

#### **ARTICLE 21. Town Information Sign**

To see if the Town will vote to raise and appropriate the sum of \$1,500 to complete the purchase and installation of the Town Information Sign, to be located between the Fire Department and Town Hall; of this amount the entirety is to come from the Unassigned Fund Balance. (Selectmen recommend adoption of this Warrant Article.) (Majority vote required.)

#### **ARTICLE 22. Expert Highway Agent**

To see if the Town will vote to instruct the Select Board to appoint an expert highway agent pursuant to NH RSA 231:64, who, under the direction of the selectmen, shall have the same power and perform the same duties as a highway agent elected by the town. (Selectmen recommend adoption of this Warrant Article.) (Majority vote required.)

#### **ARTICLE 23. Blasting Ordinance**

To see if the town will adopt a blasting ordinance that will require a 3 million dollar bond before blasting and forbids blasting within 500 feet of groundwater protection districts and 100 feet of wetlands. (The Selectmen recommend adoption of this Warrant Article.) (Majority vote required.)

→ for non-residential  
construction

#### **ARTICLE 24. Borehole Sealing Standards**

To see if the town will adopt the National Cooperative Highway Research Program standards for sealing of geotechnical boreholes, with requirement of a bond equal to that required by the DOT in the case of DOT approved borings, and the requirement that applicants are required and will be responsible for the expense of the Town hiring and independent expert to oversee the filling/sealing of boreholes. (The Selectmen recommend adoption of this Warrant Article.) (Majority vote required.)

#### **ARTICLE 25. Horizontal Directional Drilling**

To see if the Town will adopt an ordinance prohibiting Horizontal Directional Drilling within 500 feet of the Groundwater Protection district, prohibit use of drilling additives other than bentonite, and prohibit discharges of Horizontal Directional Drilling fluid to surface or ground waters. (The Selectmen recommend adoption of this Warrant Article.) (Majority vote required.)

#### **ARTICLE 26. Thermal Backfill**

To see if the Town will adopt an ordinance prohibiting thermal backfill or thermal concrete containing coal ash within the groundwater protection district. All fluidizing agents must be approved by the town before thermal backfill may be used. (The Selectmen recommend adoption of this Warrant Article.) (Majority vote required.)

✓ DES has approved

Protection



## OSHA News Release – Region 7

U.S. Department of Labor

Please note: As of January 20, 2017, information in some news releases may be out of date or not reflect current policies.

### Region 7 News Release: 12-1063-MON (SF-110)

June 7, 2012

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#### **US Department of Labor's OSHA cites Missouri-based PAR Electrical Contractors for safety violations following worker fatality in Montana**

**BILLINGS, Mont.** – The U.S. Department of Labor's Occupational Safety and Health Administration has cited Kansas City, Mo.-based PAR Electrical Contractors Inc. for three alleged safety violations following the Dec. 22, 2011, death of an employee who was electrocuted while working on a power line near the town of Two Dot, Mont., approximately 100 miles outside of Billings.

"We are committed to doing everything in our power to prevent tragic workplace incidents such as this from happening," said Trina Mailloux, acting director of OSHA's Billings Area Office. "Employers must ensure that workers are protected when working near power lines."

OSHA has issued citations for two serious violations involving exposing workers to electrocution hazards when they are working in close proximity to energized parts without approved insulating safeguards and failing to discontinue the power line work when high winds made the situation particularly hazardous. A serious violation occurs when there is substantial probability that death or serious physical harm could result from a hazard about which the employer knew or should have known.

Additionally, a citation has been issued for one repeat violation involving failing to keep new conductors under positive control in order to prevent accidental contact with energized circuits. In February 2007, OSHA cited PAR Electrical Contractors for essentially the same violation identified at a Missouri job site. A repeat violation exists when an employer previously has been cited for the same or a similar violation of a standard, regulation, rule or order at any other facility in federal enforcement states within the last five years.

The citations carry a total of \$52,500 in proposed fines. The company has 15 business days from receipt of the citations and proposed penalties to comply, request an informal conference with OSHA or contest the findings before the independent Occupational Safety and Health Review Commission.

To ask questions, obtain compliance assistance, file a complaint, or report workplace hospitalizations, fatalities or situations posing imminent danger to workers, the public should call OSHA's toll-free hotline at 800-321-OSHA (6742) or the agency's Billings office at 406-247-7494.

Under the Occupational Safety and Health Act of 1970, employers are responsible for providing safe and healthful workplaces for their employees. OSHA's role is to ensure these conditions for America's working men and women by setting and enforcing standards, and providing training, education and assistance. For more information, visit <http://www.osha.gov>.

###

U.S. Department of Labor news materials are accessible at <http://www.dol.gov>. The information above is available in large print, Braille or CD from the COAST office upon request by calling 202-693-7828 or TTY 202-693-7755.



[« Return to search form](#)

## Violation Tracker Parent Company Summary

**Parent Company Name:** Quanta Services**Ownership Structure:** publicly traded (ticker symbol PWR)**Headquartered in:** Texas**Industry:** construction & engineering**Penalty total since 2010:** \$1,102,917**Number of records:** 31

Top 10 Primary Offense Types	Penalty Total	Number of Records
wage and hour violation	\$629,371	7
workplace safety or health violation	\$473,546	24

**Notes:**

Parent-subsidiary linkages are based on relationships current as of the latest revision listed in the [Update Log](#), which may vary from what was the case when a violation occurred. The penalty dollar total above may be adjusted to account for the fact that the list of entries below may include both agency records and settlement announcements for the same case; or else a penalty covering multiple locations may be listed in the individual records for each of the facilities. Duplicate penalty amounts are marked with an asterisk in the list below.

**Associated Names:**

BRENT WOODWARD; BRINK CONSTRUCTORS; CAN-FER UTILITY SERVICES, LLC; DILLARD SMITH CONSTRUCTION; NORTH HOUSTON POLE LINE; NORTH HOUSTON POLE LINE LP; NOVA GROUP; PAR ELECTRICAL CONTRACTORS; POTELOCO; PRICE GREGORY INTL; QUANTA POWER GENERATION; SUMTER UTILITIES; SVC ELECTRIC; UTILIMAP

**Links:**

Subsidy Tracker data on financial assistance to this company by federal, state and local government agencies can be found [here](#).

Read more about this company's state and Federal tax payments (or lack thereof) on its CTJ-ITEP Corporate Tax Dodgers [page](#).

## Individual Penalty Records:

Download results as [CSV](#) or [XML](#)

Company	Primary Offense Type	Year	Agency	Penalty Amount
<a href="#">Price Gregory International, Inc.</a>	wage and hour violation	2015	WHD	\$239,784
<a href="#">Utilimap Corporation</a>	wage and hour violation	2010	WHD	\$165,976
<a href="#">DILLARD SMITH CONSTRUCTION COMPANY</a>	workplace safety or health violation	2012	OSHA	\$107,100
<a href="#">NOVA Group, Inc.</a>	wage and hour violation	2012	WHD	\$85,939
<a href="#">PAR ELECTRICAL CONTRACTORS</a>	workplace safety or health violation	2015	OSHA	\$58,435
<a href="#">Brent Woodward, Inc.</a>	wage and hour violation	2015	WHD	\$46,037
<a href="#">Nova Group, Inc.</a>	wage and hour violation	2015	WHD	\$32,800
<a href="#">Price Gregory International, Inc.</a>	wage and hour violation	2015	WHD	\$31,584
<a href="#">SERVICE ELECTRIC CO INC</a>	workplace safety or health violation	2013	OSHA	\$27,800
<a href="#">Brink Constructors, Inc</a>	wage and hour violation	2010	WHD	\$27,251

Company	Primary Offense Type	Year	Agency	Penalty Amount
<a href="#">PAR ELECTRICAL CONTRACTORS, INC.</a>	workplace safety or health violation	2014	OSHA	\$26,500
<a href="#">POTELCO INC</a>	workplace safety or health violation	2014	OSHA	\$26,500
<a href="#">PAR ELECTRICAL CONTRACTORS, INC.</a>	workplace safety or health violation	2012	OSHA	\$24,650
<a href="#">POTELCO INC</a>	workplace safety or health violation	2012	OSHA	\$21,000
<a href="#">PAR ELECTRICAL CONTRACTORS, INC.</a>	workplace safety or health violation	2011	OSHA	\$21,000
<a href="#">SUMTER UTILITIES, INC.</a>	workplace safety or health violation	2016	OSHA	\$21,000
<a href="#">POTELCO INC</a>	workplace safety or health violation	2011	OSHA	\$16,500
<a href="#">POTELCO INC</a>	workplace safety or health violation	2014	OSHA	\$14,100
<a href="#">NORTH HOUSTON POLE LINE LP</a>	workplace safety or health violation	2015	OSHA	\$14,000
<a href="#">PAR ELECTRICAL CONTRACTORS, INC.</a>	workplace safety or health violation	2015	OSHA	\$14,000
<a href="#">NORTH HOUSTON POLE LINE, L.P.</a>	workplace safety or health violation	2016	OSHA	\$12,471
<a href="#">PAR ELECTRICAL CONTRACTORS, INC.</a>	workplace safety or health violation	2013	OSHA	\$9,000
<a href="#">QUANTA POWER GENERATION, INC.</a>	workplace safety or health violation	2016	OSHA	\$8,500
<a href="#">NORTH HOUSTON POLE LINE</a>	workplace safety or health violation	2015	OSHA	\$7,000
<a href="#">SERVICE ELECTRIC COMPANY</a>	workplace safety or health violation	2013	OSHA	\$7,000
<a href="#">PRICE GREGORY INTERNATIONAL, INCORPORATED</a>	workplace safety or health violation	2015	OSHA	\$7,000
<a href="#">PAR ELECTRICAL CONTRACTORS, INC.</a>	workplace safety or health violation	2014	OSHA	\$7,000
<a href="#">PAR ELECTRICAL CONTRACTORS, INC.</a>	workplace safety or health violation	2016	OSHA	\$7,000
<a href="#">CAN-FER UTILITY SERVICES, LLC</a>	workplace safety or health violation	2013	OSHA	\$5,600
<a href="#">SUMTER UTILITIES</a>	workplace safety or health violation	2012	OSHA	\$5,390
<a href="#">PRICE GREGORY INTERNATIONAL, INC.</a>	workplace safety or health violation	2010	OSHA	\$5,000

Download results as [CSV](#) or [XML](#)



Note: our penalty amounts include not only fines and monetary settlements but also costs such as supplementary environmental projects or consumer relief that companies are often compelled to undertake as part of settlements. If the settlement includes fines paid to state governments, those are included as well.

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## News Releases from Region 01

### Connecticut Power Company Settles with EPA for Transformer Spill

08/03/2016

**Contact Information:**

David Deegan ([deegan.dave@epa.gov](mailto:deegan.dave@epa.gov))  
617-918-1017

**BOSTON** – The Connecticut Light and Power Company has agreed to pay \$47,000 to settle claims by the US Environmental Protection Agency that it violated federal regulations in its management of a transformer that spilled 50 gallons of oil containing PCBs at a location in Waterbury.

EPA alleged that violations of the federal Toxics Substances Control Act occurred at a transformer at 130 Freight St., home to a client of the power company. The transformer was owned by the power company, which is doing business as Eversource Energy. Eversource was responsible for the storage and removal of the transformer.

Eversource has since removed and shipped for disposal the PCB-contaminated transformer and contaminated soil and concrete. About 70 cubic yards of material was removed as a result of the cleanup, according to Eversource officials. Connecticut Light and Power has now properly disposed of the transformer and cleaned the area where it stood.

"The toxic substances law is in place to make sure the public and the environment are protected from the potential damage of chemicals such as PCBs," said Curt Spalding, regional administrator of EPA's New England office.

The transformer was reportedly vandalized in September of 2014 and several key components were stolen. On Sept. 24 of that year, Eversource, then known as Northeast Utilities, took the transformer off line but due to an oversight did not remove it for over a year. In January of 2016, Eversource discovered the transformer had been vandalized again and a spill had occurred. The company estimated about 50 gallons of oil with a PCB concentration of 318 parts per million had been released.

Among the violations:

- The PCB spill onto the concrete pad and soil constitutes improper disposal of PCBs.
- The transformer was stored for disposal more than 30 days without the facility receiving an EPA identification number.

- The PCB-contaminated transformer was stored for disposal more than 30 days in an area which did not meet the storage requirements of the law.
- The transformer was not disposed of within a year of the date the item was determined to be waste.
- The transformer was not inspected every 30 days for leaks and records of leak inspections were not maintained as required.

More information on PCBs and regulations on their management  
([www.epa.gov/pcbs](http://www.epa.gov/pcbs))

LAST UPDATED ON AUGUST 3, 2016

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

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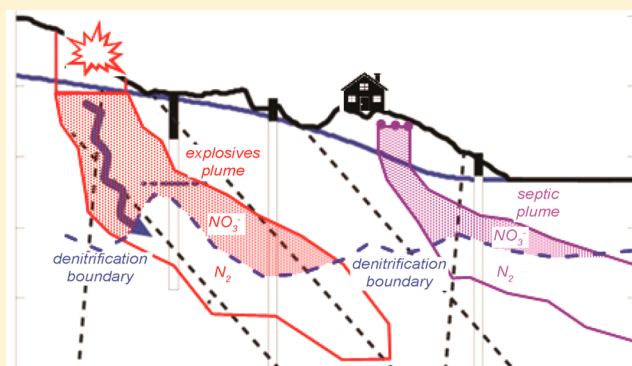
<sup>§</sup>New Hampshire Dept. of Transportation, Bureau of Materials and Research, 5 Hazen Drive, Concord, New Hampshire 03301, United States

<sup>||</sup>Hoyle, Tanner & Associates, Inc., I-93 Exit 3 Project Field Office, 77 Indian Rock Road, Windham, New Hampshire 03087, United States

<sup>⊥</sup>U.S. Geological Survey, Box 628, Montpelier, Vermont 05602, United States

## Supporting Information

**ABSTRACT:** Explosives used in construction have been implicated as sources of  $\text{NO}_3^-$  contamination in groundwater, but direct forensic evidence is limited. Identification of blasting-related  $\text{NO}_3^-$  can be complicated by other  $\text{NO}_3^-$  sources, including agriculture and wastewater disposal, and by hydrogeologic factors affecting  $\text{NO}_3^-$  transport and stability. Here we describe a study that used hydrogeology, chemistry, stable isotopes, and mass balance calculations to evaluate groundwater  $\text{NO}_3^-$  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  $\text{NO}_3^-$  (low  $\delta^{15}\text{N}$ , high  $\delta^{18}\text{O}$ ) from dissolution of unexploded  $\text{NH}_4\text{NO}_3$  blasting agents in oxic groundwater; (2) delayed and reduced breakthrough of synthetic  $\text{NO}_3^-$  subjected to partial denitrification (high  $\delta^{15}\text{N}$ , high  $\delta^{18}\text{O}$ ); (3) relatively persistent concentrations of blasting-related biogenic  $\text{NO}_3^-$  derived from nitrification of  $\text{NH}_4^+$  (low  $\delta^{15}\text{N}$ , low  $\delta^{18}\text{O}$ ); and (4) stable but spatially variable biogenic  $\text{NO}_3^-$  concentrations, consistent with recharge from septic systems (high  $\delta^{15}\text{N}$ , low  $\delta^{18}\text{O}$ ), variably affected by denitrification. Source characteristics of denitrified samples were reconstructed from dissolved-gas data ( $\text{Ar}$ ,  $\text{N}_2$ ) and isotopic fractionation trends associated with denitrification ( $\Delta\delta^{15}\text{N}/\Delta\delta^{18}\text{O} \approx 1.31$ ). 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 ( $\text{NO}_3^-$ ) contamination of groundwater.<sup>1–4</sup> Hundreds to tens of thousands of kg of  $\text{NO}_3^-$  are typically used at a construction site. Nitrate is a component of ammonium nitrate ( $\text{NH}_4\text{NO}_3$ ), which is approximately 90% of commonly used commercial explosives by weight.<sup>5</sup> Bulk emulsions injected into blasting holes typically consist of  $\text{NH}_4\text{NO}_3$  and fuel oil (ANFO). High  $\text{NO}_3^-$  concentrations in groundwater affected by explosives could be related to several different processes, including (1) leaching of  $\text{NO}_3^-$  from unexploded  $\text{NO}_3^-$ -bearing explosive compounds such as  $\text{NH}_4\text{NO}_3$ ;<sup>1</sup> (2) oxidation (nitrification) of reduced N components of explosives such as  $\text{NH}_4\text{NO}_3$ , TNT, RDX, etc.; and (3) injection of soluble  $\text{NH}_3$  or  $\text{NO}_x$  gases into

the subsurface by blasting.<sup>4</sup> 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,<sup>1,6</sup> which could be a substantial contribution to groundwater recharge locally.

Previous studies have reported (1) high concentrations of  $\text{NO}_3^-$  and related compounds in groundwater at mines, quarries,<sup>2,3</sup> and other environments exposed to heavy explosives use; (2) isotopic fractionation of N in explosive compounds caused by biodegradation;<sup>7</sup> (3) occurrence of isotopically

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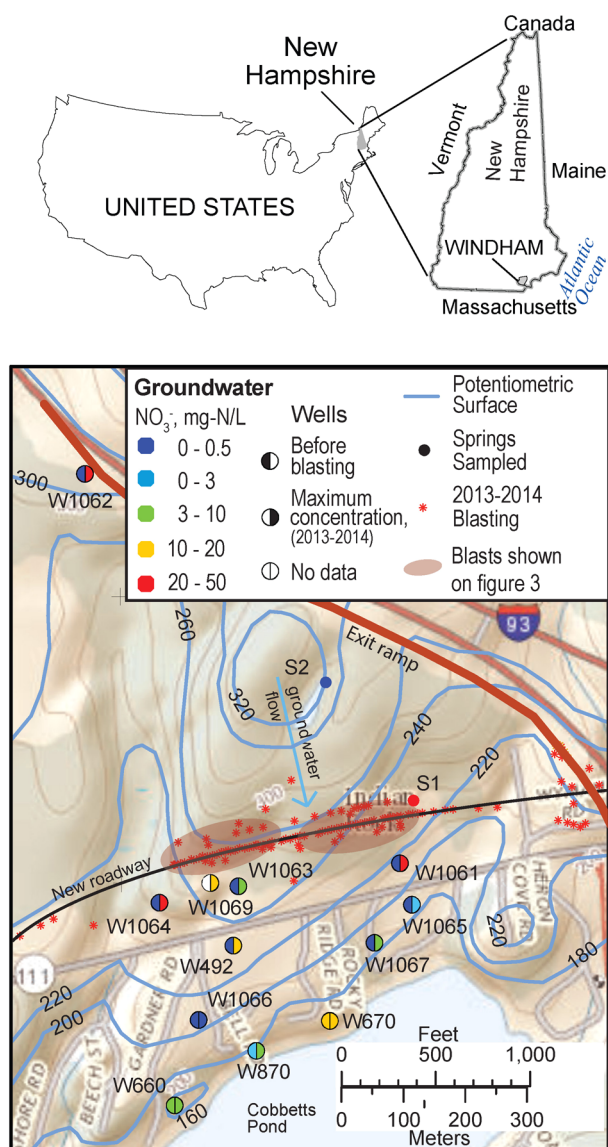
anomalous  $\text{NO}_3^-$  that may have been derived from nitrification of reduced N in explosive compounds;<sup>8,9</sup> and (4) elevated concentrations of dissolved constituents from enhanced weathering of blasted rock fragments.<sup>1</sup> In New Hampshire and elsewhere, rock excavation for highway construction commonly requires blasting with  $\text{NH}_4\text{NO}_3$ -based explosive emulsions. Elevated concentrations of  $\text{NO}_3^-$  in groundwater have been attributed to blasting in New Hampshire,<sup>10–15</sup> but direct forensic evidence of  $\text{NO}_3^-$  sources is lacking. Nitrate concentrations in groundwater in the region typically are low ( $<1$  mg-N/L),<sup>16,17</sup> 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  $\text{NO}_3^-$  sources include wastewater disposal (e.g., septic systems), fertilizers used in landscaping and agriculture, atmospheric deposition, and weathering of soils and rocks.<sup>18–22</sup>

Isotope ratios of N ( $\delta^{15}\text{N}$ ) and O ( $\delta^{18}\text{O}$ ) have been used to evaluate sources of groundwater  $\text{NO}_3^-$  contamination in agricultural, urban, and other settings,<sup>23–29</sup> but apparently have not been thoroughly tested for identifying sources of  $\text{NO}_3^-$  near blasting sites in fractured-bedrock aquifer settings. Nitrate from unexploded  $\text{NH}_4\text{NO}_3$  may be recognizable isotopically as synthetic  $\text{NO}_3^-$  if not altered by biologic activity. However, denitrification (microbial reduction of  $\text{NO}_3^-$  to  $\text{N}_2$  gas) can alter the isotopic composition of the remaining  $\text{NO}_3^-$ . Blasting-related reduced N may be microbially oxidized (nitrified), yielding biogenic  $\text{NO}_3^-$  with an isotopic composition different from that of synthetic  $\text{NO}_3^-$ . In addition, groundwater transport of  $\text{NH}_4^+$  from blasting sites can be retarded by ion exchange with solid phases in soils and aquifers. Thus, it is possible that synthetic  $\text{NO}_3^-$  could move away from a source first, followed by  $\text{NH}_4^+$  that, if oxidized gradually, could generate a secondary and possibly more persistent  $\text{NO}_3^-$  pulse with modified isotopic composition. Despite these potential complications, blasting-related  $\text{NO}_3^-$  may be distinguishable from other  $\text{NO}_3^-$  contamination sources including agriculture and wastewater disposal.

This study tested whether isotopic analyses can identify blasting-related  $\text{NO}_3^-$  in groundwater in an area of road construction. Stable isotope ratios in  $\text{H}_2\text{O}$ ,  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , and  $\text{N}_2$  were used to identify sources, transport pathways, and transformation processes of  $\text{NO}_3^-$ . 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  $\text{NO}_3^-$  sources including an unmodified synthetic  $\text{NO}_3^-$  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)  $\text{NO}_3^-$  characteristics and reduce uncertainties in source attributions. Approaches used to identify  $\text{NO}_3^-$  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  $\text{m}^3$  of bedrock was removed by blasting.<sup>30</sup> Blasting was done in 2009 to create an exit ramp<sup>31</sup> and was resumed in 2013–2014 to create a new roadway.<sup>30,32</sup> The total mass of blasting compounds used in 2013–2014 was approximately 221 000



**Figure 1.** Map<sup>40</sup> 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  $\text{NO}_3^-$  concentrations (Table S2)<sup>41–43</sup> indicated by colors on the left and right sides of the symbols, respectively.

kg, largely in the form of bulk emulsions of ANFO ( $\text{NH}_4\text{NO}_3$  plus additives) (Supporting Information Table S3).

Thin ( $<3$  m) glacial till overlies igneous and metamorphic bedrock in the study area.<sup>33</sup> The bedrock is Silurian-age metasedimentary rock intruded by multiple phases of Devonian-age granite.<sup>34–36</sup> A potentiometric-surface map (Figure 1) was produced from existing water level-data,<sup>37–39</sup> 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.<sup>40</sup> 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.<sup>41,42</sup> Nineteen open-bedrock-borehole drinking-water wells were sampled monthly during blasting activities (2013–2014) for analyses including  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ , and  $\text{NH}_4^+$  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  $\text{NO}_3^-$  concentrations had been reported.<sup>41</sup> 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.<sup>43</sup> 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 ( $\text{NO}_3^-$ ,  $\text{NH}_4^+$  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 ( $\text{O}_2$ ) concentrations were measured in the field.<sup>44</sup> Water samples were analyzed in the laboratory for selected major elements and ions (B, Ca, Mg, Na,  $\text{Br}^-$ ,  $\text{Cl}^-$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{SO}_4^{2-}$ ), dissolved gases ( $\text{O}_2$ , Ar,  $\text{N}_2$ ,  $\text{CH}_4$ ), VOCs, and stable isotope ratios ( $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  of  $\text{H}_2\text{O}$ ,  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$ ,  $\delta^{15}\text{N}$  of  $\text{NH}_4^+$  and  $\text{N}_2$ ). Samples from drinking-water wells were collected and analyzed by the NHDOT contractor for major elements and ions, and VOCs.<sup>41,42,45</sup> NHDOT data included alkalinities and total Fe concentrations for a limited number of samples, yielding charge balances given by: anion equivalents =  $1.11 \times$  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.<sup>46,47</sup> Redox conditions relevant to  $\text{NO}_3^-$  transport were evaluated using a combination of  $\text{O}_2$ ,  $\text{NO}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NH}_4^+$ , Fe, and excess  $\text{N}_2$  data<sup>48,49</sup> (see below).

Dissolved-gas concentrations were measured in the USGS Reston Groundwater Dating Laboratory.<sup>50</sup> Stable isotope ratios were measured in the USGS Reston Stable Isotope Laboratory.<sup>46</sup> 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,

$\text{N}_2$ , and  $\delta^{15}\text{N}$  of  $\text{N}_2$ ) for each sample were used to quantify the effects of denitrification on the concentration and isotopic composition of  $\text{NO}_3^-$  by reconstructing the initial recharge (predenitrification)  $\text{NO}_3^-$  concentration and isotopic composition using methods described in previous studies<sup>51–54</sup> as described below and in the Supporting Information.

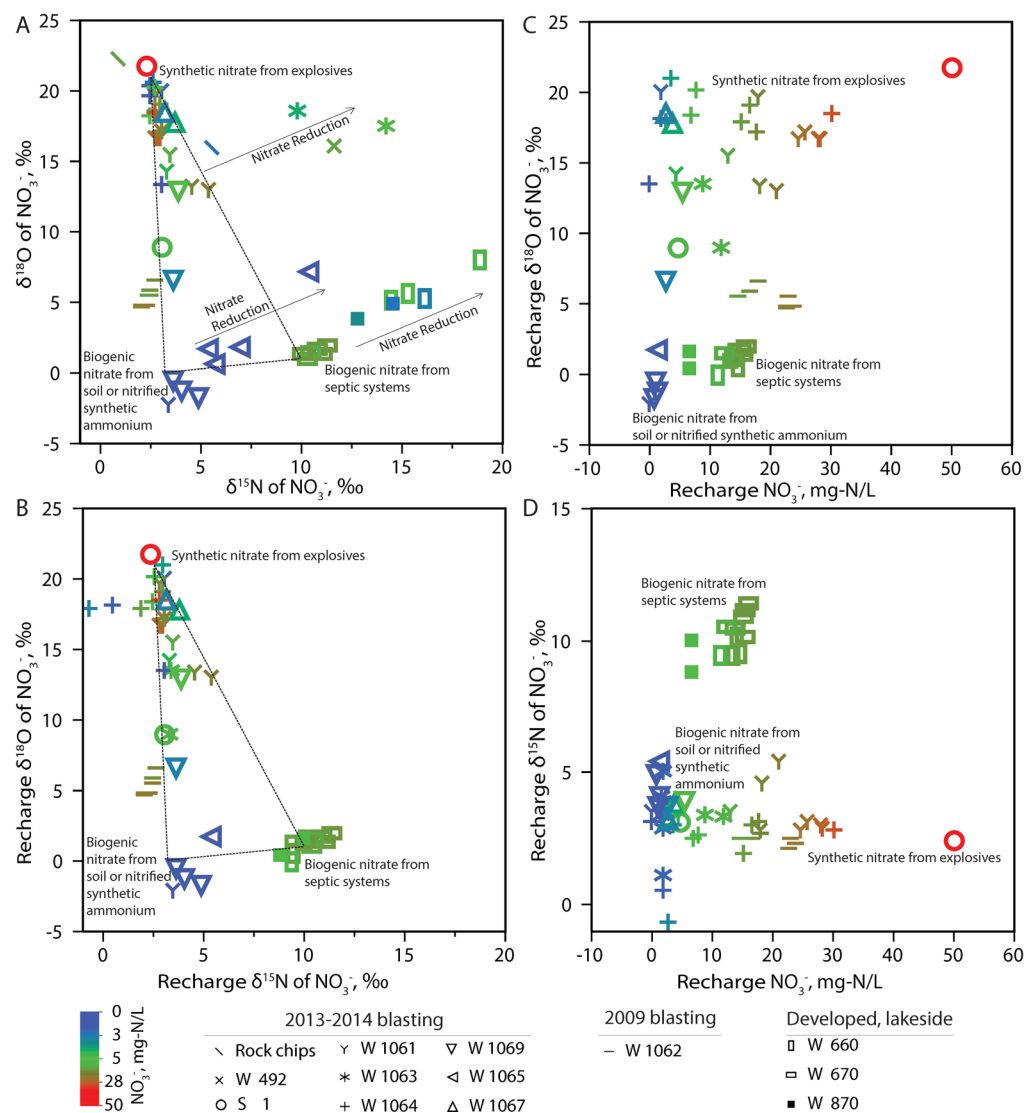
## RESULTS AND DISCUSSION

Nitrate concentrations and isotopic compositions of many samples were affected by blasting. Isotope data indicated multiple  $\text{NO}_3^-$  sources (synthetic and biogenic), but reducing conditions in the aquifer caused substantial changes in  $\text{NO}_3^-$  concentrations and isotopic characteristics in many cases. Reconstruction of initial (recharge)  $\text{NO}_3^-$  concentrations and isotopic compositions using dissolved gas data improved the definition and attribution of  $\text{NO}_3^-$  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  $\text{NO}_3^-$  concentrations reflected land use.<sup>40</sup> Groundwater beneath forested land cover adjacent to the new roadway did not have detectable  $\text{NO}_3^-$  ( $\leq 0.04$  mg-N/L, W1063, W1064) before blasting. Nitrate was not detected ( $\leq 0.04$  mg-N/L, S2) in groundwater discharging from an upgradient spring on forested land. Groundwater beneath developed land had moderate -to-high  $\text{NO}_3^-$  concentrations (e.g., 5.3 mg/L W660, 15.6 mg/L W670) throughout the study period. Groundwater  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_3^-$ -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<sup>1,6</sup> 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  $\text{NO}_3^-$  and half in the form of  $\text{NH}_4^+$ . 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<sup>55</sup> could yield a mean concentration between 10 and 600 mg-N/L, more than enough to account for documented occurrences of transient, heterogeneously distributed  $\text{NO}_3^- \pm \text{NH}_4^+$  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  $\text{NO}_3^-$ . Hydroseeding fertilizer did not contain  $\text{NO}_3^-$  and was mostly in the form of  $\text{CO}(\text{NH}_2)_2$ , but portions not assimilated by plants could have been nitrified in soils.



**Figure 2.** Isotopic and chemical data for  $\text{NO}_3^-$ . (A) Measured  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  indicating various sources and varying effects of denitrification (nitrate reduction), with  $\Delta\delta^{15}\text{N}/\Delta\delta^{18}\text{O} \approx 1.31$  (best fit to data from W660, W670, and W870); (B) Recharge (including measured and reconstructed, predenitrification)  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  indicating three major sources (end members) and possible mixtures (i.e., adjusted version of panel A); (C) Recharge  $\text{NO}_3^-$  concentrations and  $\delta^{18}\text{O}$  values; (D) Recharge  $\text{NO}_3^-$  concentrations and  $\delta^{15}\text{N}$  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  $\text{NO}_3^-$  in groundwater,<sup>56</sup> and the distributions of  $\text{NO}_3^-$  before and after blasting were consistent with septic-system sources in some residential wells.  $\text{NO}_3^-$  concentrations in residential areas were inversely proportional to lot size (Tables S1). Groundwater  $\text{NO}_3^-$  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.<sup>21,22,56</sup>

Another potential source of  $\text{NO}_3^-$  is atmospheric deposition, but total maximum annual N deposition fluxes (Table S5) are small ( $\leq 10$  kg/ha) compared to the locally high fluxes from blasting and septic systems. Background  $\text{NO}_3^-$  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,<sup>16,17</sup> consistent with relatively small  $\text{NO}_3^-$  inputs from atmospheric deposition, or from decay of organic matter, or weathering of minerals (e.g., illite, biotite) containing  $\text{NH}_4^+$  in soils or metamorphic rocks.<sup>57,58</sup>

#### Isotopic Composition of Nitrate and Ammonium.

Stable isotope ratios of N and O in groundwater  $\text{NO}_3^-$  provided evidence of multiple sources of  $\text{NO}_3^-$  (Figure 2A).  $\delta^{18}\text{O}$  values ranged from  $-2.2$  to  $+21.7$ ‰ and  $\delta^{15}\text{N}$  values ranged from  $+2.1$  to  $+18.9$ ‰. Most samples with high  $\text{NO}_3^-$  concentrations, including samples from the blasting-site spring (S1) and wells adjacent to, and downgradient from blasting (W1061 and W1064), had relatively low  $\delta^{15}\text{N}$  values ( $+1$  to  $+3$ ‰) and high  $\delta^{18}\text{O}$  values ( $+17$  to  $+23$ ‰) (Figure 2A). Similarly, leachate from blasted rock chips had  $\text{NO}_3^-$  with  $\delta^{15}\text{N} = 1$ –6‰ and  $\delta^{18}\text{O} = 16$ –22‰ (Table S2). These isotope ratios are different from those of biogenic soil  $\text{NO}_3^-$  (formed by nitrification) and more like those of common synthetic  $\text{NO}_3^-$  sources.<sup>59,60</sup> Some samples with relatively low  $\delta^{15}\text{N}$  also had low  $\delta^{18}\text{O}$ , indicating sources such as nitrification of N from



Table 1. Chemical and Isotopic Data for a Subset of Representative Settings and Sample Dates<sup>a</sup>

ID	sample date	comment	O <sub>2</sub>	SC	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	NO <sub>3</sub> <sup>-</sup>	NO <sub>3</sub> <sup>-</sup>
			mg/L	μS/cm	mg-N/L	mg-N/L	δ <sup>15</sup> N ‰	δ <sup>15</sup> N ‰	δ <sup>18</sup> O ‰
<b>S2</b>	<b>4/15/2014</b>	<b>upgradient spring, background</b>		<b>68</b>	<b>&lt;0.010</b>	<b>&lt;0.04</b>			
W1064	4/18/2013	2013 preblasting, forest	7.5	95	<0.010	<0.04			
<b>W1063</b>	<b>4/18/2013</b>	<b>2013 preblasting, forest, low O<sub>2</sub></b>	<b>0.3</b>	<b>324</b>	<b>&lt;0.010</b>	<b>&lt;0.04</b>			
W1061	4/18/2013	2013 preblasting, developed	4.0	116	<0.010	0.13		3.5	-2.2
<b>S1</b>	<b>6/25/2013</b>	<b>2013 postblast, synthetic NO<sub>3</sub><sup>-</sup></b>	<b>5.6</b>	<b>610</b>	<b>21.16</b>	<b>50.23</b>	<b>2.0</b>	<b>2.4</b>	<b>21.7</b>
<b>W1061</b>	<b>2/4/2014</b>	<b>2013 postblast, synthetic NO<sub>3</sub><sup>-</sup></b>	<b>6.0</b>	<b>412</b>	<b>0.05</b>	<b>28.43</b>		<b>2.9</b>	<b>16.7</b>
<b>W1064</b>	<b>10/16/2014</b>	<b>2013 postblast, synthetic NO<sub>3</sub><sup>-</sup></b>	<b>1.2</b>	<b>596</b>	<b>0.04</b>	<b>30.31</b>		<b>2.8</b>	<b>18.5</b>
W492	10/16/2014	2013 postblast, low O <sub>2</sub>	0.1	580	0.01	13.71		11.7	16.1
W1063	10/16/2014	2013 postblast, low O <sub>2</sub>	0.1	378	< 0.010	5.20		14.3	17.5
<b>S1</b>	<b>4/15/2014</b>	<b>2013 postblast, mixed source</b>		<b>215</b>	<b>0.02</b>	<b>4.82</b>		<b>3.1</b>	<b>8.9</b>
<b>W1061</b>	<b>10/16/2014</b>	<b>2013 postblast, mixed source</b>	<b>4.8</b>	<b>636</b>	<b>&lt; 0.010</b>	<b>21.13</b>		<b>5.4</b>	<b>13.0</b>
W1062	6/10/2014	2009 postblast	2.1	2117	0.34	14.70	11.1	2.5	5.5
<b>W1062</b>	<b>10/16/2014</b>	<b>2009 postblast, low O<sub>2</sub></b>	<b>0.1</b>	<b>2121</b>	<b>0.33</b>	<b>18.00</b>		<b>2.7</b>	<b>6.5</b>
W670	6/25/2013	septic, developed	4.9	454	0.02	16.13		11.4	1.9
<b>W660</b>	<b>6/25/2013</b>	<b>septic, developed, low O<sub>2</sub></b>	<b>0.6</b>	<b>590</b>	<b>0.01</b>	<b>5.32</b>		<b>15.3</b>	<b>5.6</b>

<sup>a</sup>SC = specific conductance. Normal and bold fonts indicate groups of samples with common sources, settings, or O<sub>2</sub> 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<sub>3</sub><sup>-</sup>, such as W670 in a residential area near Cobbetts Pond with δ<sup>15</sup>N = +10.7 ± 0.5‰ and δ<sup>18</sup>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<sub>4</sub><sup>+</sup> concentrations generally were low (<0.01 mg-N/L), but a few samples near blasting sites had elevated NH<sub>4</sub><sup>+</sup> (0.01–21.1 mg-N/L) that may represent ANFO contamination (Table 1). For example, blasting-site spring S1 had NH<sub>4</sub><sup>+</sup> = 21.1 mg-N/L with δ<sup>15</sup>N = +2.0‰, which is consistent with contamination by synthetic NH<sub>4</sub><sup>+</sup>. Blasted rock chips had δ<sup>15</sup>N = +1 to +4‰ in leachate-extractable NH<sub>4</sub><sup>+</sup> and δ<sup>15</sup>N = +2 to +5‰ in total N. This material apparently contained residues of synthetic NO<sub>3</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> from explosives, plus nonextractable N that could include soil, rock, or other explosive components, which may have been partially oxidized to NO<sub>3</sub><sup>-</sup>. Hydroseeding fertilizer samples had bulk δ<sup>15</sup>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<sub>3</sub><sup>-</sup> 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<sub>4</sub><sup>+</sup> (0.8 mg-N/L) with δ<sup>15</sup>N = +8.7‰. This δ<sup>15</sup>N value is higher than those of likely NH<sub>4</sub><sup>+</sup> 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<sub>4</sub><sup>+</sup>. Nitrate in W1062 had relatively low δ<sup>15</sup>N (2.4 ± 0.2‰) and δ<sup>18</sup>O (5.4 ± 0.7‰) values; the δ<sup>18</sup>O value was low compared to most blasting-related NO<sub>3</sub><sup>-</sup>. Data from this well may indicate that residual synthetic NH<sub>4</sub><sup>+</sup> from blasting was being gradually nitrified, yielding groundwater with a mixture of blasting-related NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup>, 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<sub>3</sub><sup>-</sup> had slightly elevated NO<sub>2</sub><sup>-</sup> (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<sub>3</sub><sup>-</sup> with spatial and temporal variability, the NO<sub>3</sub><sup>-</sup> also was variably affected by isotopic fractionation associated with denitrification as indicated by excess N<sub>2</sub> gas in some samples with low O<sub>2</sub> concentrations. Because denitrification locally affected NO<sub>3</sub><sup>-</sup> from various sources, the NO<sub>3</sub><sup>-</sup> 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<sub>3</sub><sup>-</sup> concentrations and associated isotope ratios in recharge, which, in turn, allowed for improved source attribution of NO<sub>3</sub><sup>-</sup>, 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<sub>3</sub><sup>-</sup> concentrations and altered NO<sub>3</sub><sup>-</sup> isotope ratios locally, complicating NO<sub>3</sub><sup>-</sup> source identification. Low O<sub>2</sub> concentrations (<1 mg/L) and positive correlations between δ<sup>18</sup>O and δ<sup>15</sup>N values of NO<sub>3</sub><sup>-</sup> indicated denitrifying conditions and isotope fractionation effects in some wells (Figure 2A). For example, δ<sup>15</sup>N and δ<sup>18</sup>O values of NO<sub>3</sub><sup>-</sup> in wells in residential areas (W660, W670, W870) were positively correlated (R<sup>2</sup> = 0.96, N = 10) and generally increased with decreasing NO<sub>3</sub><sup>-</sup> concentrations, consistent with varying degrees of denitrification.<sup>61</sup> Similar fractionations apparently affected NO<sub>3</sub><sup>-</sup> isotopic composition in other wells such as W1065 and W492 (Figure 2A).

For each sample the concentration of excess N<sub>2</sub> attributable to denitrification was estimated from concentrations of Ar and N<sub>2</sub> (assuming a narrow range of excess air concentrations and seasonally varying recharge temperatures, discussed further in the Supporting Information). Subsequently, the estimated concentration and δ<sup>15</sup>N value of excess N<sub>2</sub> were combined with measured values for NO<sub>3</sub><sup>-</sup> to reconstruct the initial values for NO<sub>3</sub><sup>-</sup> (NO<sub>3</sub><sup>-</sup> in recharge, prior to denitrification in the saturated zone), according to methods described previously.<sup>51,52,54</sup> Measured δ<sup>15</sup>N values of total N<sub>2</sub> 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 ( $\Delta\delta^{15}N/\Delta\delta^{18}O \approx 1$ ),<sup>61</sup> and analyses of  $NO_3^-$  in reducing groundwater commonly yield apparent  $\Delta\delta^{15}N/\Delta\delta^{18}O$  ratios between 1 and 2.<sup>26,59,62</sup> 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 ( $\pm 0.6$  mg-N/L), estimated typical uncertainties associated with the reconstruction method were approximately  $\pm 0.6$  mg-N/L for  $NO_3^-$ ,  $\pm 0.5\text{‰}$  for  $\delta^{15}N$ , and  $\pm 0.5\text{‰}$  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,<sup>16</sup> 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  $NO_3^-$  concentrations (6.6–16.1 mg-N/L) but similar  $\delta^{15}N[NO_3^-]$  values ( $+10\text{‰}$ )

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  $NO_3^-$  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.<sup>63</sup>

The synthetic  $NO_3^-$  end member in our study is at the apex of the dual isotope plot with  $\delta^{15}N \approx +2.5 \pm 0.5\text{‰}$  and  $\delta^{18}O \approx +21 \pm 1\text{‰}$  and is well represented by groundwater draining a blasted rock pile at S1 ( $\delta^{15}N = +2.4\text{‰}$ ,  $\delta^{18}O = +21.7\text{‰}$ ) (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  $\pm 2\text{‰}$  and almost all to within  $\pm 4\text{‰}$ .<sup>20,59,64–67</sup> 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  $-0.9 \pm 1.9\text{‰}$  for  $NH_4^+$  and  $+2.8 \pm 1.8\text{‰}$  for  $NO_3^-$ .<sup>65</sup> Synthetic  $NO_3^-$  typically has  $\delta^{18}O$  values near that of atmospheric  $O_2$  ( $+24\text{‰}$ ) or slightly lower. One study reported  $\delta^{18}O$  values for nitrate in  $NH_4NO_3$  ranging from  $+17$  to  $+25\text{‰}$ , with the “majority” between  $+21$  and  $+24\text{‰}$ .<sup>64</sup> Other reported mean values were  $+23 \pm 3\text{‰}$  for  $\delta^{18}O$  and  $0 \pm 2$  for  $\delta^{15}N$  for  $NO_3^-$  in synthetic fertilizer and reagent sources.<sup>60</sup> 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.<sup>68</sup>

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.<sup>69</sup> 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.

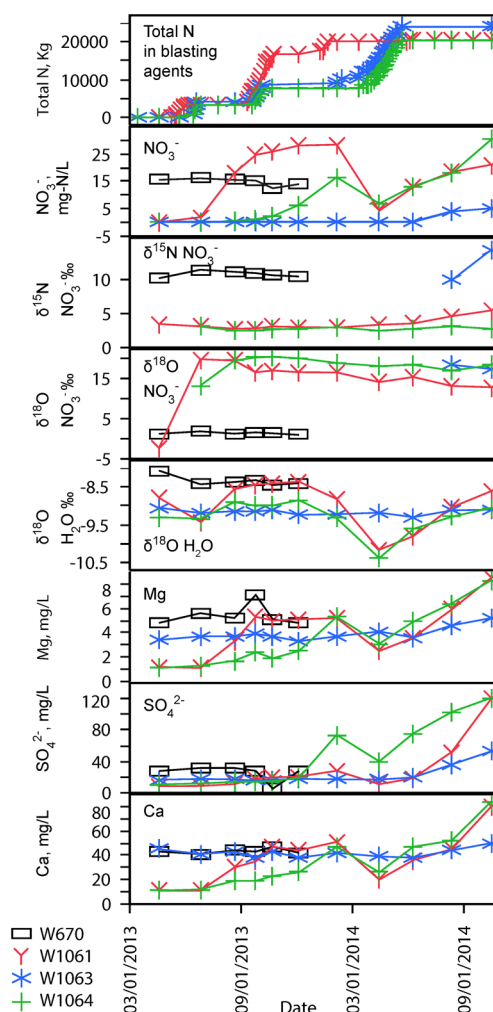
The second  $\text{NO}_3^-$  isotopic end member (Figure 2B, lower left corner of triangle), with low  $\delta^{18}\text{O}$  (Figure 2C) and low  $\delta^{15}\text{N}$  (Figure 2D), apparently occurred in some wells affected by blasting, in which case the  $\text{NO}_3^-$  may have formed by nitrification of synthetic  $\text{NH}_4^+$  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  $\text{NO}_3^-$  with low  $\delta^{15}\text{N}$  and high  $\delta^{18}\text{O}$ , some older blasting-related  $\text{NO}_3^-$  (2009, W1062) had low  $\delta^{15}\text{N}$  and low  $\delta^{18}\text{O}$  ( $+2.4\text{‰} \pm 0.2$  and  $+5.4\text{‰} \pm 0.7$ ,  $N = 7$ ), indicating a substantial component of the  $\text{NO}_3^-$  may have been nitrified synthetic  $\text{NH}_4^+$ . Nitrification of blasting-related  $\text{NH}_4^+$  was indicated in some wells by temporal sampling (see below). The isotopic composition of this biogenic  $\text{NO}_3^-$  endmember was not well constrained and may be somewhat variable ( $\delta^{15}\text{N} \approx +3 \pm 2\text{‰}$ ,  $\delta^{18}\text{O} \approx 0 \pm 2\text{‰}$ ). Slightly positive  $\delta^{15}\text{N}$  values were higher than those of most synthetic  $\text{NH}_4^+$  products, possibly indicating mixed reduced N sources or late products of previously fractionated synthetic  $\text{NH}_4^+$ . Nitrate at W1062 appeared to be a mixture of synthetic and biogenic sources, and was accompanied by elevated  $\text{NH}_4^+$  that apparently was isotopically fractionated (enriched in  $^{15}\text{N}$ ) by partial nitrification. This end member may be difficult to distinguish from  $\text{NO}_3^-$  produced by nitrification of reduced N from inorganic fertilizers or plant residues in an agricultural setting. Similar isotopic characteristics in wells with low  $\text{NO}_3^-$  concentrations could indicate natural background  $\text{NO}_3^-$  from soil sources.<sup>70</sup>

The third  $\text{NO}_3^-$  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  $\text{N}_2$ , 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  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of reconstructed  $\text{NO}_3^-$  were indistinguishable from the measured values at W670 (no denitrification); thus a septic-system  $\text{NO}_3^-$  end member was derived from measured data for W670 and reconstructed data for W660 and W870, giving  $\delta^{15}\text{N}$  of  $+10.1 \pm 0.8\text{‰}$  and  $\delta^{18}\text{O}$  of  $+1.1 \pm 0.6\text{‰}$  (Figure 2B, lower right corner of triangle).

Mixing of  $\text{NO}_3^-$  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  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  values in late samples from spring S1 (April, 2014) and wells W1062, W1063, and W1069 could indicate mixtures of synthetic  $\text{NO}_3^-$  with biogenic  $\text{NO}_3^-$  derived from nitrification of synthetic  $\text{NH}_4^+$  or other reduced N. Nitrate with a wide range of  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values may also come from nitrification, degradation, or from the postblast residues of other more complex explosive compounds containing reduced N,<sup>8,9,71</sup> but these compounds were not used in a large quantity at this site (Tables S3 and S4).

Other (nonisotopic) indicators of  $\text{NO}_3^-$  sources also were evaluated (Table S2). Perchlorate ( $\text{ClO}_4^-$ ) was analyzed in representative samples because it is a common blasting-agent component, though its use was not documented in the study area.  $\text{ClO}_4^-$  concentrations ranged from 0.03 to 0.80  $\mu\text{g/L}$ , which is within the range of values reported elsewhere for groundwater not affected substantially by local contamination sources but including domestic wastewater.<sup>72–74</sup> Thus, although  $\text{ClO}_4^-$  is a component of explosives in some settings, it apparently was not substantially enriched in blasting-affected

groundwater at this site (Table S2).<sup>1,75</sup> Some wells affected by blasting had elevated concentrations of Ca, Mg, and  $\text{SO}_4^{2-}$  (Figure 3), possibly from enhanced weathering of blasted rock.<sup>1</sup>



**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).  $\text{NO}_3^-$  concentrations and isotopic compositions are as measured.

Chloride concentrations and Cl/Br ratios were highest in some wells containing synthetic  $\text{NO}_3^-$ , 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  $\text{NO}_3^-$  from septic systems.

**Timing of Groundwater Responses to Contamination Sources.** Temporal variations in chemistry and isotopes at some wells provided additional evidence of  $\text{NO}_3^-$  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  $\text{NO}_3^-$



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  $\text{NO}_3^-$  increases at both wells were accompanied by rapid increases in  $\delta^{18}\text{O}$  of the  $\text{NO}_3^-$ , indicating that small amounts of synthetic  $\text{NO}_3^-$  quickly dominated the low background  $\text{NO}_3^-$  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  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of  $\text{H}_2\text{O}$  indicating changing recharge conditions, and in Mg,  $\text{SO}_4^{2-}$ , and Ca concentrations indicating transient dilution. The  $\text{H}_2\text{O}$  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  $\text{NO}_3^-$ , 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  $\text{NH}_4^+$  in oxic groundwater produced  $\text{NO}_3^-$  with different isotopic composition than  $\text{NO}_3^-$  leached directly from blasting compounds. For example, after blasting operations progressed westward, away from W1061 and toward W1064,  $\text{NO}_3^-$  concentrations at W1061 remained elevated but the  $\text{NO}_3^-$  had progressively lower  $\delta^{18}\text{O}$  values and higher  $\delta^{15}\text{N}$  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  $\delta^{18}\text{O}$  of  $\text{NO}_3^-$  (S1, 8.9‰), closer to the W1062 values (Figures 2A and 3), indicating a mixture of synthetic  $\text{NO}_3^-$  with biogenic  $\text{NO}_3^-$  from nitrification of reduced N. These changes are interpreted as evidence for delayed arrival of  $\text{NO}_3^-$  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  $\text{O}_2$  concentrations. This response is interpreted to indicate nitrification of sorbed  $\text{NH}_4^+$  left over from blasting. These observations may indicate that initial flushing of the synthetic  $\text{NO}_3^-$  component of the explosives was followed by delayed and longer-lived flushing of biogenic  $\text{NO}_3^-$  derived from the synthetic  $\text{NH}_4^+$  component of the explosives, possibly accompanied by some fraction of the  $\text{NH}_4^+$  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  $\text{NH}_4^+$  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,  $\text{NO}_3^-$  was not detected in this well for the first 1.5 years of this study (Figure 3); however, anoxic conditions and excess  $\text{N}_2$  gas provided evidence that denitrification had occurred. Recon-

structed data (before denitrification) indicate that well W1063 originally had approximately 2 mg-N/L  $\text{NO}_3^-$  with 1–5‰  $\delta^{15}\text{N}$  (Table S2) consistent with a synthetic or natural N source, prior to direct  $\text{NO}_3^-$  detection (5.2 mg/L, Table 1). Initial  $\text{NO}_3^-$  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  $\text{N}_2$  approximately 1.5 years after 2013–2014 blasting commenced. This sequence appears to indicate denitrification protected W1063 from earlier low-level  $\text{NO}_3^-$  contamination, but the higher flux of  $\text{NO}_3^-$  after 2013 eventually exceeded the sustainable denitrification rate in the aquifer, causing delayed breakthrough of partially denitrified synthetic  $\text{NO}_3^-$  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  $\text{NO}_3^-$  for a period of time (Figure 3 and Figures S1 and S5).

In contrast to the relatively rapidly changing  $\text{NO}_3^-$  concentrations and isotope ratios in wells affected by blasting,  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$  values of  $\text{NO}_3^-$  were affected by denitrification more in some wells and less in others, they were relatively constant over time in each well. Similarly,  $\delta^2\text{H}$  and  $\delta^{18}\text{O}$  values of  $\text{H}_2\text{O}$  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  $\text{NO}_3^-$  contamination (including construction-related explosives), combined use of various chemical and isotopic analyses, reconstruction of  $\text{NO}_3^-$  affected by denitrification, mass balance calculations, and hydrogeologic information helped to resolve  $\text{NO}_3^-$  sources and transport processes. Four groundwater  $\text{NO}_3^-$  contamination scenarios were identified in this study: (1) rapid breakthrough of synthetic  $\text{NO}_3^-$  in proximal wells downgradient of blasting (low  $\delta^{15}\text{N}$  and high  $\delta^{18}\text{O}$ ), (2) reduced and delayed blasting-related  $\text{NO}_3^-$  concentration responses in wells with anoxic (denitrifying) conditions, (3) persistent  $\text{NO}_3^-$  in wells adjacent to blasted rock from nitrification of  $\text{NH}_4^+$  (low  $\delta^{15}\text{N}$  and low  $\delta^{18}\text{O}$ ), (4) relatively stable  $\text{NO}_3^-$  concentrations and isotopic compositions consistent with septic sources (high  $\delta^{15}\text{N}$  and low  $\delta^{18}\text{O}$ ). Because of the small scale and multidisciplinary approach of this study, likely  $\text{NO}_3^-$  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  $\text{NO}_3^-$  with high  $\delta^{18}\text{O}$  is unusual in groundwater and indicates rapid transmission and lack of cycling in soils.

Denitrification caused isotopic fractionation of residual  $\text{NO}_3^-$  with both septic and blasting sources. Wells that apparently were “protected” from  $\text{NO}_3^-$  contamination by denitrification

in anoxic conditions exhibited increases in blasting-related  $\text{NO}_3^-$  only after extended periods of blasting, possibly indicating high fluxes of synthetic  $\text{NO}_3^-$  locally exceeded the supply of electron donors in the aquifer. Groundwater with blasting-related  $\text{NO}_3^-$  moved rapidly, within six months of blasting, from construction sites to downgradient wells with oxic conditions. Elevated  $\text{NO}_3^-$  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  $\text{NO}_3^-$  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  $\text{NO}_x\text{-N}$  in blasting agents (Table S4) (XLSX)

Potential nitrogen sources upgradient of wells (Table S5) (XLSX)

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### Notes

The authors declare no competing financial interest.

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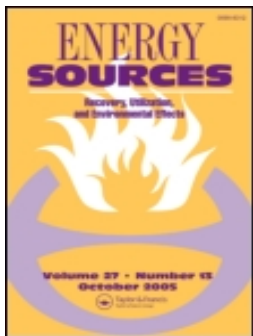


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# Physiochemical and leaching characteristics of fly and bottom ash

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## ABSTRACT

Bottom ash and fly ash are the by-products of coal in thermal power plants. They are the combustion wastes and contain many elements that may harmful to the environment. The present study investigates the physiochemical, mineral, and leaching characteristics of an Indian coal ash (bottom ash and fly ash). From the characterization of bottom ash and fly ash, it is found that the ash samples are enriched predominantly in silica, alumina, and iron oxides. A series of leaching experiments have been performed to analyze the tracing elements of metal at the different liquid to solid ratio (L/S). The L/S varies from 20:1 to 80:1. From the leaching results of the fly ash and bottom ash data, it is observed that the tracing elements of Mn, Mg, Cr, Zn, Ni, Pb, Fe, and Cu are the most abundant elements, while Hg, Mo, and Co are the least abundant elements.

## KEYWORDS

Ash disposal; bottom ash; fly ash; physiochemical; leaching characteristics

## 1. Introduction

Coal is the world's most abundant fossil fuel and its reserves are distributed in all the continents. Combustion of coal in thermal power plants generates a large amount of inorganic residues like bottom ash, fly ash slag, and flue gas desulfurization by-products, which have low values for utilization and have several environmental problems associated with their deposition (Blissett and Rowson, 2012; Kumar et al., 2013; Kumar et al., 2014). The quality of coal ash depends on the properties of coal, combustion efficiency, pulverized coal feed, and proper quality control in maintaining the particle size (Nayak et al., 1999; Gupta et al., 1998; Blissett and Rowson, 2012; Kumar et al., 2014). During hydraulic transportation and disposal, coal ash comes in contact with water. The tracing elements present in ash migrate to groundwater, surface water, and soil over a period of time. The production of a large amount of toxic metal elements in an ash disposal system of thermal power plants can pose negative environmental effects on human health and on plants (Tripathy and Mukherjee, 1997; Ugurlu, 2004; Baba et al., 2010; Blissett and Rowson, 2012). In the present study, an attempt has been made to investigate the physical, chemical, mineralogical, and leaching characteristics of fly ash and bottom ash disposed in an ash pond of the thermal power plant. The leaching test of heavy metals from fly ash and bottom ash was investigated in order to predict the environmental effect from the ash disposal on the groundwater quality.

## 2. Experimental investigations

### 2.1. Material characterization

The materials chosen for the study of particulate materials are (i) fly ash and (ii) bottom ash. Both were collected from Guru Nanak Dev thermal power plant, Bhatinda, Punjab, India. Various bench-scale tests were carried out to determine the particle size distribution (PSD) of the solid materials,

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pH value, and static settling characteristics of slurries at various concentrations. The sieve analysis method is used to obtain the PSD of the coal ash samples. A digital pH meter was used to determine the pH value of the coal ash slurry suspension at any given solid concentration. The morphology and chemical composition of the bottom ash sample were determined using scanning electron microscopy-energy dispersive X-ray spectroscopy (Model: JEOL, 6510LV). The mineralogical composition of bottom and fly ash samples has been evaluated by the X-ray diffraction (XRD) technique. The XRD patterns of the ash samples are collected by a Philips X'Pert diffractometer (Model: PW 1710), operated at 40 kV and 30 mA utilizing Cu K $\alpha$  radiation ( $\lambda = 1.542 \text{ \AA}$ ). The sample is scanned over a scattering angle  $2\theta$  from  $0 \pm 80^\circ$ . The JCPDS (Joint Committee on Powder Diffraction Standards) data files have been used for identification of the minerals present in the sample.

## 2.2. Determination of trace elements

The leaching characteristics of the fly ash and bottom ash samples were determined using the toxicity characteristic leaching procedure (TCLP) method. The collected sample was dried at  $120^\circ\text{C}$  for 12 h duration and then cooled. Extraction fluid was prepared by diluting 5.7 ml glacial acetic acid with distilled water to a volume of 1 l. The pH value of the solution was maintained as  $2.88 \pm 0.05$ . The Remi orbital shaking lubricator (Model: RS 12 plus) was used for shaking of the solution. The mixture shaking operation was performed with the period of 24 h at 40 rpm in the temperature environment of  $30^\circ\text{C}$ . At the end of the leaching experiment, liquid was filtered through a  $0.45\text{-}\mu\text{m}$  micropore membrane filter. The leaching experimentation was repeated with the variation of the L/S ratio of 40:1, 60:1, and 80:1. The final extracts were stored in a refrigerator at the temperature of  $4^\circ\text{C}$  until the tracing element determination. All the tracing elements were analyzed using atomic absorption spectrophotometer (AAS 4129, make- ECIL, India) following the standard methods (APHA, 1995).

## 3. Results and discussion

### 3.1. Physicochemical characteristics

The PSDs of both coal samples—bottom ash and fly ash—are shown in Figure 1. From Figure 1, it can be observed that the biggest particle size of bottom ash is  $1000 \mu\text{m}$ . More than 73.5% particles are coarser than  $150 \mu\text{m}$  and only 15.4% particles are finer than  $75 \mu\text{m}$ . In the fly ash, the biggest particle size is  $355 \mu\text{m}$  and 73% of the particles are finer than  $75 \mu\text{m}$ . The static settled concentrations of the fly ash and bottom ash slurries were measured by taking an initial mixture of 20% concentration (by weight). The final static settled concentration of bottom ash and fly ash slurries was observed as 52.3% and 60.8% (by weight), respectively. The pH values with variation of the solid concentration (by weight) of fly ash and bottom ash slurry have been measured at various concentrations in the range of 10–60% (by weight). The pH value of bottom ash and fly ash varies with the solid concentration in the range of 7.64–7.43 and 7.61–7.38, respectively. The pH values of both samples depict the nonreactive nature of both the ash slurries. It can be inferred that the concentration of fly ash and bottom ash slurries has negligible effect on pH value.

### 3.2. Mineralogical characteristics

The scanning electron micrographs (SEMs) of the fly ash and bottom ash at  $500\times$  magnification are shown in Figure 2. From Figure 2, it is observed that fly ash particles have smooth surfaces and a spherical morphology along with cenospheres (hollow spheres) and the particles are habitually found as agglomerates. The bottom ash particles are comparatively porous, coarser, and highly irregular in shape than the fly ash particles. The XRD results of the fly and bottom ash samples are shown in Figure 3. It seems that the major crystalline phases identified in the collected fly ash samples are quartz (56.1%), mullite (37.3%), hematite (0.2%), magnetite (0.1%), and kyanite (6.2%), whereas in the bottom the crystalline phases are quartz (53.7%), mullite (44.2%), and hematite (2.1%). Quartz and mullite are the most common phases in both fly

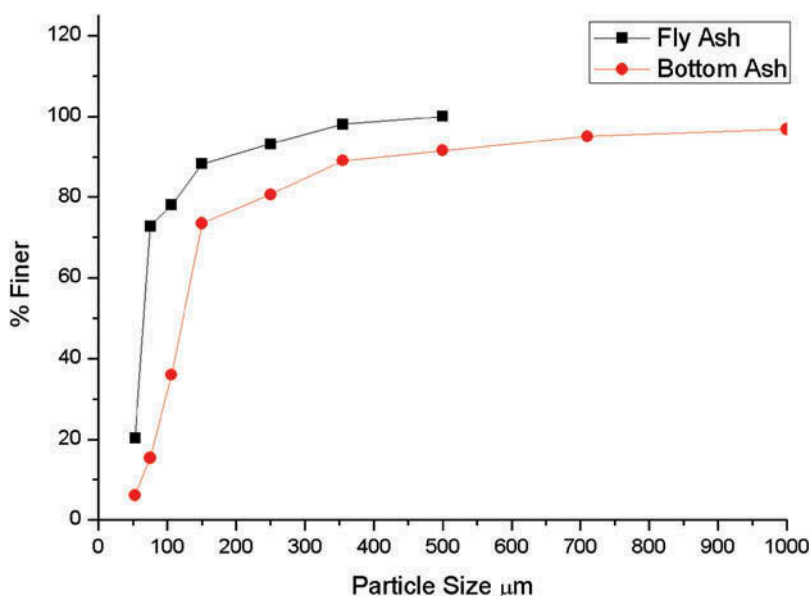


Figure 1. Particle size distribution of bottom and fly ash.

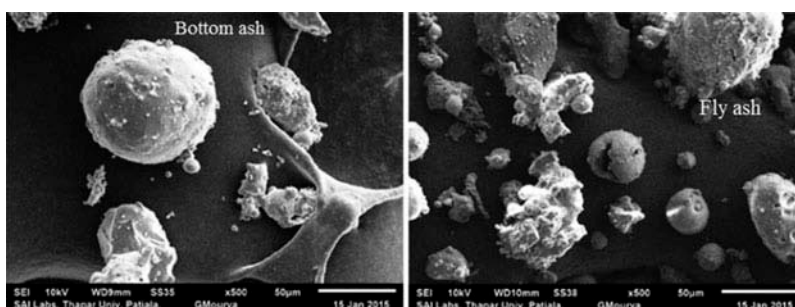


Figure 2. SEM image of bottom and fly ash.

and bottom ash. The strongest peak due to quartz ( $\text{SiO}_2$ ) is in close proximity to  $2\theta = 26.597^\circ$  and the mullite ( $\text{Al}_{4.68}\text{Si}_{1.32}\text{O}_{9.68}$ ) is in close proximity to  $2\theta = 26.202^\circ$  in the fly ash sample. Whereas in bottom ash quartz ( $\text{SiO}_2$ ) is in close proximity to  $2\theta = 26.594^\circ$  and the mullite ( $\text{Al}_{4.68}\text{Si}_{1.32}\text{O}_{9.68}$ ) is in close proximity to  $2\theta = 26.239^\circ$ .

The fly and bottom ash with a reasonable proportion of alumina and silica can be utilized as a raw material for synthetic aluminosilicate aggregates for refractory and ceramic applications (Tripathy and Mukherjee, 1997). Both bottom and fly ash samples have silica presence in a major proportion in the form of quartz, which improves the strength of the support materials and is used in the construction industry as a building material (Tripathy and Mukherjee, 1997; Nayak et al., 1999). The presence of silica in abundance increases the strength and the presence of CaO gives cementing properties after stowing. They also contain a very negligible amount of unburned carbon. Hence fly and bottom ash also can be used as a stowing material in underground coal mines (Nayak et al., 1999).

### 3.3. Leaching characteristics

The results of leaching tests for the fly and bottom ash sample are presented in Figures 4 and 5. The tracing elements like manganese (Mn), magnesium (Mg), chromium (Cr), zinc (Zn), copper (Cu), nickel (Ni),

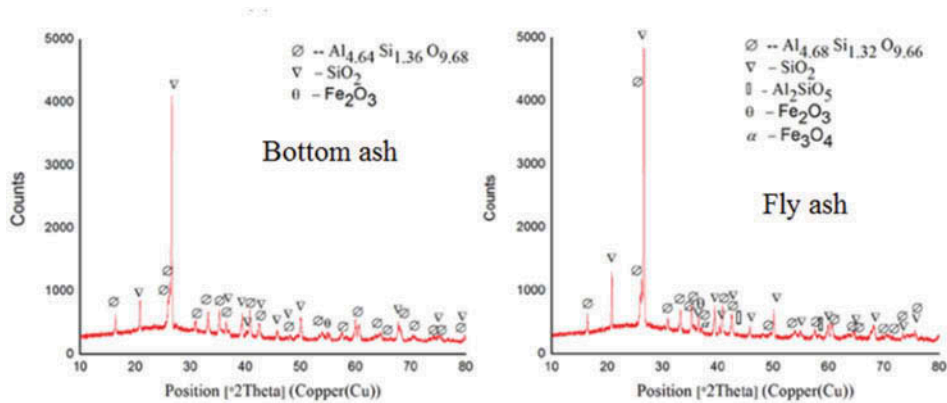


Figure 3. XRD of bottom and fly ash.

lead (Pb), iron (Fe), cobalt (Co), mercury (Hg), and molybdenum (Mo) were determined by the TCLP method. The L/S ratio was taken to be 20:1, 40:1, 60:1, and 80:1. The leaching test data of the bottom ash are shown in Figure 4. From Figure 4, it is observed that the leachate concentration of the tracing element increases with increase in the L/S ratio. The tracing element concentration of Mn, Mg, Cr, Zn, Cu, Ni, Pb, Fe, Co, Hg, and Mo increases from 112 to 135, 70 to 82, 55 to 63, 36 to 40, 33 to 36, 20 to 25, 7.50 to 9.50, 3.50 to 6, 0.22 to 0.40, and 1.50 to 1.57 mg/Kg, with the variation of L/S ratio from 20:1 to 80:1.

The tracing element result data of fly ash are presented in Figure 5, which show the similar nature of leaching characteristics as bottom ash. In the fly ash, the tracing element concentration increases from 136 to 148, 103 to 115, 50 to 58, 83 to 93, 55 to 64, 26 to 29, 10.34 to 10.74, 8.00 to 9.96, 3.30 to 3.90, 0.50 to 0.56, and 2.61 to 2.68 mg/Kg, with the variation of L/S ratio from 20:1 to 80:1. From the leaching results of the fly and bottom ash data, it is observed that the tracing elements of Mn, Mg, Cr, Zn, Ni, Pb, Fe, and Cu are the most abundant elements while Hg, Mo, and Co are the least abundant elements, present in the range of 0.20–2.66 mg/kg. The element Mn shows the maximum leachability, whereas Hg shows the minimum leachability in both fly and bottom ash samples. Similar types of analysis results have been reported in the literature with

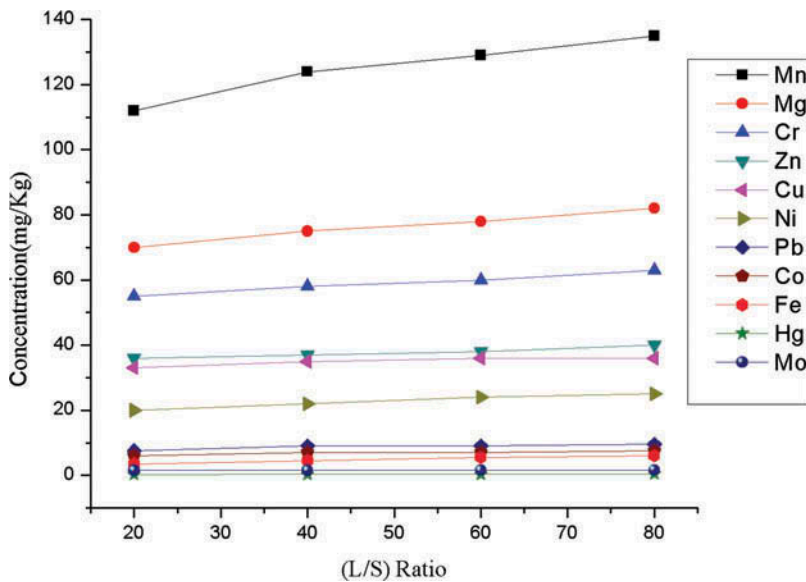


Figure 4. Concentration of different leached elements in bottom ash with variation of liquid to solid ratio.



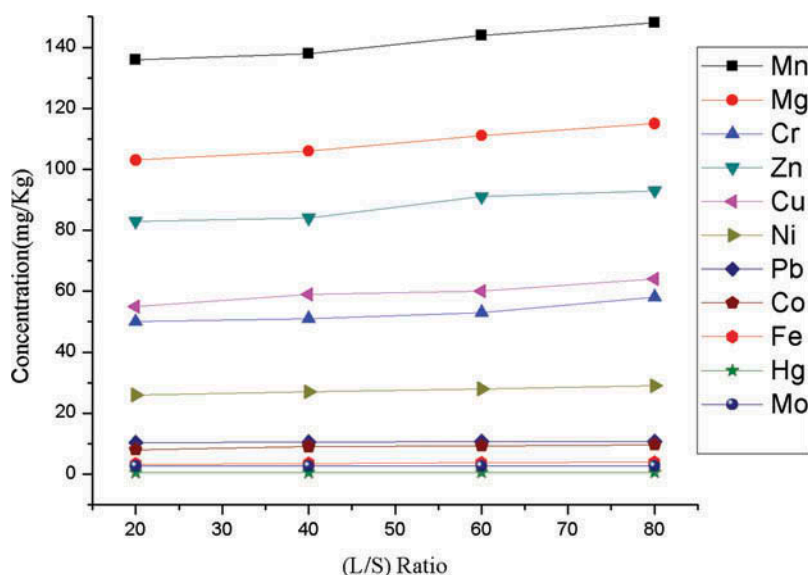


Figure 5. Concentration of different leached elements in fly ash with variation of liquid to solid ratio.

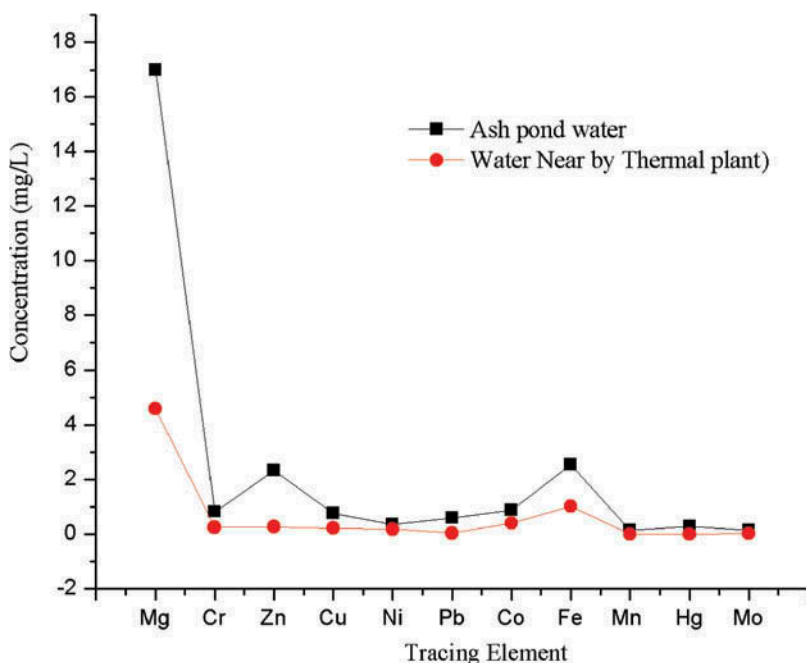
coal ash of different thermal plants (Baba et al., 2010; Blissett and Rowson, 2012; Singh et al., 2012). It is also observed that the leached concentration of the tracing elements in the fly ash is more compared with the bottom ash at the same L/S. Minimum leachability of the solution was observed with the L/S of 20:1, whereas maximum leachability of the solution was observed with L/S of 80:1. Similar result has been reported by investigators (Praharaj et al., 2002; Baba et al., 2010). The effect of the leaching characteristics from the fly ash and bottom ash waste was determined in the water of an ash pond and the water of a village close to the thermal power plants, which is shown in Figure 6. Total 11 elements were traced in the collected water: Mg, Zn, Hg, Mo, Cu, and Co were under the prescribed limits of the drinking water (IS 10500, 2009) and Cr, Pb, Mn, Ni, and Fe crossed the standard limits.

These elements may cause many harmful effects on human health like heart attack, damage of the nervous systems, lung tumors, liver failure, etc. The leaching concentration of toxic elements can be controlled by replacing the conventional slurry ash disposal systems with a high-concentration slurry ash disposal system, where evaporation controls the production of leachate (Iyer and Scott, 2001). Using good-quality coal and temperature control during the combustion process also minimize the leaching concentration. Green technology should also be adopted for controlling the toxic heavy metals pollution due to the bottom ash disposal in and around thermal power plants.

#### 4. Conclusions

Based on the present investigation on the physicochemical and leaching characteristics of fly and bottom ash of thermal power plants, the following conclusions can be drawn.

- The cenospheres of the fly ash are lightweight as compared to bottom ash.
- Mn, Mg, Cr, Zn, Ni, Pb, Fe, and Cu are the most abundant elements, while Hg, Mo, and Co are the least abundant elements, present in the range of 0.20–2.66 mg/kg.
- The tracing element analysis of the bottom ash indicates that Mn, Mg, Cr, Zn, Ni, Pb, Fe, and Cu concentrations are higher compared to Hg, Mo, and Co.



**Figure 6.** Concentration of different leached elements in the groundwater sample.

- The concentration of heavy metal elements, namely, Mg, Zn, Hg, Mo, Cu, and Co, is within the permissible limits of Indian standard (IS 10500, 2009), while the elements of concentrations of Cr, Pb, Mn, Ni, and Fe crossed the standard limits. These may cause many harmful effects on human health.

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