Identification of Groundwater Nitrate Contamination from Explosives Used in Road Construction: Isotopic, Chemical, and Hydrologic Evidence

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S *Supporting Information*

ABSTRACT: Explosives used in construction have been implicated as sources of NO_3^- contamination in groundwater, but direct forensic evidence is limited. Identification of blasting-related NO_3^- can be complicated by other NO_3^- sources, including agriculture and wastewater disposal, and by hydrogeologic factors affecting NO_3^- transport and stability. Here we describe a study that used hydrogeology, chemistry, stable isotopes, and mass balance calculations to evaluate groundwater NO_3^- sources and transport in areas surrounding a highway construction site with documented blasting in New Hampshire. Results indicate various groundwater responses to contamination: (1) rapid breakthrough and flushing of synthetic NO_3^- (low $\delta^{15}N$, high $\delta^{18}O$) from dissolution of unexploded NH_4NO_3 blasting agents in oxic groundwater; (2)

delayed and reduced breakthrough of synthetic NO_3^- subjected to partial denitrification (high $\delta^{15}N$, high $\delta^{18}O$); (3) relatively persistent concentrations of blasting-related biogenic NO_3^- derived from nitrification of NH_4^+ (low $\delta^{15}N$, low $\delta^{18}O$); and (4) stable but spatially variable biogenic NO_3^- concentrations, consistent with recharge from septic systems (high $\delta^{15}N$, low $\delta^{18}O$), variably affected by denitrification. Source characteristics of denitrified samples were reconstructed from dissolved-gas data (Ar, N_2) and isotopic fractionation trends associated with denitrification ($\Delta\delta^{15}N/\Delta\delta^{18}O \approx 1.31$). Methods and data from this study are expected to be applicable in studies of other aquifers affected by explosives used in construction.
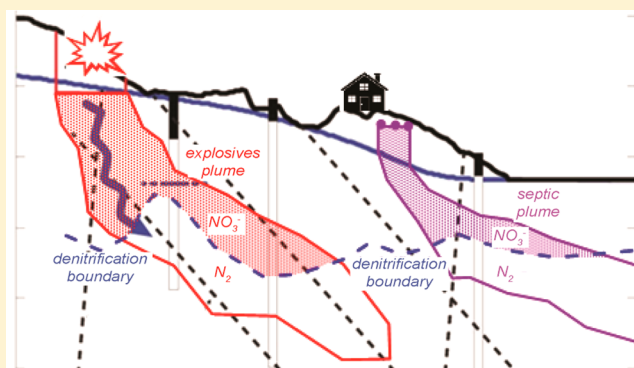
INTRODUCTION

Fragmentation of bedrock with explosives for construction and mining projects is a potential source of nitrate (NO_3^-) contamination of groundwater.[1−4] Hundreds to tens of thousands of kg of NO_3^- are typically used at a construction site. Nitrate is a component of ammonium nitrate (NH_4NO_3), which is approximately 90% of commonly used commercial explosives by weight.[5] Bulk emulsions injected into blasting holes typically consist of NH_4NO_3 and fuel oil (ANFO). High NO_3^- concentrations in groundwater affected by explosives could be related to several different processes, including (1) leaching of NO_3^- from unexploded NO_3^--bearing explosive compounds such as NH_4NO_3;[1] (2) oxidation (nitrification) of reduced N components of explosives such as NH_4NO_3, TNT, RDX, etc.; and (3) injection of soluble NH_3 or NO_x gases into

the subsurface by blasting.[4] The mass of explosive N remaining in the ground after blasting is unknown; estimates suggest that up to 6% of ANFO slurry may escape detonation,[1,6] which could be a substantial contribution to groundwater recharge locally.

Previous studies have reported (1) high concentrations of NO_3^- and related compounds in groundwater at mines, quarries,[2,3] and other environments exposed to heavy explosives use; (2) isotopic fractionation of N in explosive compounds caused by biodegradation;[7] (3) occurrence of isotopically

anomalous NO_3^- that may have been derived from nitrification of reduced N in explosive compounds;[8,9] and (4) elevated concentrations of dissolved constituents from enhanced weathering of blasted rock fragments.[1] In New Hampshire and elsewhere, rock excavation for highway construction commonly requires blasting with NH_4NO_3-based explosive emulsions. Elevated concentrations of NO_3^- in groundwater have been attributed to blasting in New Hampshire,[10−15] but direct forensic evidence of NO_3^- sources is lacking. Nitrate concentrations in groundwater in the region typically are low (<1 mg-N/L),[16,17] whereas concentrations of the order of 5− 170 mg-N/L have been observed in shallow groundwater sampled in wells and springs near blasting sites. Potential nonblasting NO_3^- sources include wastewater disposal (e.g., septic systems), fertilizers used in landscaping and agriculture, atmospheric deposition, and weathering of soils and rocks.[18−22]

Isotope ratios of N ($\delta^{15}N$) and O ($\delta^{18}O$) have been used to evaluate sources of groundwater NO_3^- contamination in agricultural, urban, and other settings,[23−29] but apparently have not been thoroughly tested for identifying sources of NO_3^- near blasting sites in fractured-bedrock aquifer settings. Nitrate from unexploded NH_4NO_3 may be recognizable isotopically as synthetic NO_3^- if not altered by biologic activity. However, denitrification (microbial reduction of NO_3^- to N_2 gas) can alter the isotopic composition of the remaining NO_3^-. Blasting-related reduced N may be microbially oxidized (nitrified), yielding biogenic NO_3^- with an isotopic composition different from that of synthetic NO_3^-. In addition, groundwater transport of NH_4^+ from blasting sites can be retarded by ion exchange with solid phases in soils and aquifers. Thus, it is possible that synthetic NO_3^- could move away from a source first, followed by NH_4^+ that, if oxidized gradually, could generate a secondary and possibly more persistent NO_3^- pulse with modified isotopic composition. Despite these potential complications, blasting-related NO_3^- may be distinguishable from other NO_3^- contamination sources including agriculture and wastewater disposal.

This study tested whether isotopic analyses can identify blasting-related NO_3^- in groundwater in an area of road construction. Stable isotope ratios in H_2O, NO_3^-, NH_4^+, and N_2 were used to identify sources, transport pathways, and transformation processes of NO_3^-. Geochemical, hydrologic, geologic, roadway-construction, and land-use data were used to corroborate the transport and fate of the N compounds. Time-series sampling of wells revealed contaminant response times and assisted isotopic identification of multiple NO_3^- sources including an unmodified synthetic NO_3^- end member from explosives that is not commonly found in groundwater. Varying degrees of denitrification were quantified, and corrections for denitrification were made to reconstruct initial (recharge) NO_3^- characteristics and reduce uncertainties in source attributions. Approaches used to identify NO_3^- sources in groundwater here can be used in fractured-rock aquifers elsewhere to determine the impacts of blasting.

■ STUDY DESIGN AND METHODS

Study Area. The study area was a New Hampshire Department of Transportation (NHDOT) highway construction site in Windham, NH (Figure 1), where 2.6 million m³ of bedrock was removed by blasting.[30] Blasting was done in 2009 to create an exit ramp[31] and was resumed in 2013−2014 to create a new roadway.[30,32] The total mass of blasting compounds used in 2013−2014 was approximately 221 000
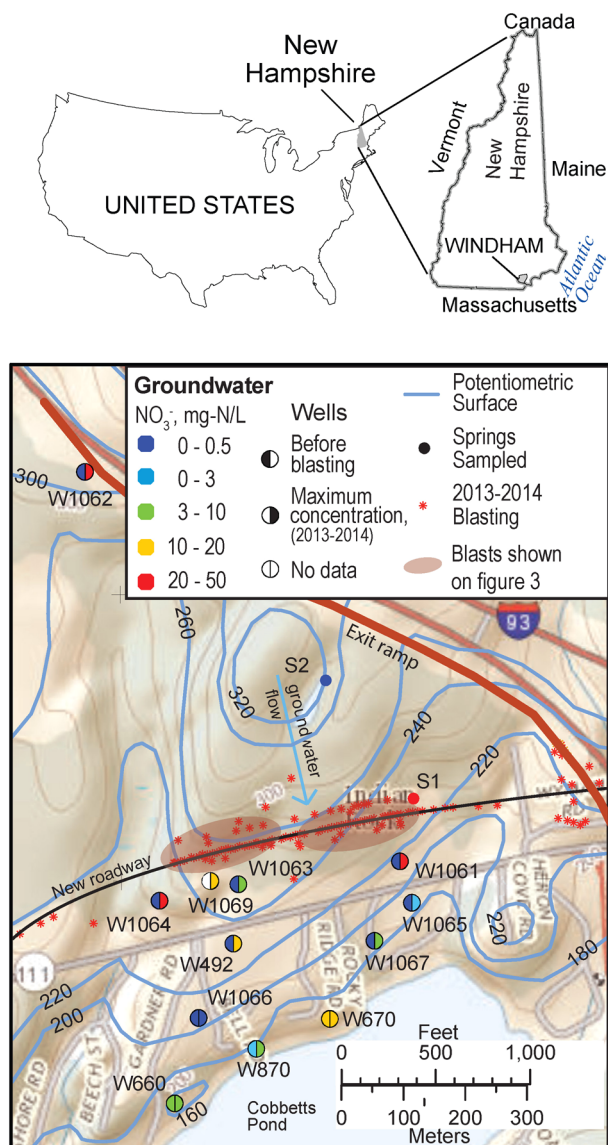

Figure 1. Map[40] of the study area near Windham, New Hampshire, showing the groundwater potentiometric surface, locations of blasting sites, wells, and springs with preblasting and maximum postblasting NO_3^- concentrations (Table S2)[41−43] indicated by colors on the left and right sides of the symbols, respectively.

kg, largely in the form of bulk emulsions of ANFO (NH_4NO_3 plus additives) (Supporting Information Table S3).

Thin (<3 m) glacial till overlies igneous and metamorphic bedrock in the study area.[33] The bedrock is Silurian-age metasedimentary rock intruded by multiple phases of Devonian-age granite.[34−36] A potentiometric-surface map (Figure 1) was produced from existing water level-data,[37−39] topography, and surface water features. In general, groundwater flow was southward through the till and fractured bedrock toward Cobbetts Pond but with considerable local variation related to topography. Forest was the dominant land cover at the blasting sites (Figure 1), whereas residential development (low to medium density) was predominant to the south.[40] Bedrock aquifer water-supply wells and septic systems for residential and commercial wastewater disposal are present in developed areas.

Well Selection and Sampling. Groundwater samples for chemical and isotopic analyses were collected between April 2013 and October 2014 in areas upgradient and downgradient

from blasting sites. Blasting related to construction of the new roadway during 2013 and 2014 was the main focus of this study; some wells also may have been affected by blasting from the 2009 construction. The selection of wells for sampling was guided in part by results from NHDOT's on-site water-quality monitoring.[41,42] Nineteen open-bedrock-borehole drinking-water wells were sampled monthly during blasting activities (2013−2014) for analyses including NO_3^-, NO_2^-, and NH_4^+ concentrations. U.S. Geological Survey (USGS) conducted one round of isotope sampling from five wells prior to blasting (W660, W670, W1061, W1063, and W1064, Figure 1) to characterize background conditions. Subsequently, wells were selected and sampled at 2 month intervals for stable isotopes and additional analytes. Quality-control samples included eight replicates (12%) and 2 field blanks (3%).

Twelve wells and two springs were sampled for the isotope study. Eleven of the wells were drinking-water supplies (public and private) and had dedicated submersible pumps. Open intervals of these wells ranged from 3 to 154 m below land surface, and the potentiometric surface was 0.3−23 m below land surface. Seven of the drinking-water wells were located in a lakeside neighborhood where elevated NO_3^- concentrations had been reported.[41] One monitoring well (W1062) was sampled by using a peristaltic pump; it had an open interval 3−30 m below land surface and a potentiometric surface 3.4 m below land surface. The monitoring well was upgradient of the 2013−2014 blasting and adjacent to the exit ramp where blasting occurred in 2009.[43] Samples of explosives used in the study area were not available for analysis; samples of rock chips from a recently blasted area and water discharging from a small spring (S1) draining a pile of recently blasted rock, were collected as possible representatives of materials most likely to be affected by blasting. Samples of hydroseed fertilizers used with reclamation planting were also obtained. Selected solid samples were analyzed for total N (blasted rock chips and fertilizers) and leachable N species (NO_3^-, NH_4^+ in blasted rock chips). An upgradient spring (S2) in a forested area was sampled to represent background conditions.

Chemical and Stable Isotopic Analyses. Temperature, specific conductance, pH, and dissolved oxygen (O_2) concentrations were measured in the field.[44] Water samples were analyzed in the laboratory for selected major elements and ions (B, Ca, Mg, Na, Br^-, Cl^-, NH_4^+, NO_3^-, NO_2^-, PO_4^{3-}, SO_4^{2-}), dissolved gases (O_2, Ar, N_2, CH_4), VOCs, and stable isotope ratios (δ^2H and $\delta^{18}O$ of H_2O, $\delta^{15}N$ and $\delta^{18}O$ of NO_3^-, $\delta^{15}N$ of NH_4^+ and N_2). Samples from drinking-water wells were collected and analyzed by the NHDOT contractor for major elements and ions, and VOCs.[41,42,45] NHDOT data included alkalinities and total Fe concentrations for a limited number of samples, yielding charge balances given by: anion equivalents = 1.11 × cation equivalents (R^2 = 0.98, n = 10). Selected major elements and ions in samples from the monitoring well, springs, solid samples, and leachates were analyzed in USGS laboratories.[46,47] Redox conditions relevant to NO_3^- transport were evaluated using a combination of O_2, NO_3^-, NO_2^-, NH_4^+, Fe, and excess N_2 data[48,49] (see below).

Dissolved-gas concentrations were measured in the USGS Reston Groundwater Dating Laboratory.[50] Stable isotope ratios were measured in the USGS Reston Stable Isotope Laboratory.[46] Isotopic measurement uncertainties varied by analysis between 0.1 and 1‰. Analytical methods and calibrations for stable isotopes and dissolved gases are described in the Supporting Information (text). Dissolved gas data (Ar,

N_2, and $\delta^{15}N$ of N_2) for each sample were used to quantify the effects of denitrification on the concentration and isotopic composition of NO_3^- by reconstructing the initial recharge (predenitrification) NO_3^- concentration and isotopic composition using methods described in previous studies[51−54] as described below and in the Supporting Information.

■ RESULTS AND DISCUSSION

Nitrate concentrations and isotopic compositions of many samples were affected by blasting. Isotope data indicated multiple NO_3^- sources (synthetic and biogenic), but reducing conditions in the aquifer caused substantial changes in NO_3^- concentrations and isotopic characteristics in many cases. Reconstruction of initial (recharge) NO_3^- concentrations and isotopic compositions using dissolved gas data improved the definition and attribution of NO_3^- sources. Temporal variations in blasting activities and groundwater responses at the wells supported source identifications. Summaries of these results are described below and results for individual wells are given in the Supporting Information.

Distribution and Potential Sources of Nitrate. Prior to blasting (Figure 1), distributions of NO_3^- concentrations reflected land use.[40] Groundwater beneath forested land cover adjacent to the new roadway did not have detectable NO_3^- (≤0.04 mg-N/L, W1063, W1064) before blasting. Nitrate was not detected (≤0.04 mg-N/L, S2) in groundwater discharging from an upgradient spring on forested land. Groundwater beneath developed land had moderate -to-high NO_3^- concentrations (e.g., 5.3 mg/L W660, 15.6 mg/L W670) throughout the study period. Groundwater NO_3^- concentrations increased (ranging from 0.05 to 30 mg-N/L) in 6 of 11 wells after blasting began (April 2013). The 6 wells were located <200 m downgradient from the new roadway (Figure 1). The NO_3^- concentration in groundwater discharging from a pile of recently blasted rock within the new roadway (spring S1, which did not exist before blasting) was 50 mg-N/L in June, 2013.

Blasting compounds were a major potential NO_3^- source to groundwater in this study (Tables S3 and S4). The blasting compounds used in 2013−2014 contained approximately 60 000 kg total N, of which 27 000 kg was in the form of NO_3^--N. Explosives were largely in the form of bulk emulsions of ANFO. Material safety data sheets indicate that smaller masses of other N compounds were present (Table S4). If 0.1 to 6% of the mass of ANFO slurry was undetonated[1,6] then there could have been as much as 60−3600 kg of N from blasting compounds released in the study area, approximately half in the form of NO_3^- and half in the form of NH_4^+. That much total N dissolved in groundwater within the blasting-affected area downgradient from the blasting sites (500 m E-W by 220 m N−S by 110 m deep) with estimated porosity of 0.0005[55] could yield a mean concentration between 10 and 600 mg-N/L, more than enough to account for documented occurrences of transient, heterogeneously distributed $NO_3^- \pm NH_4^+$ in wells, given large unknown uncertainties about the affected volume and porosity of the aquifer, and various forms of N released from exploded or unexploded blasting compounds.

Nitrogen from hydroseeding fertilizer used for reclamation of road construction sites was another potential transient source of groundwater NO_3^-. Hydroseeding fertilizer did not contain NO_3^- and was mostly in the form of $CO(NH_2)_2$, but portions not assimilated by plants could have been nitrified in soils.
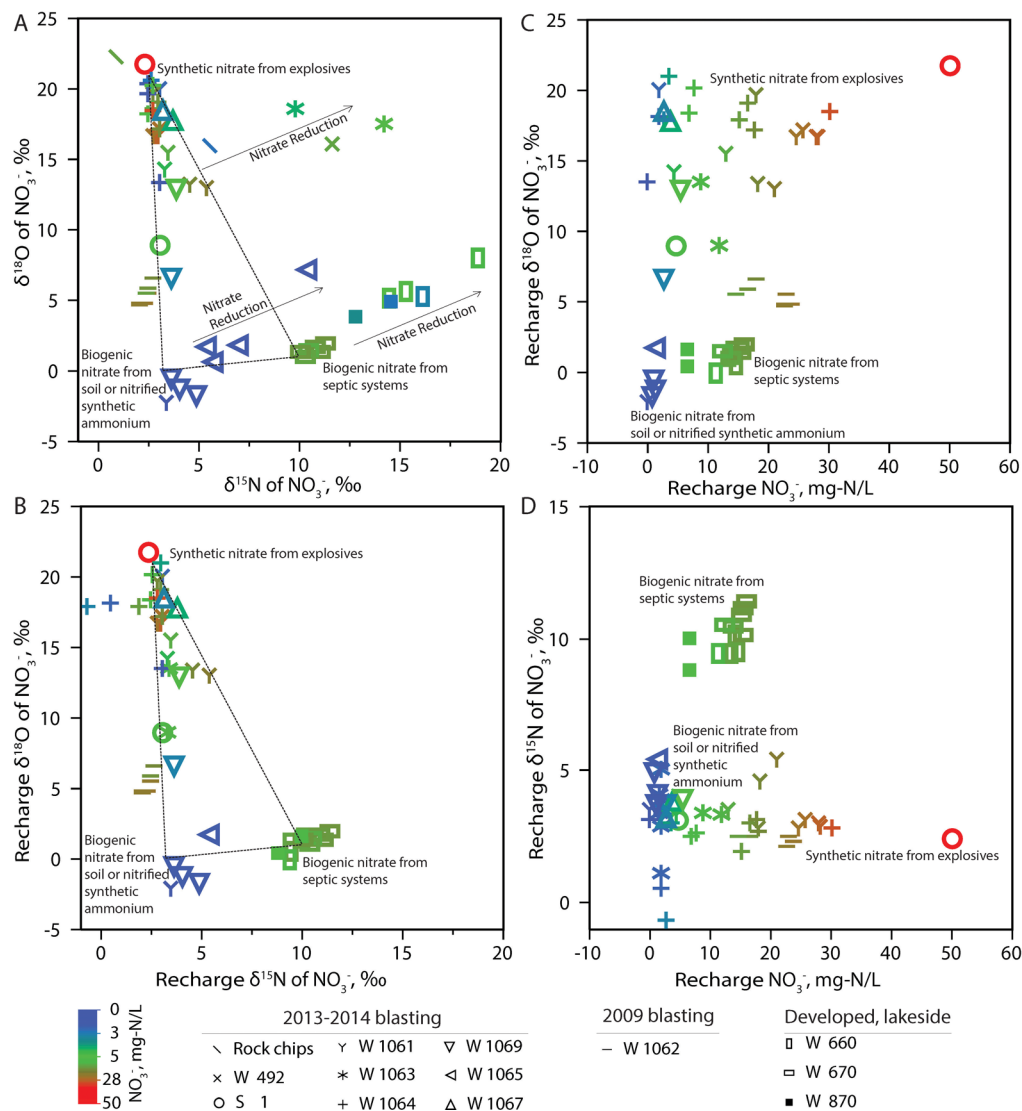
Figure 2. Isotopic and chemical data for NO_3^-. (A) Measured $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- indicating various sources and varying effects of denitrification (nitrate reduction), with $\Delta\delta^{15}N/\Delta\delta^{18}O \approx 1.31$ (best fit to data from W660, W670, and W870); (B) Recharge (including measured and reconstructed, predenitrification) $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- indicating three major sources (end members) and possible mixtures (i.e., adjusted version of panel A); (C) Recharge NO_3^- concentrations and $\delta^{18}O$ values; (D) Recharge NO_3^- concentrations and $\delta^{15}N$ values.

However, the total documented mass of N (<240 kg) in hydroseeding fertilizer applied along the new roadway was less than 0.5% of the total synthetic N used for blasting in the study area.

Septic systems are known to be potential sources of NO_3^- in groundwater,[56] and the distributions of NO_3^- before and after blasting were consistent with septic-system sources in some residential wells. NO_3^- concentrations in residential areas were inversely proportional to lot size (Tables S1). Groundwater NO_3^- concentrations similar to those observed in developed areas in this study (of the order of 2−16 mg-N/L) commonly occur in groundwater affected by septic systems elsewhere.[21,22,56]

Another potential source of NO_3^- is atmospheric deposition, but total maximum annual N deposition fluxes (Table S5) are small (≤10 kg/ha) compared to the locally high fluxes from blasting and septic systems. Background NO_3^- concentrations in oxic groundwater not affected locally by human activities are expected to be relatively low. Nitrate concentrations in New England groundwater in crystalline rock aquifers with minimal

anthropogenic influence are typically less than 1 mg/L as N or lower,[16,17] consistent with relatively small NO_3^- inputs from atmospheric deposition, or from decay of organic matter, or weathering of minerals (e.g., illite, biotite) containing NH_4^+ in soils or metamorphic rocks.[57,58]

Isotopic Composition of Nitrate and Ammonium. Stable isotope ratios of N and O in groundwater NO_3^- provided evidence of multiple sources of NO_3^- (Figure 2A). $\delta^{18}O$ values ranged from −2.2 to +21.7‰ and $\delta^{15}N$ values ranged from +2.1 to +18.9‰. Most samples with high NO_3^- concentrations, including samples from the blasting-site spring (S1) and wells adjacent to, and downgradient from blasting (W1061 and W1064), had relatively low $\delta^{15}N$ values (+1 to +3‰) and high $\delta^{18}O$ values (+17 to +23‰) (Figure 2A). Similarly, leachate from blasted rock chips had NO_3^- with $\delta^{15}N$ = 1−6‰ and $\delta^{18}O$ = 16−22‰ (Table S2). These isotope ratios are different from those of biogenic soil NO_3^- (formed by nitrification) and more like those of common synthetic NO_3^- sources.[59,60] Some samples with relatively low $\delta^{15}N$ also had low $\delta^{18}O$, indicating sources such as nitrification of N from

Table 1. Chemical and Isotopic Data for a Subset of Representative Settings and Sample Dates[a]

ID	sample date	comment	O_2 mg/L	SC μS/cm	NH_4^+ mg-N/L	NO_3^- mg-N/L	NH_4^+ $\delta^{15}N$ ‰	NO_3^- $\delta^{15}N$ ‰	NO_3^- $\delta^{18}O$ ‰
S2	4/15/2014	upgradient spring, background		68	<0.010	<0.04			
W1064	4/18/2013	2013 preblasting, forest	7.5	95	<0.010	<0.04			
W1063	**4/18/2013**	**2013 preblasting, forest, low O_2**	**0.3**	**324**	**<0.010**	**<0.04**			
W1061	4/18/2013	2013 preblasting, developed	4.0	116	<0.010	0.13		3.5	−2.2
S1	**6/25/2013**	**2013 postblast, synthetic NO_3^-**	**5.6**	**610**	**21.16**	**50.23**	**2.0**	**2.4**	**21.7**
W1061	**2/4/2014**	**2013 postblast, synthetic NO_3^-**	**6.0**	**412**	**0.05**	**28.43**		**2.9**	**16.7**
W1064	**10/16/2014**	**2013 postblast, synthetic NO_3^-**	**1.2**	**596**	**0.04**	**30.31**		**2.8**	**18.5**
W492	10/16/2014	2013 postblast, low O_2	0.1	580	0.01	13.71		11.7	16.1
W1063	10/16/2014	2013 postblast, low O_2	0.1	378	< 0.010	5.20		14.3	17.5
S1	**4/15/2014**	**2013 postblast, mixed source**		**215**	**0.02**	**4.82**		**3.1**	**8.9**
W1061	**10/16/2014**	**2013 postblast, mixed source**	**4.8**	**636**	**< 0.010**	**21.13**		**5.4**	**13.0**
W1062	6/10/2014	2009 postblast	2.1	2117	0.34	14.70	11.1	2.5	5.5
W1062	**10/16/2014**	**2009 postblast, low O_2**	**0.1**	**2121**	**0.33**	**18.00**		**2.7**	**6.5**
W670	6/25/2013	septic, developed	4.9	454	0.02	16.13		11.4	1.9
W660	**6/25/2013**	**septic, developed, low O_2**	**0.6**	**590**	**0.01**	**5.32**		**15.3**	**5.6**

[a]SC = specific conductance. Normal and bold fonts indicate groups of samples with common sources, settings, or O_2 concentrations as indicated in the comment column.

soils or reduced N components of explosive compounds. Other samples had isotopic characteristics more like those common in wastewater NO_3^-, such as W670 in a residential area near Cobbetts Pond with $\delta^{15}N$ = +10.7 ± 0.5‰ and $\delta^{18}O$ = +1.4 ± 0.3‰ prior to blasting and throughout the study.

Ammonium was present in groundwater adjacent to blasting sites and had variable N isotopic ratios. Groundwater NH_4^+ concentrations generally were low (<0.01 mg-N/L), but a few samples near blasting sites had elevated NH_4^+ (0.01−21.1 mg-N/L) that may represent ANFO contamination (Table 1). For example, blasting-site spring S1 had NH_4^+ = 21.1 mg-N/L with $\delta^{15}N$ = +2.0‰, which is consistent with contamination by synthetic NH_4^+. Blasted rock chips had $\delta^{15}N$ = +1 to +4‰ in leachate-extractable NH_4^+ and $\delta^{15}N$ = +2 to +5‰ in total N. This material apparently contained residues of synthetic NO_3^- and NH_4^+ from explosives, plus nonextractable N that could include soil, rock, or other explosive components, which may have been partially oxidized to NO_3^-. Hydroseeding fertilizer samples had bulk $\delta^{15}N$ values of −1.8‰ (N−P−K of 24−0−5) and +1.5‰ (N−P−K of 19−19−19) (Table S2), potentially similar to ANFO values, but the fertilizers did not contain NO_3^- and the relatively small masses used in the area suggest that this was not likely a major N source.

Monitoring well W1062, downgradient from the 2009 blasting in a forested area (nonresidential, northwest corner of Figure 1) area, had a relatively high concentration of NH_4^+ (0.8 mg-N/L) with $\delta^{15}N$ = +8.7‰. This $\delta^{15}N$ value is higher than those of likely NH_4^+ sources in that area, such as atmospheric deposition, forest soils, or blasting compounds, but it could indicate isotopic fractionation caused by partial nitrification of NH_4^+. Nitrate in W1062 had relatively low $\delta^{15}N$ (2.4 ± 0.2‰) and $\delta^{18}O$ (5.4 ± 0.7‰) values; the $\delta^{18}O$ value was low compared to most blasting-related NO_3^-. Data from this well may indicate that residual synthetic NH_4^+ from blasting was being gradually nitrified, yielding groundwater with a mixture of blasting-related NH_4^+ and NO_3^-, both of which were isotopically modified in comparison to the original synthetic explosive ratios. Nitrite concentrations generally were less than 0.05 mg-N/L, but some samples with blasting-related NO_3^- had slightly elevated NO_2^- (up to 2 mg-N/L in S1 and W492) providing additional evidence of active nitrogen

redox reactions (nitrification/denitrification) associated with the contamination.

While isotope data clearly indicated multiple sources of NO_3^- with spatial and temporal variability, the NO_3^- also was variably affected by isotopic fractionation associated with denitrification as indicated by excess N_2 gas in some samples with low O_2 concentrations. Because denitrification locally affected NO_3^- from various sources, the NO_3^- isotope data could not be fully evaluated on the basis of the measured values. Quantifying the effects of denitrification allowed for the reconstruction of initial NO_3^- concentrations and associated isotope ratios in recharge, which, in turn, allowed for improved source attribution of NO_3^-, as described below.

Effects of Denitrification and Reconstruction of "Initial" Nitrate Concentrations and Isotope Ratios. Chemical and isotopic data indicated that denitrification lowered groundwater NO_3^- concentrations and altered NO_3^- isotope ratios locally, complicating NO_3^- source identification. Low O_2 concentrations (<1 mg/L) and positive correlations between $\delta^{18}O$ and $\delta^{15}N$ values of NO_3^- indicated denitrifying conditions and isotope fractionation effects in some wells (Figure 2A). For example, $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- in wells in residential areas (W660, W670, W870) were positively correlated (R^2 = 0.96, N = 10) and generally increased with decreasing NO_3^- concentrations, consistent with varying degrees of denitrification.[61] Similar fractionations apparently affected NO_3^- isotopic composition in other wells such as W1065 and W492 (Figure 2A).

For each sample the concentration of excess N_2 attributable to denitrification was estimated from concentrations of Ar and N_2 (assuming a narrow range of excess air concentrations and seasonally varying recharge temperatures, discussed further in the Supporting Information). Subsequently, the estimated concentration and $\delta^{15}N$ value of excess N_2 were combined with measured values for NO_3^- to reconstruct the initial values for NO_3^- ($NO_3^{-\circ}$ in recharge, prior to denitrification in the saturated zone), according to methods described previously.[51,52,54] Measured $\delta^{15}N$ values of total N_2 gas were +0.7 ± 0.1‰ in oxic samples, consistent with undenitrified atmospheric sources, and ranged from −0.4 to +2.5‰ in suboxic samples, indicating partial to complete denitrification

(Figure S2). Precision of excess N_2 calculations was limited in part by apparent variation in groundwater recharge conditions (temperature and excess air entrainment). Oxic samples (assumed to have no excess N_2) had calculated recharge temperatures ranging from about 4–15 °C and excess air concentrations of approximately 1 to 4 cm^3STP/L (Figure S2). Excess N_2 concentrations for all samples were calculated by assuming excess air = 2.5 cm^3STP/L and allowing temperature to vary accordingly. Reconstructed $\delta^{15}N$ values of NO_3^- were determined by mass balance and reconstructed $\delta^{18}O$ values were estimated by using the observed correlation between $\delta^{15}N$ and $\delta^{18}O$ (Figure 2A). Laboratory studies indicate that the relative rates of change of $\delta^{15}N$ and $\delta^{18}O$ during denitrification are approximately equal ($\Delta\delta^{15}N/\Delta\delta^{18}O \approx 1$),[61] and analyses of NO_3^- in reducing groundwater commonly yield apparent $\Delta\delta^{15}N/\Delta\delta^{18}O$ ratios between 1 and 2.[26,59,62] In the current study, we derived a local $\Delta\delta^{15}N/\Delta\delta^{18}O$ ratio of 1.31 from the array of data representing residential wells (Figure 2A). In tables, figures, and text, "recharge" NO_3^- concentrations and isotopic compositions were reconstructed for samples with more than 1.2 mg/L excess N_2 and were left equal to measured values for samples that had no detectable excess N_2. Considering the variation of excess N_2 in oxic samples (±0.6 mg-N/L), estimated typical uncertainties associated with the reconstruction method were approximately ±0.6 mg-N/L for NO_3^-, ± 0.5‰ for $\delta^{15}N$, and ±0.5‰ for $\delta^{18}O$ (see Supporting Information text and Table S2), overall uncertainties could be larger, especially for samples with low recharge NO_3^- concentrations.

Wells with groundwater considered most likely to have been affected by denitrification (W492, W660, W870, W1063, W1064, W1065, and W1066, see Supporting Information text) were characterized by measurable excess N_2–N concentrations (>1 mg/L:), low O_2 concentrations (<1 mg/L), and/or elevated $\delta^{18}O[NO_3^-]$ and $\delta^{15}N[NO_3^-]$ values. Some samples without measurable excess N_2 may have been denitrified if their initial NO_3^- concentrations were low. Samples with low O_2 (<1 mg/L) had excess N_2 concentrations ranging from near zero to approximately 10 mg-N/L, indicating up to 10 mg-N/L of NO_3^- loss by denitrification.

Reducing conditions are common in fractured metamorphic bedrock aquifers in the region,[16] but it is not clear what controlled the distribution of denitrified and undenitrified samples locally. Wells exhibiting evidence of denitrification were greater than 50 m deep, suggesting deep, long aquifer flow paths encountered reducing conditions. Six wells with anoxic groundwater and evidence of denitrification were in an area adjacent to and downgradient from the new roadway, and in residential areas toward the lake. Relatively high alkalinities in some reduced samples could indicate reactions with carbonate or organic C phases in the aquifer; whereas total dissolved Fe concentrations in a few samples were not clearly related to O_2 or excess N_2 concentrations (Table S2). It is considered likely that some wells sampled groundwater from multiple depths and redox conditions, reflecting heterogeneity of flow paths and reactions.

Reconstructed initial NO_3^- concentrations and isotopic compositions (Figures 2B–D) produced a more coherent picture of NO_3^- sources and mixing than the unadjusted measured data (Figure 2A). For example, isotope data from 3 residential-area wells that were variably affected by denitrification (W660, W670, W870) had variable $NO_3^-{}^\circ$ concentrations (6.6–16.1 mg-N/L) but similar $\delta^{15}N[NO_3^-]^\circ$ values (+10‰)

after reconstruction (Figure 2B–D, Table S2). Approximately half of the NO_3^- in the groundwater at well W660 had been lost to denitrification after recharge. Wells W1066 and W1063 had similar excess N_2 concentrations, similar reconstructed $NO_3^-{}^\circ$ concentrations and $\delta^{15}N$ values (Table S2), consistent with a shared source and flow path.

Evidence for Multiple Sources of Nitrate and Source Mixing. After adjustment for effects of denitrification (Figure 2B), the "reconstructed-initial" NO_3^- isotopic compositions plot nearly within a triangular area in the dual isotope plot, providing evidence for three distinct sources (end members define a triangle) of NO_3^- in groundwater recharge: (1) synthetic NO_3^- from blasting, (2) biogenic NO_3^- from microbial nitrification of synthetic NH_4^+, limited contributions from soil NH_4^+, and possibly other explosive or fertilizer compounds, and (3) biogenic NO_3^- from septic systems. Values of $\delta^{18}O$ and $\delta^{15}N$ of NO_3^- that do not plot near end members may represent mixed sources of NO_3^- (Figure 2B), in some cases related to temporal effects of blasting-related NO_3^- transport or mixing of water from fractures within open boreholes.[63]

The synthetic NO_3^- end member in our study is at the apex of the dual isotope plot with $\delta^{15}N \approx + 2.5 \pm 0.5‰$ and $\delta^{18}O \approx + 21 \pm 1‰$ and is well represented by groundwater draining a blasted rock pile at S1 ($\delta^{15}N = +2.4‰$, $\delta^{18}O = +21.7‰$) (Figure 2B), consistent with reported isotope data for synthetic NO_3^-. Although samples of explosives were not available for this study, literature data indicate most such products have fairly distinctive isotopic compositions, whereas limited sampling in a given area may or may not be representative of all products used locally. Synthetic NO_3^- and NH_4^+ reagents and fertilizers, including NH_4NO_3, typically have $\delta^{15}N$ values near that of atmospheric N_2 (0‰), mostly to within ±2‰ and almost all to within ±4‰.[20,59,64–67] For example, one compilation yielded mean $\delta^{15}N$ values for synthetic fertilizer components (including NH_4^+ and NO_3^- separated from NH_4NO_3 but not including lab reagents) of −0.9 ± 1.9% for NH_4^+ and +2.8 ± 1.8‰ for NO_3^-.[65] Synthetic NO_3^- typically has $\delta^{18}O$ values near that of atmospheric O_2 (+24‰) or slightly lower. One study reported $\delta^{18}O$ values for nitrate in NH_4NO_3 ranging from +17 to +25‰, with the "majority" between +21 and +24‰.[64] Other reported mean values were +23 ± 3‰ for $\delta^{18}O$ and 0 ± 2 for $\delta^{15}N$ for NO_3^- in synthetic fertilizer and reagent sources.[60] In some environments, NO_3^- with low $\delta^{15}N$ and high $\delta^{18}O$ could indicate direct atmospheric contributions. However, atmospheric deposition is not a likely source for the NO_3^- in S1 or the wells adjacent to blasting (Table 1) because the NO_3^- concentrations in these samples were much higher than NO_3^- concentrations in atmospheric deposition or uncontaminated groundwater in the area of the study. Also, high atmospheric NO_3^- $\delta^{18}O$ values typically are not observed in groundwater except in arid regions.[68]

A previous study reported "post-blast" solid residues and water extracts had total-N $\delta^{15}N$ values of the order of 2–30‰ higher than preblast NH_4NO_3 prills, presumably because of various isotope effects of the explosions.[69] With the possible exception of one blasted rock sample with elevated $\delta^{15}N$-[NO_3^-], our data indicate that most of the NO_3^- entering groundwater from blasting sites was not affected substantially by blasting reactions. Our data were interpreted to indicate that much of the blasting-related NO_3^- came from unexploded NH_4NO_3 that dissolved in the groundwater recharge and moved away from blasting sites.

The second NO_3^- isotopic end member (Figure 2B, lower left corner of triangle), with low $\delta^{18}O$ (Figure 2C) and low $\delta^{15}N$ (Figure 2D), apparently occurred in some wells affected by blasting, in which case the NO_3^- may have formed by nitrification of synthetic NH_4^+ or other reduced N compounds in explosives or in soils disturbed by blasting. For example, whereas recent (2013, S1) blasting produced groundwater dominated by synthetic NO_3^- with low $\delta^{15}N$ and high $\delta^{18}O$, some older blasting-related NO_3^- (2009, W1062) had low $\delta^{15}N$ and low $\delta^{18}O$ (+2.4‰ ± 0.2 and +5.4‰ ± 0.7, N = 7), indicating a substantial component of the NO_3^- may have been nitrified synthetic NH_4^+. Nitrification of blasting-related NH_4^+ was indicated in some wells by temporal sampling (see below). The isotopic composition of this biogenic NO_3^- endmember was not well constrained and may be somewhat variable ($\delta^{15}N \approx +3 \pm 2‰$, $\delta^{18}O \approx 0 \pm 2‰$). Slightly positive $\delta^{15}N$ values were higher than those of most synthetic NH_4^+ products, possibly indicating mixed reduced N sources or late products of previously fractionated synthetic NH_4^+. Nitrate at W1062 appeared to be a mixture of synthetic and biogenic sources, and was accompanied by elevated NH_4^+ that apparently was isotopically fractionated (enriched in ^{15}N) by partial nitrification. This end member may be difficult to distinguish from NO_3^- produced by nitrification of reduced N from inorganic fertilizers or plant residues in an agricultural setting. Similar isotopic characteristics in wells with low NO_3^- concentrations could indicate natural background NO_3^- from soil sources.[70]

The third NO_3^- isotopic end member was identified in samples that were interpreted to be affected by septic systems. Samples from septic-proximal well W670 did not have measurable excess N_2, indicating no denitrification and that W670 might stand alone as a representative of this end member. After adjustment for effects of denitrification at wells W660 and W870, the calculated $\delta^{15}N$ and $\delta^{18}O$ values of reconstructed $NO_3^{-\circ}$ were indistinguishable from the measured values at W670 (no denitrification); thus a septic-system NO_3^- end member was derived from measured data for W670 and reconstructed data for W660 and W870, giving $\delta^{15}N$ of +10.1 ± 0.8‰ and $\delta^{18}O$ of +1.1 ± 0.6‰ (Figure 2B, lower right corner of triangle).

Mixing of NO_3^- from various combinations of these sources can result in isotope ratios that plot inside the triangle formed by end members (Figure 2B). For example, moderate $\delta^{15}N$ and $\delta^{18}O$ of NO_3^- values in late samples from spring S1 (April, 2014) and wells W1062, W1063, and W1069 could indicate mixtures of synthetic NO_3^- with biogenic NO_3^- derived from nitrification of synthetic NH_4^+ or other reduced N. Nitrate with a wide range of $\delta^{15}N$ and $\delta^{18}O$ values may also come from nitrification, degradation, or from the postblast residues of other more complex explosive compounds containing reduced N,[8,9,71] but these compounds were not used in a large quantity at this site (Tables S3 and S4).

Other (nonisotopic) indicators of NO_3^- sources also were evaluated (Table S2). Perchlorate (ClO_4^-) was analyzed in representative samples because it is a common blasting-agent component, though its use was not documented in the study area. ClO_4^- concentrations ranged from 0.03 to 0.80 $\mu g/L$, which is within the range of values reported elsewhere for groundwater not affected substantially by local contamination sources but including domestic wastewater.[72−74] Thus, although ClO_4^- is a component of explosives in some settings, it apparently was not substantially enriched in blasting-affected

groundwater at this site (Table S2).[1,75] Some wells affected by blasting had elevated concentrations of Ca, Mg, and SO_4^{2-} (Figure 3), possibly from enhanced weathering of blasted rock.[1]
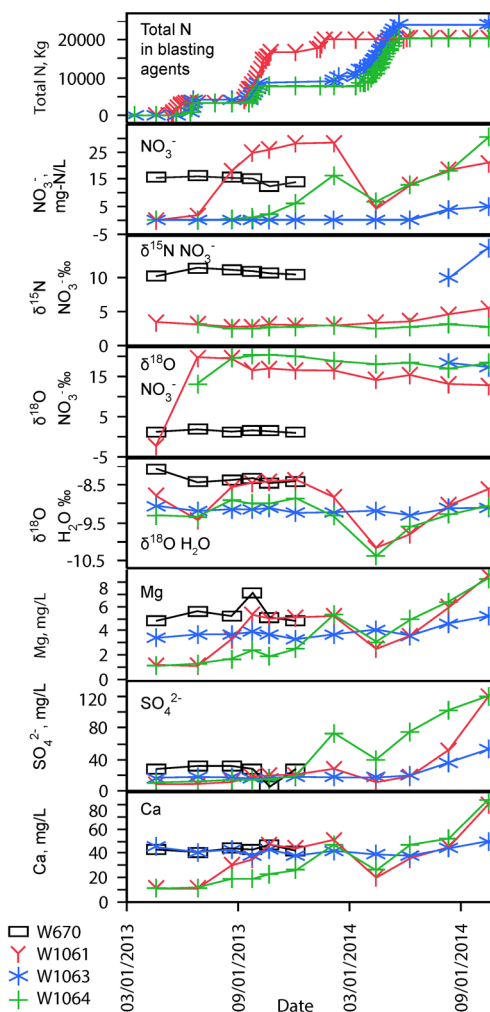

Figure 3. Temporal variations in cumulative total N used in blasting compounds compared with selected chemical and isotopic data from representative wells, illustrating various response patterns. Chemical and isotopic data are from well W670 (septic source), and wells W1061, W1063, and W1064 (adjacent to blasting). Blasting N records are from hypothetical potential recharge contributing areas (buffers) extending 100 m on both sides of a flow vector upgradient from the wells (see Figure 1). NO_3^- concentrations and isotopic compositions are as measured.

Chloride concentrations and Cl/Br ratios were highest in some wells containing synthetic NO_3^-, consistent with proximity to roads and construction sites affected by both blasting and road salt, but this was not a consistent feature of blasting-contaminated samples (Figure S4). Chloride concentrations, specific conductance, Cl/Br ratios, and B concentrations were elevated above background values in some residential-area wells, consistent with domestic wastewater NO_3^- from septic systems.

Timing of Groundwater Responses to Contamination Sources. Temporal variations in chemistry and isotopes at some wells provided additional evidence of NO_3^- sources, transformations, and transport processes. Blasting along a 500 m section of new roadway (Figure 1) occurred over a period of 18 months (April 2013 to October 2014). The timing of NO_3^-

concentration changes in some wells was related to recorded changes in the cumulative mass of N compounds used for blasting upgradient of wells (Figures 1 and 3; Tables S3 and S4).

Wells W1061 and W1064 were adjacent to blasting areas, had short, fractured-bedrock flow paths from local recharge zones, and were therefore representative of rapid temporal changes in groundwater in response to changing blasting inputs. Nitrate concentrations increased abruptly at W1061 after June 2013, within 1−3.5 months after upgradient blasting began, and more gradually (3−5 months) at W1064 (Figure 3). Initial NO_3^- increases at both wells were accompanied by rapid increases in $\delta^{18}O$ of the NO_3^-, indicating that small amounts of synthetic NO_3^- quickly dominated the low background NO_3^- that had biogenic isotopic characteristics. Nitrate concentrations decreased briefly in these wells in March−April 2014 possibly due to recharge driven dilution, and then subsequently increased (Figure 3). Coincident variations were recorded in the δ^2H and $\delta^{18}O$ values of H_2O indicating changing recharge conditions, and in Mg, SO_4^-, and Ca concentrations indicating transient dilution. The H_2O isotope data could indicate rapid infiltration of cold-season meteoric water in March−April 2014, possibly associated with dilution of the solutes. The early spring dilution followed a winter without blasting and may have been facilitated by enhanced recharge from till removal and rock fracturing and removal. Sulfate trends lagged behind NO_3^-, Mg, and Ca trends, possibly because of the time or geochemical conditions required to oxidize sulfide minerals in blasted rock.

Nitrification of sorbed or recharged NH_4^+ in oxic groundwater produced NO_3^- with different isotopic composition than NO_3^- leached directly from blasting compounds. For example, after blasting operations progressed westward, away from W1061 and toward W1064, NO_3^- concentrations at W1061 remained elevated but the NO_3^- had progressively lower $\delta^{18}O$ values and higher $\delta^{15}N$ values (Table 1, Figure 3). Spring S1 had a similar temporal trend (not shown, see Table 1). Some samples of groundwater taken in 2014 that were affected by 2013 blasting had lower $\delta^{18}O$ of NO_3^- (S1, 8.9‰), closer to the W1062 values (Figures 2A and 3), indicating a mixture of synthetic NO_3^- with biogenic NO_3^- from nitrification of reduced N. These changes are interpreted as evidence for delayed arrival of NO_3^- that was related indirectly to blasting and derived from microbial nitrification of reduced N from explosives, disturbed soils, or rocks.

Nitrate concentrations measured in well W1062 varied between 14.7 and 23.8 mg/L and increased with increasing O_2 concentrations. This response is interpreted to indicate nitrification of sorbed NH_4^+ left over from blasting. These observations may indicate that initial flushing of the synthetic NO_3^- component of the explosives was followed by delayed and longer-lived flushing of biogenic NO_3^- derived from the synthetic NH_4^+ component of the explosives, possibly accompanied by some fraction of the NH_4^+ itself after partial nitrification and retardation during transport. The low yield of this well, likely associated with low-transmissivity fractures in the bedrock, may have contributed to a delay in NH_4^+ flushing, providing an example of possible results in other low transmissivity rocks.

Another type of delayed response was exhibited by W1063. Although blasting occurred adjacent to well W1063, NO_3^- was not detected in this well for the first 1.5 years of this study (Figure 3); however, anoxic conditions and excess N_2 gas provided evidence that denitrification had occurred. Recon-

structed data (before denitrification) indicate that well W1063 originally had approximately 2 mg-N/L $NO_3^{-\circ}$ with 1−5‰ $\delta^{15}N$ (Table S2) consistent with a synthetic or natural N source, prior to direct NO_3^- detection (5.2 mg/L, Table 1). Initial NO_3^- concentrations were present before the start of the 2013−2014 blasting and may have been related to upgradient blasting in 2009. Nitrate concentrations subsequently increased with corresponding increases in excess N_2 approximately 1.5 years after 2013−2014 blasting commenced. This sequence appears to indicate denitrification protected W1063 from earlier low-level NO_3^- contamination, but the higher flux of NO_3^- after 2013 eventually exceeded the sustainable denitrification rate in the aquifer, causing delayed breakthrough of partially denitrified synthetic NO_3^- from blasting. Fractures intersecting well W1063 (12 m of casing, Table S1) are connected to a deeper anaerobic flow system that may have promoted denitrification of blasting-related NO_3^- for a period of time (Figure 3 and Figures S1 and S5).

In contrast to the relatively rapidly changing NO_3^- concentrations and isotope ratios in wells affected by blasting, NO_3^- concentrations and isotope ratios at wells in developed areas affected by septic-systems were relatively stable throughout the study. Wells W660 and W670 in developed land-use settings adjacent to many homes with small lot sizes and septic systems had moderately high NO_3^- with elevated Mg, Cl, and Ca, that changed by less than 25% between April 2013 and October 2014 (Figure 3, Table S2). Magnesium and Ca were consistently elevated in the septic-affected wells, possibly indicating contributions from water softeners. Although $\delta^{15}N$ and $\delta^{18}O$ values of NO_3^- were affected by denitrification more in some wells and less in others, they were relatively constant over time in each well. Similarly, δ^2H and $\delta^{18}O$ values of H_2O were relatively constant in these wells (Figure 3 and Figure S3), consistent with recharge containing larger components of recycled groundwater and less responsive to rapid infiltration of precipitation or snowmelt (at seasonal or event time scales) than in some of the blasting-affected wells.

Implications for Nitrate Source Identification Studies. In an area with multiple sources of groundwater NO_3^- contamination (including construction-related explosives), combined use of various chemical and isotopic analyses, reconstruction of NO_3^- affected by denitrification, mass balance calculations, and hydrogeologic information helped to resolve NO_3^- sources and transport processes. Four groundwater NO_3^- contamination scenarios were identified in this study: (1) rapid breakthrough of synthetic NO_3^- in proximal wells downgradient of blasting (low $\delta^{15}N$ and high $\delta^{18}O$), (2) reduced and delayed blasting-related NO_3^- concentration responses in wells with anoxic (denitrifying) conditions, (3) persistent NO_3^- in wells adjacent to blasted rock from nitrification of NH_4^+ (low $\delta^{15}N$ and low $\delta^{18}O$), (4) relatively stable NO_3^- concentrations and isotopic compositions consistent with septic sources (high $\delta^{15}N^\circ$ and low $\delta^{18}O^\circ$). Because of the small scale and multidisciplinary approach of this study, likely NO_3^- sources could be distinguished by various lines of evidence; the isotopic evidence could be especially useful in areas where some of the other evidence may be lacking or ambiguous. Synthetic NO_3^- with high $\delta^{18}O$ is unusual in groundwater and indicates rapid transmission and lack of cycling in soils.

Denitrification caused isotopic fractionation of residual NO_3^- with both septic and blasting sources. Wells that apparently were "protected" from NO_3^- contamination by denitrification

in anoxic conditions exhibited increases in blasting-related NO_3^- only after extended periods of blasting, possibly indicating high fluxes of synthetic NO_3^- locally exceeded the supply of electron donors in the aquifer. Groundwater with blasting-related NO_3^- moved rapidly, within six months of blasting, from construction sites to downgradient wells with oxic conditions. Elevated NO_3^- was flushed over a time scale of months to years. Nitrate breakthrough times in denitrifying groundwater (Wells W1063 and W492) were on the order of a year, but may depend on loading rates. Groundwater from septic systems had persistent NO_3^- concentrations, distinctive isotopic compositions, and elevated specific conductance.

These results highlight the transient, heterogeneous, and complex nature of groundwater contamination associated with blasting-related construction in crystalline rock terrains. However, with careful study design and appropriate choices in monitoring of isotopes and gases in concert with general chemistry, it is possible to determine N sources to groundwater near blasting operations and to disentangle the complexities associated with multiple sources and geochemically altered N compounds in many aquifer systems.

ASSOCIATED CONTENT

Supporting Information
The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.5b03671.

Descriptions of sampling protocols, quality control, stable isotopic analyses, nitrate reconstruction calculations, and additional observations about individual wells (text); a map and cross sections of the study area and figures summarizing selected chemical and isotopic data (Figures S1−S5) (PDF)
Well construction information (Table S1) (XLSX)
Chemical and isotopic data (Table S2) (XLSX)
Blasting records and masses of blasting agents used (Table S3) (XLSX)
Concentrations of total N and NO_x-N in blasting agents (Table S4) (XLSX)
Potential nitrogen sources upgradient of wells (Table S5) (XLSX)

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Notes
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