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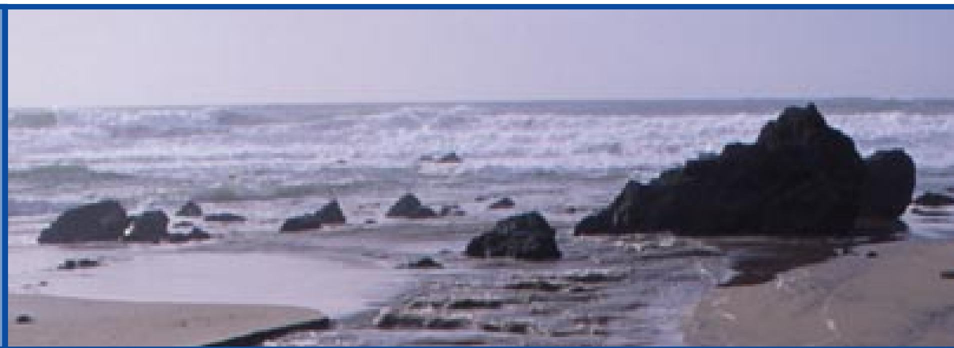

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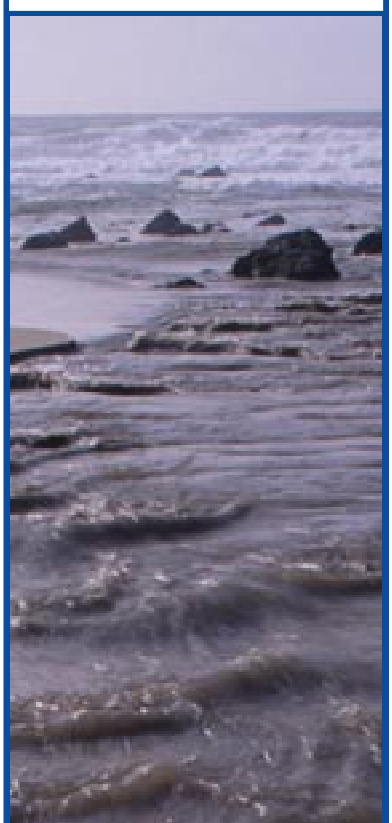

Distinguishing sources of groundwater nitrate by ^{1}H NMR of dissolved organic matter

by Jianhang Lu, Andrew C. Chang, Laosheng Wu

Abstract

Dissolved organic matter (DOM) originating from a certain source usually carries characteristic marks in its molecular structures that can be recognized by spectroscopic analysis. Sources of water-borne contaminants, such as nitrate, can be identified by recognition of the characteristics of DOM entrained in the water. In this study, DOM in groundwaters sampled from a dairy/crop production area (Chino Basin, CA) was analyzed by ^{1}H nuclear magnetic resonance (^{1}H NMR). Results showed that DOM derived from natural soil organic matter has a characteristic resonance at a chemical shift region of 4.0-4.3 ppm, while DOM derived from dairy wastes has a characteristic resonance at a lower chemical shift region of 3.2-3.6 ppm. These signature resonances were then used to distinguish the origins of nitrate in the groundwater. It was found that disposal of dairy wastes on croplands is the primary source of nitrate contamination in groundwater underlying the Chino Basin dairy area.

1. Introduction

The chemical composition and structural nature of dissolved organic matter (DOM) in soils and aquatic environments vary with their origins (Ghosh and Schnitzer, 1980; Gschwend and Wu, 1985). DOM derived from a certain source usually carries structural marks related to the characteristics of its parental materials and/or decomposition history. For example, fulvic acids derived from organic waste-treated soils occur in a less oxidized state than those extracted from naturally occurring soil organic matter (Sposito et al., 1978). DOM fractions from urban waste composts are rich in aliphatic structures compared to DOM from soil, surface, and ground waters, as indicated by wet chemistry

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Andrew Chang Named Director of WRCA's Parent Unit

Andrew Chang, UC Riverside professor and agricultural engineer, has been appointed director of UC Center for Water Resources.

Chang, who previously served as associate director of the Center for Water Resources, is a nationally and internationally recognized research scientist in water quality management and water reuse, and has worked on some of the state's critical water-quality issues.

"He will bring a great deal of experience in developing and managing research programs to the operation of the center," said Steve Angle, dean of the College of Natural and Agricultural Sciences. "As more and more faculty, specialists and advisors are involved in water-related issues in various respects," Chang said, "the Center will make an effort to coordinate their activities through funding research projects, organizing workshops and conferences, and developing forums for policy discussions."

The UCR campus was chosen to host the center for a five-year period after proposals from UC Berkeley, UC Davis and UC Riverside were considered. UC Center for Water Resources is a multicampus research unit that houses several systemwide water resources related research and outreach programs, namely, the Water Resources Center, Salinity and Drainage Program, Regional Water Quality Program, and Prosser Trust.

The 2005 Salinity and Drainage Conference (scheduled for March 22) will highlight 20 years of UC research to understand the salinity and drainage problem in San Joaquin Valley. The 25th Biennial Groundwater Conference (scheduled for Oct. 25 and 26) will be the 50-year anniversary of the conference.For more information about the Center, go to www.waterresources.ucr.edu.

Reprinted from ANR Report*, vol. 18, no. 7, January 2005, with permission. Read more about Andrew Chang's research in the cover article, about distinguishing between two sources of nitrate in groundwater in the Chino Basin of southern California.*

Water Resources Center Archives

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Mission *To maintain and continue to develop a collection of current and historical water-related materials to meet the needs of the University of California and the people of the state.*

Newsletter by Nancy Novitski except as otherwise noted.

Collecting the Papers on Dividing the Waters

An exciting recent addition to WRCA is a large collection of water law and policy materials from the Dividing the Waters project, a network of state and federal judges who preside over complex water-related litigation.

The Dividing the Waters Collection (MS 2003/1) consists of 23 cartons of materials submitted by judges and water management agencies, including books, articles, conference proceedings, court pleadings, and judicial orders and decisions. Materials in the collection are organized by topic (for example, general stream adjudication materials, water law issues, Indian reserved water rights, other federal reserved water rights) and by jurisdiction (18 states plus interstate materials).

The transfer of these materials to WRCA greatly facilitates public access. The collection is available for on-site viewing, except for a few items to which access is restricted. To search the collection contents, researchers may use the online finding aid, which describes and provides an inventory of the collection (see URL below).

The Dividing the Waters Collection was originally developed by Andrea Gerlak (now assistant professor of earth and environmental sciences at Columbia University) during her internship with the Office of the Special Master, Arizona General Stream Adjudication. It has been updated by Kathy Dolge, project administrator for Dividing the Waters.

The Dividing the Waters project began in 1992 to bring together judges and other judicial officers (special masters, commissioners, referees) who are responsible for general stream adjudications. These massive proceedings to determine existing water rights, usually involving thousands of parties, are pending in most western states.

The project soon expanded to involve judges who preside over other water-related litigation including interstate litigation pending before the U.S. Supreme Court and environmental and water quality litigation (such as litigation concerning California's Bay-Delta and Central Valley regions). Presently, 160 judges and judicial officers from around the United States, predominately from the West, are involved in the Dividing the Waters network.

The project also provides ongoing educational programs for judges, such as conferences and specialized workshops on topics such as alternative dispute resolution and water-related science, and supports publications, including forthcoming books and articles on general stream adjudications and Indian water rights.

Hosted by the Arizona Supreme Court in Phoenix, the Dividing the Waters project received initial funding in 1992 from the Ford Foundation and in recent years from the Hewlett and General Service Foundations. John E. Thorson, formerly Special Master for the Arizona Supreme Court and now an Administrative Law Judge for California, and Dan Hurlbutt, Idaho District Court Judge, are the original conveners of the project. They have been joined in recent years by Colorado Supreme Court Justice Gregory Hobbs and California Court of Appeal Justice Ron Robie.

The finding aid for the Dividing the Waters Collection is online at www.lib.berkeley.edu/WRCA/mss.html#D *(click on "finding aid" next to "Dividing the Waters Collection"). To learn more about the Diving the Waters project, visit* www.dividingthewaters.org.

Arthur Littleworth Oral History Completed

by Germaine LaBerge

Water—what subject could be more important in the arid western United States? For fifty years, the Regional Oral History Office (ROHO) of the University of California, Berkeley, has been documenting a broad variety of subject areas critical to the history of California and the United States. In 1965 the UC Water Resources Center suggested and provided funding for the California Water Resources Oral History Series. This translates into interviewing individuals who have been major players in the California water world of the 20th century. The latest addition to this series is a full-life oral history with Arthur Littleworth, one of the preeminent water law attorneys in the United States.

Two interviewers from ROHO tape-recorded eight interviews with Arthur Littleworth at the Riverside law offices of Best Best & Krieger between 2002 and 2004. The resulting transcripts (from 17 tapes) will be available in a bound volume sometime in 2005, after which time a copy will be available for viewing at WRCA. Already part of WRCA's collection are legal materials relating to several of Littleworth's cases, which he donated in 2003.

At Best Best & Krieger, Littleworth practiced general law until he was given his first water rights case in 1961 (*Fallbrook*). Over the years he gained such expertise that Governor Jerry Brown asked him to join the Governor's Commission to Review California Water Rights Law, 1977-1978, along with former Chief Justice Donald Wright, California Water Resources Director Ron Robie, and Stanford Law School Dean Charles Meyers, among others. With Eric Garner, Littleworth is co-author of *California Water*, a definitive book on the subject of water law in California (WRCA call no. R L176 N5). Closer to Berkeley, Littleworth and his firm represented the East Bay Municipal Utility District (EBMUD) in the years-long lawsuit over its rights to American River water (*Environmental Defense Fund v. EBMUD*). Retired EBMUD general counsel Robert B. Maddow (who himself has recorded an oral history) has written a fine introduction to the upcoming volume.

Arthur Littleworth talked about his entire career during the course of the interviews, including his experience as Special Master for the United States Supreme Court (1987-2004). *Kansas v. Colorado* involved a 1949 compact between the two states regarding their use of water from the Arkansas River. The question was: had Colorado's well pumping materially depleted the quantity of water available and therefore violated the compact? And if so, what kind of damages, how to calculate the damages, and what remedy? Stay on the lookout for Arthur Littleworth's oral history for answers to these questions—and a fascinating read!

Germaine LaBerge is a retired interviewer for ROHO.

To learn more about the California Water Resources Oral History Series, visit http://www.lib.berkeley.edu/WRCA/oralhist.html. *To learn more about ROHO, visit* http://bancroft.berkeley.edu/ROHO.

Special Report on South Bay Salt Pond Restoration

WRCA has extra copies of a 16-page special report from the October-December 2004 issue of *Bay Nature* magazine, entitled *South Bay Challenge: Reclaiming the Salt Ponds for People and Nature.* If you'd like a copy, stop by 410 O'Brien Hall or email us at waterarc@library.berkeley.edu. The report is also online: *www.baynature.com/2004octdec/saltponds.html*

California Colloquium on Water

Fall 2004 Summary

A broad range of speakers graced last fall's Colloquium line-up with some interesting parallels: two speakers discussed the formation of governmental agencies, and the other two speakers discussed the effects of fluid withdrawal from the ground.

For the first time, these lectures are available as streaming video on the Colloquium web site (www.lib.berkeley.edu/WRCA/ccow.html). PowerPoint presentations are also online for those speakers who used them. Also, videotapes of the lectures are available for loan at WRCA, and CDs of PowerPoint presentations are available for viewing at WRCA.

Peter Douglas, Executive Director of the California Coastal Commission, started the fall on an inspirational note with his September talk, "Saving the Coast: A Job That's Never Done." He described the political and technical difficulties—and rewards—of planning and regulating development and natural resource use along the coast in keeping with the requirements of the Coastal Act.

Mark Zoback's October 12 lecture, "Fluids and Faulting: Water and Earthquakes in California," came on the heels of an earthquake in Parkfield, CA—the very location of the San Andreas Fault Observatory at Depth (SAFOD), where the Stanford professor of geophysics researches fluid pressure in the fault zone. He noted that the injection of water and other fluids in the ground, and fluid removal, have been correlated with changes in earthquake frequency.

In November Donald Pisani, Merrick Professor of History at the University of Oklahoma, spoke about the idealism surrounding the birth of the U.S. Bureau of Reclamation in the early 1900s. Several key individuals hoped that the urban poor could move onto Reclamation farms to improve their quality of life. Success was mixed at best, however, as indicated in Pisani's title: "When Myth Trumps History: The Reclamation Bureau and the Family Farm, 1902-1935."

Rounding out the semester in December was Robert Glennon, Morris K. Udall Professor of Law & Public Policy at the University of Arizona and author of the book *Water Follies: Groundwater Pumping and the Fate of America's Fresh Waters*. Glennon detailed the environmental consequences of overpumping groundwater: rivers go dry, ecosystems change for the worse, land subsides and cracks, and as supplies of water for drinking and agriculture diminish, the costs of providing water increases.

Spring 2005 Schedule

This spring's Colloquium opened February 8 with "The Nature of Indian Water Rights." If you missed this lecture by Olney Patt, Jr., Executive Director of the Columbia River Inter-Tribal Fish Commission, you will soon be able to watch it on the Colloquium Web site as streaming video (www.lib.berkeley.edu/WRCA/ccow.html). The video will also be available for loan at WRCA.

Visit the Web site for more information about the lectures to come. You can view the flyer for each lecture and the brochure for the spring semester in PDF format.

March 8

"The Gravel Pirates: Strip-Mining the Russian River Water Supply"
L. Martin Griffin, Jr., MD, MPH
Founder, Friends of the Russian River

April 12

"The Influence of ENSO Phase on Floods & Sediment Transport in California Coastal Streams"
Edmund Andrews
Hydrologist & Chief of River Mechanics Project, U.S. Geological Survey

May 10

"The Continuing Battle to Restore the San Joaquin River"
Hamilton Candee
Senior Attorney & Co-Director, Western Water Project, Natural Resources Defense Council

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analysis (Gigliotti et al., 2002). These structural characteristics are the signatures of DOMs, reflecting their sources and formation history, and thus can be used to distinguish them. Albaiges et al. (1986) have illustrated that the presence of specific organic substances in groundwater could be traced to the leachate from a nearby sanitary landfill.

Since DOM moves with water, it can serve as a tracer to indicate the flowpath of a water and movement of water-borne contaminants, such as nitrate. Using DOM as a water tracer has significant advantages over artificial tracers (such as dyes, bromide, isotope- or fluorescence-labeled chemicals), because: (1) DOM is ubiquitous in soil and groundwater, thus no application of tracer is needed; (2) DOM is naturally entrained in water and is ready for sampling, therefore there is no waiting time for tracer distribution. This property is particularly important for groundwater infiltration studies, due to the lengthy process of surface recharge. If an artificial tracer is used, it needs to be applied several to tens of years before tracer-sampling, otherwise the distribution of tracer cannot faithfully represent the flowpath of water movement; (3) using DOM as a tracer is environment-friendly since no artificial chemical is introduced to the natural system. If the signature of DOM from different sources can be determined, qualitative information on the pathway of a water flow and the source of water-entrained pollutants (such as nitrate) accompanied by DOM might be inferred.

The structural characteristics of DOM can be characterized by spectroscopic analysis, such as ultraviolet absorbance (Gauthier et al., 1987), infrared spectrum (Lobartini and Tan, 1988; Witelski et al., 1991), fluorescence spectrum (Cabaniss and Shuman, 1987; De Haan and De Boer, 1987), ^{1}H nuclear magnetic resonance (NMR) (Wilson, 1984; Grasso et al., 1990), and ^{13}C NMR (Hatcher et al., 1980; Schnitzer and Preston, 1986). Among these methods, NMR is most useful in recognizing the chemical structure of DOM molecules because its signal is directly related to chemical functional groups. While ^{13}C NMR is more desirable for elucidating structural information because it examines the actual carbon skeleton rather than protons (Hatcher et al., 1980; Lobartini and Tan, 1988), the lack of availability of sufficient quantities of DOM samples often prevents application of the method (Grasso et al., 1990). Using ^{1}H NMR, DOM in a river water and DOM in the pore water of a lake sediment have been shown to exhibit different molecular structures (Grasso et al., 1990).

Nitrate is a pollutant often accompanied by DOM in groundwater underlying many agricultural and waste disposal sites. Overuse of chemical fertilizers and improper organic waste disposal are by far the most common causes of nitrate contamination (Pionke and Urban, 1985; Stone et al., 1998). Concentrations of nitrate and other contaminants have been found to be elevated in groundwater underlying agricultural sites on which both organic wastes (Meek et al., 1974; Robertson et al., 1984) and inorganic chemical fertilizers (Kitchen et al., 1997) have been applied. In some areas where agricultural lands and dairy waste disposal sites are adjacent or interlaced, there is a need to identify the source of nitrates in the groundwater (Franco and Cady, 1997; Williams et al., 1998). Identifying pollutant sources is crucial not only to planning mitigation and cleanup, but also to the community that must participate in any scientific or regulatory decision making (Williams et al., 1998). One means to distinguish the source of nitrate is measurement of the isotopic ratio of $^{15}N/^{14}N$. Nitrate derived from organic wastes (sewage or manure) has been found to be more ^{15}N-enriched than nitrate derived from inorganic fertilizer or from the decomposition of natural soil organic matters (Flipse and Bonner, 1985). The isotopic ratio of $^{18}O/^{16}O$ can also be used in conjunction with the ratio of $^{15}N/^{14}N$ (Kendall, 1998). However, the isotopic method is not always applicable and convincing because: (1) the ratio of $^{15}N/^{14}N$ can be significantly modified by many reactions taking place within the hydrologic system, such as ammonia volatilization, nitrification, denitrification, ion exchange, and plant uptake (Kendall, 1998); (2) source identification becomes very difficult when mixing of point and non-point sources occurs (Kendall, 1998); and (3) isotopic ratios sometimes are hard to determine in environmental samples due to analytical difficulties (Mengis et al., 2001).

Based on the hypothesis that DOM is conservative and moves with the water, if one can distinguish the source of the groundwater by recognizing the characteristics of the DOM it carries, the origin of a nitrate pollutant might be qualitatively identified. In this study, DOMs in nitrate-contaminated groundwater in an aquifer underlying a concentrated dairy/crop production area were

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characterized by ^{1}H NMR assay. The results were used to distinguish the sources of nitrate, whether it originated from application of chemical fertilizers or from disposal of dairy wastes.

2. Description of the study area

2.1. History of crop production and dairy

The Chino Basin of the Santa Ana River Watershed became a citrus and crop production area in southern California more than 70 years ago. Beginning in the early 1960s, it was gradually transformed into a dairy production region for the Los Angeles metropolitan area. The

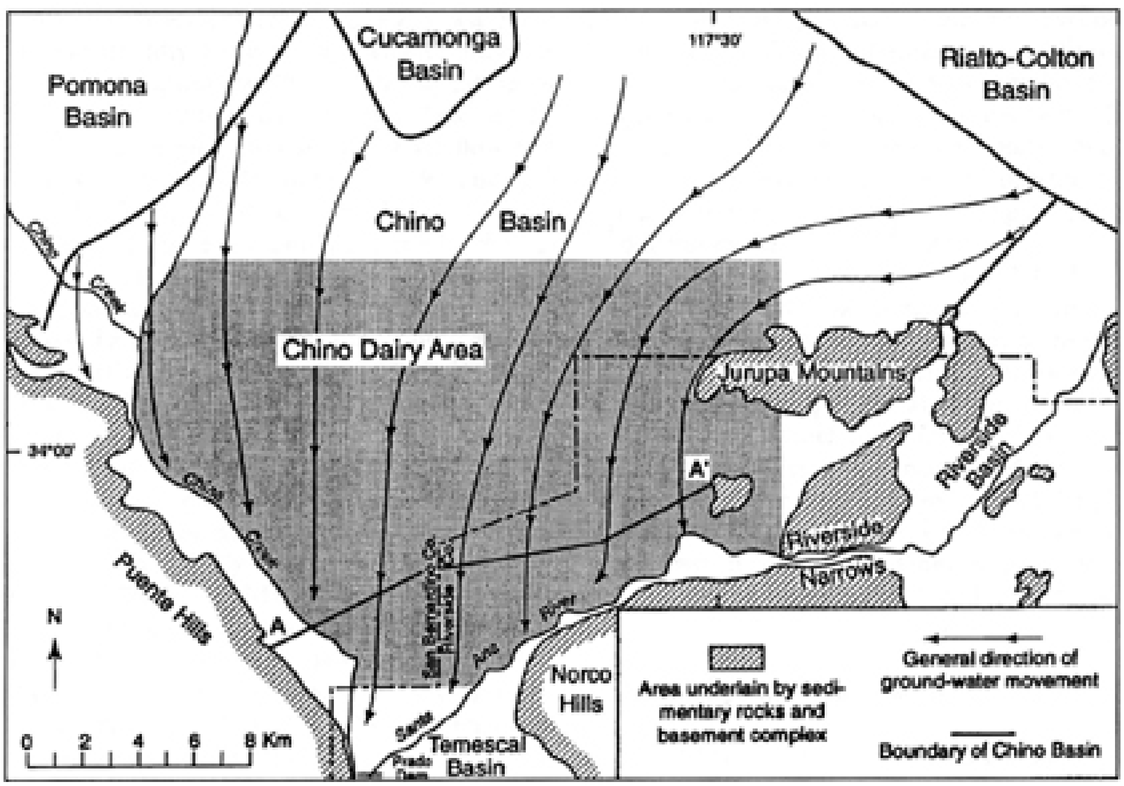

Fig. 1. Location of the Chino dairy area and general direction of groundwater flow in the Chino Basin (redrawn from Fig. 2 in French, 1972).

300 km^2 dairy area (shaded area in Fig. 1) is located 85 km east of Los Angeles. There were 300 dairies with >180,000 head of milking cows in the mid-1970s. The animal population reached its peak at 300,000 head in the mid 1980s. Since then, the number of dairies has been declining because of urban encroachment from the north, and the total animal population has been maintained at 250,000 heads (Schneider et al., 1990). The majority of the wastes produced by dairy cows were spread on irrigated pastures and croplands in the same vicinity. Due to a shortage of available land, the proportion of disposal acreage to the dairy cow population was as high as 1 ha to 35 cows. The disposal of waste severely overloaded the soil with organic solids, nitrate, and dissolved minerals (Adriano et al., 1971).

2.2. Geohydrology

The dairy area is situated on top of a large groundwater watershed of southern California—the Chino Basin (Fig. 1). The basin is filled with 30 to 400 m depth of alluvium which is underlain by sedimentary rocks and pre-Tertiary age rocks of the southern California batholith. The basement rocks do not contain or transmit fresh water and the area's aquifer is contained in the alluvial materials, which are poorly sorted gravel, sand, silt, and clay. Clay layers exist throughout the basin, creating semi-confining conditions in places, and horizontally stratify the alluvium into several layers (Fig. 2).

The Chino basin aquifer is recharged primarily by snowmelt from the San Gabriel Mountains at the northern border of the basin. In addition, deep percolation from precipitation and irrigation on the valley floor also contribute to inflows of the aquifer. Since the broad alluvial plain slopes gently from the north to the south (French, 1972), groundwater moves through the alluvium from

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north to south and rises to the surface along the Santa Ana River between the Riverside Narrows and the Prado Dam (Figs. 1 and 2). A sheet steel wall was driven to the base of the water-bearing sediments underneath the Prado Dam to intercept the subsurface flow. The water flowing over the dam is used to recharge the aquifers of the lower Santa Ana River Watershed in Orange County. There are >500 production wells tapping the Chino Basin aquifer. Annual yields from these wells are the major source of domestic and irrigation water in San Bernardino and Riverside Counties.

As the aquifer receives precipitation and irrigation recharge from the basin floor, total dissolved solids (TDS) and nitrate (derived from nitrogen-containing fertilizers) accumulating in the root zone are transported to groundwater along with the inflows. The water quality degradation within the dairy area appears to be confined to the unsaturated zone underneath dairies and dairy waste disposal sites, and the contaminant flow has reached groundwater immediately beneath (Rees et al., 1995; USDA, 1988; Adriano et al., 1971). The TDS concentrations of pore waters in the unsaturated zone underneath a dairy were 10,400, 6020, 3980, and 1350 mg L^{-1} at depths of 1.5, 3.1, 4.6, and 7.6 m from the ground surface, respectively (Rees et al., 1995). The nitrate concentrations in the same pore waters were >7000 mg L^{-1} near the surface, decreased by nearly two orders of magnitudes (110 mg L^{-1}) at a depth of 3.1 m, and varied from 100 to 40 mg L^{-1} at a depth of 23 m (Rees et al., 1995). As the groundwater rises toward the surface, it comes into contact with more salts and nitrate accumulated in the vadose zone. Adriano et al. (1971) reported that the nitrate concentrations of waters from the top of the groundwater table range from 198 to 326 mg L^{-1}. Contrarily, water from intermediate and deep layers of the aquifer had a TDS concentration of about 210 to 230 mg L^{-1} and a nitrate concentration of <9 mg L^{-1}, and the water quality did not seem to vary temporally. The intermediate and deep layers of the aquifer remain uncontaminated or are only slightly affected, possibly because the transit time for pollutants in the leachate to move through the vadose zone is longer than the establishment of the major dairies in this area. The transit time was expected to be as long as 25-50+ years (Adriano et al., 1971).

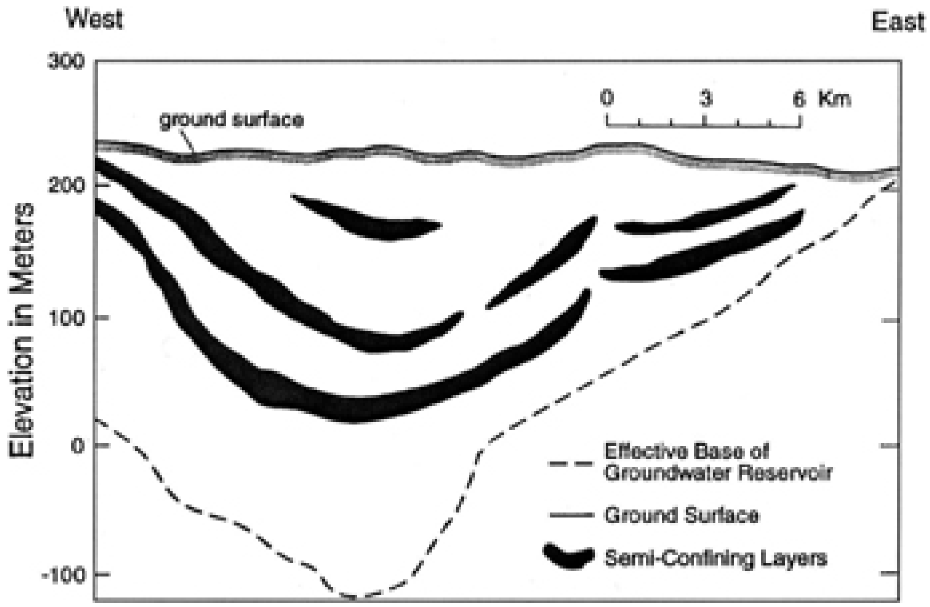

Fig. 2. A hydrostratigraphic cross section (location shown by the line A-A' in Fig. 1) of the Chino Basin groundwater aquifer.

2.3. Possible source of nitrates

Since the early 1970s, water pumped from some wells in the Chino Basin and water discharged at the Prado Dam have experienced considerable increases in nitrate and/or TDS concentrations. The land-applied dairy wastes appeared to be a logical source of the pollution. Prior to the establishment of dairies, however, the entire Chino Basin (from the foothills of the San Gabriel Mountains in the north to the Prado Dam in the south) was in cultivation of truck crops, viniculture, and citrus. Therefore, nitrate in the groundwater might also be the result of chemical fertilization practices. In order to evaluate the water quality changes and to develop a management strategy, the source of nitrates in the groundwater needs to be identified. Since both nitrate and DOM are entrained in water, nitrate originating

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from inorganic nitrogen-containing fertilizer is accompanied by natural soil-borne DOM, while nitrate originating from dairy wastes is coupled with dairy waste-borne DOM. Provided that the sources of DOM in the groundwater of the Chino Basin could be distinguished by ^{1}H NMR assay, the cause of the elevated nitrate concentration in the groundwater might be deduced.

3. Methods and materials

3.1. Water sampling

The Water Master of the Santa Ana River Watershed conducts a groundwater quality survey in the Chino Basin annually (Wildermuth Environmental Inc., 2002). The water samples used for this study were collected from 23 wells surveyed by the Water Master in 1998. One well (No. 3) is located in an abandoned vineyard upgradient (north) of the dairy area. Its water is not expected to be affected by wastes from dairies, and thus is considered as an upgradient control representing the groundwater quality affected by chemical fertilization practices in crop production in this area. Since the region upgradient of the dairy area has been entirely urbanized, no other suitable control well was found. Three wells (Nos. 10, 11, and 12) are located downgradient of the dairy area where groundwater is rising and moving toward the Santa Ana River. The remaining 19 sampling wells are scattered in the midst of the dairy/crop production area.

The water table depths of these wells are difficult to measure because most of the wells are sealed at the top. Moreover, with so many wells of various depths and varying perforation lengths tapping the aquifer, the groundwater table depth and water table drawdown of each well would be affected by the pumping of wells in the surrounding areas. We were unable to obtain information on the perforation depths to determine from which layers of the aquifer these wells withdrew their waters.

3.2. Sample analyses

The samples were stored in an ice chest during the sampling trips and then filtered first by a glass fiber filter with 0.45 mm pores and followed by a silver filter with 0.2 mm pores upon arrival at our laboratory. One liter of filtered water was freeze-dried, and then re-dissolved in 10 mL of heavy water (99.9% D_2O). Through this solvent substitution process, the protons associated with water were eliminated from the sample and the DOM in the groundwater was concentrated. Then, the heavy water aliquots were analyzed on a GN 500 MHz superconducting NMR spectrometer. The PRESAT pulse sequence was used to alleviate effects of the strong residual water signal on the NMR spectra. A total of 128 scans were collected for each spectrum using a sweep width of 6024 Hz. Line broadening of 5 Hz was applied during the data processing and chemical shifts were reported relative to tetramethylsilane. For convenience in comparing the results, the same NMR experimental settings were used for all water samples. The iron and manganese contents of the water were <0.10 and 0.05 mg L^{-1}, respectively, and the presence of these paramagnetic elements should not have a significant effect on the linewidth of signals.

Nitrate concentrations of the waters were determined using a Technicon auto-analyzer. Total organic carbon (TOC) concentrations of the waters were determined by an ultravioletepersulfate oxidation method on a Dohrmann DC-80 TOC analyzer. The electrical conductivity (EC) and pH of the water samples were also measured.

4. Results and discussion

4.1. Water quality and contamination of the wells

The pH, EC, concentrations of nitrate and TOC in the groundwater samples are listed in Table 1. In order to evaluate the groundwater quality and distinguish the sources of pollutants, one needs to know from which layer of the aquifer the water samples were withdrawn. Since no information on the depths of water table in these wells is available, EC values are used to roughly estimate from which layers of the aquifer the wells withdrew their waters. On irrigated cropland, salts concentrate into the leachate and enter groundwater through the vadose zone. In the Chino Basin, the salts entering the aquifer through surface recharge tended to remain within the water located near the water table (Rees et al., 1995) and the TDS content in the naturally occurring groundwater underneath was much lower than that of the water contaminated by crop production drainage and/or dairy waste disposal (Adriano et al.,

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Table 1.
Chemical properties of groundwater in the Chino Basin.

Well description	Well no.	pH	EC ($\mu S\ cm^{-1}$)	Nitrate ($mg\ L^{-1}$)	Total organic carbon ($mg\ L^{-1}$)
Upgradient control well	3	7.7	624	29.0	8.9
Downgradient wells	10	7.1	1474	46.7	12.1
	11	7.4	1232	56.1	18.6
	12	7.2	1526	53.9	8.7
Wells in the midst of dairy/crop production area					
Wells pumping from deep layers of the aquifer	4	7.7	415	22.1	4.2
	8	7.6	530	15.2	7.0
	14	7.8	337	14.9	5.8
	23	7.6	457	15.7	3.1
Wells pumping from shallow layers of the aquifer	1	7.2	1711	268.4	3.9
	2	7.7	999	118.8	4.1
	5	6.9	2300	510.3	9.0
	6	7.4	896	68.4	2.7
	13	7.6	835	113.5	7.0
	15	7.2	1795	229.9	3.8
	16	7.8	623	38.3	3.7
	17	7.7	890	91.9	2.8
	18	7.3	1137	179.4	5.8
	20	7.2	1626	202.9	7.1
	21	7.0	650	22.5	2.4
	22	7.8	662	63.9	2.7
	24	7.2	1432	82.9	6.4
	25	7.5	1021	60.4	2.8
	28	7.6	1244	187.9	3.3

1971; Rees et al., 1995). Therefore, the EC, which measures the salinity of a water, might be reasonable as an indicator of the aquifer layer from which the sampled well withdrew its water. In general, water with higher EC, therefore with higher salt content, would be more likely to originate from wells whose perforation zones tapped contaminated groundwater near the ground water table, while water with lower EC would be withdrawn more likely from wells tapping deep layers of the aquifer, which are not contaminated or less contaminated. Based on their locations and EC values, the 23 sampled wells were classified into the following four groups:

(i) Upgradient control well (No. 3). The EC of water from this well was 624 $\mu S\ cm^{-1}$. The TDS concentration of this water, estimated by the following equation (Richards, 1954):

$$TDS\ (mg\ L^{-1}) = 0.68 \times EC\ (\mu S\ cm^{-1})$$

was 424 $mg\ L^{-1}$, approximately twice the TDS concentration expected in the naturally occurring groundwater in this area, which was 210-230 $mg\ L^{-1}$ as represented by water in the intermediate and deep layers of the aquifer (Rees et al., 1995). Because the upgradient well is located in a vineyard, it appears that water in this well has been affected by leachates from crop irrigation, and the salinity level of the water has risen above the expected background level. The nitrate concentration of the same water was 29.0 $mg\ L^{-1}$, which was about 2-3 times that of the naturally occurring groundwater (10-15 $mg\ L^{-1}$) in the Chino Basin (Rees et al., 1995).

(ii) Downgradient wells (Nos. 10, 11, and 12). The downgradient wells are situated in the shallow area of the aquifer where groundwater is rising and approaching the ground surface. Water from these wells was high in salinity (EC = 1232-1526 $\mu S\ cm^{-1}$), indicating that the rising groundwater originated primarily from water near the surface section of the aquifer. Water from these wells also had elevated nitrate concentrations (46.7-56.1 $mg\ L^{-1}$).

(iii) Wells pumping from deep layers of the aquifer (Nos. 4, 8, 14, and 23). The EC values of water from this group of wells were low, ranging from 337 to 530 $\mu S\ cm^{-1}$. Since their EC values were close to that of the naturally occurring water in this region (Rees et al., 1995), it is safe to conclude that contamination by TDS and nitrate had not occurred in the layers of the aquifer where these wells were pumping water. The nitrate nitrogen concentration of the corresponding groundwater varied from 14.9 to 22.1 $mg\ L^{-1}$ (Table 1), which is slightly higher than that of the naturally occurring groundwater.

(iv) Wells pumping from shallow layers of the aquifer (Nos. 1, 2, 5, 6, 13, 15, 16, 17, 18, 20, 21, 22, 24, 25, and 28). These wells have an apparent elevated EC (623-2300 $\mu S\ cm^{-1}$ with a mean of 1188 $\mu S\ cm^{-1}$) and elevated nitrate concentration (22.5-268.4 $mg\ L^{-1}$ with a mean of 149.3 $mg\ L^{-1}$). Obviously these wells have been contaminated by TDS and nitrate through leachates from the irrigated field. However, it is not yet clear where the nitrate originated—application of chemical fertilizer, disposal of dairy wastes, or both?

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4.2. [1]H NMR of DOM in groundwater

The [1]H NMR spectra of DOM in the groundwater samples are shown in Figs. 3-6. For the convenience of discussion, they are organized by the four groups discussed above, namely upgradient control (Fig. 3), downgradient control (Fig. 4), wells pumping from deep layers of the aquifer (Fig. 5), and wells pumping from shallow layers of the aquifer (nitrate- and TDS-contaminated wells) in the dairy area (Fig. 6). In general, the distribution of the resonance signals is largely similar to those of DOMs from soil, surface, and ground waters (Grasso et al., 1990; Ma et al., 2001). These NMR spectra are dominated by broad unresolved humps (characteristic of complex mixtures) with some sharp signals indicative of specific functional groups or structures. These types of spectra are difficult to interpret precisely, but some general structural information can be determined and used as "fingerprints" of aquatic organic materials from particular sources (Fujita et al., 1996; Ma et al., 2001).

Signal assignments were made according to data in the literature (Grasso et al., 1990; Peuravuori and Pihlaja, 1998). Briefly, resonances at the 0-2.0 ppm chemical shift region are attributed to protons on aliphatic carbons; resonances at 2.0-3.3 ppm are attributed to protons on carbons next to aromatic, carboxylic, carbonyl, or other electron-drawing groups; resonances at 3.3-6.5 ppm are attributed to protons on carbons next to oxygen atoms (such as methoxy groups and aldehydes), and protons associated with oxygen (alcoholic, phenolic, and car-

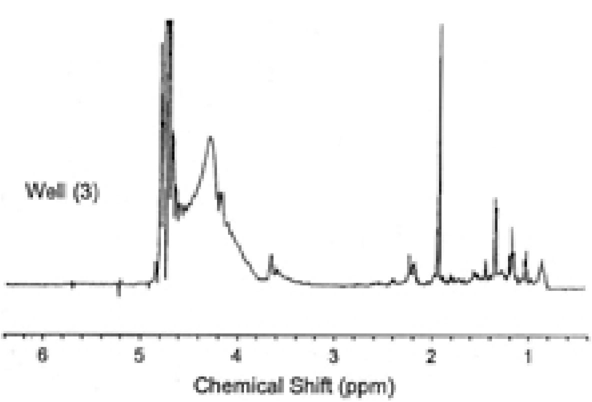

Fig. 3. [1]H NMR spectrum of DOM in water from the up-gradient control well.

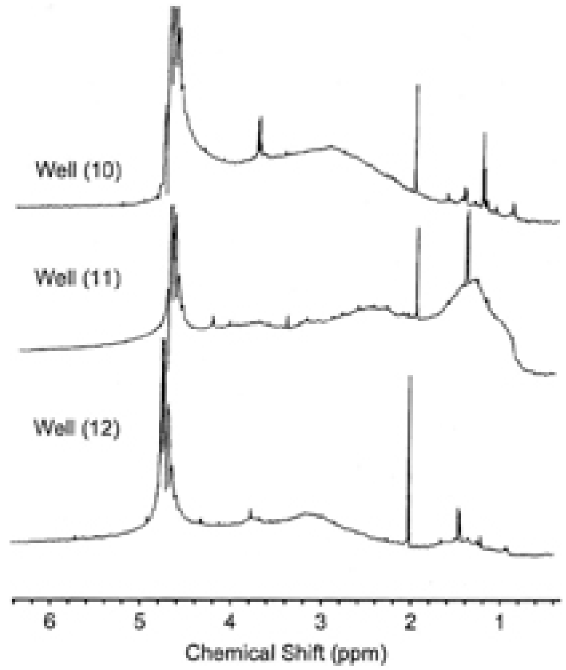

Fig. 4. [1]H NMR spectra of DOM in waters from the downgradient wells.

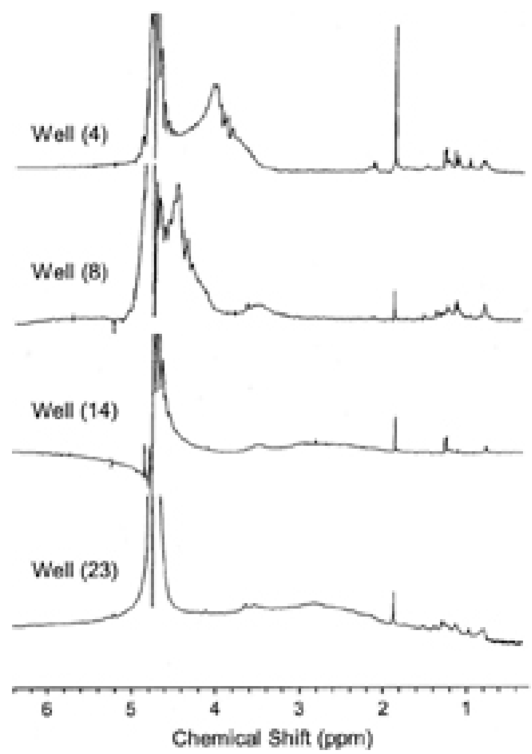

Fig. 5. [1]H NMR spectra of DOM in waters from wells pumping from deep layers of the aquifer.

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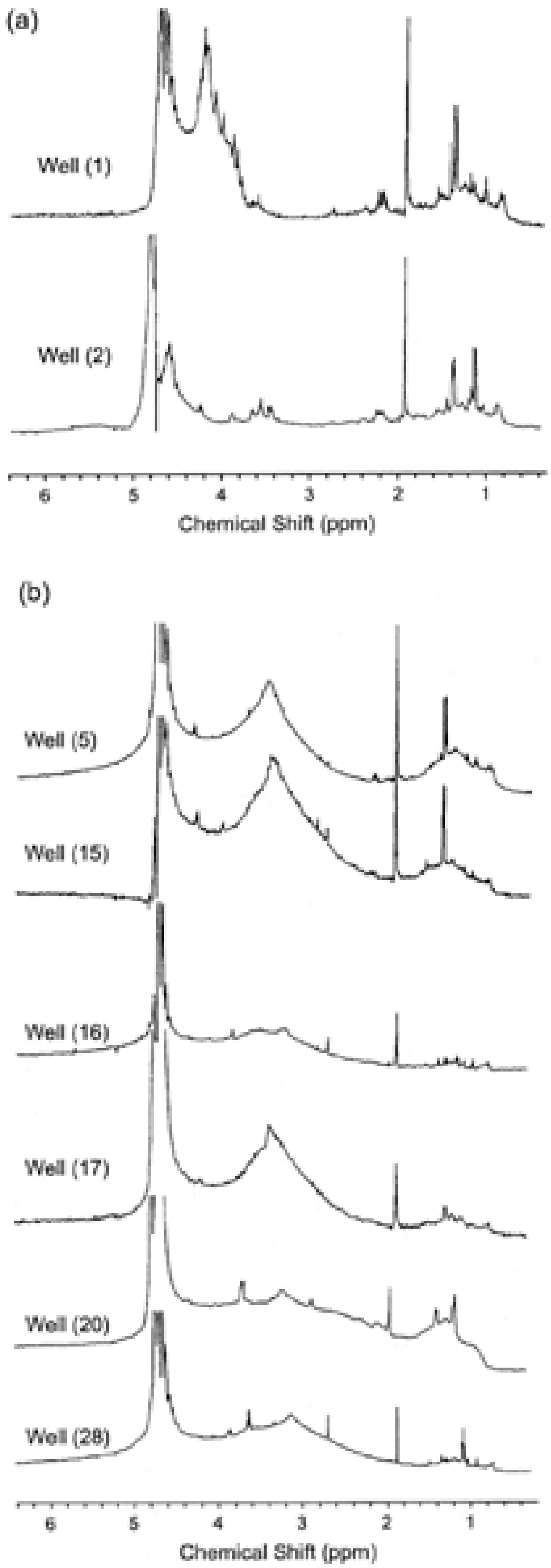

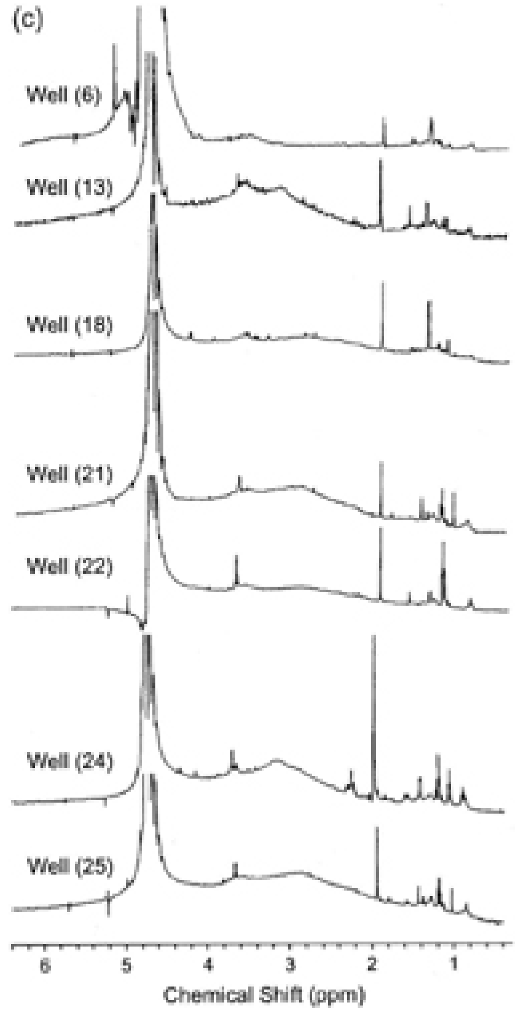

Fig. 6. ^{1}H NMR spectra of DOM in waters from wells in the dairy area contaminated by nitrates and total dissolved solids (TDS): (a) spectra showing a prominent resonance signal at 4.0-4.3 ppm; (b) spectra showing a prominent resonance signal at 3.3-3.6 ppm; and (c) spectra showing a trace of a resonance signal at 3.3-3.6 ppm.

boxylic groups) or nitrogen (such as amines); and resonances at 6.5-9.0 ppm are attributed to protons associated with aromatic carbon atoms. Aside from these rules, a strong resonance at about 4.7 ppm is attributed to the residual water which is not removed during the freeze-dying of DOM samples or hydrogen deuterium oxide (HDO) impurity in the heavy water solvent (Hinedi et al., 1997; Peuravuori and Pihlaja, 1998).

Several characteristics are common in the ^{1}H NMR spectra of all water examined, including the following: (1) all samples contain the strong residual water signal at 4.6-4.7 ppm; (2) no distinctive resonance signal at >6.5

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ppm is observed (data not shown), indicating there are no aromatic structures in the DOMs of these water samples, which agrees well with previous observations of DOM from natural sources (Grasso et al., 1990); (3) a series of well-resolved signals at 0.8-2.2 ppm occurs in all of the water samples, which are attributed to protons associated with aliphatic carbons. Since the molecular skeletons of natural DOM are mainly composed of aliphatic carbons (Grasso et al., 1990; Gigliotti et al., 2002), these signals are very complicated due to the interactions of nearby protons, and thus are difficult to interpret. The most useful resonance signals, which might be used to identify sources of the contaminants, are in the chemical shift region of 2.2-4.6 ppm.

An overview of all the NMR spectra of the well waters showed that two resonance signals are prominent in the chemical shift region of 2.2-4.6 ppm. One centers around 4.0-4.3 ppm (such as in well Nos. 3, 4, and 8) and the other centers around 3.2-3.6 ppm (such as in well Nos. 5, 15, and 17). Both of them are poorly resolved resonances. The 4.0-4.3 ppm signal is a strong resonance, usually accounting for >50% of the total signal intensity of a sample where it occurs, while the intensity of the 3.2-3.6 ppm signal varies with the wells (Fig. 6b and c). The two prominent resonance signals might be considered as the signatures of DOM from different sources because: (1) DOMs in the Chino Basin have two major sources (i.e. natural soil organic matter in crop production fields and dairy waste disposal on the fields), and there are two and only two kinds of strong signals in all the spectra; (2) all the wells pumping from shallow layers of the aquifer (more severely contaminated) either contain one of these two strong signals or contain both. For example, well Nos. 1 and 3 contained a signal at 4.3 ppm, and well Nos. 5 and 17 contained a signal at 3.5 ppm, while well Nos. 2 and 15 contained both signals at 3.5 ppm and 4.5 ppm; (3) signals in the wells that pumped from deep layers of the aquifer (such as well Nos. 14 and 23), which are likely less contaminated, were much less pronounced. For example, all of the signals at 2.2-4.6 ppm were barely recognizable in well Nos. 14 and 23. The signal at 4.0-4.3 ppm is attributed to natural soil-borne DOM, since it occurs in the spectrum of the upgradient control well (No. 3), which for sure has been contaminated by the drainage from chemical fertilization. The 3.3-3.6 ppm signal is attributed to dairy waste-borne DOM since it occurs in the spectra of the majority of the wells in the dairy/crop production area. These assignments are in accordance with the structural characteristics of DOMs from different sources. Animal waste-borne DOM (dairy wastes in this case) was found to be less oxidized than agricultural soil-borne DOM (Sposito et al., 1978). In other words, the molecules of dairy waste-borne DOM contain fewer oxygen atoms in their structure, which cause its characteristic proton resonance signal to occur in the lower chemical shift region.

4.3. Identification of nitrate source

As indicated by their elevated EC and nitrate concentration, the groundwaters of wells pumping from shallow layers of the aquifer in the dairy/crop area and wells in the downgradient area have been nitrate-contaminated. By recognizing the characteristic signal of the ^{1}H NMR spectrum of DOM, the sources of nitrates in these groundwaters can be inferred qualitatively:

(i) Wells pumping from shallow layers of the aquifer. The characteristic resonance of soil-borne DOM (4.0-4.3 ppm) is observed in 2 of the 15 wells (Fig. 6a). The signal is also slightly recognizable in well Nos. 5, 15, and 18. Contrarily, the characteristic resonance of dairy waste-borne DOM (3.2-3.6 ppm) is observed in all of the wells, with strong intensity in six wells (Fig. 6b) and lower intensity in the other eight wells (Fig. 6c). Therefore, it is reasonable to conclude that for the majority of the wells located in the dairy/crop production area, the nitrate and TDS contamination in these wells are primarily caused by disposal of dairy wastes. Only two wells (Nos. 1 and 2) are mainly contaminated by chemical fertilizer application on croplands. Moreover, the average nitrate concentration in the wells with strong intensity of the characteristic signal (well Nos. 5, 15, 16, 17, 20, and 28) is 210.2 mg L^{-1}, which is much higher than that of wells with weaker signals (well Nos. 6, 13, 18, 21, 22, 24, and 25), which is 87.1 mg L^{-1}.

(ii) Downgradient wells (Nos. 10, 11, and 12). Since their nitrate concentrations are much lower than those of wells pumping from shallow layers of the aquifer, groundwaters in these downgradient wells are not severely contaminated. In their spectra (Fig. 4), the

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characteristic resonances of dairy waste-borne DOM at 3.2-3.6 ppm are weak, but still recognizable. However, the characteristic resonance of agricultural soil-borne DOM at 4.0-4.3 ppm is totally absent, indicating that the slight nitrate contamination is more likely caused by disposal of dairy wastes, rather than by application of chemical fertilizer on cropland. Considering the location of these wells and their geohydrological settings, it would be reasonable to conclude that the nitrate and TDS in the rising groundwater near the Santa Ana River originated primarily from the upper section of the aquifer that had been contaminated by disposal of dairy wastes.

5. Conclusions

Due to differences in their chemical composition and molecular structure, DOMs in groundwater, that originated from various sources exhibit different characteristic resonances in their ^{1}H NMR spectra. DOM derived from soil organic matter has a signature resonance at a chemical shift region of 4.0-4.3 ppm, while DOM indigenous to dairy wastes has a signature resonance at a lower chemical shift region of 3.2-3.6 ppm. Though these resonance signals are poorly resolved and are difficult to interpret precisely, they are useful for distinguishing the sources of water-borne contaminants accompanied by DOM, such as nitrates.

By recognizing the ^{1}H NMR spectra of DOM, the sources of nitrates in groundwater of the Chino Basin dairy area are qualitatively inferred. The majority (13 of 15 wells) of nitrate-contaminated wells located in the dairy/crop production area showed characteristics of contamination by disposal of dairy wastes, while only 2 of the 15 sampled wells showed characteristics of contamination by leachates from chemical fertilization practices in crop production. The ^{1}H NMR assay also showed that nitrate and TDS in the rising groundwater near the Santa Ana River originated primarily from the upper section of the aquifer that had been contaminated by dairy wastes. Chemical fertilizers used in crop production did not appear to have a significant role in the elevated nitrate and TDS concentrations in the groundwater of the Chino Basin.

Acknowledgements

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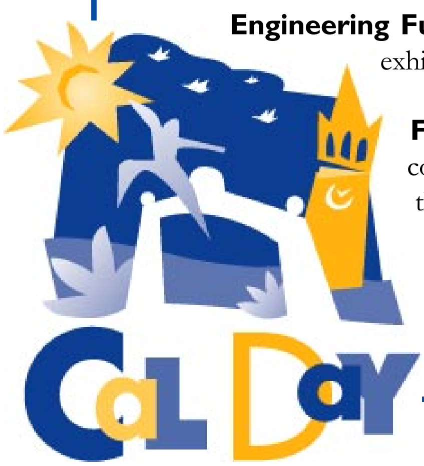

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Staff Update

Farewell, Gabby

Who could ask for more from a student assistant than spunk, diligence, and continuity? Gabby Ventura gave all that and more during her tenure at WRCA. After three years of shelving, filing, picking up deliveries, assisting with ordering books, and helping with a smattering of special projects, we must finally bid Gabby farewell. This spring she left the familiar Berkeley sights for a last-minute semester abroad in Madrid, just before graduating with a double major in political science and rhetoric. Gabby and her unique handwriting and emotive smiley-faces will be greatly missed. The staff wish her luck in public policy or wherever her path may lead.

Farewell, Nancy

After almost 2½ years as Public Services Library Assistant, I will be leaving WRCA in late March to live with my grandfather in Eugene, OR. From checking out books to organizing the Colloquium to designing this newsletter, I have truly enjoyed my time at WRCA. It has been a great opportunity to learn about water issues and to meet lots of wonderful people. A comprehensive list of thank-yous to my fellow staff members is impossible, so I will limit myself to the following: thank you to Paul, for quirky style; to Trina, for impeccable copyediting skills; and to Linda, for making the library a fun place for staff and patrons alike. Thanks also to Paige, Gabby, Grayson, Celia, and the other students who have worked here during my tenure—your poise continues to amaze me. Last but not least, thank you to all the patrons of WRCA, for keeping me on my toes and for making this job what it is.

Welcome, Grayson

A fall addition to the WRCA student staff, Grayson Vincent hails from all the way over in Daytona Beach, Florida. She is currently a sophomore and plans to major in statistics. Grayson is involved in several campus organizations, including the Undergraduate Marketing Association and the Alpha Phi Omega service fraternity. She also serves as activities chair of her sorority. Grayson is excited about joining the WRCA team, an enthusiasm matched by the staff in welcoming her.

Welcome, Celia

Celia Bein has just re-joined WRCA as a student employee. Celia's first stint was in spring 2004, after which she left Berkeley to study abroad at the University of Queensland, in Brisbane, Australia. She has now returned to Berkeley and, to the delight of the staff, to WRCA as well. Although she enjoyed studying in Brisbane, Celia is ready to finish her fourth year as a political science major here at Cal, and is contemplating law school after graduation. This semester Celia is especially looking forward to playing intramural volleyball, doing a darkroom photography class, and participating in the UC Berkeley Model United Nations.

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