-16	-25.0	0.3	2.2	19.7	11.5	14.0	0.708050
Other								
F23	Mg(NO <sub>3</sub> ) <sub>2</sub>	1.5	0.2	0.0	24.5	11.7	16.5	0.706624
F24	Mg(NO <sub>3</sub> ) <sub>2</sub>	-	0.0	0.8	22.4	-	-	0.711934
F25	MgSO <sub>4</sub>	-	-	-	-	21.4	11.2	0.708145
F26	FeSO <sub>4</sub>	-	-	-	-	-1.8	15.1	-
F27	CuSO <sub>4</sub>	-	-	-	-	6.1	8.9	-

<sup>a</sup>  $\delta^{13}\text{C}_{\text{Total}}$  and  $\delta^{15}\text{N}_{\text{Total}}$  were analyzed from the whole fertilizer and  $\delta^{15}\text{N}_{\text{NO}_3}$ ,  $\delta^{18}\text{O}_{\text{NO}_3}$ ,  $\delta^{34}\text{S}_{\text{SO}_4}$ ,  $\delta^{18}\text{O}_{\text{SO}_4}$ , and  $^{87}\text{Sr}/^{86}\text{Sr}$  were determined from the water-soluble fraction. A dash (-) indicates that the concentration of the compound was undetectable or too low for analysis. <sup>b</sup> There was no fertilizer available for analysis. <sup>c</sup> Data from Antich et al. (18).

results are discussed with explanations regarding the origin of the fertilizer components, contrasting the isotope data with the chemical results and conclusions of Otero et al. (21), and evaluating their isotope signatures to be used as tracers for the fertilizers contaminations in future studies.

### Fertilizer Classification

Following the nomenclature of the commission proposal of the European Communities (COM2001 0508), a **straight fertilizer** contains only one of the primary nutrients (N, P, or K) and a **compound (or NPK) fertilizer** has at least two of them. Compound fertilizers are usually labeled with three numbers (e.g., NPK 10-10-15, which is 10% nitrogen, 10% phosphate (as P<sub>2</sub>O<sub>5</sub>), and 15% potassium (as K<sub>2</sub>O)). A **secondary nutrient fertilizer** contains a certain amount of S, Ca, Mg, and/or Na; a **micronutrient fertilizer** a certain amount of B, Co, Cu, Fe, Mn, Mo, and/or Zn.

The 27 fertilizers analyzed are classified into three major groups: **straight fertilizers**, **compound fertilizers**, and **others** (includes secondary nutrient and micronutrient fertilizers). Seven of the eight straight fertilizers contain nitrogen as primary nutrient (F1-F7) and one potassium (F8) (Table 1). The group of compound fertilizers includes six fertilizers (F9-F14) used for fertigation or foliar application (FF NPK) and eight fertilizers (F15-F22) used for basal and top dressing (BT NPK). The former are commonly used for intensive farming, the latter are used for extensive farming and horticulture. The group classified as others includes three fertilizers with secondary nutrients (F23-F25) and two with micronutrients (F26 and F27). All are mineral fertilizers, except F16, which is an organomineral fertilizer. They were

all collected from different commercial suppliers from Spain and are used in different types of crops (herbaceous, vegetables and cereals crops, fruit trees, and vineyards).

### Background of Fertilizer Isotopic Published Data

A large number of fertilizer nitrogen and nitrate oxygen isotopic data have been already published. Shearer et al. (22) characterized several fertilizers, soils, and shelf chemicals to evaluate the analytical reproducibility of the  $\delta^{15}\text{N}$  measurements and to determine their isotopic compositions; Freyer and Aly (23) inquired into the origin of their isotopic values. Most studies use the isotopic data to evaluate their usefulness for tracing sources of nitrate contamination (5, 8, 24-27) and/or to apply them in environmental case studies (4, 6, 28-32).

Fertilizer sulfate isotopic data ( $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ ) in environmental studies is less common. Mizota and Sasaki (15) analyzed the  $\delta^{34}\text{S}_{\text{SO}_4}$  of 45 commercial fertilizers (for two of them the  $\delta^{34}\text{S}_{\text{S}}$ ) that affect the  $\delta^{34}\text{S}_{\text{SO}_4}$  of different soils in Japan, Hawaii, Australia, New Zealand, and Brazil. Robinson and Bottrell (12) analyzed the  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  of one superphosphate to discriminate the contribution of fertilizers as the source of sulfur in pristine and polluted river catchments in New Zealand. Montcaster et al. (13) analyzed the  $\delta^{34}\text{S}_{\text{SO}_4}$  of six fertilizers to distinguish between anthropogenic sulfate and sulfate derived by pyrite oxidation in a limestone aquifer in England.

Published data regarding strontium isotopic ratios are found in Borg and Banner (33), where they evaluate the possible sources of Sr isotopes in a limestone aquifer in Barbados and analyze three different fertilizers (one N-, one

P-, and one K-based fertilizer). Martin and McCulloch (17) used Nd and Sr isotopes as well as trace elements to study the geochemistry of river sediments and soils in a fertilized catchment in Australia; they reported the isotopic composition of six phosphate fertilizers. Böhlke and Horan (19) analyzed the Sr isotopes of 11 fertilizers for a geochemistry study of agriculturally affected groundwaters in Maryland. The carbon isotopic composition of fertilizers is not found in the literature.

## Methods

Before analysis, the 27 fertilizers were homogenized and powdered. A split of the pulverized fertilizers was dissolved in distilled water, stirred during 24 h, and filtered with a Millipore filter of 0.45  $\mu\text{m}$  pore size. The solid fertilizer was analyzed to determine the isotopic composition of carbon ( $\delta^{13}\text{C}_{\text{total}}$ ) and nitrogen ( $\delta^{15}\text{N}_{\text{total}}$ ) whereas the dissolved fertilizer provided the isotopic composition of dissolved nitrate ( $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ), dissolved sulfate ( $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$ ), and strontium  $^{87}\text{Sr}/^{86}\text{Sr}$ .

The  $\delta^{13}\text{C}_{\text{total}}$  and  $\delta^{15}\text{N}_{\text{total}}$  were determined directly from the pulverized solid fertilizer with a Carlo Erba elemental analyzer coupled in continuous flow with a Finnigan Matt delta C or an Isochrom continuous flow mass spectrometer.

For  $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$  analyses, the dissolved nitrate from fertilizers was separated using anion-exchange columns of Bio-Rad AG 1-X8( $\text{Cl}^-$ ) 100–200 mesh resin. Next they were eluted with HCl and converted to  $\text{AgNO}_3$  by the addition of silver oxide following a modified method from Silva et al. (34). The purified silver nitrate solution was then freeze-dried. The  $\delta^{15}\text{N}_{\text{NO}_3}$  was determined with a Carlo Erba elemental analyzer coupled in continuous flow with a Finnigan Matt delta C mass spectrometer, and the  $\delta^{18}\text{O}_{\text{NO}_3}$  was analyzed in duplicate by on-line pyrolysis with a Eurovector TC/EA (high temperature) elemental analyzer coupled with a Micromass Isoprime mass spectrometer.

For  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  analysis, sulfate from the dissolved fertilizers was precipitated as  $\text{BaSO}_4$  by the addition of  $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$  in acid media ( $\text{pH} < 2$ ) to prevent  $\text{BaCO}_3$  precipitation. The  $\delta^{34}\text{S}_{\text{SO}_4}$  was determined from  $\text{BaSO}_4$  with an elemental analyzer coupled in continuous flow with a Delta C Finnigan Matt mass spectrometer. The  $\delta^{18}\text{O}_{\text{SO}_4}$  was measured in duplicate by on-line pyrolysis with a ThermoQuest TC/EA unit coupled with a Finnigan Matt delta C mass spectrometer.

Notation is expressed in terms of  $\delta$  per mil (‰). The standards used were air (atmospheric  $\text{N}_2$ ) for nitrogen, V-SMOW (Vienna Standard Mean Oceanic Water) for oxygen, V-CDT (Vienna Canyon Diablo Troilite) for sulfur, and V-PDB (Vienna PeeDee Belemnite) for carbon. The isotope ratios were calculated using international and internal laboratory standards. Precision ( $\equiv 1\sigma$ ) calculated, after correction of the mass spectrometer daily drift, from standards systematically interspersed in analytical batches were for total carbon  $\pm 0.4\text{‰}$ , for total nitrogen  $\pm 0.3\text{‰}$ , for nitrate nitrogen  $\pm 0.3\text{‰}$ , for nitrate oxygen  $\pm 0.5\text{‰}$ , for sulfate sulfur  $\pm 0.5\text{‰}$ , and for sulfate oxygen  $\pm 0.5\text{‰}$ .

For the strontium isotopic analysis, aliquots of 50 mL of dissolved fertilizers were dried and then taken up in 14 M  $\text{HNO}_3$ . The Sr was separated using Sr-spec resin (Eichrom Industries), and  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were determined by standard mass spectrometry on a Finnigan Matt-262. Isotope ratios were normalized to  $^{87}\text{Sr}/^{86}\text{Sr} = 0.1194$  and NBS-987 standard  $^{87}\text{Sr}/^{86}\text{Sr} = 0.710282$ , the standard deviation was 0.000018. In addition, as Sr water-soluble fraction represents 5–100% of the total Sr fertilizer content (21), an acetic and total acid digestion were conducted in some fertilizers to detect changes in the isotopic ratio. Fertilizers used for this experiment were F18 and F22, with 32 and 44% of Sr detected, respectively, in the water-soluble fraction. Results showed a maximum difference of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of 0.000074 between these three

methods. Martin and McCulloch (17) also analyzed one fertilizer by sequential acid dissolution and found that the fertilizer solution  $^{87}\text{Sr}/^{86}\text{Sr}$  composition after a  $\text{HCl} + \text{H}_2\text{O}_2$  digestion was indistinguishable from the bulk sample.

Nitrogen and oxygen isotopes of dissolved nitrate and  $\delta^{15}\text{N}_{\text{total}}$  were performed at the Environmental Isotope Laboratory of the University of Waterloo (Canada) and at the Serveis Científicotècnics of the University of Barcelona (Spain). Sulfur and oxygen isotopic analyses of dissolved sulfate and  $\delta^{13}\text{C}_{\text{total}}$  were prepared at the Mineralogia Aplicada i Medi Ambient Laboratory and analyzed at the Serveis Científicotècnics of the University of Barcelona. Strontium isotopes were performed at the University of País Vasco (Spain).

## Results

Results are shown in Table 1. Fertilizers have carbon isotopic compositions ( $\delta^{13}\text{C}_{\text{total}}$ ) covering a wide range of values, from  $-41.3$  to  $+1.5\text{‰}$  with a median value of  $-25.8\text{‰}$ . All NPK fertilizers, except F21, show a  $\delta^{13}\text{C}_{\text{total}}$  between  $-23.6$  and  $-34.3\text{‰}$ ; F3 (urea) has the lowest value ( $-41.3\text{‰}$ ); F1, F21, and F23 have the highest with values of  $-8.3\text{‰}$ ,  $-3.0\text{‰}$ , and  $+1.5\text{‰}$ , respectively.

Total nitrogen isotopic compositions ( $\delta^{15}\text{N}_{\text{total}}$ ) are very similar for all types of fertilizers, ranging from  $-1.7$  to  $+3.9\text{‰}$  with a median value of  $+0.0\text{‰}$ . Fertilizer nitrogen isotopic composition of dissolved nitrates ( $\delta^{15}\text{N}_{\text{NO}_3}$ ) varies between  $-1.6\text{‰}$  and  $+5.6\text{‰}$  with a median value of  $+1.1\text{‰}$ ; differences by fertilizer group were not detected. The oxygen isotopic composition of dissolved nitrates ( $\delta^{18}\text{O}_{\text{NO}_3}$ ) ranges from  $+18.0$  to  $+25.1\text{‰}$  with a median value of  $+22.1\text{‰}$ , except F9, with a higher composition of  $+48.5\text{‰}$ .

The sulfur isotopic composition of dissolved sulfates ( $\delta^{34}\text{S}_{\text{SO}_4}$ ) covers a wide range of values, from  $-6.5\text{‰}$  (F11) to  $+21.4\text{‰}$  (F25), with a median composition of  $+6.0\text{‰}$ . Except for F11 and F25, the other fertilizers have  $\delta^{34}\text{S}_{\text{SO}_4}$  between  $-1.8\text{‰}$  and  $+11.7\text{‰}$ . The oxygen isotopic composition of dissolved sulfates ( $\delta^{18}\text{O}_{\text{SO}_4}$ ) varies from  $+7.7\text{‰}$  (F9) to  $+16.5\text{‰}$  (F23) with a median value of  $+12.7\text{‰}$ . Neither the  $\delta^{34}\text{S}_{\text{SO}_4}$  nor the  $\delta^{18}\text{O}_{\text{SO}_4}$  show any difference by fertilizer group.

Isotopic ratios of dissolved strontium ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) have a median ratio of 0.70823, with values ranging from 0.70335 (F7) to 0.71522 (F8). Additionally, as occurred with other isotopes, no differences exist between fertilizer groups.

Figure 1 shows the nitrogen compounds isotopic composition data from the literature, together with results from the present study. A histogram with the  $\delta^{15}\text{N}_{\text{NH}_4}$  data reported in other studies is also presented. Values of the  $\delta^{15}\text{N}_{\text{total}}$  range from  $-3.3$  to  $+3.9\text{‰}$ , with a median value of  $+0.2\text{‰}$ . The  $\delta^{15}\text{N}_{\text{NO}_3}$  varies from  $-7.5$  to  $+6.6\text{‰}$ , with a median value of  $+1.8\text{‰}$ . The  $\delta^{15}\text{N}_{\text{NH}_4}$  has values from  $-7.4$  to  $+3.6\text{‰}$  with a median value of  $-0.6\text{‰}$  and the  $\delta^{18}\text{O}_{\text{NO}_3}$  ranges from  $+17.4$  to  $+48.5\text{‰}$ , with a median value of  $+22.1\text{‰}$ .

Sulfate isotopic composition data from the literature together with our analyses are shown in Figure 2. The  $\delta^{34}\text{S}_{\text{SO}_4}$  varies from  $-6.5$  to  $+21.6\text{‰}$ , with a median composition of  $+5.7\text{‰}$ , and three main groups are differentiated. The first group corresponds to fertilizers with the lowest isotopic composition (from  $-7$  to  $+3\text{‰}$ ) with a mode near  $+1\text{‰}$ . A second group is characterized by values between  $+4\text{‰}$  and  $+13\text{‰}$ , with a mode close to  $+7\text{‰}$ . And in the third group are those fertilizers with the highest sulfur isotopic compositions (from  $+16$  to  $+22\text{‰}$ ) with most of them close to  $+21\text{‰}$ . Only one value of  $\delta^{18}\text{O}_{\text{SO}_4}$  has been found in the literature with the same composition as those of the present study.

A histogram with  $^{87}\text{Sr}/^{86}\text{Sr}$  published data and our analyses is presented in Figure 3. It is worth noting that we determined the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio in the water-soluble fraction, whereas other authors have previously digested fertilizers with HCl and  $\text{HNO}_3$  (19),  $\text{HNO}_3$  and HF (17), or unspecified methods (33)

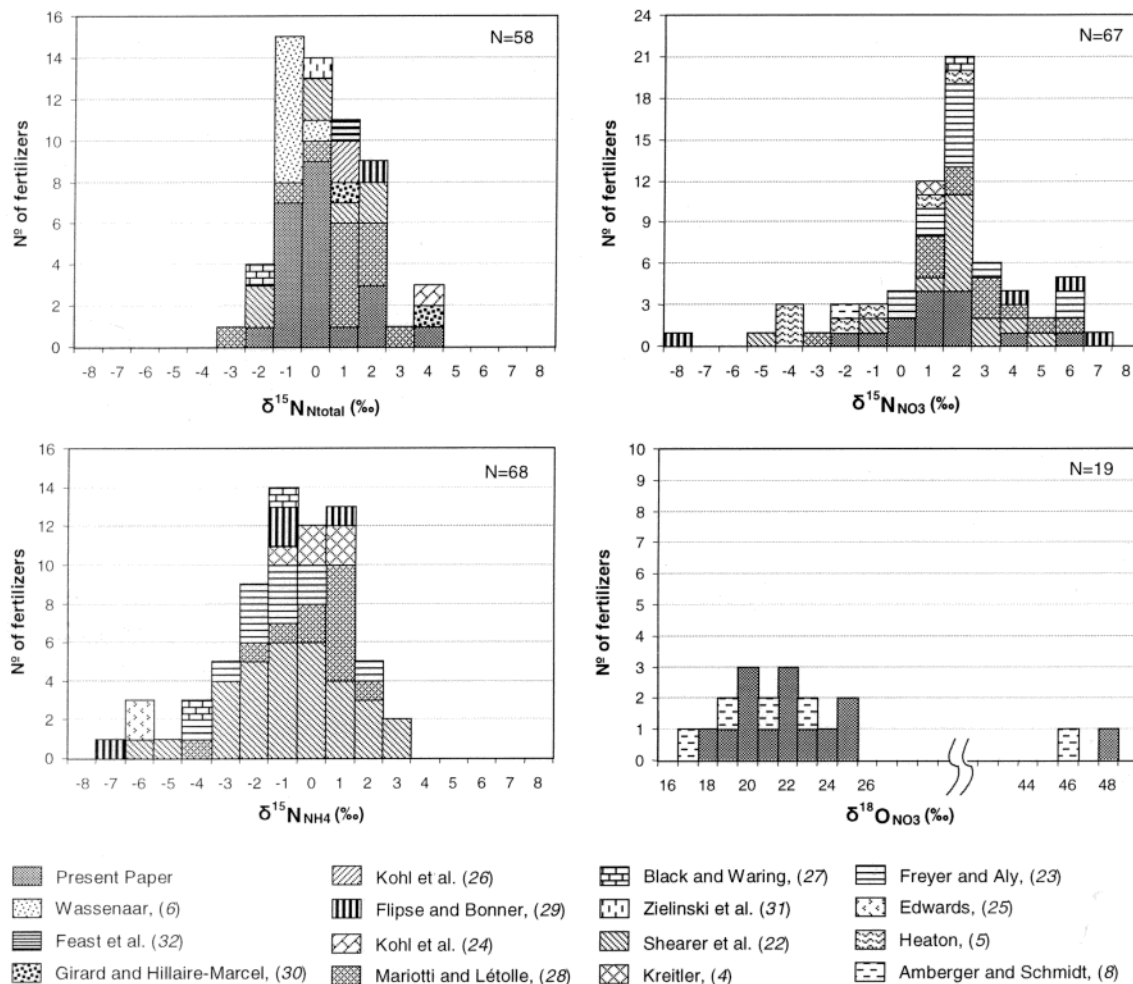


FIGURE 1. Histograms of total nitrogen ( $\delta^{15}\text{N}_{\text{Ntotal}}$ ), ammonium ( $\delta^{15}\text{N}_{\text{NH}_4}$ ), and nitrate ( $\delta^{15}\text{N}_{\text{NO}_3}$  and  $\delta^{18}\text{O}_{\text{NO}_3}$ ) isotopic compositions of fertilizers including compiled data from different publications and the present analyses.

determining the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of the total Sr content. In all studies, strontium isotopic ratios do not show significant differences, and they extend within the same range of values (with the exception of two high radiogenic values), varying from 0.70335 to 0.83518 and with a median value of 0.70881.

As can be observed in Figures 1–3, histograms of the present fertilizers show the same modes and range of values as the compiled published data. This means that the 27 sampled fertilizers of the present study are representative of the fertilizers isotopic chemistry provided by the main worldwide suppliers. This is especially important in the case of sulfate–oxygen, where fewer data were available from literature.

## Discussion

No correlation can be observed between the isotopic compositions of the different fertilizer compounds and/or with the chemistry data. This is due to the fact that most fertilizers are made up of a physical mixture of single-nutrient materials of different origin; hence, each one has its particular isotopic composition. Fertilizer isotopic signatures will be discussed as fingerprints of their components origin in the manufacture process, and their usefulness as tracers of contamination will be evaluated.

**Origin of the Fertilizer Isotopic Signatures.** Raw materials used to provide carbon content for the fertilizer industry are mainly carbon dioxide and/or carbonates. Carbon dioxide is commonly used for urea manufacture, which procedure consists of reacting ammonia and carbon dioxide at high

pressure (140–200 bar) and high temperature (180–190 °C) forming ammonium carbamate, which is finally dehydrated to obtain the synthetic urea (35). The carbon isotopic composition of the straight fertilizer F3 (urea), with the highest content of total organic carbon, is  $-41.3\text{‰}$ . This negative value can be explained by an organic origin of the commercial  $\text{CO}_2$  used, which is normally obtained as a byproduct from fuel combustion by petrochemical companies (R. González, personal communication).

NPK fertilizers (except F21) have  $\delta^{13}\text{C}_{\text{Ctotal}}$  values between  $-34\text{‰}$  and  $-24\text{‰}$ , and except for F15–F17, the total carbon (TC) content corresponds to the content of the total organic carbon (TOC) (1). In this case, the carbon content is related again to an organic origin. On the other hand, F15–F17 have a higher TC content than TOC concentration. Otero et al. (21) provide two possible explanations: (i) not all the organic carbon has been detected since the solubility of these fertilizers is less than 100%, and/or (ii) there is another source of carbon (e.g. carbonates). Their negative carbon isotopic composition seems to indicate an organic origin for the carbon concentration.

Fertilizers F1, F21, and F23 have no TOC content and their  $\delta^{13}\text{C}_{\text{Ctotal}}$  have the highest values ( $-8.3\text{‰}$ ,  $-3.0\text{‰}$ , and  $+1.5\text{‰}$ , respectively) coinciding with the carbonatite signatures that range from  $-10$  to  $+3\text{‰}$  (36) (Figure 4). The carbonatite origin for some components of F21 is supported by the REE patterns reported by Otero et al. (21), which were not applicable to F1 and F23 as they do not have an appreciable REE content. F23 has a  $\delta^{13}\text{C}_{\text{Ctotal}}$  that also matches

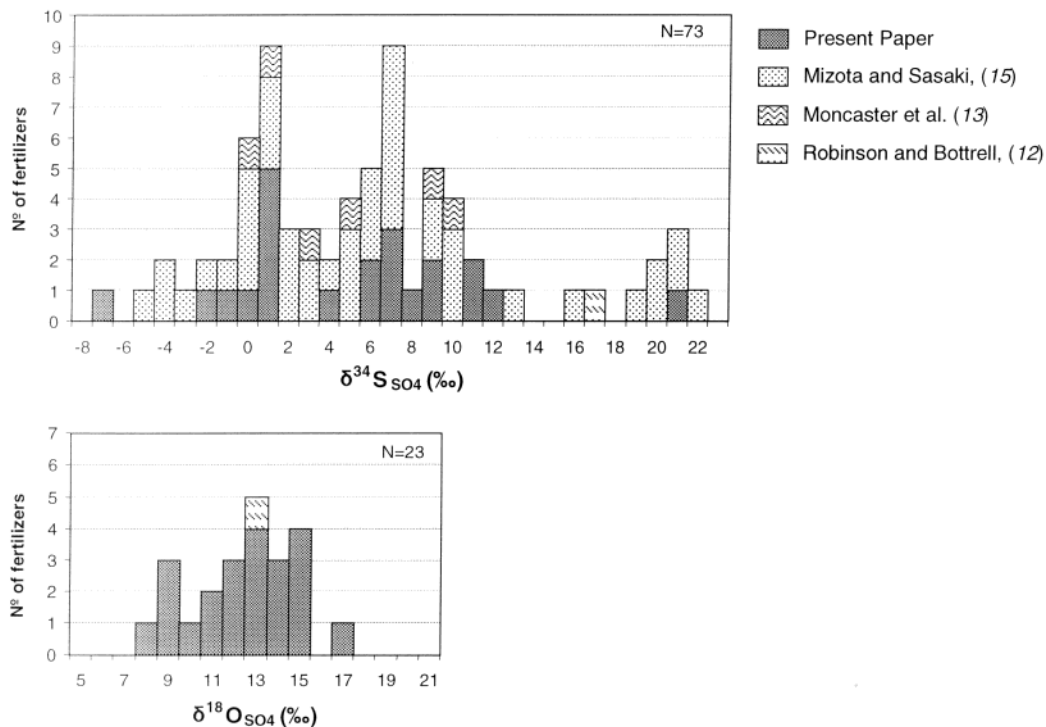


FIGURE 2. Histograms of sulfate-sulfur ( $\delta^{34}\text{S}_{\text{SO}_4}$ ) and sulfate-oxygen ( $\delta^{18}\text{O}_{\text{SO}_4}$ ) isotopic compositions of fertilizers from literature compiled data and the present analyses.

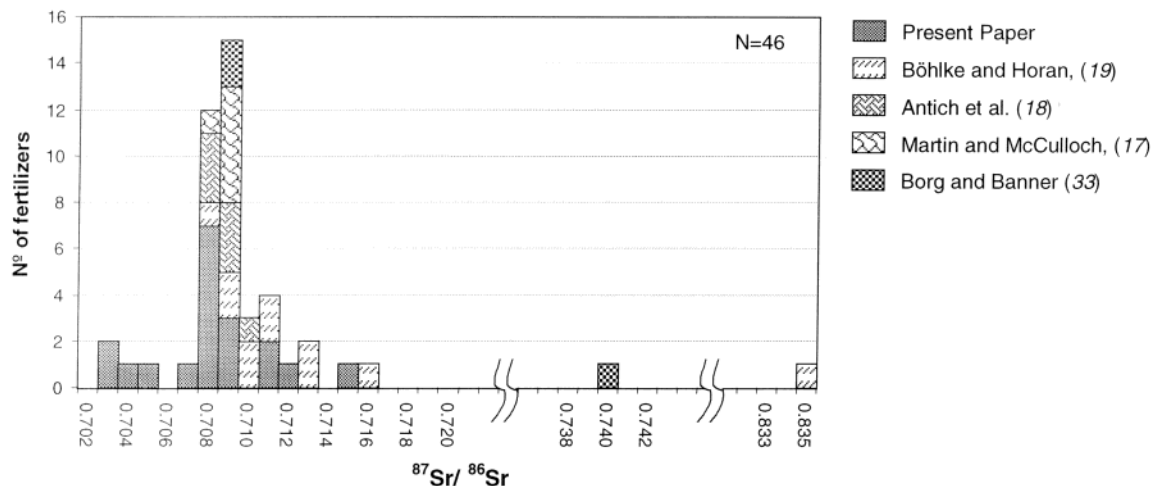


FIGURE 3. Histogram of fertilizer strontium isotopic composition ( $^{87}\text{Sr}/^{86}\text{Sr}$ ) extracted from previous published data and the present study.

with the marine carbonate compositions, ranging from  $-3$  to  $+2\text{‰}$  (38), and F1 has a composition close to atmospheric  $\text{CO}_2$  ( $-7\text{‰}$ ; 38), which seems to be the origin of its low TC content (0.03 ppm) as this fertilizer is a synthetic  $\text{NH}_4\text{NO}_3$  produced with atmospheric  $\text{N}_2$  and  $\text{O}_2$ .

The  $\delta^{15}\text{N}$  of total nitrogen as well as the  $\delta^{15}\text{N}_{\text{NO}_3}$  values are in accordance with the compositions of the primary constituents used by the fertilizer industry. Fertilizer nitrogen compounds (synthetic ammonia, ammonium, nitrate, and urea) are manufactured by different industrial processes using, as nitrogen source, atmospheric nitrogen ( $0\text{‰}$ , 39) (Figure 5) and, as nitrate oxygen source, atmospheric oxygen ( $+22.5\text{‰}$ , 42) (43) (Figure 6). Another current, though less important, nitrate source for fertilizer manufacture are the Chilean nitrate deposits, with a  $\delta^{15}\text{N}$  also close to  $0\text{‰}$  (from  $-5$  to  $+5\text{‰}$ ) and a  $\delta^{18}\text{O}$  value between  $+35.6\text{‰}$  and  $+50.4\text{‰}$  (40). Fertilizers inherit these isotopic signatures, all reaching similar values of  $\delta^{15}\text{N}_{\text{Total}}$ ,  $\delta^{15}\text{N}_{\text{NO}_3}$ ,  $\delta^{18}\text{O}_{\text{NO}_3}$ , and  $\delta^{15}\text{N}_{\text{NH}_4}$  (see Figure 1). Only fertilizer F9 and another from the literature

data have the typical  $\delta^{18}\text{O}$  Chilean nitrate value. Nitrate nitrogen isotopic values, compared to the atmospheric nitrogen, are slightly enriched in  $^{15}\text{N}$  (median value of  $\delta^{15}\text{N}_{\text{NO}_3} = +1.8\text{‰}$ ) as the ammonium nitrogen is enriched in  $^{14}\text{N}$  (median value of  $\delta^{15}\text{N}_{\text{NH}_4} = -0.6\text{‰}$ ). Freyer and Aly (23) explain the difference between the  $\delta^{15}\text{N}_{\text{NO}_3}$  and the  $\delta^{15}\text{N}_{\text{NH}_4}$  of about  $2.5\text{‰}$  by an isotopic exchange occurring after the oxidation of ammonia in the nitric acid production involved in the fertilizer manufacture.

In the production of synthetic fertilizers, two major sources provide sulfate: sulfuric acid and marine evaporites. As over 60% of world sulfuric acid production is used in the fertilizer industry (35), it is expected to find its signature in fertilizers. This acid is used to digest the phosphate rock and also to provide sulfur as a secondary nutrient. The raw materials used for the acid production are metal sulfides (mainly pyrites), sulfates, sulfurous gases such as  $\text{H}_2\text{S}$ , and native S. The different  $\delta^{34}\text{S}$  values of these materials result in a heterogeneity of fertilizer compositions. However, in Figure

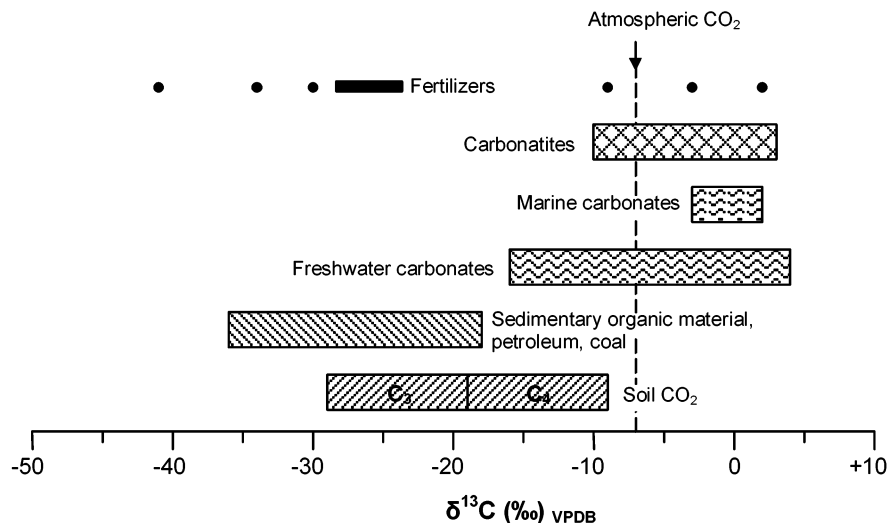


FIGURE 4.  $\delta^{13}\text{C}$  values for the main carbon reservoirs (data from refs 36–38). Fertilizer data correspond to the present analyses; rectangle includes most of the data; dots represent single values.

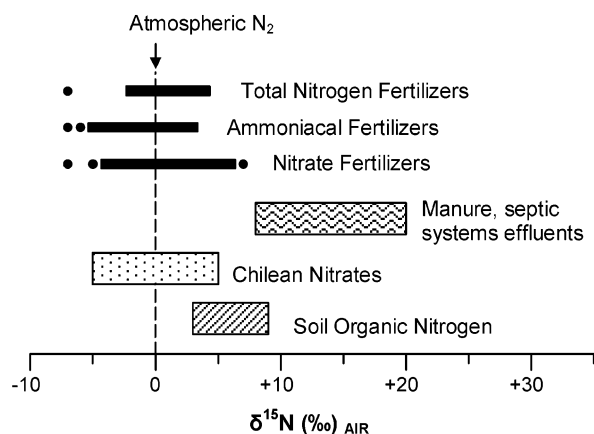


FIGURE 5.  $\delta^{15}\text{N}$  compositions of different nitrogen compounds (data from refs 5–7, 38, 40, and 41). Fertilizer values correspond to the compiled data of Figure 1; rectangles include most of the data; dots represent single values.

2 three groups of samples can be observed. The first group has compositions close to 1‰, corresponding to the mean value for pyrite found in the Iberian Pyritic Belt, one of the world's major massive sulfide districts (44, 45) (Figure 7). Additionally, a Spanish-manufactured sulfuric acid (Probus  $\text{H}_2\text{SO}_4$  1 N) was analyzed, and an isotopic value of +1.2‰ was obtained. The second group, with sulfur compositions near +7‰, can correspond to other sulfide deposits exploited by the fertilizer industry as Kuroko (Japan) or the Australian VHMS with  $\delta^{34}\text{S}$  values between 0‰ and +12‰ (48, 46). The third group of fertilizers is characterized by  $\delta^{34}\text{S}_{\text{SO}_4}$  close to the present day (+21‰; 47) or Tertiary (from +16 to +23‰; 38) seawater sulfate as it seems to correspond to F25 ( $\text{MgSO}_4$ ). However, Mizota and Sasaki (15) describe other sources of sulfur different from the actual marine evaporite deposits (brimstone,  $\text{H}_2\text{S}$ , sulfate, etc.), which can account for the enriched isotopic compositions of fertilizers.

Regarding the sulfate oxygen isotopic compositions, F25 has a  $\delta^{18}\text{O}_{\text{SO}_4}$  of +11.2‰ that corroborates a Tertiary marine sulfate origin (from +11 to +16‰, 38) (Figure 8). On the other hand, fertilizers characterized by a  $\delta^{34}\text{S}_{\text{SO}_4}$  compatible with the  $\text{H}_2\text{SO}_4$  manufactured from sulfides show a range of  $\delta^{18}\text{O}_{\text{SO}_4}$  values between +7.7‰ and +16.5‰ (Figure 2). Indeed, the previous Spanish-manufactured  $\text{H}_2\text{SO}_4$  has an isotopic composition of +12.9‰, corresponding to the median value of the histogram.

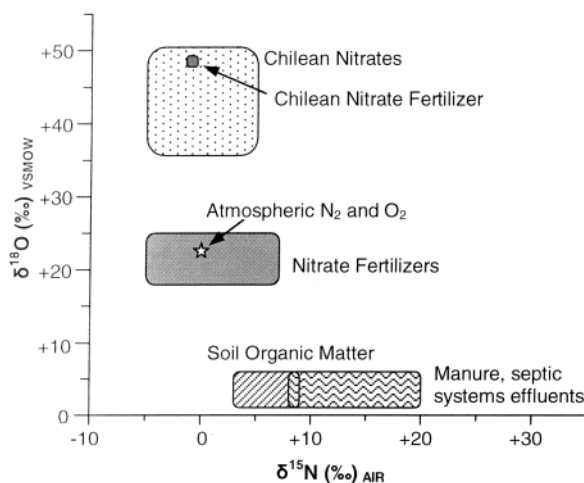


FIGURE 6. Isotopic compositions of various nitrate compounds and atmospheric  $\text{N}_2$  and  $\text{O}_2$  (data from refs 5–7 and 38–42). Fertilizer nitrate–nitrogen isotopic values correspond to the compiled data of Figure 1, whereas nitrate–oxygen values are from the present analyses.

Strontium in fertilizers can be associated to sulfates, phosphates, carbonates, or potassium used for the fertilizer manufacture. Figure 3 shows that most fertilizers have values between 0.708 and 0.709 in accordance with the late Tertiary and modern seawater values (Figure 9). Moreover, as strontium does not fractionate during the mineral precipitation, these  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios are compatible with a marine carbonate, sulfate, or phosphorite origin of this element. During geological times, these deposits inherited the seawater  $^{87}\text{Sr}/^{86}\text{Sr}$  composition, varying between 0.7066 and 0.7092 (38). Otero et al. (21) studied the REE patterns and the ratio  $\text{La}/\text{Lu}$  normalized to PAAS (post-archean Australian average shale),  $(\text{La}/\text{Lu})_{\text{PAAS}}$ , of fertilizers having an appreciable REE content (BT NPK) in order to identify the source of phosphate rock—phosphorites or carbonatites—used for their manufacture. The importance of this lies in the fact that the different origin implies different REE and heavy metal content: the use of carbonatites can potentially result in higher contents of REE, Sr, Ba, and Th, while phosphorites in higher contents of some metals of environmental concern, such as Cd, U, and As, and a higher sum of heavy metals (21). These authors found that REE patterns and the  $(\text{La}/\text{Lu})_{\text{PAAS}}$  ratio of fertilizers F15–F19 and F22 correspond to a phosphorite origin, which is in accordance with the observed strontium isotopic ratio.

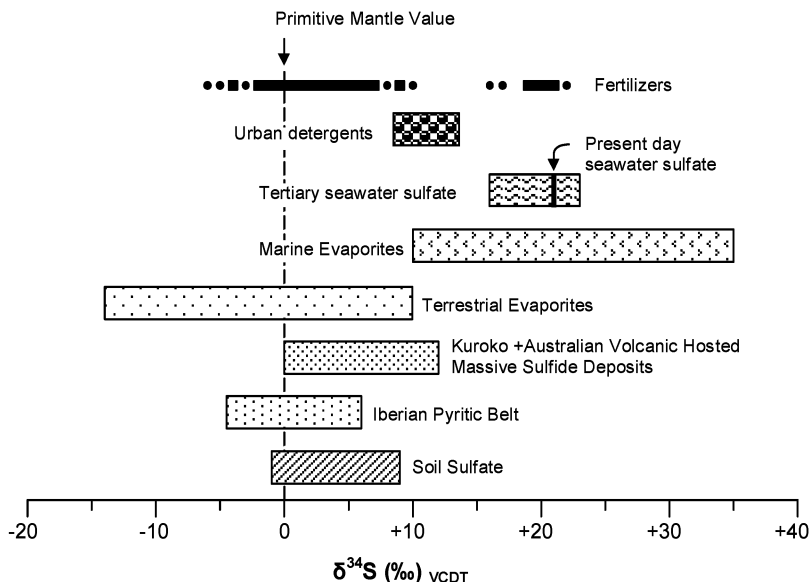


FIGURE 7.  $\delta^{34}\text{S}$  values of some major sulfur reservoirs and selected materials (data from refs 14, 15, 38, 44–49, and Soler et al. (unpublished data)). Fertilizer values correspond to the compiled data of Figure 2; rectangles include most of the data; dots represent single values.

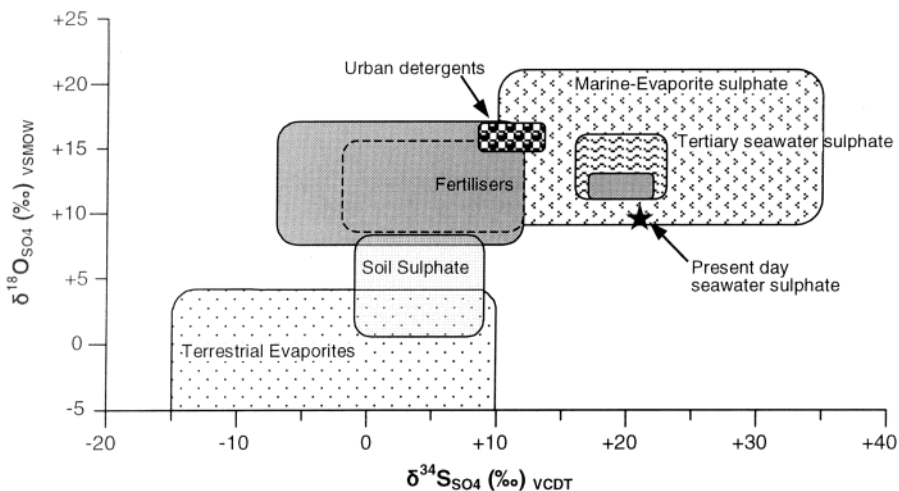


FIGURE 8. Sulfate isotopic composition of some selected materials (data from refs 14, 15, 38, 47, 49–51, and Soler et al. (unpublished data)). Fertilizer values correspond to the compiled data of Figure 2; 80% of them plot within the dashed line.

Fertilizers F7, F14, F20, F21, and F23 have the lowest strontium isotopic ratios. Carbonatite deposits have typical values ranging from 0.7018 and 0.7054 with mean values near 0.7035, and they usually have high contents of strontium and REE (52). This seems to be the strontium origin for F14, F20, and F21, whose Sr contents are 12, 4451, and 4535 ppm, respectively, which in turn corroborates the F20 and F21 carbonatite origin found by Otero et al. (21) as they have the highest REE contents (1330 and 1637 ppm, respectively); the REE patterns and  $(\text{La}/\text{Lu})_{\text{PAAS}}$  ratios are in accordance with a carbonatite origin. Moreover, the F21 carbon isotopic composition indicates the same origin. Nonetheless, fertilizers F7 and F23 have no phosphate content (<0.5% and <0.25%, respectively) although the strontium isotopic ratio in F7 has a clear carbonatite origin. The 0.70662 ratio of the F23 could correspond to a carbonatite, marine carbonate, or a mixing of both origins for strontium, which coincides with the source of carbon found by the  $\delta^{13}\text{C}$ .

The most radiogenic fertilizer ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.835$ ) analyzed by Böhlke and Horan (19) also has a composition coherent with its chemistry. This fertilizer is a NPK 0–0–60, made up entirely of sylvite (KCl), a mineral that can contain significant amounts of rubidium-substituting potassium into its crystalline structure. Rubidium is an element that naturally decays

to  $^{87}\text{Sr}$  increasing the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio to a very radiogenic composition. The second most radiogenic fertilizer ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.740$ , from ref 33) and fertilizer F8 ( $^{87}\text{Sr}/^{86}\text{Sr} = 0.715$ ) also follow this assumption since they are potassic fertilizers. In addition, F8 has high Rb and Br contents (26 and 47.7 ppm, respectively), characteristic elements of the potash evaporite deposits (53).

Fertilizers F10, F12, and F24 have intermediate ratios (from 0.71093 to 0.71193), which could also be explained by an evaporite origin of their potassium content (>20, 10.66, and 0.03 ppm, respectively). Also, they can be the end result of different sources of strontium associated to the different components mixed for the fertilizer production.

It is worth noting that to trace the source of phosphate rock—phosphorites or carbonatites—in fertilizers, implies different REE and heavy metal content as disclosed in Otero et al. (21). REE patterns and  $(\text{La}/\text{Lu})_{\text{PAAS}}$  ratios can be used for those fertilizers having an appreciable REE content (BT NPK fertilizers). Nevertheless, the strontium ratio can be determined in almost all fertilizers.

**Usefulness of the Isotopic Compositions to Trace Fertilizer Contaminations.** Fertilizers have a relatively low content of carbon with a wide range of  $\delta^{13}\text{C}_{\text{total}}$  signatures coinciding with most of their geologic and biological  $\delta^{13}\text{C}$

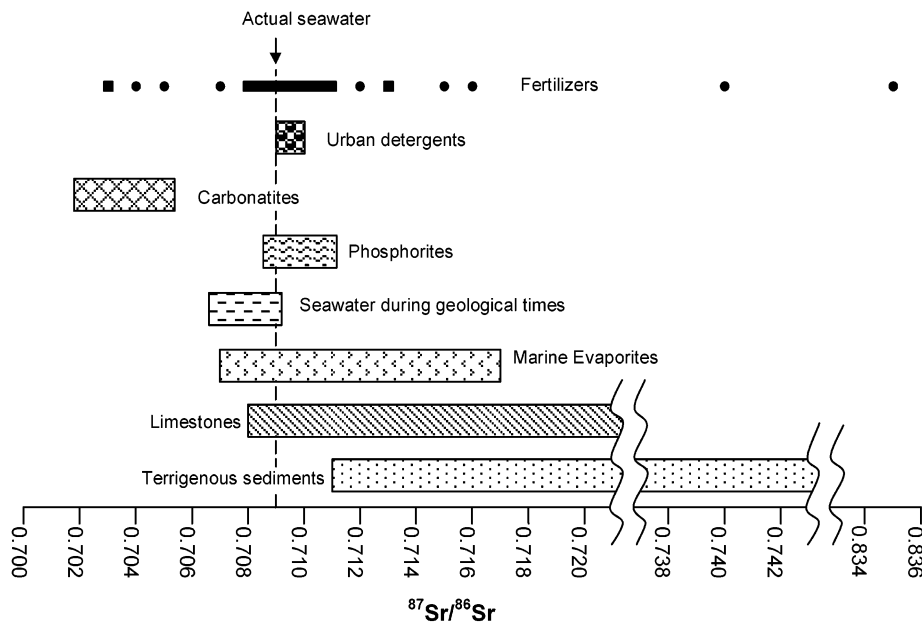


FIGURE 9. Strontium isotopic ratios of selected materials (data from refs 18, 38, 52, and 53). Fertilizer values correspond to the compiled data of Figure 3; rectangles include most of the data; dots represent single values.

compositions (Figure 4). Most NPK fertilizers have  $\delta^{13}\text{C}_{\text{total}}$  values that coincide with those of a sedimentary organic carbon, soil  $\text{CO}_2$ , and some freshwater carbonates. Other fertilizers (straight and others) coincide with marine carbonates, carbonatites, and the atmospheric  $\text{CO}_2$  compositions. This fact together with the high carbon content of natural environments, which could buffer the relatively small fertilizer carbon inputs in contaminated areas, makes it difficult to use the  $\delta^{13}\text{C}_{\text{total}}$  of fertilizers as a tracer.

In contrast, fertilizer nitrogen isotopic compositions of total nitrogen and/or nitrate have a narrow range of values ( $-4$  to  $+6\text{‰}$ ), which are generally lower than other natural or anthropogenic nitrogen sources (Figure 5). Soil organic nitrogen has a  $\delta^{15}\text{N}$  between  $+4\text{‰}$  and  $+9\text{‰}$  (5), and animal manure or sewage wastes have values typically higher than  $+8\text{‰}$  (6, 7, 41). Nitrogen compounds, however, can be affected by fractionation process, which change their isotopic compositions: urea and ammoniacal compounds of synthetic fertilizers and animal or human wastes are usually partially lost to the atmosphere by volatilization. Under aerobic conditions (river systems, aquifer unsaturated zone, etc.), the residual ammonium is nitrified to nitrate, and nitrate can be, under anaerobic conditions, denitrified into  $\text{N}_2$ . All these reactions produce an overall enrichment in  $^{15}\text{N}$  and  $^{18}\text{O}$  between the original nitrogen compound and the dissolved  $\text{NO}_3^-$  (9, 54). This can produce difficulties in tracing nitrate contaminations (55), however, when sources are well-characterized, the coupled use of the  $\delta^{15}\text{N}$  together with the  $\delta^{18}\text{O}$  allows us to identify these reactions and trace nitrogen contaminations in natural environments (7, 20, 11, 56, among others).

Despite the wide range of fertilizer sulfur isotopic signatures, which coincide with most of the reported compositions of major sulfur reservoirs (Figure 7), by coupling  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  values, fertilizer compositions are different from natural sulfates as marine evaporite deposits—except those manufactured from these deposits—sulfates resulting from sulfide oxidation (57) and soil sulfates (50, 51) (Figure 8). Nevertheless, the range of fertilizer compositions can coincide with other local anthropogenic sulfate sources such as detergents ( $\delta^{34}\text{S}_{\text{SO}_4}$  from  $+8.5$  to  $+13.6\text{‰}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  from  $+14.7$  to  $16.9\text{‰}$ ; Soler et al. (unpublished data)) or urban and industry wastes, etc. that must be taken into account in each local case study.

The sulfate molecule, similar to nitrate, is susceptible to reduction by bacterial activity under anaerobic conditions, resulting in  $\delta^{34}\text{S}_{\text{SO}_4}$  and  $\delta^{18}\text{O}_{\text{SO}_4}$  fractionation. However, the  $E_h$  conditions required to produce these reduction reactions are much lower than those required for nitrate (58). Therefore, as their isotopic compositions are different from other sources of sulfate contamination, they can be also used to trace fertilizer contaminations in soils and waters. Moreover, they have also been used to distinguish between fertilizer sulfate and sulfate derived by pyrite oxidation (13) or potash mine tailing contamination (59, 60).

Regarding strontium, fertilizers have a wide range of  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios coinciding with much of the geological materials in the earth. However, most of these agrochemicals have very similar ratios (0.708–0.709) overlapping those of late Tertiary and modern seawater compositions and, therefore, with the contemporaneous chemical sediments (sulfates, carbonates, phosphorites) (Figure 9). In specific areas, these values are also similar to other anthropogenic sources of pollution such as the mixed urban and industrial wastes (0.70839–0.70844) but slightly different from the detergents ratios (0.70913–0.71008) (61).

The power of Sr isotopes lies in the fact that the  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio of surface water and groundwater is determined primarily by the isotopic characteristics of the watershed area as natural processes do not produce fractionation. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is a conservative tracer that persists in the water until it becomes mixed with other waters containing dissolved strontium of different compositions. Thus, when the strontium isotopic composition of natural and anthropogenic sources is different, the isotopic signature of the dissolved strontium in fluvial and groundwaters will show a mixing of different endmembers and can be a powerful added tool when nitrate or sulfate fertilizer isotopic signatures are overwhelmed. However, if mineral dissolution and/or cation exchange processes exist in soils and aquifers, they must be taken into account. Antich et al. (61) used the  $^{87}\text{Sr}/^{86}\text{Sr}$  coupled with chemical data to distinguish between detergents, fertilizers, and natural sources of strontium in a river basin. The coupled use of strontium isotopic ratios with sulfur isotopic composition has been successfully used by Soler et al. (14) as tracers of natural (weathering of sediments) and anthropogenic (fertilizers, industrial, and/or urban wastes) chemicals in streamwaters.



Nitrogen (or nitrate) and sulfate are principal components of fertilizers, and when the coupled use of  $\delta^{15}\text{N}_{\text{NO}_3}-\delta^{18}\text{O}_{\text{NO}_3}$  and  $\delta^{34}\text{S}_{\text{SO}_4}-\delta^{18}\text{O}_{\text{SO}_4}$  occurs, improved differentiation of fertilizers from natural compounds and other anthropogenic sources of pollution is obtained even if fractionation processes are active. Strontium, on the other hand, has an isotope ratio that is unaffected by fractionation effects. Therefore, the multi-isotopic approach appears to be an excellent tool for environmental studies to constrain and quantify fertilizer contribution to water pollution.

## Acknowledgments

This study has been financed by CICYT Project REN2002-04288-CO2-02 of Spanish Government and partially by SGR01-00073 of the Catalanian Government. We would like to thank the Serveis Científicotècnics of the University of Barcelona (Spain).

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Received for review July 24, 2003. Revised manuscript received March 2, 2004. Accepted March 15, 2004.

ES0348187