Mass balance and isotope effects during nitrogen transport through septic tank systems with packed-bed (sand) filters

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ABSTRACT

Septic tank systems are an important source of NO3− to many aquifers, yet characterization of N mass balance and isotope systematics following septic tank effluent discharge into unsaturated sediments has received limited attention. In this study, samples of septic tank effluent before and after transport through single-pass packed-bed filters (sand filters) were evaluated to elucidate mass balance and isotope effects associated with septic tank effluent discharge to unsaturated sediments. Chemical and isotopic data from five newly installed pairs and ten established pairs of septic tanks and packed-bed filters serving single homes in Oregon indicate that aqueous solute concentrations are affected by variations in recharge (precipitation, evapotranspiration), NH4+ sorption (primarily in immature systems), nitrification, and gaseous N loss via NH3 volatilization and/or N2 or N2O release during nitrification/denitrification. Substantial NH4+ sorption capacity was also observed in laboratory columns with synthetic effluent. Septic tank effluent δ15N−NH4+ values were almost constant and averaged +4.9‰ ± 0.4‰ (1σ). In contrast, δ15N values of NO3− leaving mature packed-bed filters were variable (+0.8 to +14.4‰) and averaged +7.2‰ ± 2.6‰. Net N loss in the two networks of packed-bed filters was indicated by average 10–30% decreases in Cl−-normalized N concentrations and 2–3‰ increases in δ15N, consistent with fractionation accompanying gaseous N losses and corroborating established links between septic tank effluent and NO3− in a local, shallow aquifer. Values of δ18O–NO3− leaving mature packed-bed filters ranged from −10.2 to −2.3‰ (mean −6.4‰ ± 1.8‰), and were intermediate between a 2/3 H2O−O+1/3 O2−O conceptualization and a 100% H2O−O conceptualization of δ18O–NO3− generation during nitrification.

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Apparent N loss in single-pass (non-recirculating) packed-bed filters serving single homes and other small decentralized facilities has been observed in numerous studies (Brandes, 1980; Ronayne et al., 1984; Bushman, 1996; Crites and Tchobanoglous, 1998; Harrison et al., 2000; Bayley et al., 2003). This apparent N loss has often been attributed to denitrification or NH4+ sorption (used in this paper to describe both specific adsorption and ion exchange). However, evidence to support denitrification or sorption has been scant. Also, timescales over which N attenuation mechanisms may operate have not always been well characterized; this has implications for interpretation of packed-bed filter data insofar as early-time NH4+ sorption prior to sorption site saturation may bias results if studies occur over timescales shorter than those required to achieve sorption site saturation. Furthermore, effects of dilution with precipitation (rain, snowmelt) or concentration in response to evapotranspiration are often ignored. Thus, some of the apparent N loss observed in studies of packed-bed filters may in fact reflect dilution rather than an actual loss due to a removal process such as volatilization, denitrification, or sorption. The distinction between sorption and volatilization or denitrification is important because volatilization and denitrification essentially remove N from the packed-bed filter, whereas sorbed NH4+ remains in the reactive fixed N pool at the site and may be remobilized.

The purpose of this study was to characterize N losses and the associated isotopic effects that occur in single-pass packed-bed filters used for single-family septic tank effluent disposal. The focus was on field investigations, in which a combination of newly installed and mature packed-bed filters provided data on temporal aspects of packed-bed filter performance. Cl− concentrations were used to normalize N concentrations to account for effects of dilution and evapotranspiration. Stable isotope analyses of N and O in NH4+, NO3−, and H2O provide additional evidence for solute fate and document the nature and variability of isotopic signatures of septic tank-derived NO3− that may enter ground water. Laboratory sand column sorption experiments complemented the field investigations.

2. Study design and methods

In this study, five newly installed packed-bed filters in the vicinity of La Pine, Oregon, were monitored over a period of years to provide information on maturing (through mature phase) packed-bed filters. Ten additional packed-bed filters in the vicinity of Bend, Oregon, were sampled once to provide additional information on mature systems (0.9 to 9.1 yr of operation). Coarse volcanic sand from a packed-bed filter under construction near La Pine was used in laboratory column experiments.

2.1. Study area

La Pine and Bend are located in Oregon’s upper Deschutes Basin (Fig. 1). Septic tanks are used in both areas, with particularly widespread use in the rural-residential community of La Pine. As of 2004, 6550 homes in the La Pine area were served by septic tanks, at least 900 of which were connected to packed-bed filters (B.J. Rich, Deschutes County Environmental Health Division, written commun., 2008). Local geology consists of Quaternary and Tertiary basaltic and andesitic flows, vent deposits, and pyroclastic rocks, and (chiefly volcanic) sediment. Precipitation, ranging from about 40 to 50 cm/yr over most of the La Pine area and 20 to 40 cm/yr near Bend (Taylor, 1993), falls primarily from November through March. Mean annual air temperatures are similar: 7.2 °C near La Pine and 8.0 °C near Bend.

2.2. Maturing packed-bed filters

Deschutes County Environmental Health Division (DCEHD) and Oregon Department of Environmental Quality (ODEQ) installed five single-pass packed-bed filters in the La Pine area during fall 2000. Three of the new systems (53110A, 17346B, 17186H) contained polyvinyl chloride half-pipes at the bottom that emptied into collection buckets (representing “bottomless” systems commonly used in the region of the study); the other two (50663F, 5233OS) were installed with plastic liners on the bottom that fed into collection chambers (representing “lined” systems commonly used in the region). Samples of septic tank fluid (considered equivalent to septic tank effluent and referred to as such in this paper) and packed-bed filter effluent were collected, usually as paired samples, approximately six times per year between late 2000 and late 2003. Samples were analyzed for N species and Cl−. The resulting data set (Oregon Department of Environmental Quality, 2005) provides temporal characterization of packed-bed filter effluent from early in their operation into a period of apparent maturity, and thus these packed-bed filters are referred to as the maturing packed-bed filter network. For this study, we used samples with complete analyses of NO2−+NO3−, NH4+, Kjeldahl N (NH4+ plus organic N), and Cl−. Because NO2− typically represents a negligible component of NO2−+NO3−, we henceforth refer to NO2−+NO3− as NO3−. NO3− concentrations in four packed-bed filter samples, collected May 31, 2001, and analyzed by the U.S. Geological Survey (USGS), were 0.03% to 0.34% of NO2−+NO3−.

Additional samples were collected for analysis of N and O isotopes in NH4+, NO3−, and H2O. Samples of septic tank effluent...
were analyzed for δ¹⁵N–NH₄⁺ and packed-bed filter effluent for δ¹⁵N–NO₃⁻.

Samples were collected by dipping clean bottles into the centroid of the septic tank chamber or packed-bed filter collection bucket, and sub-sampling from this primary collection bottle. Samples for N speciation were unfiltered and preserved with H₂SO₄ to pH < 2 (plus refrigeration). Samples for isotope analysis were filtered (0.45 µm) and either preserved with H₂SO₄ to pH < 2 (plus refrigeration) (NH₄⁺) or with KOH to pH > 11 (plus freezing) (NO₃⁻). Samples for Cl⁻ analysis were filtered.

N and Cl⁻ concentrations were analyzed by ODEQ in Portland, Oregon: NO₃ by automated cadmium reduction; NH₄⁺ by automated phenate; Kjeldahl N by Kjeldahl digestion and colorimetry (automated phenate); Cl⁻ by automated ferricyanide (Clesceri et al., 1998). Method reporting levels for N species were: NO₃⁻, 0.01 mg N/L; NH₄⁺, 0.02 mg N/L; and Kjeldahl N, 0.2 mg N/L. Total N was calculated as NO₃⁻ plus Kjeldahl N.

N isotopes in NH₄⁺, N and O isotopes in NO₃⁻, and H and O isotopes in H₂O were analyzed by isotope-ratio mass spectrometry at the USGS Reston Stable Isotope Laboratory (http://isotopes.usgs.gov) by modifications of methods described previously (Supplementary data). δ¹⁵N and δ¹⁸O values are reported relative to N₂ in air and O in VSMOW, respectively, and normalized to published values for international isotopic reference materials (Supplementary data).

In addition to routine ambient monitoring by DCEHD/ODEQ, DCEHD collected an additional set of samples from four of these sites on May 31, 2001. These samples were filtered (DCEHD) and analyzed (USGS) for N and Cl⁻ concentrations, and N isotopes. Samples for N species were preserved by chilling (4 °C). Kjeldahl N was analyzed by automated-segmented flow colorimetry (Fishman, 1993). Analytical methods for NO₃⁻, NH₄⁺, and Cl⁻ concentrations were identical to those used in the column experiments (below). Samples for isotope analysis were preserved and analyzed as described above.

2.3. Mature packed-bed filter synoptic

DCEHD and ODEQ sampled 10 existing, single-pass, packed-bed filter systems in October, 2001. These packed-bed filters were identical in structure to the lined packed-bed filters in the maturing packed-bed filter network; they were chosen because their ages (duration of use: 0.9 to 9.1 years) were likely to have resulted in mature conditions, and all systems had sampling access. Techniques of sample collection, processing, and analysis were identical to those used for the maturing packed-bed filter network. This part of the study is referred to as the mature packed-bed filter network.

2.4. Column experiments

Sorption of NH₄⁺ to packed-bed filter sediment was evaluated with a 76-cm tall, 9.5-cm inside diameter acrylic column under unsaturated conditions using synthetic septic tank effluent containing NH₄HCO₃ and NaCl. The sorption experiment was followed by a desorption experiment with 2 M KCl. An additional experiment was done to measure pre-existing exchangeable NH₄⁺ on fresh packed-bed filter sediment. Experimental details and analytical methods are described in the Supplementary data.

3. Results and discussion

3.1. NH₄⁺ sorption in sand columns

No detectable NH₄⁺ was present in water exiting the sediment column during the sorption experiment with synthetic septic tank effluent (Fig. 2a). Based on Cl⁻ breakthrough, over 10 (partially saturated) pore volumes passed through the column during the sorption experiment, which ran for approximately 6 days. No NO₃⁻ was detected in the column effluent, suggesting that nitrification was negligible, and thus indicating that sorption was likely responsible for the observed NH₄⁺ attenuation. The absence of measurable nitrification may reflect the lack of introduction of nitrifying bacteria from septic tank effluent and the short timeframe for any endogenous sediment-bound nitrifying bacteria to multiply.

Fig. 2 – Breakthrough curves for sand column experiments with synthetic septic tank effluent. (a) Sand column NH₄⁺ adsorption. (b) Sand column NH₄⁺ desorption using 2 M KCl. C = concentration exiting column; Co = concentration entering column.
Column effluent near the end of the sorption experiment, at 10.72 L cumulative volume of effluent, contained cations not added to the synthetic septic tank effluent: Ca$^{2+}$ (30.8 mg/L), Mg$^{2+}$ (19.8 mg/L), and K$^{+}$ (9.13 mg/L). These cations probably represent cations exchanged during NH$_4^+$ sorption, although mineral and volcanic glass dissolution also may have contributed to some extent.

NH$_4^+$ strongly sorbs to mineral surfaces (Hem, 1985), and clay minerals play a particularly important role in NH$_4^+$ sorption reactions (Nommik and Vahtras, 1982). However, large amounts of clay are not required for measurable NH$_4^+$ sorption, and considerable NH$_4^+$ retardation has been observed in coarse-grained aquifers with low (<0.1%) clay content (Ceazan et al., 1989; Buss et al., 2004; Böhlke et al., 2006). Thus, the essentially complete apparent sorption of NH$_4^+$ (Ceazan et al., 1989; Buss et al., 2004; Böhlke et al., 2006).

Mg$^{2+}$ (19.8 mg/L), and K$^+$ (9.13 mg/L). These cations probably confirm the hypothesis that the attenuated NH$_4^+$ tributed to some extent.

mineral and volcanic glass dissolution also may have contributed to some extent.

The desorption experiment was done to determine if NH$_4^+$ had been sorbed (Fig. 2b). By the termination of the desorption experiment, 97% of the sorbed NH$_4^+$ had been recovered, indicating that sorption was essentially fully reversible.

To evaluate the possibility that some of the desorbed NH$_4^+$ might have been NH$_4^+$ that was attached to sediment surfaces prior to the sorption experiment, a column was packed with fresh sediment and subjected to 2 M KCl treatment. No NH$_4^+$ was detected in the effluent, indicating that prior to introduc-

[Table 1 - Chemical and isotopic data from the mature packed-bed filter network]

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<th>Site</th>
<th>Sample</th>
<th>Date</th>
<th>System age (years)</th>
<th>NO$_3^-$ (mg N/L)</th>
<th>NH$_4^+$ (mg N/L)</th>
<th>TKN$^a$ (mg N/L)</th>
<th>Cl$^-$ (mg/L)</th>
<th>$\delta^{15}$N-NH$_4^+$ (‰)</th>
<th>$\delta^{15}$N-NO$_3^-$ (‰)</th>
<th>$\delta^{18}$O-H$_2$O (‰)</th>
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$\delta^{15}$N-NH$_4^+$ data normalized to +0.4‰ for IAEA-N1 and +53.7‰ for USGS26, $\delta^{18}$O-H$_2$O data normalized to +4.7‰ for IAEA-N3 and +180.0‰ for USGS32, $\delta^{18}$O-NO$_3^-$ data normalized to -27.9‰ for USGS34 and +25.6‰ for IAEA-N3, $\delta^2$H-H$_2$O data normalized to 0.0‰ for VSMOW and -55.50‰ for SLAP, $\delta^2$H-H$_2$O data normalized to 0.0‰ for VSMOW and -428.0‰ for SLAP.

$^a$ TKN, total Kjeldahl N.

3.2. N and Cl$^-$ fluxes from packed-bed filters

Septic tank effluent consisted almost entirely of reduced N (Table 1 and Supplementary data). N from septic tank effluent was oxidized efficiently within packed-bed filters, and NO$_3^-$ was the primary N species in recharge to ground water from packed-bed filters, particularly for mature systems. For example, for samples collected after the first year of operation in the maturing packed-bed filter network, >99% (median and mean) of total N in septic tank effluent was reduced N (n=63), whereas 98% (median and mean) of total N in packed-bed filter effluent was NO$_3^-$ (n=63). Most N and Cl$^-$ in these samples was introduced during household water use. Ground water used for domestic purposes in the vicinity of the maturing network is currently dilute, typically containing <1 mg N/L of NO$_3^-$ and <4 mg/L of Cl$^-$ (Hinkle et al., 2007), whereas concentrations in packed-bed filter effluent are considerably greater: NO$_3^-$, 55 mg
N/L (median) or 58 mg N/L (mean), and Cl−, 45 mg/L (median) or 48 mg/L (mean), for the 63 post-first-year maturing-network samples.

In the vicinity of La Pine (maturing network), the estimated average volume of septic tank effluent loaded to packed-bed filters is about 430 L/day (Morgan et al., 2007, p. 22). For the mature network, estimated average septic tank effluent fluxes would be about 25% greater, based upon site-specific occupancy data. At the scale of individual 33 m² packed-bed filters, potential recharge from septic tank effluent (flux prior to evapotranspiration losses) averages about 480 to 600 cm/yr for these systems, greatly exceeding the ~50 cm/yr of precipitation that falls on these systems.

3.3. Mass balance and isotope effects in the mature packed-bed filter network

Cl− data are consistent with an evapotranspiration effect in the mature packed-bed filters (Table 1). The ratio of Cl− in packed-bed filter effluent, Cl− in septic tank effluent, and matching for evapotranspiration and concentration (by evapotranspiration) in the packed-bed filters. An alternative explanation—Cl− might be mobilized from packed-bed filter sediment surfaces—does not appear likely for <1 m of volcanic sands that have been in use in packed-bed filters for long periods of time. Furthermore, background concentrations of Cl− on the order of a few mg/L in ground water near and upgradient from these systems (Caldwell, 1998) and the absence of detectable Cl− in column experiment effluent prior to loading with Cl− (Fig. 2a) argue against a solid-phase Cl− source.

Cl− data were used to calculate N mass balances. Packed-bed filter N attenuation is apparent in Cl−-normalized N concentrations. The ratio of Cl−-normalized N in packed-bed filter effluent, (N/Cl−)PBFE, to Cl−-normalized N in septic tank effluent, (N/Cl−)STE, is a measure of the fraction of original septic tank N remaining in the packed-bed filter effluent after adjusting for evapotranspiration and dilution (N∗):

\[ N^* = \frac{(N/Cl^-)_{PBFE}}{(N/Cl^-)_{STE}} \] (1)

Values of N∗ for matched pairs of packed-bed filter effluent and septic tank effluent samples from the mature packed-bed filter network ranged from 0.52 to 0.85, with median 0.69 and mean 0.71.

For this network, septic tank effluent δ15N-NH₄⁺ ranged from +4.5 to +5.6‰ (median and mean +5.0‰). Packed-bed filter effluent δ15N-NH₄⁺ ranged from +5.1 to +14.4‰ (median +7.8‰, mean +8.5‰). The differences between the median and mean values of δ15N-NH₄⁺ for septic tank effluent (+5.0‰) and δ15N-NH₄⁺ for packed-bed filter effluent (+7.8‰ or +8.5‰) are interpreted to indicate isotopic fractionation, and combined with the approximately 30% decrease in Cl−-normalized N, are consistent with N loss by a combination of NH₃ volatilization prior to nitrification (Kreitler, 1975, 1979; Hübner, 1986) and N₂ or N₂O release during subsequent nitrification and denitrification within the packed-bed filters (Delwiche and Steyn, 1970; Hübner, 1986; Mariotti et al., 1988; Högberg, 1997). Correlation between δ15N-NO₃ and sample temperature was significant (r² = 0.76; p < 0.01), indicating more N loss by volatilization or denitrification at higher temperatures (temperature data available for 9 of the 10 sites; data not shown). Packed-bed filter effluent δ18O-NO₃ ranged from −7.5 to −3.2‰, and were not correlated with δ15N-NO₃ values (r² = 0.03; not statistically significant).

3.4. Mass balance and isotope effects in maturing packed-bed filter systems

The ratio of Cl− in packed-bed filter effluent to Cl− in septic tank effluent, for the 86 matched (by date) pairs of ODEQ samples from the five systems in the maturing packed-bed filter network was 1.03 (median) and 1.06 (mean), consistent with a small overall net evapotranspiration effect (Table S2 in Supplementary data). Eight matched pairs of septic tank effluent and packed-bed filter effluent yielded an average δ18O enrichment in packed-bed filter effluent of 0.24‰ relative to septic tank effluent (Table S3 in Supplementary data), which could be consistent with a minor amount of evaporation (isotopically fractionating) and transpiration (non-fractionating).

The greater apparent evapotranspiration in the mature packed-bed filter samples, compared with the maturing packed-bed filter samples, may reflect the relatively dry climate conditions during the mature packed-bed filter network sampling. Mature packed-bed filter samples were collected during October, 2001, a particularly dry October with precipitation in Bend of 0.74 cm for the month, compared with the calendar year total of 24.5 cm (National Climatic Data Center, 2005). Generally more arid conditions of Bend (location of mature packed-bed filter survey) compared with La Pine (location of maturing packed-bed filter monitoring) also may have contributed to these differences by affecting antecedent moisture in packed-bed filters.

N attenuation in the maturing packed-bed filters was most pronounced during the first several months of operation, as demonstrated by N/Cl− ratios (Fig. 3; N/Cl− ratios shown instead of N∗ because many early-time septic tank effluent samples were not analyzed for Cl−). Three packed-bed filters (53110A, 17346B, 50663F) yielded N/Cl− ratios of <0.3 when sampled 2 to 7 months after installation, whereas N/Cl− ratios typically were >1 in mature systems. Low N/Cl− ratios were not due to an absence of septic tank effluent in the packed-bed filters because the packed-bed filter effluent samples contained sufficient Cl− (several tens of milligrams per liter; Table S2 in Supplementary data) to indicate that septic tank effluent had passed through the packed-bed filters. These early-time data indicate that considerable N attenuation occurred in these packed-bed filters during the first months of operation. In the remaining two packed-bed filters, observed early-time N attenuation was comparable to that at later time. The substantial N attenuation in early-time data from some packed-bed filters is consistent with the results of column studies, and indicates that N loss to NH₄ sorption might occur in packed-bed filters early in their life cycle, but that sorption may be limited by saturation of sorption sites and/or development of nitrifying conditions. Some early-time N loss also might be accounted for by microbial assimilation during
establishment of microbial communities in the packed-bed filters. N attenuation also is indicated by samples collected after the first several months of monitoring, but N/Cl ratios appear to have reached a quasi-steady-state before the end of the first year of operation. Cl−-normalized N losses in post-first-year samples averaged about 10% (Table 2). The difference in N attenuation between the post-first-year maturing packed-bed filter network samples (about 10%) and the mature packed-bed filter network samples (about 30%) could reflect system variability (e.g. water or nutrient loading, packed-bed filter sediment grain-size distribution) or seasonal variability (e.g. temperature or precipitation prior to sampling). The mature network with greater average attenuation was near Bend, Oregon, which has the drier average climate.

A subset of samples from the network of five maturing systems was analyzed for isotopes (27 pairs of samples; Fig. 4, and Table S3 in Supplementary data). Isotope data from the first year of packed-bed filter operation are sparse. The first isotope sample from site 17346B (Fig. 3), with a N/Cl− ratio of 0.38, had a relatively low δ15N–NO3 value of +1.4‰, which could be consistent with a combination of isotopic fractionation during nitrification and sorption of isotopically enriched NH4+. Other isotope data representing the first year of packed-bed filter operation plot beyond the apparent sorption phase in Fig. 3, and have δ15N–NO3 values similar to those of post-first-year data.

In samples collected more than 1 year after commencement of packed-bed filter operation (21 pairs), δ15N–NH4+ values in septic tank effluent exhibited little variation, ranging from +4.2 to +5.1‰, with median and mean of +4.8‰ (Fig. 4a). Values of δ15N–NO3 were more variable, ranging from +0.8 to +10.3‰, with median and mean of +6.5‰ (Fig. 4a). The average increase of 1.7‰ between NH4+ and NO3− in the maturing systems after 1 year of operation and the average 10% N attenuation (Table 2) are consistent with isotopic fractionation resulting from gaseous N (NH3, N2, and(or) N2O) losses.

δ18O–NO3 values also were variable (Fig. 4b). Evaluating the set of post-first-year samples from the maturing packed-bed filter network as a whole, δ18O–NO3 values did not increase systematically with increasing δ15N–NO3, as is commonly observed in denitrifying ground water (Böttcher et al., 1990; Aravena and Robertson, 1998). Correlation between post-first-year δ18O–NO3 and δ15N–NO3 values was low (r² = 0.04) and not statistically significant. These data might indicate that NH3 volatilization was more important than denitrification as a mechanism of N loss in these packed-bed filters, as fractionations from NH3 volatilization will affect δ15N but would not have a direct effect on δ18O values established subsequently during nitrification. Upon closer inspection, though, relations between δ18O–NO3 and δ15N–NO3 values suggest the possibility that different processes might have occurred in bottomless and lined packed-bed filters. Post-first-year samples from lined packed-bed filters exhibited a positive correlation

<table>
<thead>
<tr>
<th>Packed-bed filter</th>
<th>N*</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>53110A</td>
<td>1.00</td>
<td>0.99</td>
</tr>
<tr>
<td>17346B</td>
<td>0.90</td>
<td>0.90</td>
</tr>
<tr>
<td>50663F</td>
<td>0.76</td>
<td>0.73</td>
</tr>
<tr>
<td>17186H</td>
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<td>0.83</td>
</tr>
<tr>
<td>52330S</td>
<td>0.93</td>
<td>0.90</td>
</tr>
</tbody>
</table>

Analysis restricted to samples collected more than one year after commencement of packed-bed filter operation, to avoid early-time data that might be associated with sorption; complete data in Table S2 in Supplementary data.

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The $\delta^{18}H$ and $\delta^{18}O$ values of $H_2O$ range from about $-116$ to $-102\%$ and $-15.3$ to $-13.1\%$, respectively. These values differ consistently from site to site (Fig. 4c), and they do not appear to record seasonal isotopic variations in precipitation (Table S3 in Supplementary data). More than 90% of the water passing through these packed-bed filters is domestic well water, which is derived from local ground water (Section 3.2). The $\delta^{18}O$–$NO_3^-$ values also do not appear to be related to seasonality (Table S3 in Supplementary data). Some of the variation in $\delta^{18}O$–$NO_3^-$ could be due to variation in the $\delta^{18}O$ of $H_2O$ during nitrification, but the variation in $\delta^{18}O$–$NO_3^-$ is greater (factor of four) than the variation in $\delta^{18}O$ of $H_2O$. As a group, the $\delta^{18}O$–$NO_3^-$ values plot between a hypothetical line representing 100% unfractionated $H_2O$–$O$ as a source of $O$ incorporated in $NO_3^-$ during nitrification (Sigman et al., 2005) and a hypothetical line representing a mixture of 2/3 $H_2O$–$O$ and 1/3 atmospheric $O_2$–$O$ as sources of $O$ incorporated in $NO_3^-$ during nitrification (Amberger and Schmidt, 1987) (Fig. 4c). Values of $\delta^{18}O$–$NO_3^-$ from the mature packed-bed filter network fall between these hypothetical lines, too (Table 1). Both the variability of $\delta^{18}O$–$NO_3^-$ values and the deviation of these values from the 2/3 $H_2O$–$O$/1/3 $O_2$–$O$ model could be due to fractionation of $O$ isotopes derived from either $H_2O$ or $O_2$, as has been observed with $O$ isotopes during $FeS_2$ oxidation to $SO_4^{2-}$ (Balci et al., 2007), or to partial isotopic equilibration between $H_2O$–$O$ and intermediate nitrogen oxide species during $N$ oxidation (Casciotti et al., 2007).

3.5. From septic tank to ground water

Following discharge from septic tanks, $N$ may be affected by dilution with precipitation, concentration by evapotranspiration, $NH_4^+$ sorption, $NH_3$ volatilization, nitrification, and/or denitrification. Results of this study indicate that after several months of packed-bed filter operation, $NH_4^+$ sorption appeared to be minimal. Nitrification in packed-bed filters was efficient, with about 98% of $N$ exiting packed-bed filter sediments occurring as $NO_3^-$, as has been observed with $O$ isotopes during $FeS_2$ oxidation to $SO_4^{2-}$ (Balci et al., 2007), or to partial isotopic equilibration between $H_2O$–$O$ and intermediate nitrogen oxide species during $N$ oxidation (Casciotti et al., 2007).

Fig. 4 – Relations among isotopic data in the maturing packed-bed filter network (data from Table S3 in Supplementary data). (a) $\delta^{15}N$–$NO_3^-$ in packed-bed filter effluent and $\delta^{15}N$–$NH_4^+$ in septic tank effluent collected simultaneously. (b) $\delta^{15}N$–$NO_3^-$ and $\delta^{18}O$–$NO_3^-$ in packed-bed filter effluent. (c) $\delta^{18}O$–$H_2O$ and $\delta^{18}O$–$NO_3^-$ in packed-bed filter effluent.

($r^2=0.71$; $p<0.01$), whereas post-first-year samples from bottomless packed-bed filters exhibited weak, negative correlation ($r^2=0.19$; not statistically significant) (Fig. 4b). These relations could reflect the preferential existence of denitrification in the lined packed-bed filters. However, gravel (>15 cm) placed on top of the liner in lined packed-bed filters would reduce the potential for development of a capillary fringe above the liner in the bottom of the sand material that otherwise might facilitate denitrification. Furthermore, the relation between $\delta^{18}O$–$NO_3^-$ and $\delta^{15}N$–$NO_3^-$ values for lined packed-bed filters is more complex when young (first-year) samples are considered (Fig. 4b); it is not clear if this reflects a time lag for development of denitrifying microbial populations, or if the larger number of samples simply provides a more comprehensive picture of the true complexity in these systems.
outgoing NO₃ are interpreted to reflect net, average N loss by NH₃ volatilization and(or) N₂ or N₂O degassing during nitrification/denitrification. Variability in δ¹⁸O-NO₃ values that is largely independent of seasonality and of variability in δ¹⁸O-H₂O values, and δ¹⁸O-NO₃ composition intermediate between 2/3 H₂O-O and 100% H₂O-O, may reflect differences in the nitrification process, partial isotopic equilibration among O-containing species during development of δ¹⁸O signatures in wastewater NO₃, or subsequent fractionations. Some of this variability could possibly be related to changes in the saturation state of sediments in the packed-bed filters or to transient abundances of intermediate nitrogen oxides during nitrification. Temporal variability in packed-bed filter δ¹⁵N-NO₃ and δ¹⁸O-NO₃ values demonstrates a potential limitation of relying on isolated samples of septic tank-derived NO₃ in studies of septic tank-impacted environments.

Although this study was focused on mounded packed-bed filter treatment systems, it is possible that similar processes occur where septic tank effluent passes through naturally emplaced unsaturated-zone sediment. A literature review by Fogg et al. (1998) indicated that unsaturated-zone water impacted by septic tank effluent typically had δ¹⁵N-NO₃ values of +7 to +15‰. Additional studies may indicate if there are systematic reasons for the large range of reported δ¹⁸N values for septic tank-derived NO₃ in unsaturated-zone and ground water. To date, characterization of δ¹⁸O of septic tank-derived NO₃ has been scarce, and additional δ¹⁸O characterization of this important NO₃ source term may indicate if the relatively low values reported here are typical or unusual. This is important because previously reported data produced by different isotopic analytical methods in the absence of reference materials may not be comparable (Révész and Böhlke, 2002; Böhlke et al., 2003). Further work within the unsaturated zone might also help clarify specific N loss mechanisms and isotopic characteristics of NO₃ delivered to the water table.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.scitotenv.2008.08.036.

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