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AQUIFER DENITRIFICATION: CORRELATION OF ^{15}N ISOTOPIC
ENRICHMENT AND FIRST-ORDER RATE CONSTANTS

By

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University of North Dakota
Honors Program Committee
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For Graduation
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Grand Forks, North Dakota

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ABSTRACT

Denitrification is the process by which potentially dangerous nitrate is biogeochemically reduced into harmless nitrogen gas. This process is mediated by bacteria in the presence of suitable electron donors, such as organic carbon, sulfide, and ferrous iron. Due to its potential utility in the remediation of contaminated environments, the process of denitrification has received considerable attention. However, a relationship between the rate constant of the reaction and isotopic enrichment of ^{15}N , which occurs as a direct result of the chemical reaction, has received little consideration. A strong correlation between these two factors could lead to a technique to estimate denitrification rates based on ^{15}N isotopic enrichment.

Mariotti, et al. (1981, 1982) were among the first researchers to investigate this relationship. After observing lab experiments, they proposed the hypothesis that a negative correlation exists between ^{15}N enrichment and reaction rates. That is, higher rates of denitrification result in lower (less negative) values of isotopic enrichment. This hypothesis was tested herein using bromide tracer tests carried out in seven different sites across eastern North Dakota and western Minnesota.

A decent correlation exists; however, the correlation is a positive one, where the highest denitrification rates resulted in the highest (most negative) enrichment values. Furthermore, significant variability, particularly that of the Larimore site, remains unexplained. Further research, including investigation of bacteria types, variations due to temperature, and more correlation studies are suggested.

INTRODUCTION

Nitrate contamination has long been recognized as a leading source of pollution in groundwater systems. A potential carcinogen, nitrate (NO_3^-) originates from a variety of common and necessary human activities, such as agriculture and sewage treatment (Feast, 1998). The process that removes nitrate contamination from the soil and groundwater is a biogeochemical process known as denitrification.

Although denitrification has been observed to occur naturally and in the laboratory, few have examined naturally occurring systems without alterations designed to enhance the rate of denitrification. The latter allows for detection of denitrification in a shorter, more cost effective, time frame but may obscure our understanding of the natural process. If a method for detecting denitrification can be developed that does not depend on amended samples, our understanding of the process could be significantly increased.

One such method is the correlation of denitrification reaction rates with ^{15}N isotopic enrichment. Isotopic enrichment is a well-known phenomenon that occurs in chemical reactions involving elements with stable isotopes, in this case the isotope ^{14}N , with a mass of 14 amu (atomic

mass unit), and ^{15}N a much less common nitrogen isotope. Geochemists have studied stable isotopes for many decades for a variety of geological purposes (Faure, 1998).

Mariotti et al. (1981, 1982) were the first researchers to recognize the link between denitrification rates and isotopic enrichment. Using lab experiments on amended soil samples from France, they proposed the hypothesis that higher rates of denitrification resulted in lower (less negative) values of isotopic enrichment and conversely, lower reaction rates lead to higher (more negative) values of enrichment. This conclusion has gone largely unchallenged, and has been used by several researches to interpret their findings (Mariotti, 1988, Smith, 1991, Green, 1998, Bates, 1998, Mengis, 1999).

This thesis is intended to investigate that hypothesis using data derived from tracer tests conducted since 1997 by the University of North Dakota, under the direction of Dr. Scott F. Korom. These tests are *in situ*, involve no added electron donors, and represent a naturally occurring process.

TECHNICAL BACKGROUND

Denitrification

Denitrification is the name given to a biogeochemical process whereby nitrous compounds containing nitrate (NO_3^-) are broken down into nitrogen gas (N_2). As noted earlier, nitrates are a harmful pollutant, but N_2 is a very stable gas and the main component of our atmosphere.

Denitrification is an oxidation-reduction reaction. This is a reaction where the number of electrons in the valence shells of some of the participating elements changes. Some elements lose electrons and are termed electron donors. These elements undergo oxidation when they lose an electron. Other elements gain electrons and are termed electron acceptors. These elements undergo reduction as their valence shell gains an electron charge. Any oxidation must be accompanied by reduction and vice versa (Faure, 1998).

Denitrification is primarily accomplished through nitrogen-digesting bacteria, which use nitrates as electron acceptors when the preferred acceptor, oxygen, is not readily available. The conversion of nitrates to N_2 covers several intermediate steps and may react to completion or stop at any intermediate depending on the environmental conditions. The steps are shown below; note that the

oxidation state of the nitrogen atom changes from +5 to zero:



The other necessary condition for denitrification is the availability of an electron donor for the bacteria to use as an energy source (Feast, 1998). Commonly, this source is organic carbon originating from the decay of organic material, but inorganic materials such as pyrite, which contains ferrous iron and sulfide, may also contribute (Schlag, 1999). The sources of electron donors available depend on the geological processes that formed the aquifer and its environment.

Therefore, in order for denitrification to occur, nitrous compounds, nitrogen digesting bacteria, suitable electron donors, and an anaerobic environment must be present (Korom, 1992).

Isotopic Enrichment

When a bacterium breaks the N-O bond in NO_3 , it preferentially selects the lighter ^{14}N isotopes over the heavier ^{15}N isotopes because it requires slightly less energy to break the bond of the lighter isotope. This results in an elevated fraction of ^{15}N to ^{14}N in the remaining nitrate (Faure, 1998). This ratio can be measured

using mass spectrometry and is known as the fractionation factor (α). The mass spectrometer measures the isotopic ratios of the sample and compares them to a standard based on nitrogen derived from the atmosphere. The fractionation factor is then reported in delta (δ) notation as parts per thousand or permil (‰). The $\delta^{15}\text{N}$ value is calculated as follows:

$$\delta^{15}\text{N} = 10^3 \times ((^{15}\text{N}_{\text{sample}} / ^{14}\text{N}_{\text{sample}}) / (^{15}\text{N}_{\text{standard}} / ^{14}\text{N}_{\text{standard}}) - 1) \quad (1)$$

where ^{15}N and ^{14}N are concentrations in permil (‰) and 10^3 is a constant used to report units of permil (Mariotti, 1981).

When the change in isotopic concentration of a sample is compared to the natural log (ln) of the remaining nitrate fraction, a value known as the enrichment factor, ε , is found. The enrichment factor is calculated by way of the Raleigh equation as described by Mariotti et al. (1981). The equation is as follows:

$$\varepsilon = \frac{10^3 \times \ln((10^{-3} \times \delta^{15}\text{N}_t + 1) / (10^{-3} \times \delta^{15}\text{N}_{t=0} + 1))}{\ln(N_t / N_{t=0})} \quad (2)$$

where ε = enrichment factor in ‰, 10^3 = constant required to give ε units of ‰, N_t = the concentration of NO_3^- -N at time (t), and $\delta^{15}\text{N}_t$ for the remaining NO_3^- -N at time (t). The more negative the number calculated, the greater the enrichment of the ^{15}N in the remaining nitrate.

Reaction Rates

A reaction rate is generally defined as the rate at which the mass or volume of some material A is changing time. This can be expressed mathematically as

$$\frac{dA}{dt} = r \quad (3)$$

where r is the reaction rate.

Two types of reactions comprise most naturally occurring processes: Zero-order reactions and first-order reactions. Zero-order reactions are those in which r can be defined as a constant (k) such that

$$\frac{dA}{dt} = k \quad (4)$$

where the units of the rate constant are simply mass/time. This means that the reaction proceeds at the same rate regardless of the reactant concentration (Vesilind and Morgan, 2003).

First-order reactions are those in which change in the amount of a material is proportional to the amount of material itself; they are mathematically expressed as

$$\frac{dA}{dt} = kA \quad (5)$$

where the units of the rate constant are in $1/\text{time}$ or time^{-1} . Therefore the rate of this reaction is dependent on the amount of material present (Vesilind and Morgan, 2003).

In order to solve for rate constants the above equations are simply integrated and rearranged such that

$$\frac{C_t - C_o}{t} = -k \quad (4a)$$

$$\frac{\ln C_t - \ln C_o}{t} = -k \quad (5a)$$

where C_t is the concentration of the material in question at time t and C_o is the initial concentration. When the reaction involves a tracer, the terms C_t and C_o are replaced with the relative concentrations of the reactant and the tracer, respectively.

The rate constants in (4a) and (5a) may also be found graphically by plotting the change in concentration vs. time for a zero-order reaction, or the \ln of the change in concentration vs. time for first-order reactions. The slopes of the lines produced from these plots are the rate constants.

PREVIOUS WORK ON DENITRIFICATION

As noted earlier, the first researchers to investigate the nature of denitrification using ^{15}N tracers were Andre Mariotti, and his colleagues. In two papers published in 1981 and 1982, he and his fellow scientists modeled the process of denitrification as a single step, unidirectional process. This important assumption allows for the application of a well-known model of kinetic isotope theory, namely Raleigh distillation, as discussed previously, to be applied to denitrification.

Evaluation of this process by Mariotti, et al. in 1982 revealed that although denitrification in the subsurface was actually much more complicated than the assumed single step reaction, calculations based on these assumptions did not vary significantly from experimental results. Furthermore, denitrification was found in his experiments to most closely resemble a first-order reaction.

In their second publication (Mariotti et al., 1982), the researchers examined denitrification in various experimental conditions. The controlling factors were found to be electron donor availability and temperature, both of which affected the rate of the reaction. Values of enrichment ranged from -11‰ to -33‰. When enrichment was plotted as a function of rate constant, a high correlation

was found. Thus they formed the hypothesis that lower (less negative) enrichment values are obtained for higher denitrification rates, and that higher rates of denitrification result in lower (more negative) values of enrichment (Mariotti et al., 1982). This hypothesis has been assumed to be correct and implemented by subsequent researchers in both soils and aquifer sediments.

With the general theory of the denitrification process in place, Mariotti et al. (1988), proved its usefulness with an investigation of nitrate concentrations in a French chalk aquifer. Following the lead of other scientists who had noted decreases in nitrate levels with depth or displacement in aquifers, they showed how isotopic fractionation could be used to identify the cause of this decrease. The principal causes of these decreases were identified as dilution, absorption by vegetation, or denitrification. Dilution is a physical process that does not alter isotopic variations, only changing their absolute abundances through mixing. In other words, dilution occurs without isotopic enrichment. When root systems absorb nitrates the N-O bonds are broken and fractionation can occur. However, this is a very rapid process, occurring over a very short time frame, so enrichment that results is usually close to zero (Mariotti et al., 1988). Thus,

whenever isotopic fractionation is observed to occur in conjunction with reduction of nitrous ion species, it assumed to be attributed to denitrification. This process was found occurring in the chalk aquifer, verifying the results of their earlier research.

Enrichment values calculated from the chalk aquifer were very small, ranging from -4.7‰ to -5‰. These values were assumed to be the combination of two processes. First, the rate of denitrification was assumed to be fairly high. Second, it was shown that the high porosity and low permeability of the chalk could result in the formation of dead end pores where water could stagnate and allow denitrification to run to completion. This would decrease the overall enrichment as these waters diffused back into the main flow channels (Mariotti et al., 1988).

An investigation by Smith, et al. in 1991 used the methods established by Mariotti and his colleagues to show that denitrification was occurring in polluted sand aquifers near Cape Cod, MA. Isotopic fractionation was found to vary with depth creating a zone of denitrification, which existed within the first 10 meters below the water table. This zone coincided with the occurrence of the contaminant plume. Larger values of enrichment were found (-13.9‰), lying between the values published by Mariotti et

al. (1988) and others. This led to the conclusion that the rate of denitrification in the Cape Cod aquifer must be proceeding at a slower rate than the rate of the French aquifer. The authors also confirmed the assumption that denitrification could be modeled as a single step process due to the excellent agreement of theoretical and observed data (Smith et al., 1991).

Green et al. (1998) revealed another important use of nitrogen isotopes in a study of the groundwater system beneath the Island of Jersey near the United Kingdom. This aquifer system was widely polluted by nitrate contamination. Through close observation, other scientists discovered that different sources of nitrates had unique isotope ratios. Thus, by examining isotope ratios it was possible to trace, or identify, the source of the nitrate species. The most common sources of contamination and isotopic ratios are reported as: nitrified soil organic nitrogen (+4‰ to +9‰), nitrogenous fertilizers (-4‰ to +4‰), and animal and sewage wastes (>+10‰) (Green et al., 1998). Using these facts the authors concluded that the widespread pollution was due to infiltration of nitrates from agricultural activity.

Isotopic analysis of wells across the island revealed that denitrification was occurring in response to the

pollution, but only in deep groundwater. A very low enrichment factor of -3‰ was found and attributed to a combination of rapid denitrification by the method proposed by Mariotti et al. (1982) and mixing with shallow groundwaters. It was noted that the regional hydrology complicated isotopic analysis. Nevertheless, denitrification was determined to be insufficient to deal with the island's nitrate pollution (Green et al., 1998).

A study by Feast et al. (1998) is more notable for an excellent summation of the denitrification model than for its actual scientific conclusions in regards to denitrification rates. The purpose of the study was to determine the fate of nitrate contamination in an aquifer system near Norfolk, England. The chalk bedrock, which contains the main aquifer for the region showed no signs of significant in situ denitrification. However, denitrification was found to occur in the layer of glacial till above the chalk bedrock, with an enrichment factor of -7‰. Interestingly, the nitrates in the areas where denitrification was occurring were isotopically very different than those polluting the aquifer system, and thus thought to be related to nitrates introduced into the soil long before it was cultivated.

Grischek et al. (1998) studied denitrification along the Elbe River in Germany. Using the isotopic methods and the precedent of a single step reaction, as established by previous researchers, denitrification was determined to occur in the groundwater feeding the river. An enrichment factor of -14‰ was found and later confirmed through laboratory simulations of the groundwater environment. Denitrification was found to proceed at a rate sufficient to impact nitrate infiltration to the river, but analysis showed that the availability of solid organic carbon was likely the limiting factor as it was the main electron donor (Grischek et al., 1998).

Mengis et al., (1999) studied groundwater interactions within a riparian zone to determine the effects of denitrification. The recharge zone was below an actively cultivated field and shallow groundwater in this area showed isotopic ratios which reflected this. Deep groundwater in this area contained significantly less nitrate, along with available electron donors, such as carbon or sulfur compounds, leading to the hypothesis that denitrification was occurring in this zone. Tracer tests were conducted and it was found that enrichment associated with denitrification was occurring in both nitrogen and oxygen isotopes. The nitrogen isotopes were found to become

1.5 times more enriched than the oxygen isotopes.

Enrichment values remained within ranges reported in other studies (Mariotti et al., 1982, Smith et al., 1991, Green et al., 1998). However, it was also observed that denitrification rates reduced with depth, most likely due to the elimination of electron donors. The utility of using both nitrogen and oxygen isotopes to prove the existence of denitrification is shown by this research (Mengis, 1999).

ANALYTICAL METHODS

Data used for this study came from the emplacement of several large in situ mesocosms (ISMs) in groundwater systems across eastern North Dakota and western Minnesota (see Figure. 1). These ISMs are essentially large hollow pipes (16 in diameter, 5 ft long) that are emplaced below the water table. They allow for precise and direct observation of groundwater geochemistry for an extended length of time (over 2 years in some cases). Precise protocols were developed for sampling on about a monthly basis and samples were analyzed by the North Dakota Department of Health and the University of North Dakota Water Quality Lab. For more detailed discussion on the development of the ISMs see Schlag (1999).

Among the data collected were concentrations of NO_3^- and Br^- , as well as $^{15}\text{N}/^{14}\text{N}$ isotopic ratios. The NO_3^- was, of course, the anion of interest, whereas Br^- was used as a groundwater tracer to determine the effects of dilution on the sample. Any reduction in the amount of NO_3^- that could not be accounted for by dilution of the Br^- tracer could be attributed to denitrification. As further evidence, sites that showed significant decrease in nitrate were accompanied by enrichment of the ^{15}N isotope. As demonstrated by Mariotti et al. (1988), this is



Figure 1. Locations of ISM research sites

sufficient evidence to confirm denitrification.

To calculate isotopic enrichment values for each site, the numerator of equation (2) was calculated using the $^{15}\text{N}/^{14}\text{N}$ ratios observed during the duration of the tests. In most cases, due to the expense of isotopic analysis, only four or five samples were analyzed for isotopic composition per site, per experiment. Enrichment values were then calculated by plotting the numerator of equation (2) vs. the log of concentration change. The slope of this line was the enrichment factor of a particular tracer experiment. Enrichment ranged from a low of -5‰ at the Luverne site to a high of -44‰ for the fourth Larimore test. The linear

regressions from which enrichments were determined were greater than 0.92 for each experiment.

Next, rate constants for each experiment were calculated. Mariotti et al. (1982) described denitrification as a first-order rate reaction. To test this, each site was modeled as a first-order reaction and a zero-order reaction to determine which better fit the data. To accomplish this, NO_3^- data were first corrected for dilution using the Br^- data, and the remaining NO_3^- was attributed to denitrification. Then, the natural log was taken of the actual NO_3^- concentration divided by the NO_3^- concentration corrected for dilution. This was done to correct for the combined rate constants of dilution and denitrification.

From this, reaction rates were calculated. This is simply the process of determining reaction rate constants graphically. This was done for both zero-order and first-order reactions as was described previously in the Technical Background section of the paper. Whichever method yielded a better statistical fit for the data was the reaction model that was most appropriate. Data and figures for the Luverne site are given as an example (Figures 2-5).

Luverne	Research WRRL NO3-N mg/L	WRRL Br mg/L	15N/14N per mil	Ln of NO3- NO	Numerator of Equation 2
at/mole wt	14.00674	79.905			
Date					
8/7/2001	ND				
09/04/2001	69.2	39.2	-1.91	4.24	0.00
10/17/2001	69.2	41.85			
11/15/2001	64.6	41.0			
12/17/2001	63.6	40.6			
1/11/2002	51.4	36.4	-0.2	3.94	1.71
2/19/2002	52.65	37.85			
4/23/2002	47.9	35.6			
7/8/2002	41.9	32.2			
9/16/2002	38.6	30.1	1.02 average of	3.65	2.93
11/12/2002	37.2	30.3	1.09 & 0.95		
1/8/2003	37.1	30.6			
3/25/2003	31.9	26.7	2.18 average of	3.46	4.09
			2.16 & 2.20		

Date	Days	Br (mg/L)	NO3-N (mg/L)	NO3-N Corr for Dillution (mg/L)	NO3-N Denitrified (mg/L)	Denitrification Rate (mg/L/day)	Ln (Act/Corr)
09/04/2001	0	39.20	69.20	69.200	0.000		0.000
10/17/2001	43	41.85	69.20	73.878	4.678	0.109	-0.065
11/15/2001	72	41.00	64.60	72.378	7.778	0.108	-0.114
12/17/2001	104	40.60	63.60	71.671	8.071	0.078	-0.119
1/11/2002	129	36.35	51.40	64.169	12.769	0.099	-0.222
2/19/2002	168	37.85	52.65	66.817	14.167	0.084	-0.238
4/23/2002	231	35.60	47.90	62.845	14.945	0.065	-0.272
7/8/2002	307	32.20	41.90	56.843	14.943	0.049	-0.305
9/16/2002	377	30.10	38.60	53.136	14.536	0.039	-0.320
11/12/2002	434	30.30	37.20	53.489	16.289	0.038	-0.363
1/8/2003	491	30.60	37.10	54.018	16.918	0.034	-0.376

Figure 2. Tracer test data for the Luverne site.

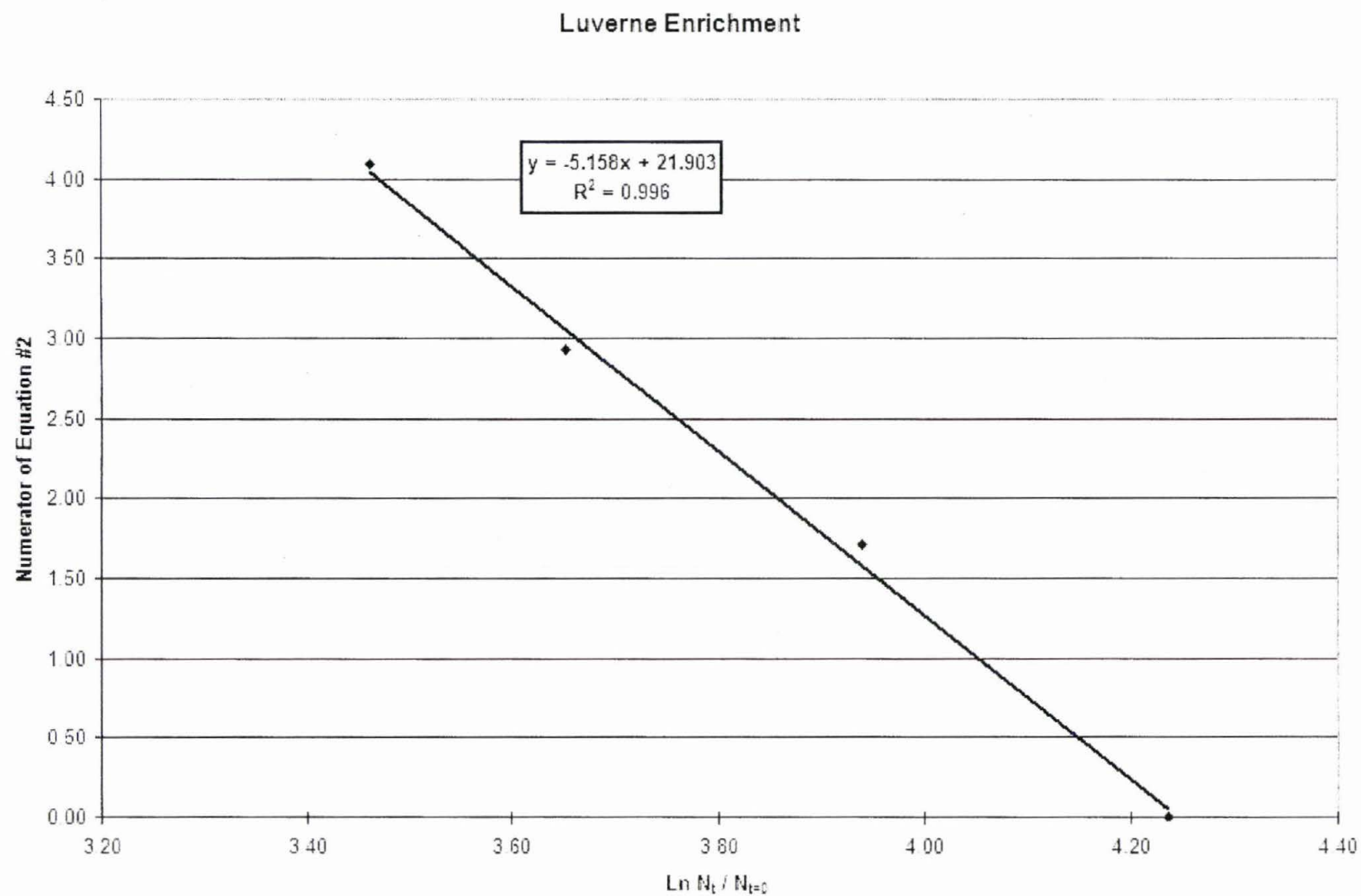


Figure 3. Plot of Luverne isotope data showing an enrichment of - 5%.

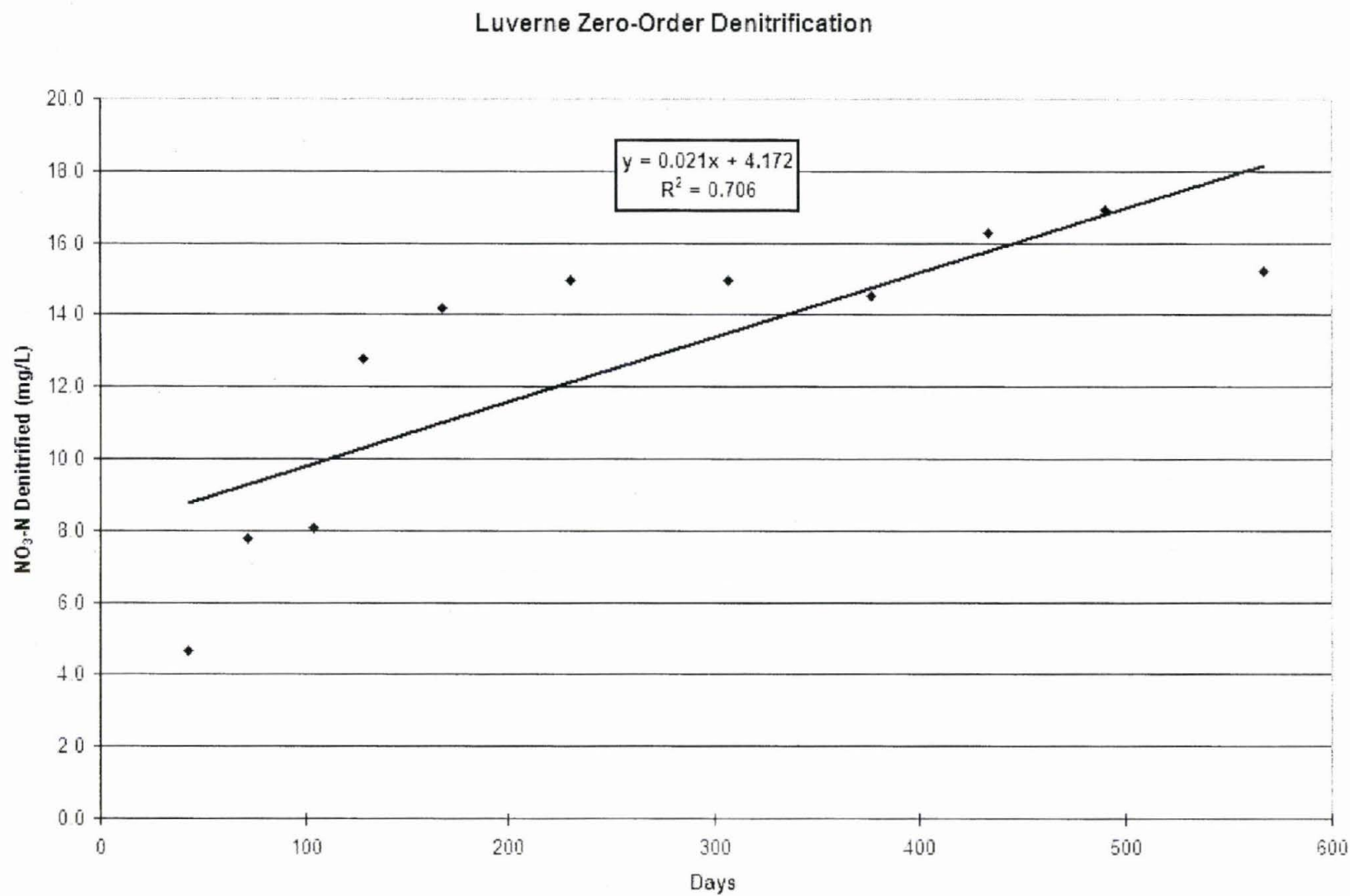


Figure 4. Plot of zero-order reaction model for the Luverne site. The slope of the line is the rate constant.

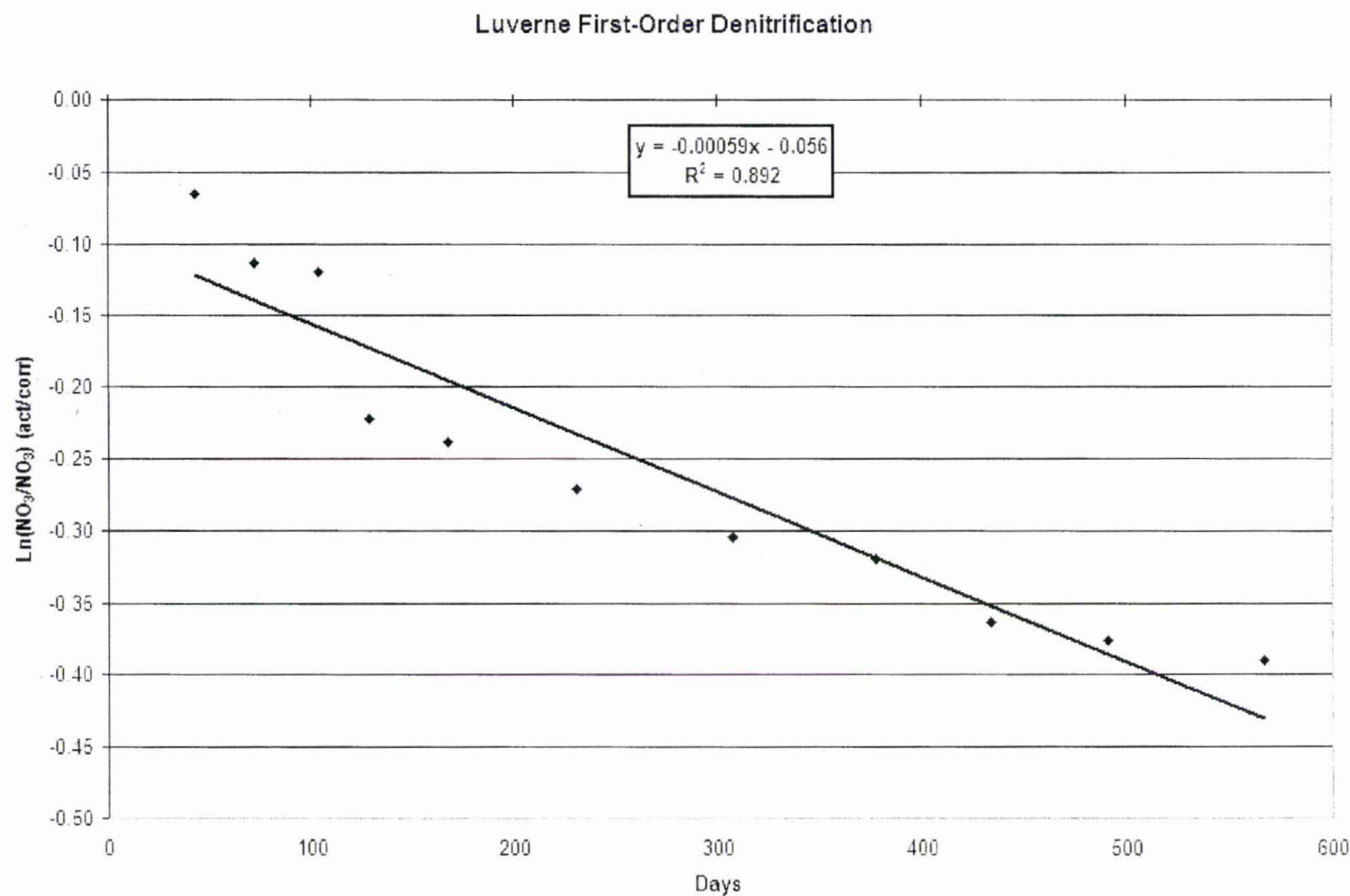


Figure 5. Plot of first-order reaction model for the Luverne site showing a better linear regression than the zero-order model. The slope of the line is the rate constant.

Once all the enrichment factors and rate constants were calculated for each site, they were plotted against one another to determine if a correlation did indeed exist between isotopic enrichment and reaction rates. The enrichment data were compared both to the first-order and zero-order reaction constants. An attempt was made to plot additional data from the literature, but was met with limited success, as will be discussed in the next section.

DISCUSSION

Plotting all the enrichment data vs. reaction rate constants showed the best correlation occurring between enrichment and first-order rate constants, as predicted by Mariotti et al. (1982). However, the correlation which resulted was a positive one where the greatest enrichment resulted from the greatest reaction rates. An R^2 value of 0.74 is not ideal, but indicates that 74% of the variation in the data are explained by the linear regression. Although the data can be subdivided, in both the cases of zero-order and first-order rate constants, the most meaningful interpretation comes from correlation of all the data under a single reaction rate order.

Enrichment vs. First Order K

Of the nine tests that showed denitrification, five grouped together along a relatively straight line while four others were more scattered (see Figure 6). These five sites exhibited enrichment factors ranging from -5‰ to -15‰ and rate constants ranging from 0.00047 day^{-1} to 0.0011 day^{-1} . The R^2 values of the linear regressions for the reaction constants were >0.81 for all five sites and were ≥ 0.90 for four of the five. All five showed high

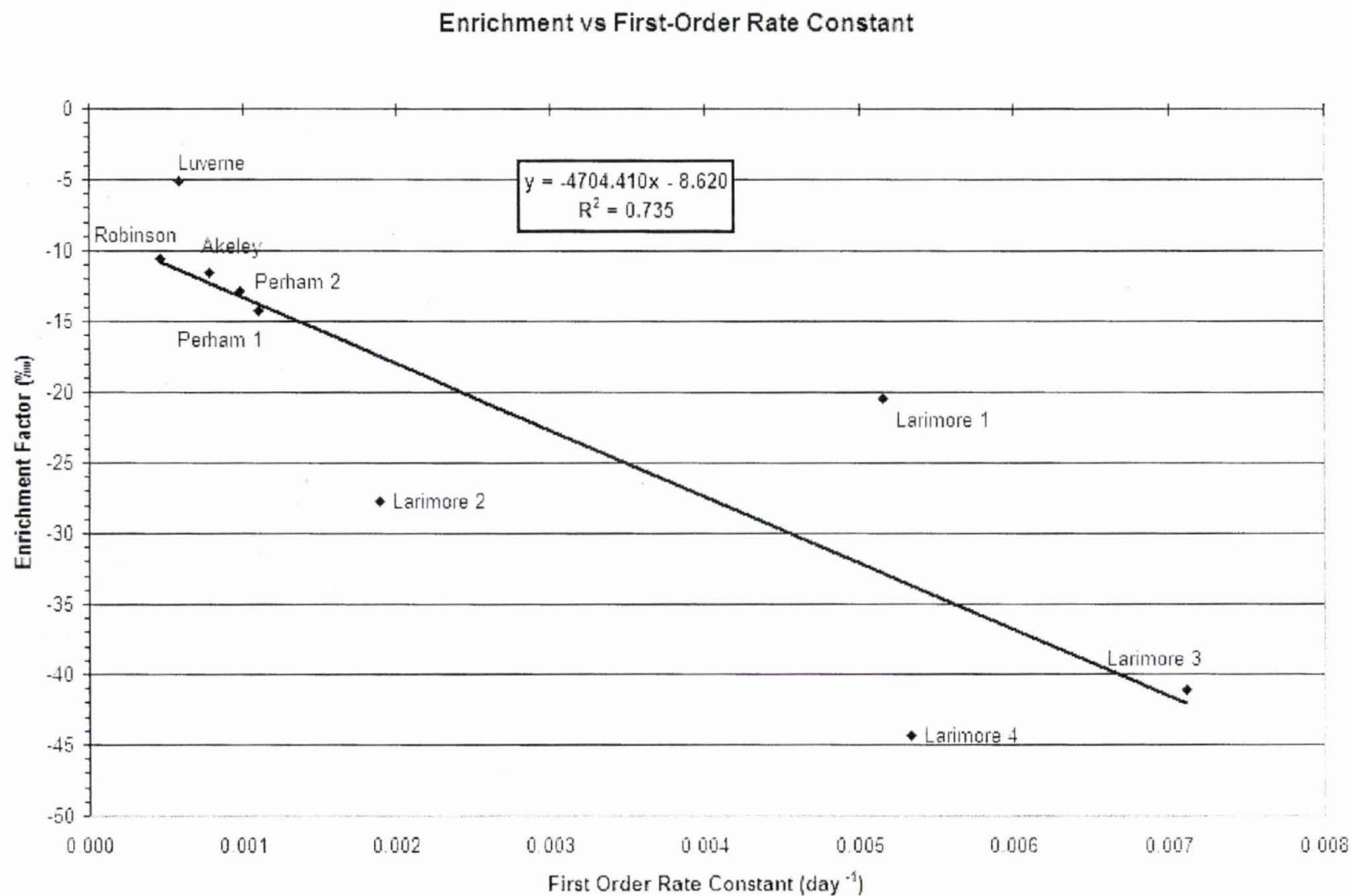


Figure 6. Enrichment vs. first-order reaction rate constants showing a R^2 value of 0.74.

agreement with the calculated enrichment values. Thus these values seem reliable and useful.

The four points showing the most scatter belong to the four Larimore tracer tests, repeated at the same site between 1997 and 2002. Although all four show very good agreement with regards to enrichment, only tests 2 and 4 have reasonably strong agreement with first-order reaction rates. Furthermore, only test 2 has a higher R^2 value for a first-order rate constant than for a zero-order rate constant.

When only data whose R^2 for first-order rate constant exceeds their R^2 for zero-order rate constants is considered, the agreement almost becomes 0.90 (see Figure 7). Also, the slope of the line changes noticeably. Although this lends strong support for describing denitrification as a first-order reaction, it ignores the Larimore tests that indicate a zero-order reaction is occurring.

Enrichment vs. Zero-Order K

Trying to describe the data in terms of zero-order reactions, however, does not work as well as for the first-order data. Plotting all the data vs. zero-order rate constants resulted in a similar pattern of 5 reasonably

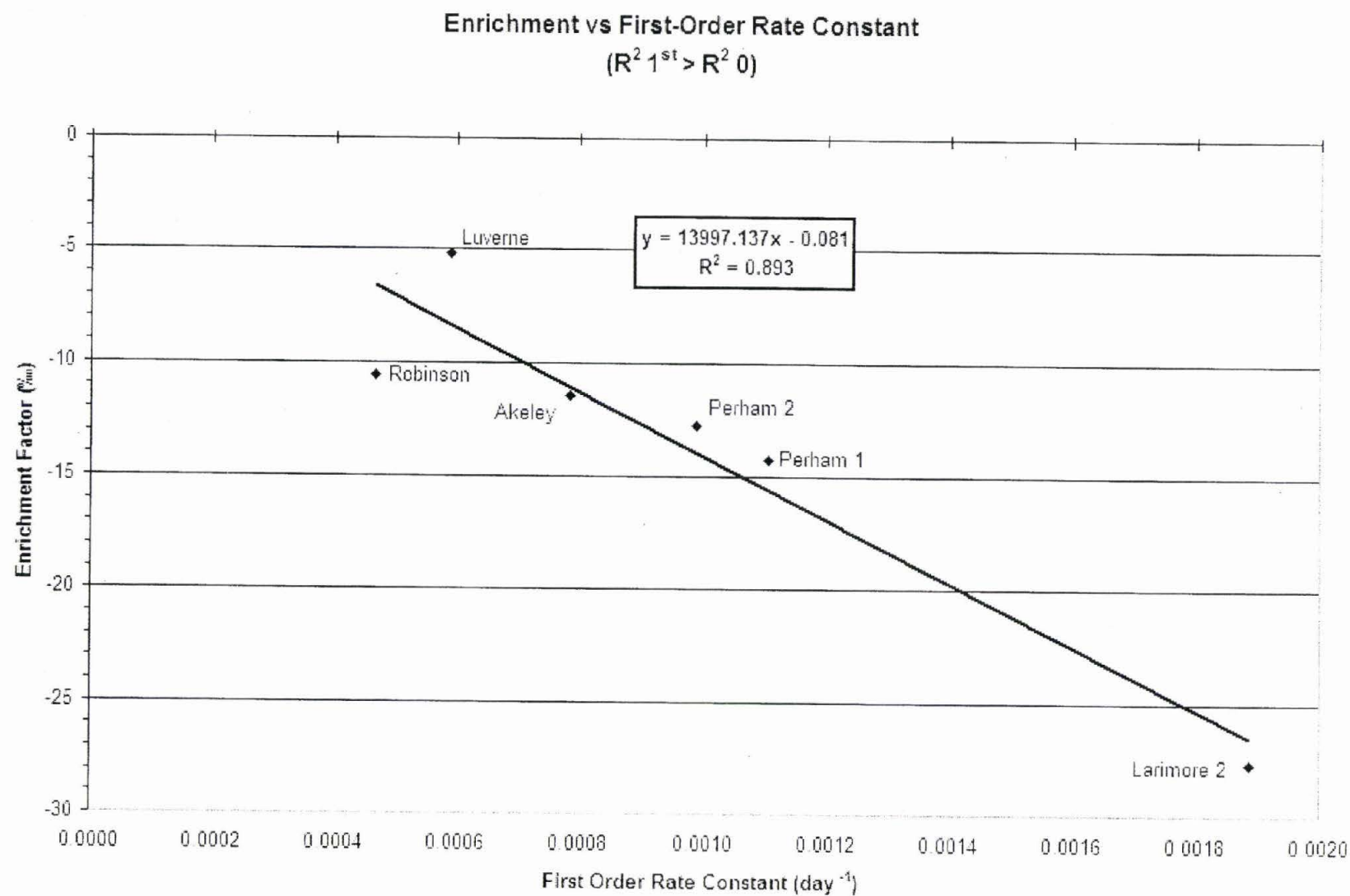


Figure 7. Enrichment vs. first-order rate constant of only those experiments which had a better linear regression for the first-order model.

grouped points and four other more anomalous points. Again the highest rates of denitrification correlated with the highest enrichment values. In this case, however, the R^2 of the zero-order correlation is only 0.70. Also only three tests showed reaction rates that favored zero-order over first order, those being Larimore tests 1, 3, and 4. An attempt to correlate those three tests resulted in a very poor R^2 value of 0.35.

The Larimore Site

As mentioned earlier all four tracer tests performed at Larimore were conducted under virtually the same conditions. The amount of variability found in these samples is therefore surprising. The only other comparable tests were conducted at the Perham sites where two separate tests were carried out in ISMs separated by several miles. However, the results of the two tests came up very similar.

Denitrification at the Larimore site is very high compared to the other study locations. The rates measured were as much as five times greater than other reaction rates observed. As a result NO_3^- concentrations fell rapidly and reached very low levels by the end of each experiment, levels much lower than those observed at other sites. For this reason, denitrification at the Larimore site

correlates better as a zero-order reaction. Unfortunately, this reduces the ability to correlate denitrification reaction rates, as the rest of the sites appear to be first-order reactions.

Data from the Literature

An attempt was made to find data in the literature to further support the model developed here. Unfortunately, the author was unable to find in situ denitrification rates in association with enrichment values. As noted earlier, enrichment values are relatively common in the literature for in situ conditions but relative reaction rates (fast or slow) are generally inferred from these values (Mariotti, 1988, Smith, 1991, Feast, 1998). Thus, the findings here that higher denitrification rates result in higher enrichment factors is very unusual. However, due to the relatively small amount of data currently available only provisional conclusions can be made at this time.

CONCLUSIONS

When applied to the sites considered in this study, the hypothesis, purposed by Mariotti et al. (1981, 1982), that denitrification reaction rates can be correlated with enrichment values, was found to be generally correct. However, a positive correlation was observed in this study, contrary to the negative correlation observed by Mariotti et al. (1982). A correlation coefficient of 0.74 with the first-order reaction rate model suggests that under a majority of conditions, denitrification behaves as a first-order reaction. However, the regional model as described herein requires further development, in particular with regards to the Larimore site. Such investigations could include analysis of the bacteria responsible for denitrification, as well as detailed analysis of the effects of temperature on the process. On a broader scope, more studies of this nature are needed to more firmly establish the correlation between ^{15}N isotopic enrichment and first-order reaction coefficients.

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