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Natural and Anthropogenic Nitrate Contamination of Groundwater in a Rural Community, California

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Contamination of small basins impacts the quality of groundwater resources and the health of residents dependent on local, limited water supplies. Understanding contaminant sources is crucial not only to planning mitigation and cleanup but also to the rural community, who must participate in any scientific or regulatory effort. Groundwaters, rock, and soil samples representative of the Sierra Pelona Valley in an arid, “Mediterranean” climate region of southern California indicate significant anthropogenic nitrate contamination. Groundwater nitrate from diverse sources can be differentiated on the basis of chemical and isotopic compositions. Samples analyzed for dissolved or leachable ion concentrations as well as δ^{15}N provide both chemical and isotopic signatures that distinguish between potential contaminant sources. Data indicate a predominance of anthropogenic, organic human and/or animal waste and decay of irrigation-enhanced vegetation. Natural nitrate sources are minor but include low concentration soil nitrate from decay of sparse, natural vegetation and nitrogen-bearing rock units. Anthropogenic sources almost certainly contribute more than half of the nitrate found in the basin as a whole and provide the dominant source in the ≈40% of water wells that routinely or occasionally exceed the nitrate-N public drinking water standard concentration of 10 mg/L.

Introduction

In southern California, approximately one-third of wells originally drilled for water production exceed health and safety standards in at least one chemical parameter (*1*), with total dissolved solids (TDS), nitrate (NO_3-N), and volatile organic compounds (VOC) as the most common contaminants.

Nitrate is found naturally at moderate concentrations in many environments, but is often enriched to contaminant levels by anthropogenic activities involving nitrogen compounds as fertilizers or byproducts of organic compounds from agriculture, septic systems, and bird or livestock manure (*2, 3*). The United States Environmental Protection Agency (EPA) considers nitrate in drinking water harmful at levels exceeding the maximum contaminant level (MCL) of 10 mg/L (measured as NO_3-N). Such levels have become common in groundwaters of the Sierra Pelona Basin, California (Figure 1), particularly over the past two decades of rapid population growth in the region (Figure 2a). In such rural communities where there is no centralized water supply, local groundwater is the major source of drinking water and is generally produced from private water wells located near each residence. In such settings, routine water quality testing is not required, and government agencies have little enforcement power, making cooperation of community residents crucial to both investigation and minimization of impact of any contaminant.

Increasingly detailed water quality investigations (*4*−*6*) indicate that a significant percentage (20−40%) of wells in the Sierra Pelona area produce water that routinely or occasionally exceeds the MCL of nitrate (Figure 2a,b). When earlier, government-sponsored studies (*4, 5*) concluded, on the basis of surface loading computations, that residential septic systems were the major sources of nitrates in groundwater, community residents questioned the adequacy of these studies for source identification (*7, 8*). The chemical and isotopic study described here represents a portion of a larger effort (*6*) to spatially and temporally quantify the occurrence of high nitrate groundwaters, address source identification, and document nitrate transport from the surface to groundwater. Although constraints on contaminant source and transport processes specifically within the Sierra Pelona groundwater basin were foci of these investigations, the results should assist regulators weighing different management strategies to control water quality problems in similar areas, which have limited recharge due to arid climatic conditions, are unsewered, and are commonly used for livestock.

Natural Setting. *Environment.* The Sierra Pelona Valley watershed and basin (Figure 1) lie within relatively arid foothills north of the San Gabriel Mountains of southwestern California. The climate of this region is generally classified as “Mediterranean” or “summer dry subtropical” (*10*), implying that significant precipitation falls only in winter and early spring. Annual rainfall in the Sierra Pelona area [26.2 cm average (*11*)] shows a highly skewed distribution, with modal annual rainfall of 17 cm but abnormal, high rainfall seasons (>46 cm) that occur only every 8−10 years. During the period of this study (1991−1994), rainfall varied from normal (17 cm) in 1991−1992, to flood conditions (63 cm) in 1992−1993, and returning to normal (20 cm) in 1993−1994.

Low average precipitation and long, high temperature dry seasons typical in Sierra Pelona limit natural vegetation to sparse chaparral consisting of grasses, low shrubs, and occasional patches of juniper woodland (*5*). Annual growth of this sparse cover is restricted by the harsh climate; consequently, natural plant detritus makes up only a minor portion of soils in the Sierra Pelona watershed. Decay and nitrification of this organic matter provides a continuous but small source of nitrate over the surface of much of the Sierra Pelona Valley.

Geology. The geology of the small Sierra Pelona Valley is quite complex (*12, 13*), with folded and faulted metamorphic (Pelona formation) and igneous (Transverse Range batholith) basement overlain by additionally folded and faulted Tertiary age sediments and volcanics (Vasquez and Tick Canyon formations). These rock units (Figure 1b) have all been

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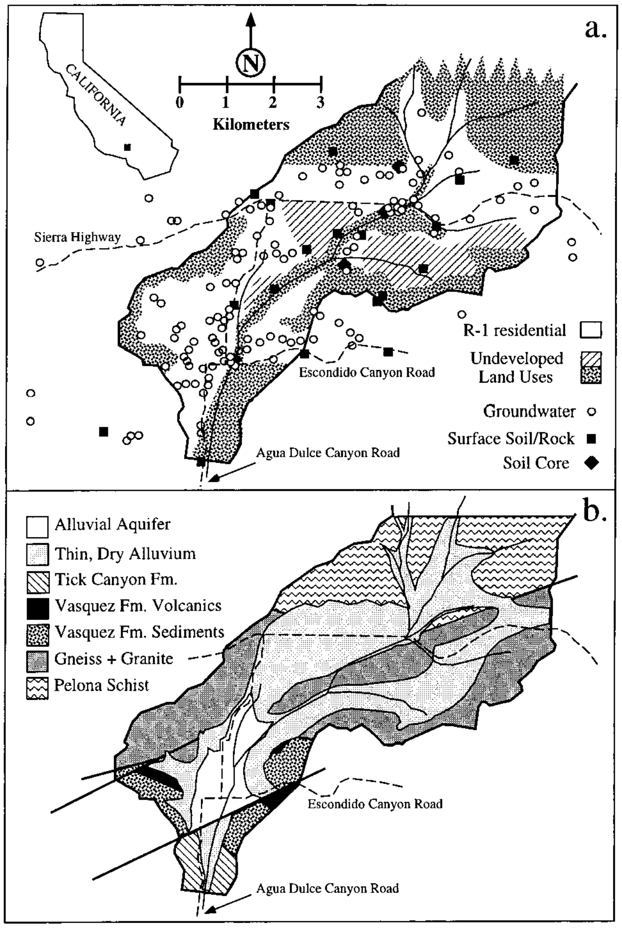

FIGURE 1. Maps of the Sierra Pelona watershed (heavy outline). Drainages (thin solid lines) and major roads (dashed lines) shown for reference. (a) Location map of sampling (symbols). Unshaded areas are rural residential (R-1) zones typically developed to ≥ 2 acre lots. Diagonal shading indicates R-1 regions as yet undeveloped, while dotted shading shows unoccupied land uses [airport, flood plain, hillside management, national/regional parks, and open space (*5, 6*)]. (b) Simplified geologic map of basement and alluvial unit outcrop areas. Saturated alluvial aquifer is distinguished from non-water-producing alluvium.

incised by erosion, and the valleys partially filled with Quaternary sedimentary alluvium. From the northeast (headwater) to the southwestern (outflow) portions of this watershed (Figure 1b), basement rock units can be described as follows:

Muscovite-rich, coarse-grained schists of the Precambrian Pelona formation outcrop on Sierra Pelona ridge and most of the watershed north of Sierra Highway (Figure 1b). Although primarily coarse, well-foliated schist, this unit also contains occasional veinlets and mappable layers of quartzite and marble (*12*). Because of its resistance to weathering and the typically steep terrain, this rock commonly outcrops or is near the surface.

Granitic and gneissic rocks (Figure 1b) represent likely Mesozoic intrusion into meta-sediments of the Pelona formation (*12*). Grain size, texture, and mineralogy vary from medium-grained massive granites to layered gneissic zones with as much as 50% highly foliated, mica-rich material.

Tertiary age rocks in the Sierra Pelona region include the Oligocene Vasquez and Miocene Tick Canyon formations, which both occur only in the southern, downstream portion of the basin (Figure 1b). The older, Vasquez formation is a sequence of non-marine, exclusively granite-clast conglomerates and sandstones, interbedded with basaltic to andesitic flows and shallow intrusives (*12*). Subangular to subrounded boulder to sand size Vasquez sediments are cemented by calcite, clays, and iron oxides producing a range of colors from white to deep red. The Miocene Tick Canyon formation (*12, 13*) is similarly made up of variable (conglomerate to silt), gray to reddish-brown sediments, unconformably overlying folded and eroded Vasquez at the southernmost end of the Sierra Pelona watershed (Figure 1b).

Erosional valleys of Quaternary to Holocene age are partially filled with weakly consolidated alluvial sediments (Figure 1b) derived from local bedrock hills. These sediments were deposited and re-eroded in several stages, leaving incised terraces in many of the canyons. Gravel and pebble size clasts of Pelona schist and granitic rocks are common in the generally coarse to fine sand that dominates this alluvium.

Hydrology. Surface waters from the Sierra Pelona catchment area flow generally southwestward in a branched array of overland streams (solid lines, Figure 1). Although rapid percolation occurs locally in the coarse, permeable sediments of Agua Dulce Canyon (south of Sierra Highway, Figure 1), the generally steep topography, shallow bedrock, and infrequent but strong rainfall events encourage runoff and outflow from the southern basin boundary. Percolation of rainfall on the Sierra Pelona watershed itself represents the only natural recharge to groundwaters in the Sierra Pelona basin.

In this rural area, groundwaters are extracted primarily from individually owned water wells drilled near to residences (Figure 1a) on parcels of 2 acres or more. Large portions of the watershed are undeveloped or are unusable for residential purposes (Figure 1a). Disposal/recharge of wastewaters is similarly local, with each residence using a septic tank and leach field system. Within a small (1.62 km^2) region in the south central portion of the basin (alluvial aquifer, Figure 1b), wells produce primarily from permeable and water-saturated alluvial fill typically greater than 50 m in thickness (*4, 5*). In all other areas, water wells must produce from basement rock fractures, since alluvial cover is either absent (26.7 km^2, Figure 1b) or insufficiently thick to ensure a reliable water supply during irregular drought-recharge cycles (16.2 km^2 of thin, dry alluvium, Figure 1b).

Previous Work. Initial groundwater research (*4*) involved water quality data from state and county records as well as four new water samples taken for chemical analysis in 1981. Of the 17 wells studied, NO_3−N varied from 0.2 to 42 mg/L, with an average of 6.9 mg/L. Four of 17 wells exceeded the public drinking water nitrate MCL of 10 mg/L (as NO_3-N). Average water quality was determined to be acceptable. Montgomery (*4*) concluded that extraction and use of that groundwater reserve slightly exceeded long-term recharge. Community residents responded with their own, independent groundwater quality investigation (*7*). Thirty-two wells sampled in 1982 ranged in NO_3-N concentration from 0.98 to 12.3 mg/L with an average value of 3.8 mg/L. Only two of the 32 wells analyzed exceeded the nitrate MCL.

Hydrogeologic and geochemical investigations (*5*) included collection of information on water quality, a well survey, characterization of land use and assessment of groundwater quality and quantity. Historical information was compiled from all government agencies, and 48 new wells were sampled for water quality, showing an NO_3-N average of 5.8 mg/L. Fourteen of 74 wells exceeded the MCL for nitrate, with a cluster near the center of the basin exhibiting the highest frequency of nitrate contamination. Their report (*5*) concluded that septic tank effluent was the primary source of the nitrate contamination. They also asserted that population growth could easily overwhelm the small volume alluvial aquifer and the low storage capacity fractured reservoir.

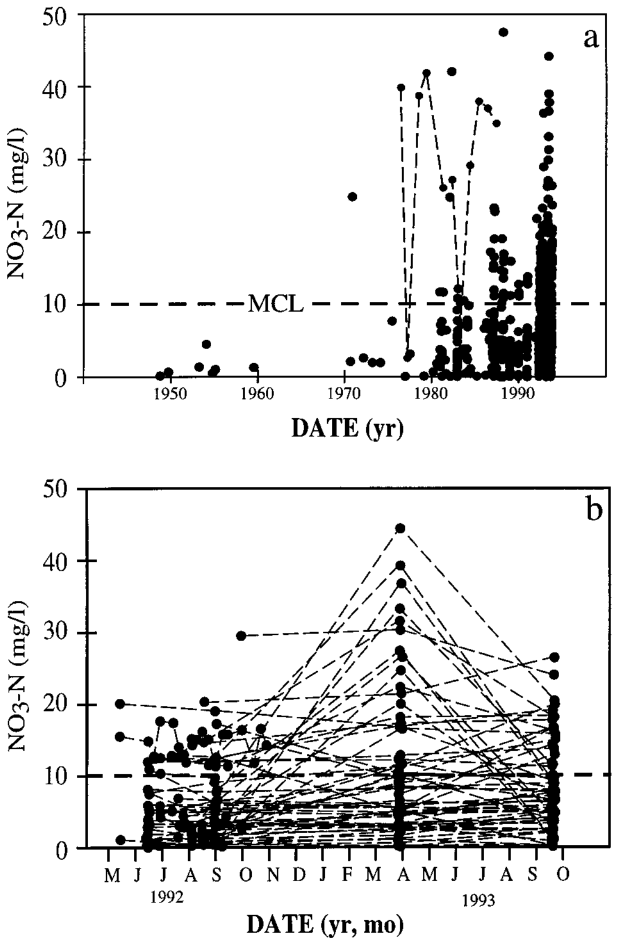

FIGURE 2. Nitrate-N concentration data of Sierra Pelona region. Public drinking water maximum contaminant level (MCL) shown for reference. Connected symbols (dashed lines) monitor variability of individual wells. (a) All available well water analyses (*5, 6*). (b) Analyses from this study.

A preliminary suite of nitrogen stable isotope ratio analyses were performed on six groundwaters and six soil samples from the Sierra Pelona region (*8*). Their consultant concluded that dominantly natural soil and rock nitrogen were present.

More recent geochemical and hydrological sampling, analysis, and modeling (*6*) will be discussed in this and a related manuscript (*9*). Published and new NO$_3$-N concentration data from groundwaters of the Sierra Pelona area (Figure 2a) illustrate a history of high and generally increasing levels of nitrate contamination. This increase roughly follows the region's population growth over the last half century (ref 6 and references cited therein). Repeat samplings of individual wells (dashed lines, Figure 2a,b) show the erratic nature and rapid variability of contaminant superimposed on the long-term increase of nitrate in the basin (*6*).

Description of Approach. Research discussed in this paper focuses on several primary questions: (1) Do significant sources of natural nitrate exist in the rocks or soils of the basin? (2) Do natural and/or anthropogenic nitrates show chemical or isotopic signatures that provide constraints on source and transport of contaminants? (3) Do chemical and isotopic data provide mass balance constraints on contamination? To address these questions, groundwaters as well as surface rocks, soils, and a few shallow soil profiles were sampled (*6*). Groundwaters and leachates from rocks and soils were then subjected to chemical and stable isotopic analysis.

Methods

Rock and Soil Sampling. Rock and soil sampling in the Sierra Pelona region involved an areally distributed suite of locations (filled squares, Figure 1a) where representative outcrops of each rock type (Figure 1b) and soils from undisturbed natural settings could be obtained. Clean, hand samples representative of each outcrop were collected and stored in labeled, air-tight plastic bags for laboratory processing. Surface samples of the uppermost 0.3 m of soil were collected by shovel, after clearing above-ground portions of plants. Roughly 2 kg of soil was taken at each site and stored in sealed plastic bags until processed.

Soil borings (filled diamonds, Figure 1a) were performed in four areas of differing land use (*6*), providing soil profiles (Figure 4) to depths as great as 11.6 m. Continuous cores were taken from the surface to termination using a dry auger, split tube core drill, and a truck-mounted hydraulic drilling rig. Samples representing each foot (0.3 m) penetrated were cut directly from the core tube into sealed plastic-lined containers for transport. Solid samples were air dried prior to leaching for chemical or isotopic analysis.

Well Sampling. Wells of more than 150 cooperating property owners in the Sierra Pelona basin (*6*) were repetitively sampled for geochemical and stable isotopic analysis. Sample locations covering all occupied regions (open circles, Figure 1a) represent approximately 8% of wells in the Sierra Pelona basin, with a distribution that representatively mimics that of residences. Blind, alphanumeric identification codes (*6*) and only rough locations (Figure 1a) of these wells were utilized to maintain cooperator anonymity. Despite records searches of all regulatory agencies (*6*), little data concerning construction of the wells sampled were uncovered. Although typical of many rural areas, this lack of information severely limits 3D hydrologic interpretations.

Water samples were collected from outlets on pumped water lines, as near to the wellhead as possible. The water tap was allowed to run for a few minutes while an electrical conductivity (EC) meter monitored removal of standing water from the well and pipelines. Fresh groundwater was then collected into a clean polyethylene container and rinsed at least twice with the water to be sampled. Aliquots were dispensed into appropriate acidified and unacidified sample bottles for geochemical and isotopic analysis and transported, on ice, to the laboratory.

Laboratory Operations. Chemical analyses of groundwaters and soil extracts were performed in University of California, Riverside, laboratories using appropriate standard procedures (*6*). For data discussed in the present paper, nonacidified samples were analyzed for chloride (Cl$^-$) using EPA Standard Method 325.2/407D. Aliquots stabilized with H$_2$SO$_4$ were analyzed for ammonium (NH$_4$-N), nitrate (NO$_3$-N), and nitrite (NO$_2$-N) nitrogen (EPA Methods 350.1/417F, 353.2/418F, and 354.1/419, respectively).

Stable isotope ratio measurements on dissolved nitrate or ammonia in acid-stabilized Sierra Pelona groundwaters or rock/soil leachates were performed using the standard techniques of steam distillation and Devardas' alloy reduction (*14*). N-bearing condensates were pH neutralized, and the nitrogen was collected quantitatively onto a molecular sieve (*15*). Quantitative conversion to N$_2$ was accomplished by the sealed tube Cu/copper oxide method (*16, 17*). Cooling rates were controlled to prevent formation of nitrogen oxides. N$_2$ was purified cryogenically, collected by adsorption at -196 °C onto a molecular sieve (*16, 18*) and then quantitatively desorbed at ≈ 70 °C for δ^{15}N analysis by direct comparison in a V.G. PRISM isotope ratio mass spectrometer.

Results and Discussion

Rock and Soil Samples. *Concentration of Nitrogen Compounds.* Concentrations of leachable NO$_3$-N from bedrock

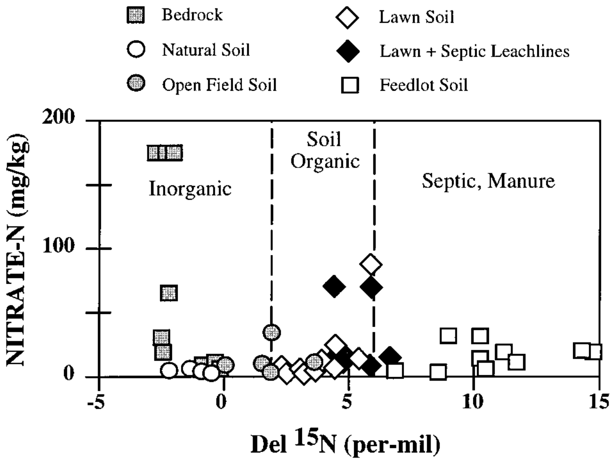

FIGURE 3. Rock and soil nitrate concentrations and ^{15}N isotope ratios. Interpretive isotope ranges (*2, 3, 6, 22*) are shown.

outcrops in the Sierra Pelona region ranged from 0.3 mg/kg to a surprisingly high 177 mg/kg (Figure 3). With the exception of hematite-stained, red sediments of the Vasquez formation (Figure 1b), leachable nitrate is generally low in basement rocks. Vasquez sediments from a single outcrop indicate significant but very variable concentrations of KCl-leachable nitrate, from negligible ($\leq$0.8 mg/kg) in a white sandstone to a high of 177 mg/kg in red sandstone.

Leachable NH_4-N, ranging from 0.7 to 26.9 mg/kg, has also been measured in a number of basement rocks of the Sierra Pelona region (*6*). Although most rock samples release negligible ammonium, notable concentrations were liberated from Pelona schist fragments subjected to 1.0 N KCl solution leaching immediately after the sample was pulverized. Leaching using 0.1 N KCl produced far lower concentrations, and negligible amounts were measured in deionized water leachate.

Surface soil samples in undisturbed, natural sites have variable (0.5−5.8 mg/kg) but typically low (Figure 3) concentrations of KCl-leachable NO_3-N. Similarly, leachable NH_4-N in such sediment samples is invariably low (0.8−2.2 mg/kg). Soils from regions disturbed by anthropogenic land use effects (Figures 3 and 4a−d) show significantly greater variability in leachable nitrate abundance. Soil samples from an open field (Figure 4a) and from irrigated lawn environments (Figure 4b) show elevated near-surface concentrations (as high as 80 mg/kg) of leachable NO_3-N, which rapidly decrease with depth to near-background values (~2.0 mg/kg) a few feet below the surface. Only in a residential lawn area adjacent to a septic leach field (Figure 4c) and at an abandoned animal containment facility (Figure 4d) were significant soil nitrate concentrations observed at depth. In those core holes, consistently elevated 8−22 mg/kg concentrations were observed throughout deep intervals in the vadose soil profile (Figure 4c,d).

Nitrogen Isotope Ratios. Isotope ratios of nitrogen (δ^{15}N) in rock and soil leachates cover a wide composition range, from −3.0‰ to +15‰ (Figures 3 and 4e−h). Isotope ratios from basement rock outcrops and surface soils in undisturbed natural sites almost universally fall in the narrow range from −2.8‰ to 0.0‰.

Surface and deep soil samples from an open field (Figure 4e), having only sparse natural vegetation, show a limited isotopic range from −0.3‰ to +3.7‰. A similar range (Figure 4f) is seen for deep soil samples from both a moderately irrigated lawn and a well-watered lawn profile 30 m away from septic leach lines [site 1, boring 1.2 (*6*)]. Significantly heavier nitrogen isotopic compositions (+4.0‰ to +6.6‰) are however observed in the surface soils of these sampling locations (Figure 4f) as well as in shallow and deep soils (Figure 4g) in drilled profiles within 5 m of the residential septic leach field. Still heavier isotope ratios (+6.8‰ to +14.6‰) pervade all depths in the soil borings (Figure 4h) beneath an abandoned pig farm.

Natural Nitrate. *Inorganic Nitrate in Rocks.* Rock and barren soil samples collected from the Sierra Pelona basin illustrate several potential sources of nitrogen. In particular, occasionally high levels of leachable nitrate are seen in red-bed sediments of the Vasquez formation, while modest levels of leachable ammonium are observed in schists of the Pelona formation (Figures 1b and 3).

NO_3-enriched sedimentary rocks of Tertiary age have previously been documented in California (*19*). In their investigation, enrichment trends were similar to the Sierra Pelona situation, in that concentrations were highest in hematite-stained and cemented terrigenous deposits of the Tulare formation, but far greater levels of nitrate were observed [as high as 3000 mg/kg (*19*)]. Metamorphic rocks, somewhat similar to the Pelona formation have also been shown to contain modest quantities of nitrogen (*20, 21*), dominantly associated with micaceous phases. Although leachable nitrogen was not investigated in their whole-mineral and whole-rock analyses, NH_4 concentrations [tens to hundreds of mg/kg (*20, 21*)] support Sierra Pelona results reported here.

Nitrogen isotopic compositions of N-bearing leachates from rocks as well as soil samples in sparsely vegetated areas (Figures 3 and 4e) cluster at ^{15}N-depleted values (<2‰) often considered typical of inorganic, fertilizer nitrogen (*2, 3*). No published studies of nitrogen-bearing sediments include isotopic data, and little information on δ^{15}N in metamorphic rocks is available (*21*). Their study reports values significantly $_{15}$N enriched relative to the isotopic ratios measured in the present study, although comparison of whole rock N (*21*) with leachable N in the present study is likely to be inappropriate.

Organic Nitrate in Soils. Degradation and oxidation of natural organic material in the soil provides modest to significant quantities of nitrate to the uppermost layers of soil in some locations in the Sierra Pelona basin. As discussed earlier, the arid climate limits annual growth of native chaparral, whose decay therefore constitutes only a minor source of surface nitrate. Undisturbed natural soils and those from unirrigated sites (Figure 4a) indicate NO_3-N concentrations less than 40 mg/kg, confined to the uppermost 0.3 m of the soil profile. It is likely that much of this annual nitrate load is assimilated in plant growth rather than serving as a source of groundwater contamination.

Nitrogen isotopic compositions of natural soil nitrate in the Sierra Pelona basin (Figure 4e) appear slightly more ^{15}N depleted (−2‰ to +4‰) than published ranges of soil nitrate [+2‰ to +6‰ (*2, 3*)]. This is likely due to the presence of inorganic "rock" nitrogen and the limited amount of plant−organic contribution in this arid region.

Anthropogenic Nitrate. *Enhanced Organic Soil Nitrate.* Human activities such as irrigation, landscaping, and growing of crops often enhance the amount of organic litter incorporated into the soil. Nitrification of such enhanced levels of plant material apparently increases the near-surface abundance (30−100 mg/kg) of NO_3-N in soil profiles beneath lawns (Figure 4b,c). Increases in surface nitrogen, however, do not routinely provide increased quantities of NO_3-N to depths greater than 1 m into the soil profile (Figure 4b), most likely because the increased rate of plant growth serves to assimilate this nitrate before it percolates below the root zone. Isotopic compositions of nitrified plant organic material (Figures 4f) appear similar to literature compilations [+2‰ to +6‰ (*2, 3*)] and are also similar to the upper range of those observed in natural soils (Figure 4e).

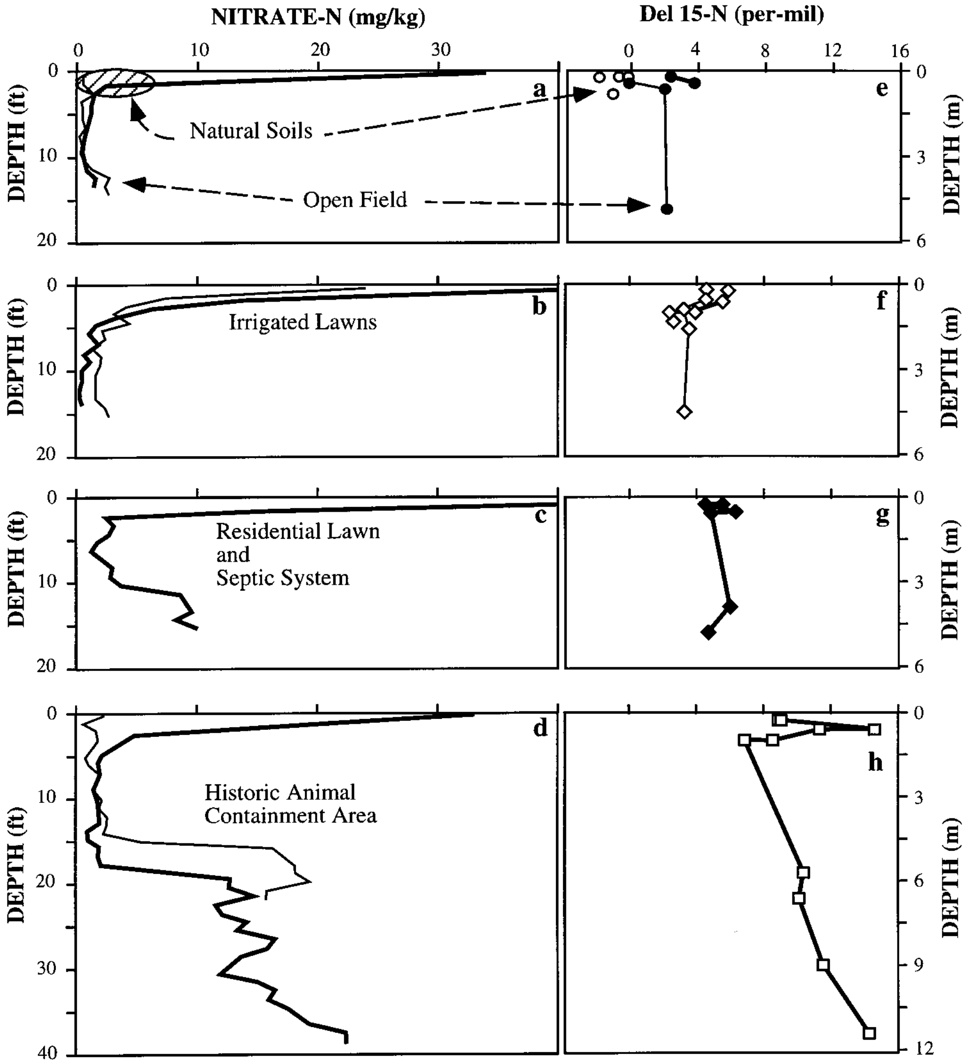

FIGURE 4. (a–d) Rock and soil nitrate concentration profiles. Curves illustrate profiles in soil core samples from different localities. Shaded envelope encloses data from nine undisturbed natural soil sites. (e–h) Rock and soil nitrate ^{15}N isotope ratio profiles. Symbols as in Figure 3.

Septic Nitrate. In deep portions of a soil profile affected by a nearby septic leach line (Figure 4c), nitrate concentrations are significantly enhanced. Leachable NO_3-N of nearly 10 mg/kg appears at depths where natural and lawn soil profiles (Figure 4a,b) show negligible concentrations.

Animal Waste Nitrate. Although no Sierra Pelona resident volunteered their animal containment facility for investigation, data from published studies clearly show consistent high to extreme levels of nitrate in the subsurface (*2, 3, 22*). In the Sierra Pelona basin, soil cores beneath an abandoned pig farm (Figure 4d) show consistent 15–22 mg/kg concentrations of leachable NO_3-N from 4 to at least 12 m below the surface.

Nitrogen isotopic compositions of such animal waste nitrate (Figure 4h) are significantly more ^{15}N enriched (+7.5‰ to +15.5‰) than other nitrates in this study. Such values agree well with published ranges of animal waste nitrate (*2, 3, 22*) that has not undergone extensive ammonia volatilization or bacterial denitrification. The effect of either of these processes would be to produce isotopically heavier soil nitrate and a general inverse correlation between isotopic composition and nitrate concentration. Such features are not observed in any soil profiles here (Figures 4a–h), implying that ammonia volatilization and bacterial denitrification have only a minor effect on nitrate balance in the dry, permeable soils and sediments of the Sierra Pelona region.

Groundwater Samples. *Concentration of Nitrogen Compounds.* Both nitrite and ammonia were found to be negligible in waters sampled from the Sierra Pelona basin (*6*). Nitrate, however, was generally significant (Figures 2 and 5–7), often a major, component and occasionally the dominant anion. NO_3-N concentrations in historical data (Figure 2a) (refs 5 and 6 and references cited therein) as well as that from this study (Figure 2b) vary from below detection to more than 45 mg/L. Despite erratic historical sampling and short-term variability (Figure 2b), a general, basinwide increase in frequency and magnitude of NO_3-N contamination is apparent (Figure 2). The percentage of sampled wells producing waters in excess of the nitrate MCL as well as the inferred basinwide mean NO_3-N concentration (Figure 2a) increased significantly over the last few decades (*6*).

Nitrogen Isotope Ratios. Groundwater samples from the Sierra Pelona basin show a wide range in nitrate $\delta^{15}N$, from −2‰ to +10‰ (Figure 5). Modal compositions are in the "natural soil" range of +3‰ to +5‰ (*2, 3*). Only a small number of samples show "inorganic" or fertilizer compositions more depleted than +2‰ (*2, 3*); however, a significant percentage of analyses, particularly those with high NO_3-N concentration, show organic "septic or manure" nitrate signatures, more ^{15}N enriched than +6‰ (*2, 3*).

Chemical Composition. Major anion and cation analyses of Sierra Pelona groundwaters (*6*) illustrate wide ranges in

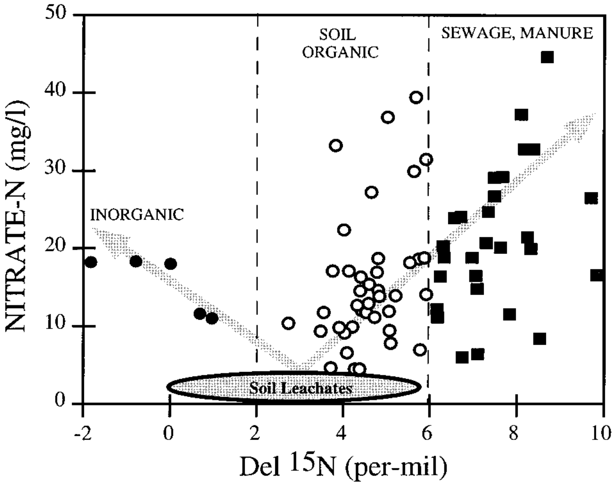

FIGURE 5. Nitrate concentrations and ^{15}N isotope ratios in groundwaters. Different symbols used for δ^{15}N interpretive ranges (*2, 3, 6, 22*) for distinctive nitrate sources. Isotopic range of leachates from deep, vegetated soils is indicated by shaded envelope.

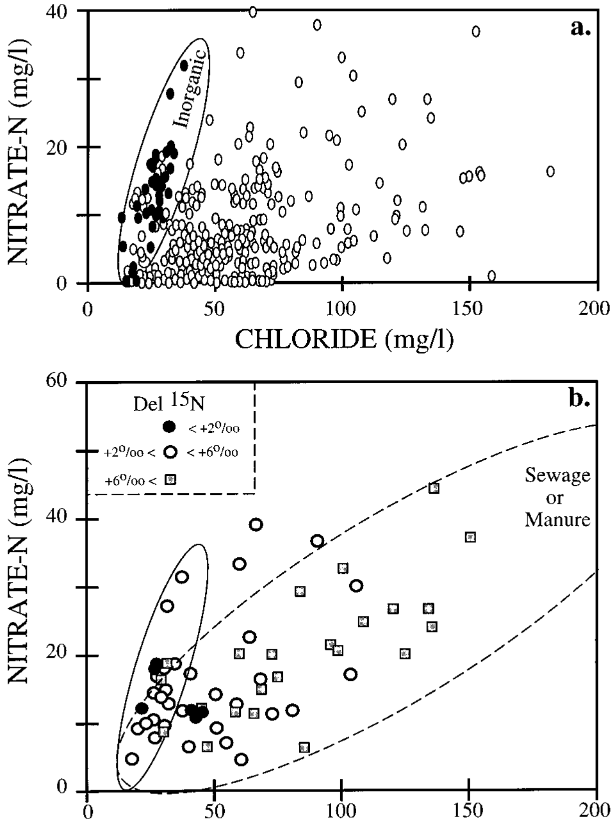

FIGURE 6. Nitrate-N vs chloride groundwater compositions in Sierra Pelona. (a) Analyses from this study. Unusual, low Cl$^-$, low SO_4^{2-}, inorganic type (*6*) waters (envelope and filled symbols) have been distinguished. (b) Isotopically analyzed groundwaters distinguished by their δ^{15}N isotopic composition. Solid envelope as in panel a; dashed envelope encloses data with high δ^{15}N sewage or manure source.

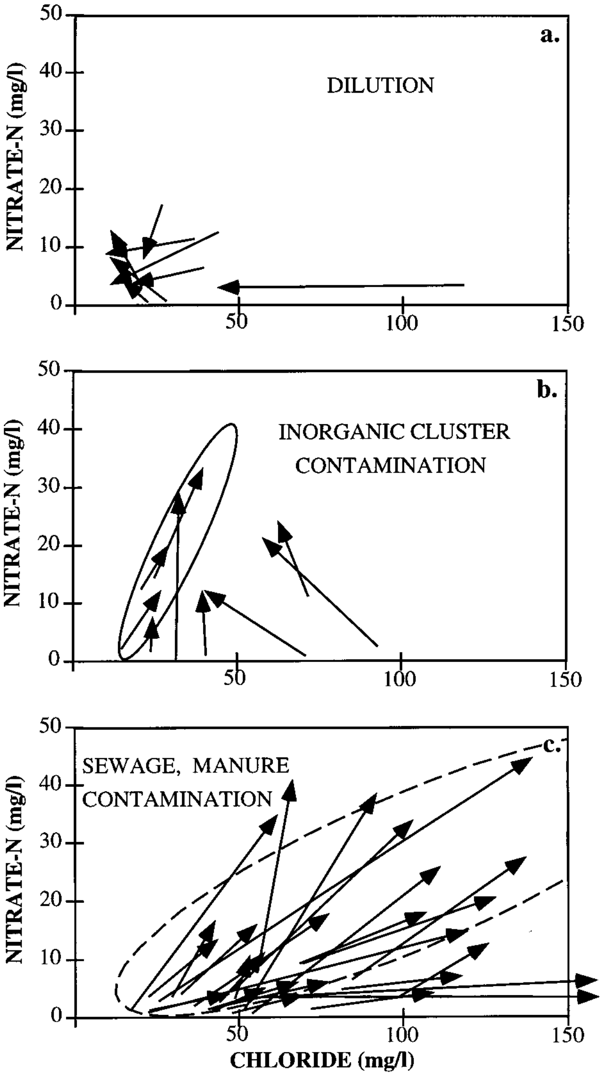

FIGURE 7. Changes in groundwater nitrate and chloride between 1992 and spring 1993 samplings (arrows) as shown on Figure 2b. (a) Wells that show dilution of contaminant. (b) Wells that show increased inorganic type (*6*) nitrate contamination. Envelope as in Figure 6a. (c) Wells that show increased sewage or manure contamination. Dashed envelope as in Figure 6b.

both concentration and composition. Significant variations in anion chemistry are seen both spatially and temporally. For example, nitrate/chloride ratios (Figure 6) and sulfate/chloride ratios (*6*) as well as absolute concentrations can differ by over an order of magnitude. Spatial clustering (*6*) of waters having distinctive, identifiable SO_4/Cl ratios is reportedly produced by interaction with differing aquifer host rocks (*6*). Contaminant chemistry appears superimposed upon this natural chemical variability (*6*). Temporal changes in dissolved ion chemistry in individual wells (Figures 2b and 7), occur rapidly, permitting monitoring of contaminant incorporation and movement within the basin (*6*).

Nitrate Contaminant Sources and Mass Balance. Since the arid and permeable soil in this study area is unsuitable for denitrification (*22, 23*) and no evidence exists for isotopic enrichment by volatilization or denitrification processes, groundwater isotopic compositions likely indicate the nitrate's sources or their mixture of sources. We can be relatively certain that the small percentage of waters analyzed as ^{15}N depleted (<2‰, Figures 5 and 6b) obtain their nitrate from a dominantly inorganic source, either rock nitrogen (Figure 3) or from unspecified fertilizer use (*2, 3, 22*). Similarly, we can be quite sure that isotopically enriched groundwater samples (>6‰, Figures 5 and 6b) obtain much of their nitrate from animal waste sources such as sewage or manure (Figure 4g,h), (*2, 3, 22*). Nitrate transport modeling (*6, 9*) of the Sierra Pelona region, however, shows conclusively that a consistent near-surface water flux (far in excess of that supplied by rainfall) is necessary to move nitrate to reach groundwater table at significant depth. We infer that sewage nitrate, mobilized by the near-constant water flux of the septic leach system, is a more likely source of isotopically enriched nitrate contaminant than is manure from a relatively dry environment.

Sources for intermediate isotopic composition groundwater nitrates (+2‰ to +6‰, Figures 5 and 6b) are far less certain. Such compositions could reflect soil nitrification of plant detritus (Figure 4f), (*2, 3, 22*) grown either under natural or irrigated conditions. Based on the modeling described above (*6*, *9*), we infer that irrigation water flux makes it a more likely source for such contamination. Isotopically intermediate waters (Figures 5 and 6b) could also indicate mixtures between ^{15}N-depleted (inorganic or soil) and enriched (sewage or manure) contaminants. The somewhat fan-shaped data array of intermediate to enriched compositions (Figure 5) supports mixing of a relatively low δ^{15}N soil-source component (≈+2‰), similar to undisturbed natural soil samples (Figures 3 and 4e) with nitrate-rich high δ^{15}N sewage/manure sources (shaded arrow to right, Figure 5).

Mass balances of various nitrate sources can be computed using methods based on isotopic and major ion chemistry (*6*). Different methods of identifying and defining contaminant and dilutant end-member compositions lead to a variety of mass balance estimates. A very conservative estimate of anthropogenic animal waste contribution (>12%) can be computed using only those groundwater analyses in which correlation of contaminant NO_3^- and Cl^- (*24*) can be distinguished from background variability (*6*) in chloride from low nitrate waters ($Cl^- > 70$ mg/L, Figure 6a). Isotopic groupings (Figure 5) provide a somewhat less conservative estimate. Of nitrate in the samples analyzed, only 5.9% appears to be of inorganic origin while at least 39.7% shows clearly anthropogenic sewage/manure isotopic signatures. The remaining 54.4% shows intermediate isotopic signatures or represents nitrate present at concentrations lower than convenient for our isotopic analyses. More sophisticated mass balance computations (*6*) involving both chemical and isotopic signatures (Figures 5 and 6b) indicate that anthropogenic contributions are likely >40%. The rapid contaminant influx, which occurred with flood recharge of spring 1993 (*6*) (Figures 2b and 7b,c), gives the least conservative estimate of anthropogenic contaminant contribution. Chemically (*6*) and isotopically inferred inorganic sources (*6*) (Figures 6a,b and 7b) appear responsible for approximately 10% of the total nitrate load in 1993 groundwaters. Nitrate contaminants linked to significant increases in chloride (Figures 6b and 7c), however, account for roughly 49% of the total basinwide nitrate observed in 1993 groundwaters. Natural and irrigation-enhanced plant detritus nitrates and various indeterminant mixtures account for no more than 31% of the nitrate in the Sierra Pelona basin.

Summary. Chemical and stable isotopic studies of groundwaters, rock, and soil from the Sierra Pelona basin in Los Angeles County, California, indicate the presence of both natural and anthropogenic sources of nitrate contamination. Rocks and natural soils may supply as much as 10% of the observed contamination while definitively anthropogenic, most likely sewage and less likely domestic animal, waste contributes more than 49%. Although there is a large remainder (31%) from indeterminant sources, transport modeling (*6, 9*) and water quality histories (Figure 2a,b) imply that residential growth in the second half of the 20th century has affected this basin to the extent that average produced groundwater from the Sierra Pelona area is now approaching the federal drinking water standard MCL of 10 mg/L for nitrate-N.

Investigations funded by governmental agencies but studying groundwater contamination in rural areas such as the Sierra Pelona basin succeed only with the support and cooperation of members of the community. Similarly, solutions to such contamination will be best achieved by cooperation between government regulators and residents. Many of the most direct mitigation steps to confront anthropogenic nitrate contamination [proper construction, repair or upgrading of septic systems and water wells, and control of animal waste (*6*)] are up to individual land owners. In rural areas, only the most draconian and expensive options [limitations on growth, construction of centralized sewer or water supply (*6*)] are under direct control of government agencies.

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Literature Cited

(1) *Metropolitan's role in the development of groundwater in southern California.* Metropolitan Water District of Southern California, Los Angeles, Discussion Paper, December 1990.

(2) Komor, S. C.; Anderson, H. W., Jr. *Ground Water* **1993**, *31* (2), 260−270.

(3) Rolston, D. E.; Fogg, G. E.; Grismer, M. E.; Benjamin, A.; Decker, D.; Louie, D. *Identificationand evaluation of methods for determining sources of nitrate contamination in groundwater.* Final report to California Water Resources Board and Regional Water Quality Control Board, Central Coast Region, San Luis Obispo, CA, 1994.

(4) Montgomery, J. M. (Consulting Engineers Inc.) *Phase I Agua Dulce/Mint Canyon Hydrogeologic Investigation.* Report to County of Los Angeles, Board of Supervisors, 1982.

(5) CH2M-Hill. *Phase II: Stages I, II, III, Agua Dulce Hydrogeologic Investigation.* Final reports to County of Los Angeles, Department of Public Works, 1988.

(6) Williams, A. E.; Lund, L. J.; Kabala, Z. *Investigation of nitrate contamination in the Sierra Pelona groundwater basin, Agua Dulce.* Final Report to California Regional Water Quality Control Board, Los Angeles Region, Monterey Park, CA, 1996.

(7) *A study of water quality, quantity and usage.* Agua Dulce Ad Hoc Committee report to Agua Dulce Town Council, Agua Dulce, CA, Feb 1983.

(8) *Agua Dulce Water Committee Presentation.* Agua Dulce Water Committee report to California Regional Water Quality Control Board, Monterey Park, CA, March 1990.

(9) Kabala, Z. J.; Schaad, D. E.; Williams, A. E.; Lund, L. J.; Johnson, J. Modeling nitrate contamination transport in the vadose zone of the Sierra Pelona basin. *Environ. Sci. Technol.* Submitted for publication.

(10) Bailey, H. P. *The climate of southern California;* University of California Press: Berkeley, CA, 1966; 87 pp.

(11) *Climatological Data, California;* U.S. National Oceanic and Atmospheric Administration: Washington, DC, 1994.

(12) Muehlberger, W. R. *Bull. Am. Assoc. Petrol. Geol.* **1958**, *42*, 1812−1844.

(13) Dibblee, T. W., Jr. *Geologic map of the Boquet Reservoir Quadrangle, Los Angeles County,California;* U.S. Geological Survey (scale 1:62500): Denver, 1961.

(14) Bremner, J. M.; Edwards, A. P. *Soil Sci. Am. Proc.* **1965**, *29*, 504−507.

(15) Velinsky, D. J.; Pennock, J. R.; Sharp, J. H.; Cifuentes, L. A.; Fogel, M. L. *Mar. Chem.* **1989**, *26*, 351−361.

(16) Macko, S. A. Ph.D. Dissertation, University of Texas, Austin, 1981.

(17) Kendall, C.; Grim, E. *Anal. Chem.* **1990**, *62*, 526−529.

(18) Mariotti, A. *Nature* **1983**, *303*, 685−687.

(19) Strathouse, S. M.; Sposito, G.; Sullivan, P. J.; Lund, L. J. *J. Environ. Qual.* **1980**, *9*, 54−60.

(20) Honma, H.; Itihara, Y. *Geochim. Cosmochim. Acta* **1981**, *45*, 983−988.

(21) Haendl, D.; Muhle, K.; Nitzsche, H.-M.; Stiehl, G.; Wand, U. *Geochim. Cosmochim. Acta* **1986**, *50*, 749−758.

(22) Rees, T. F.; Bright, D. J.; Fay, R. G.; Christensen, A. H.; Anders, R.; Baharie, B. S.; Land, M. T. *Geohydrology, water quality, and nitrogen geochemistry in the saturated and unsaturated zones beneath various land uses, Riverside and San Bernardino counties, California*: U.S. Geological Survey Water Resource Investigation Report 94-4127; U.S. Geological Survey: Denver, 1995.

(23) Gambrell, R. P.; Gilliam, J. W.; Weed, S. B. *J. Environ. Qual.* **1975**, *4*, 311−316.

(24) Walker, W. G.; Bouma, J.; Keeney, D. R.; Magdoff, F. R. *J. Environ. Qual.* **1973**, *2*, 475−480.

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