Atlantic. Saito *et al.* (*13*) reported lower Miocene sediments at the intersection of the MAR with the Atlantis Fracture Zone. The offset of the MAR axis at the Atlantis Fracture Zone is only 30 km (*14*), and Saito's lower Miocene sediments were recovered from within the offset zone, about 10 km from one of the two offset axes; thus, their maximum possible distance from a spreading axis, either immediately north or immediately south of the fracture, is 20 km. If we assume a spreading rate of 2 cm/year, the maximum age of these sediments would be 1 million years if their occurrence is to be explained by sea-floor spreading. However, if they were deposited in the lower Miocene, they must be at least 15 million years old; that is, they are one order of magnitude too old to be accounted for by sea-floor spreading.

Within the offset of the MAR at the St. Paul Fracture Zone a ridge trending east-west is capped by a protrusive, predominantly ultramafic body which emerges at the St. Paul Islets. Recently obtained radiometric ages of rocks from this body, particularly a potassium-argon age of 835 million years for a brown hornblende mylonite (*5*), are inconsistent with sea-floor spreading. In the offset at the Romanche Fracture Zone we found the summit of the transverse ridges to be covered by thick MnO_2 crusts and by phosphatized limestones Miocene or older (*15*).

A summary of the data indicates that: (i) the Vema transverse ridge is essentially an ultramafic body (*2*); (ii) the petrology and chemistry of its ultramafic rocks suggest mantle derivation, and their textures suggest tectonic emplacement (*2*, *3*); (iii) sedimentary rocks and fossils from the Vema transverse ridge are explained if it is assumed that they formed in a narrow and shallow primitive Atlantic and if extensive vertical tectonic motions occurred without much lateral spreading; and (iv) there are indications that the Vema transverse ridge is older than the adjacent sea floor.

We conclude that the Vema transverse ridge constitutes a nonspreading, mantle-derived protrusive block which became emplaced along a preexisting crustal fracture and is now plastered at the boundary between adjacent spreading plates or subplates. Present indications suggest that similar quasi-static ultramafic protrusions exist at other major fracture zones of the Atlantic, such as the Atlantis, St. Paul, and Romanche fracture zones. Thus, sea-floor spreading in the equatorial Atlantic can be viewed as operating in parallel spreading belts separated at the MAR offsets by thin nonspreading blocks (*16*). The presence of these relatively static, mantle-derived protrusive bodies at the offsets of the MAR can be considered within a broader scheme: it can be related to the possible presence of a stagnant mantle zone below the MAR (*17*), and it can be linked to the origin of the offsets themselves, as discussed in detail elsewhere (*16*).

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Fertilizer Nitrogen: Contribution to Nitrate in Surface Water in a Corn Belt Watershed

Abstract. *Measurements of nitrate concentration and relative enrichment in nitrogen-15 were made on samples of the surface waters of a typical Illinois corn belt watershed and the effluent of the subterranean tiles that drain the cropped land in the region. From these measurements, we estimate that at the time of peak nitrate concentration in the spring of 1970 a minimum of 55 to 60 percent of the nitrogen found as nitrate in the surface waters of this watershed originated from fertilizer nitrogen.*

As nitrate concentrations in surface waters in the United States continue to increase [see, for example, Harmeson and Larson (*1*)], even occasionally surpassing the U.S. Public Health Service (PHS) limit of acceptability, two questions among others become increasingly important: (i) What fractional responsibility must the rising rate of application of inorganic nitrogen fertilizers bear for the increase in the nitrate concentration? (ii) What will nitrate concentrations in surface waters be in the future, given a continuation in present trends or given a change in fertilization practices?

Until now, efforts to answer these and related questions have been based on the apparently straightforward technique of analyzing the relationship between nitrogen fertilizer applied to the soil and the concentration of nitrate and other nitrogenous constituents in water that drains from cropped land. The interpretation of such data is, however, far from straightforward because the large preexisting reservoir of nitrogen in the soil and the biological transformations it undergoes—particularly the cycling of NH_4^+ through bacterial protoplasm—serve as a buffer between the input of inorganic nitrogen and the discharge of nitrate to subsurface water.

We report here some results based on a different approach and aimed at providing an answer for the first question for a typical central Illinois corn belt watershed. In addition, we are hopeful that this new approach to the problem of estimating the impact of fertilizer nitrogen on surface water nitrate will help to generate the data needed to predict future nitrate levels.

The study has been carried out in the Sangamon River watershed. In 1922 a mainstream dam on that river

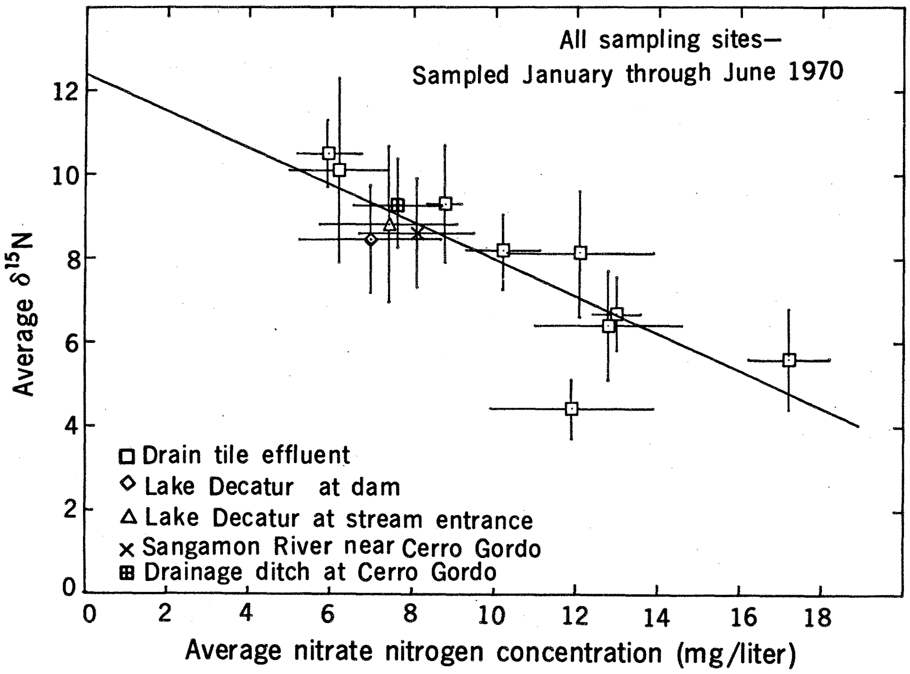

Fig. 1. Relative enrichment in ^{15}N plotted against nitrate nitrogen concentration. Each point represents the average of samples taken at various times during the indicated months. The period January to July 1970 was chosen since after this time most drain tiles virtually stopped flowing. Therefore, the magnitude of the "standard deviation" indicated is affected by the real temporal variation as well as the experimental error in the determination of the values (about ±1 unit for both parameters).

created Lake Decatur, which serves as the source of drinking water for the city of Decatur, a growing metropolitan area of about 100,000 people. Measurements by the Illinois State Water Survey on water samples from the Sangamon River about 34 miles above Lake Decatur show an increase in the nitrate concentration over the past decade that roughly parallels the increase in the use of nitrogen fertilizer in that time. The median value for 1956 to 1961 for the nitrate nitrogen concentration was 2.0 mg/liter while for 1966 to 1969 it was 7.4 mg/liter (*2*). The PHS acceptable standard for drinking water is 10 mg of nitrate nitrogen per liter.

There are no significant sources feeding nitrogen into the river or lake other than erosion or those directly related to cropping; feedlots, industrial discharge, and municipal sewage effluent are all virtually absent. The watershed is heavily cropped with most of the land planted in alternate years in corn and soybeans. During the times of peak river discharge, which are generally also the times of maximum nitrate concentration, a significant fraction of the water entering the river—and hence the lake—is drained from the cropped fields by a subterranean drainage system. Virtually all the agricultural fields of the region are drained by subterranean tiles, which discharge water into drainage ditches that ultimately empty into the river. To a first approximation it may be assumed that each tile course drains a specific area, although there is probably some lateral movement of groundwater. The water drained from that area is often conveniently available at the point at which it is discharged into the ditch.

Our work is based on measurements of the natural enrichment in ^{15}N of soil nitrogen, fertilizer nitrogen, and the nitrogen of surface water nitrate, as well as on measurements of nitrate concentrations. The stable isotope ^{15}N accounts for approximately 0.37 percent of the nitrogen found in the atmosphere, the dominant isotope ^{14}N accounting for the remainder. Many physical and biochemical processes, such as evaporation, denitrification, nitrification, and so on, tend to fractionate isotopes according to mass. In these processes ^{14}N is favored, and the substrate for the process is enriched in ^{15}N (*3*).

It is possible to detect variations as small as 0.1 percent in ^{15}N levels. The parameter $\delta^{15}N$ used in this study is the per mil enrichment in ^{15}N compared to its enrichment in air. Thus, the 0.1 percent alluded to above is expressible as $\delta^{15}N = |1|$. The values of $\delta^{15}N$ were measured on a Consolidated-Nier (model 21-201) mass spectrometer with dual-sample collection. Background correction for masses 28 and 29 allows $\delta^{15}N$ to be determined to ± 1 unit. Samples were prepared for the mass spectrometer by reducing the nitrate in the samples to NH_4^+, after distilling off any NH_4^+ initially present (*4*). Extreme care was taken that none of the sample was lost during the preparation, since any sample loss could result in a spurious value of $\delta^{15}N$ through isotope fractionation.

Compared to air, soil is generally enriched in ^{15}N (*5*). This probably results from the fact that nonsymbiotic nitrogen fixation does not significantly fractionate the isotopes (*6*), while denitrification favors ^{14}N (*3*) which leaves soil nitrogen enriched in ^{15}N. Virgin soil was brought into the laboratory from fields in the study region and incubated at 22°C under aerobic conditions (200 g of dry soil with 40 ml of water stirred in) in order to produce nitrate from reduced soil nitrogen. The nitrogen of the nitrate produced in this manner was substantially enriched in ^{15}N: $\delta^{15}N = +13$. On the other hand, nitrogen from the fertilizer used in the study region was found to be considerably less enriched in ^{15}N; for example, for anhydrous ammonia fertilizer, $\delta^{15}N = +3.7$.

If the only possible sources of nitrate nitrogen found in the surface waters are soil nitrogen, for which $\delta^{15}N = +13$, and fertilizer nitrogen, for which $\delta^{15}N = +3$ (*7*), then measurements of $\delta^{15}N$ for the surface waters should provide a means for assigning the fraction of the nitrate in them which originated from fertilizer. Thus, if the only sources of nitrate nitrogen were from soil and fertilizer and if the lake water were to have a value of $\delta^{15}N = +7.5$, a linear interpolation between +13 and +3 would allow one to say unequivocally that 55 percent (±10 percent due to experimental error) of the nitrate was derived from fertilizer.

In fact, the situation in this watershed closely approximates the ideal situation. Water is available from two distinctly different types of environment, namely, surface water (drainage ditch, river, lake, Decatur tap water) and subsurface water (which is accessible for collection at the point at which it emerges from the subterranean tiles and empties into the drainage ditch). The only conceivable sources of nitrogen found in the drain-tile effluent, in

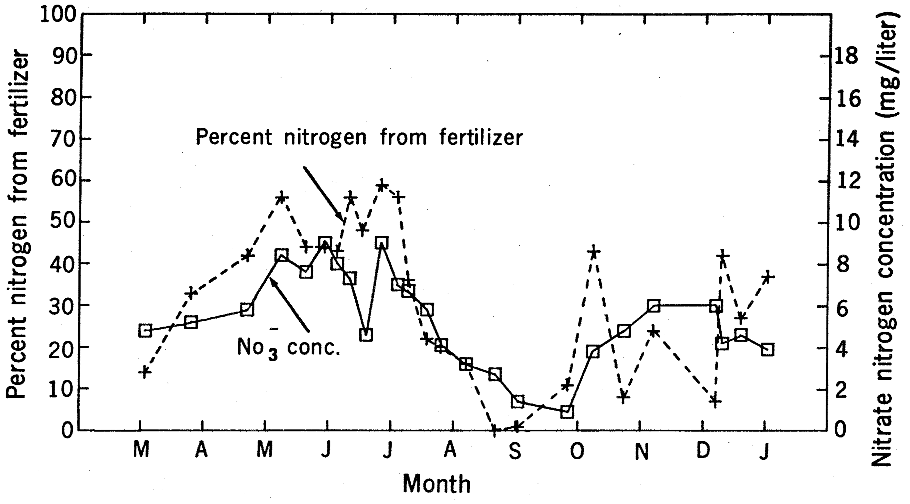

Fig. 2. The minimum percentage of nitrate nitrogen originating from fertilizer nitrogen and the concentration of nitrate nitrogen in Lake Decatur as a function of time. The percentage of nitrogen originating from fertilizer (dashed line) was calculated from measurement of the ^{15}N content of each sample, as described in the text. The data plotted were generated by samples taken at the water department intake at the dam of Lake Decatur. Samples were taken from 2 March 1970 to 10 January 1971.

addition to soil organic matter and fertilizer nitrogen, are rain water and atmospheric nitrogen fixed by soybeans. Preliminary measurements (9 for nitrate and 19 for Kjeldahl nitrogen) made under conditions certain to maximize the concentration of nitrogen suggest that rain may contribute 12 to 17 percent as much nitrogen as is put on the land as fertilizer. If instead one uses Aldrich's estimate [cited in (*2*)] for this region of 5 pounds of nitrogen per acre added in rain, the value is about 8 percent of the fertilizer nitrogen applied in 1970. Even the higher value is just greater than the experimental error of the δ^{15}N measurement. The contribution of atmospheric nitrogen fixed by soybeans is also relatively small. Under the assumption that 75 pounds of nitrogen is fixed per acre and that the partition between harvested crop and stubble returned to the land is 86 : 14 (*8*), nitrogen fixation by soybeans contributes less than 10 percent of the quantity of nitrogen added by fertilizer. Even this is probably an overestimate since nitrogen fixation is considerably reduced by the carry-over of nitrogen fertilizer applied to the previous year's corn and by the natural fertility of these soils (*8, 9*). The fact that atmospheric nitrogen fixed by soybeans is ultimately added to the soil as organic matter in stubble also considerably dampens its impact.

The surface water receives nitrogen from other sources as well as from the drain-tile effluent. While it is possible to calculate the relative contributions from various sources of nitrogen and to conclude that they are minimal sources compared to nitrogen originating in soil organic matter and nitrogen fertilizer, this assumption is so central to the argument of this paper that experimental verification seems in order. In Fig. 1 δ^{15}N values are plotted against nitrate concentration. The regression line was established by measurements made on samples of drain-tile effluent alone. Figure 1 shows that there is a significant negative correlation between δ^{15}N and nitrate concentration. (Since $n = 13$, the hypothesis that the variables are not related may be rejected at the 99 percent confidence level if the regression coefficient, r, is greater than $|0.735|$. Here $r = -0.832$.) Each set of values in Fig 1 represents repeated measurements between January and July 1970 on water sampled from one location. Thus, the variation indicated by the error bars includes the real temporal variation as well as the experimental error. The claim that the data of Fig. 1 support the notion that soil organic nitrogen and fertilizer nitrogen are the dominant contributors to the surface waters is based on the fact that the data generated by these waters fall on the regression line established by the subsurface water drained from the cropped land (tile water). We take this to be strong evidence that the nitrate nitrogen in the two water systems comes from identical sources; that is, the nitrate nitrogen found in the surface waters during the time when the points fall on the same regression line comes predominantly from the subsurface water, which is typified by the tile water on which our measurements were made.

We interpret the negative correlation seen in Fig. 1 (drain tiles only) in the following manner. As indicated earlier, the two main sources of nitrogen that might contribute to the nitrate in tile effluent are soil organic matter (through mineralization to nitrate) and inorganic fertilizer (largely ammonia, converted to nitrate through nitrification). The fact that δ^{15}N varies with the average nitrate concentrations of different tile effluents indicates that two or more sources which differ in δ^{15}N contribute to the observed variations in nitrate concentrations. The significant negative correlation between nitrate concentration and δ^{15}N means that the nitrogen source responsible for the elevated nitrate concentrations is characterized by a δ^{15}N value significantly lower than that of the source responsible for the minimum nitrate concentration. As noted, our preliminary experiments suggest that the δ^{14}N value of nitrate produced from the reduced nitrogen of the soil from the study area is about + 13 and the average δ^{15}N for inorganic fertilizers used in the area is about +3. As evident in Fig. 1, δ^{15}N values for tile effluents decrease from about + 10 to + 4 with increasing concentration of nitrate. These results suggest strongly that the tiles that yield minimum average nitrate nitrogen concentrations (about 5 to 6 mg/liter) receive most of their nitrogen from soil organic matter, and that the higher nitrate concentrations (up to about 18 mg/liter) reflect the increasing contribution of fertilizer nitrogen. The spread of the data is further confirmation that the nitrogen in rain and that fixed by soybeans are not dominant contributors. If they were, then all of the points would be bunched around a single value, since rainfall contributes nitrogen uniformly to the effluent of all the tiles as, to a lesser extent, does fixation by soybeans.

We conclude that the nitrate that entered Lake Decatur during the spring period of heavy groundwater flow represented a mixture of nitrate derived predominantly from soil organic nitrogen and from inorganic fertilizer. We can estimate the relative contribution of these two sources from a linear interpolation between $\delta^{15}N = +13$ and $\delta^{15}N = +3$, the isotope values representative of these two sources (*10*).

This is shown in Fig. 2, from which we conclude that fertilizer nitrogen contributed 55 ± 10 percent of the nitrate entering Lake Decatur during the spring months of 1970.

We have assumed that the nitrogen transformations in the soil do not significantly discriminate between ^{14}N and ^{15}N, so that the $^{15}N : ^{14}N$ ratio observed in the effluent nitrate reflects the $^{15}N : ^{14}N$ ratio of the source nitrogen. In fact, almost all the biological nitrogen transformations in the soil do have an isotope effect. A quantitative correction for these isotopic fractionations is not yet possible. It is possible, however, to predict the direction of the isotope fractionation in each nitrogen transformation from data already available (*3*). With one exception, these effects are such that they tend to minimize the apparent contribution of fertilizer nitrogen to surface water nitrate. The exception, nitrogen fixation, contributes only a small quantity of nitrogen compared with the fertilizer nitrogen. On these grounds, we regard our estimate of 55 ± 10 percent to be a minimum.

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11. This work was supported in part by PHS grant ES-00139.

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The Xenon Record of Extinct Radioactivities in the Earth

Abstract. *Analyses of xenon from well gas rich in carbon dioxide reveal a large excess of radiogenic xenon-129 from the decay of extinct iodine-129. Smaller excesses observed in the heavy xenon isotopes are from fission. These results place narrow limits on any age difference between the earth and the oldest meteorites. The occurrence of excess radiogenic xenon-129 in well gas also suggests that any quantitative degassing of existing solid materials to form the atmosphere must have been limited to a very early period of the earth's history, approximately the first 10^8 years. Alternatively, this observation is consistent with a model of the earth's continuous, but still incomplete, degassing since its time of formation.*

There is unambiguous evidence from several radioactive dating methods that most meteorites formed about 4.6×10^9 years ago (*1, 2*). This age is obtained by comparing present concentrations of certain long-lived radioactive nuclides, ^{238}U, ^{235}U, ^{87}Rb, and ^{40}K, with the concentrations of their respective stable decay products, ^{206}Pb, ^{207}Pb, ^{87}Sr, and ^{40}Ar. It has recently been established that two radioactive nuclides, ^{129}I and ^{244}Pu, were incorporated into meteorites at the time of their formation (*3*), but essentially the entire inventory of these two nuclides has decayed over the life-span of 4.6×10^9 years of meteorites. These two nuclides are now referred to as extinct radioactivities.

The half-lives of ^{129}I and ^{244}Pu are 17×10^6 (*4*) and 82×10^6 (*5*) years, respectively, and their decay products identified in meteorites are radiogenic ^{129}Xe (^{129r}Xe) from ^{129}I and fissiogenic $^{131\text{-}136}Xe$ ($^{131\text{-}136f}Xe$) from ^{244}Pu. Because it is not possible to calculate the age of a body solely from the concentration of a stable decay product, total meteorite ages cannot be obtained by either ^{129}I-^{129r}Xe or ^{244}Pu-$^{131\text{-}136f}Xe$ dating. However, early $^{129}I : ^{127}I$ and $^{244}Pu : ^{238}U$ ratios in meteorites decreased rapidly because of the shorter half-lives of the nuclides in the numerator, and since the nuclides in each ratio display similar geochemical behavior, measurements of the $^{129r}Xe : ^{127}I$ and $^{131\text{-}136f}Xe : ^{238}U$ ratios present in meteorites today are used to define the $^{129}I : ^{127}I$ and $^{244}Pu : ^{238}U$ ratios present when the meteorites formed (*6, 7*). For example, it has been found that chondrite meteorites were formed when the $^{129}I : ^{127}I$ ratio was about 1.1×10^{-4} (*8*) and the $^{244}Pu : ^{238}U$ ratio was about 0.013 (*7*). In several different achondrites the initial $^{129}I : ^{127}I$ ratio was found to vary from 10^{-8} to 10^{-5}, and the initial $^{244}Pu : ^{238}U$ ratio varied from 0.002 to 0.006 (*9*), which suggests that the achondrites formed later than the chondrites. Meteorite age differences of a few million years have been detected by measurements of $^{129r}Xe : ^{127}I$ and $^{131\text{-}136f}Xe : ^{238}U$ ratios (*9, 10*).

The chronology of early events for the earth is not so well established. The earth's interior is inaccessible, and the rocks and minerals of the earth's crust show a wide range of ages with an upper limit of about 3.5×10^9 years. Further, the continuous formation of new crustal material along oceanic ridges suggests that even today the earth's crust is not completely isolated from its mantle. Thus, the fundamental assumption of all radioactive dating, that the system has remained isolated or closed over the time period being measured, may not be valid for the accessible portions of the earth. Age estimates of the earth based on $^{207}Pb : ^{206}Pb$ ratios are undoubtedly among the more reliable since chemical fractionation would alter neither the ratio of the two parents, $^{235}U : ^{238}U$, nor the ratio of the decay products, $^{207}Pb : ^{206}Pb$. The

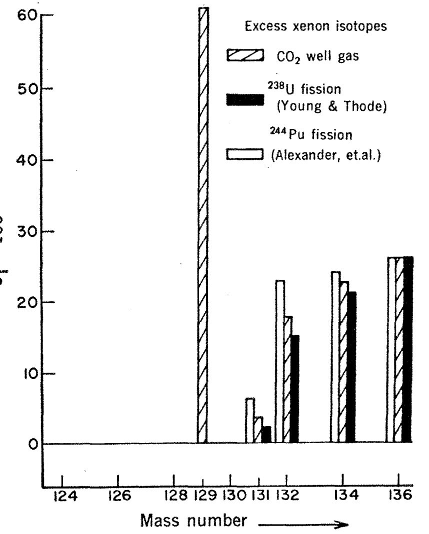

Fig. 1. The excess xenon isotopes found in CO_2 gas wells relative to atmospheric xenon (*16*). The excess for each isotope of mass number i is expressed as δ_i, which is defined by Eq. 1 (see text). The enrichment at each mass number is compared with that expected from the fission of ^{244}Pu (*20*) and ^{238}U (*19*).