

# Sources and Transformations of Nitrogen Compounds along the Lower Jordan River

Michal Segal-Rozenhaimer, Uri Shavit,\* Avner Vengosh, Ittai Gavrieli, Efrat Farber, Ran Holtzman, Bernhard Mayer, and Avi Shaviv

## ABSTRACT

The Lower Jordan River is located in the semiarid area of the Jordan Valley, along the border between Israel and Jordan. The implementation of the water sections of the peace treaty between Israel and Jordan and the countries' commitment to improve the ecological sustainability of the river system require a better understanding of the riverine environment. This paper investigates the sources and transformations of nitrogen compounds in the Lower Jordan River by applying a combination of physical, chemical, isotopic, and mathematical techniques. The source waters of the Lower Jordan River contain sewage, which contributes high ammonium loads to the river. Ammonium concentrations decrease from 20 to 0–5 mg N L<sup>-1</sup> along the first 20 km of the Lower Jordan River, while nitrate concentrations increase from nearly zero to 10–15 mg N L<sup>-1</sup>, and  $\delta^{15}\text{N}$  (NO<sub>3</sub>) values increase from less than 5‰ to 15–20‰. Our data analysis indicates that intensive nitrification occurs along the river, between 5 and 12 km from the Sea of Galilee, while further downstream nitrate concentration increases mostly due to an external subsurface water source that enters the river.

MANY OF THE CLASSICAL STUDIES on nitrogen transformations in water bodies are based on either chemical and isotopic approaches or mass balance calculations. This study investigated the nitrogen compounds in the water column along the Lower Jordan River via physical, chemical, and isotopic analyses and solutions of the mass transport equation. This combined approach improves the ability to identify the sources and to quantify the transformations of nitrogen compounds along the river.

The Lower Jordan River is a damaged ecosystem. It is located in the semiarid area of the Jordan Valley along the Israel–Jordan border (Fig. 1). The river has been altered dramatically in the last several decades. Water quantity has decreased from about  $1300 \times 10^6$  m<sup>3</sup> yr<sup>-1</sup> to a mere 100 to  $200 \times 10^6$  m<sup>3</sup> yr<sup>-1</sup> (Salameh and Naser, 1999). The historical tributaries included the Sea of Galilee ( $540 \times 10^6$  m<sup>3</sup> yr<sup>-1</sup>), the Yarmouk River ( $480 \times 10^6$  m<sup>3</sup> yr<sup>-1</sup>), and local streams and runoff (Hof, 1998). Since the implementation of water supply projects in Israel, Jordan, and Syria, the Sea of Galilee and the Yarmouk River are blocked and no fresh surface water flows into the river except for negligible contribu-

tions from small springs and rare flood events. Currently, the only two water sources at the starting point of the Lower Jordan River are the effluent of the Bitania wastewater treatment plant and the Saline Water Carrier (Sites 1 and 2 in Fig. 1). The Bitania source includes poorly treated human and animal waste effluents. The Saline Water Carrier contains a mixture of saline spring water diverted from the Sea of Galilee and urban sewage effluent. As a result of the degradation of water quantity and quality, the Lower Jordan River has become brackish (Salameh, 1996, p. 13–16, 65; Farber et al., 2004).

Nitrogen is a major nutrient in aquatic systems and is essential for the growth of aquatic life forms. Yet, in excess, it can harm the ecosystem, depriving water use applications, and reduce the water body vitality (Curtis et al., 1975; Pauer and Auer, 2000). The potential transformation processes that are likely to affect the concentration of nitrogen compounds in the river are mineralization (conversion of organic N to NH<sub>4</sub><sup>+</sup>), immobilization (conversion of NH<sub>4</sub><sup>+</sup> or NO<sub>3</sub><sup>-</sup> to organic N [Jansson and Persson, 1982; Peterson et al., 2001]), nitrification (conversion of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup> [Curtis et al., 1975]), ammonium volatilization (Freney et al., 1983; Nelson, 1982), and denitrification (conversion of NO<sub>3</sub><sup>-</sup> to gaseous N<sub>2</sub> or N<sub>2</sub>O [Jones, 1985; Sain et al., 1977; Seitzinger et al., 2002; Master et al., 2003]). Mixing with water from external sources (e.g., surface runoff, tributaries, and ground water infiltration) can also affect the in-stream nitrogen cycle.

The Jordan River was recognized as a unique aquatic ecosystem and its future management was addressed by the Israel–Jordan peace treaty (Governments of Israel and Jordan, 1994). Beyond its religious and historical significance, and despite its low water quality, the Jordan River gained the attention of the peace treaty since it serves as a secondary water resource, mainly for irrigation and fishpond recharge, for both Israel and Jordan. A better understanding of the riverine environment is required for the implementation of the peace treaty, in which the two countries jointly agreed to improve the ecological sustainability of the river system. To provide some of the needed information, a joint Israeli–Palestinian–Jordanian project is currently underway (Shavit et al., 2002; Farber et al., 2004), investigating water quantity and quality of the Lower Jordan River.

The chemical compositions of water samples collected during this joint project showed that the Lower Jordan River is characterized by three sections; the upper (northern) section, where the initial high salinity decreases downstream; the middle section, where salinity variation is less significant; and the lower (southern) section, where salinity increases with the river flow. Our chemical analyses, flow rate measurements, and detailed mass balance calculations indicate that water from a

M. Segal-Rozenhaimer, U. Shavit, R. Holtzman, and A. Shaviv, Faculty of Civil and Environmental Engineering, Technion, Israel Institute of Technology, Haifa, Israel. A. Vengosh and E. Farber, Department of Geological and Environmental Sciences, Ben Gurion University, Beer Sheva, Israel. I. Gavrieli, Geological Survey of Israel, Jerusalem, Israel. B. Mayer, Departments of Physics & Astronomy and Geology & Geophysics, University of Calgary, Calgary, AB, Canada T2N 1N4. Received 22 June 2003. \*Corresponding author (aguri@tx.technion.ac.il).

Published in J. Environ. Qual. 33:1440–1451 (2004).

© ASA, CSSA, SSSA

677 S. Segoe Rd., Madison, WI 53711 USA

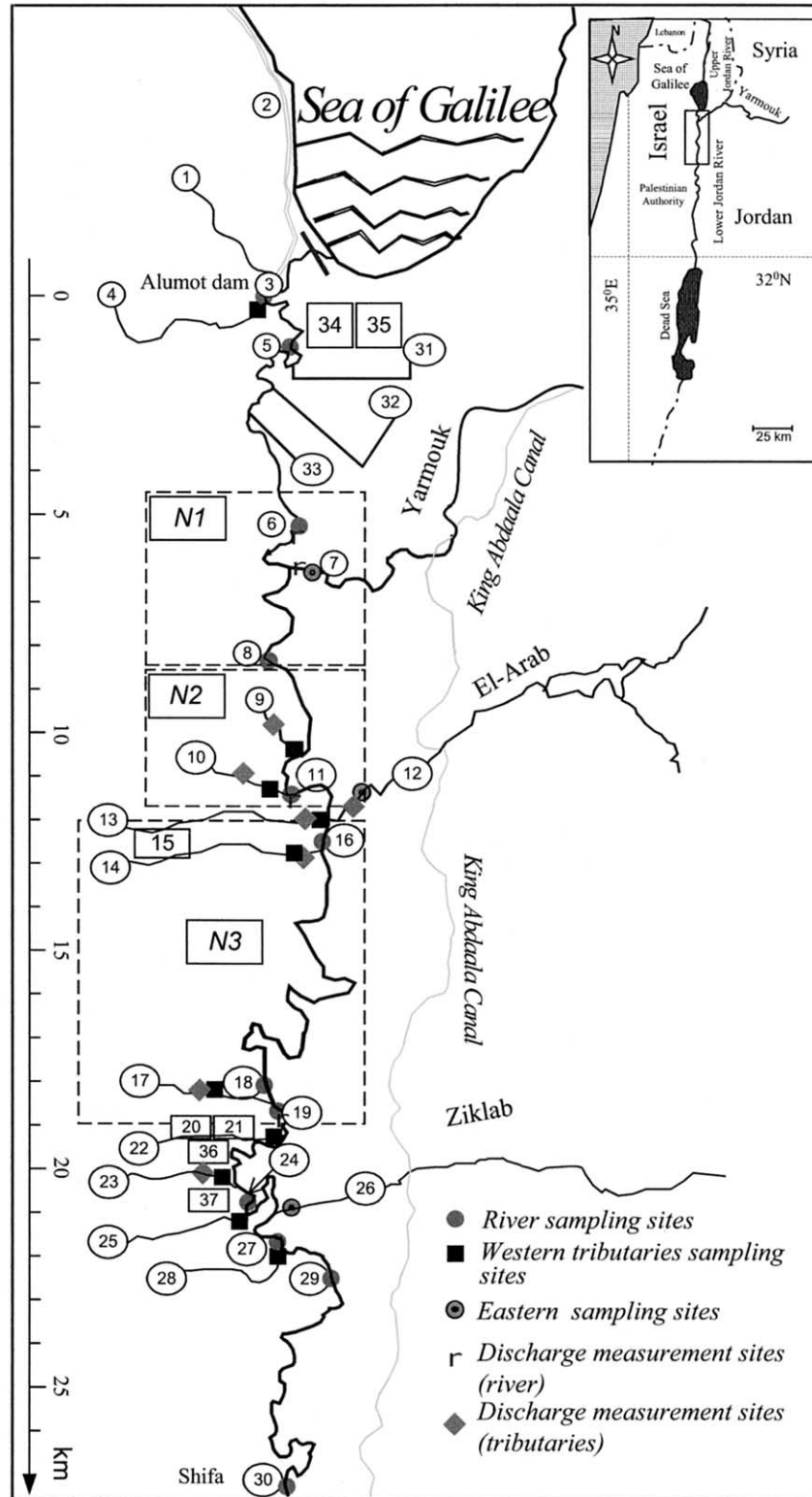


Fig. 1. A map of the study area between the Sea of Galilee and Shifa. Sampling and measurement sites include sites along the river, tributaries, drainages, fishponds, and soil samples. Agricultural drainages are marked as straight lines. Segment N1 is Dalhamiya (Site 6) to Gesher (Site 8), N2 is Gesher (Site 8) to Nave Ur (Site 11), and N3 is Nave Ur (Site 16) to Hamadiya (Site 19). For site information see Table 1.

nonpoint ground water source enters the river, modifying the river water chemistry. The nature of the non-point source was investigated and the results are reported in Farber et al. (2004) and Holtzman (2003). In

this paper we investigate the riverine nitrogen cycle along the upper (northern) section of the Lower Jordan River. It was found that the most significant variations of nitrogen compounds occur along this section. Based

on geochemical and mass balance studies, new information about the nitrogen sources and transformations within the Lower Jordan River is provided.

## MATERIALS AND METHODS

### Study Area

The Lower Jordan River stretches between Alumot dam (downstream from the Sea of Galilee, 32°42' N, 35°35' E, 210 m below sea level) and the Dead Sea (31°47' N, 35°33' E, 416 m below sea level in 2003), with a catchment area of 14 930 km<sup>2</sup> (Efrat, 1996, p. 237–242, 245–251). The aerial length of the river is 100 km, while the true length as the river flows is about 200 km (Tahal, Israeli Water Division Office, Israeli Office of National Foundation, TAHAL-Consulting Engineering LTD, personal communication, 2000). Our study focuses on the northern part of the river, from Alumot dam (Site 3 in Fig. 1) to the station at Shifa (Site 30). The land on both sides of the river is used for agriculture [e.g., date (*Phoenix dactylifera* L.) plants] and fishponds. Tributaries to the river consist of natural streams and artificial canals (e.g., agricultural and fishpond drainage), which are characterized by significant fluctuations in seasonal flow and chemical compositions.

### Sampling and Analytical Procedures

Samples include river water sampled along the Lower Jordan River, its tributaries, fishponds, agricultural drainage canals, and leachates from soil adjacent to the river (Table 1).

In the discussion we distinguish between three different segments in the northern part of the Lower Jordan River, 5 to 20 km from the Sea of Galilee. Figure 1 shows the boundaries of these segments: Dalhamiya to Gesher (N1), Gesher to Nave Ur (N2), and Nave Ur to Hamadiya (N3).

Water samples were collected at Sites 1 to 30 during field trips in February, March, April, and June 2001. In August 2001, additional sites were sampled (31 to 37). In January 2002, samples were taken only from Sites 1 to 11 and 30 to 32, excluding Sites 4, 9, and 10. Samples that were collected in January, February, March, and April represent the wet winter season. Samples that were collected in June and August represent the hot, dry summer when both evaporation and irrigation become more significant. Surface water was sampled usually in the middle of the Lower Jordan River and its tributaries from bridges or the banks. Electrical conductivity, water temperature, pH, turbidity, and dissolved oxygen were measured in the field.

Water samples were stored at 4°C before chemical analyses, which were conducted within 72 h after sampling. All water samples were filtered through 0.45- $\mu$ m Millipore (Billerica, MA) membranes. Nitrate and nitrite concentrations were determined using an automated spectrometric cadmium reduction method using a QuickChem 8000 analyzer (Lachat, Milwaukee, WI) (Eaton et al., 1995, p. 4–88). Ammonium was determined by an automated spectrometric method with sodium salicylate and hypochlorite using the same instrument (Eaton et al., 1995, p. 4–81). Measurements of total nitrogen contents were obtained by converting all N compounds to

**Table 1. A list of the sampling sites including site number (Fig. 1), site name, location, and a general description.**

Site	Site name	Description	Aerial distance from Alumot dam km
1	Bitania	sewage input, surface†	0
2	Saline Water Carrier	saline input, surface†	0
3	Alumot‡	river	0.1
4	Yavneal stream	surface tributary, west	0.4
5	Beit-Zera bridge	river	1.3
6	Dalhamiya bridge	river	5.6
7	Yarmouk River	surface tributary, east	6.3
8	Gesher	river	8.5
9	Canal 81	surface tributary, west	10.6
10	Canal 78	surface tributary, west	11.5
11	Nave Ur north	river	11.6
12	El-Arab stream	surface tributary, east	12.1
13	Canal 76	surface tributary (fishponds drainage), west	12.1
14	Canal 74	surface tributary (fishponds drainage), west	12.7
15	Nave Ur fishpond	fishpond, west	12.5
16	Nave Ur south	river	12.7
17	Doshen canal	surface tributary (fishponds drainage), west	18.5
18	Hamadiya north	river	18.2
19	Hamadiya south	river	19.0
20	Hamadiya zor fishpond	fishpond, west	19.2
21	Hamadiya H fishpond	fishpond, west	19.2
22	Hamadiya south canal	surface tributary (fishponds drainage), west	19.3
23	Harod stream	surface tributary (+sewage effluents), west	20.5
24	Gate 48	river	21.0
25	Canal 48	surface tributary, west	21.1
26	Ziqlab stream	surface tributary, east	21.0
27	Maoz Hayim	river	22.0
28	Nimrod stream	surface tributary (+sewage effluents), west	22.0
29	Shiech Hussain bridge	river	22.7
30	Shifa station	river	27.7
31	Robed drainage	subsurface agricultural drainage, west	1.5
32	Kochvani drainage	subsurface agricultural drainage, west	2.5
33	Z drainage	subsurface agricultural drainage, west	3
34	avocado plant	soil sample	1.0
35	banana plant	soil sample	1.0
36	date plant	soil sample	19.8
37	alfalfa field	soil sample	21.0

† Starting point of the Lower Jordan River.

‡ Alumot is the first sampling point of the river. Alumot dam is a dirt dam, which separates the Sea of Galilee and the Lower Jordan River.

ammonium using a single digestion with  $\text{H}_2\text{SO}_4\text{-H}_2\text{O}_2$  without prior filtration (Thomas et al., 1967), and subsequent determination of inorganic ammonium concentrations. Precision of the nitrogen compound analysis was  $\pm 5\%$  based on standard calibration. Total organic carbon (TOC) was measured using unfiltered samples analyzed by a TOC 5000A organic carbon analyzer (Shimadzu, Kyoto, Japan). All determinations of C and N concentrations were performed in the Technion laboratories, Haifa, Israel. Sulfate and chloride concentrations were determined at the Geological Survey of Israel using ion chromatography.

### Flow Rate Measurements

Discharge measurements in the Lower Jordan River and tributaries were made with a portable acoustic Doppler velocimeter (3D Argonaut-ADV; SonTek/YSI, San Diego, CA) and a portable electromagnetic current meter (2000 Flo-Mate; Marsh-McBirney, Frederick, MD). The ADV was mounted on a vertical pole held by a construction bridge and floats. By cruising the floating construction across the river, both water velocity and river bathymetry profiles were determined. Flow rate was obtained by integrating the measured velocity across the stream using a power law curve fit and first-order Simpson integration. The flow rate measurement uncertainty was 10%. A detailed description is given by Holtzman (2003).

### Isotopic Analyses

One to two liters of water were collected for the determination of the isotopic composition of nitrate ( $\delta^{15}\text{N}$  and  $\delta^{18}\text{O}$ ). Filtered water samples were passed through a cation exchange resin (2 mL of 50W-X4,  $\text{H}^+$  form; Bio-Rad Laboratories, Hercules, CA) and subsequently through an anion exchange resin (2 mL AG 1-X8 resin,  $\text{Cl}^-$  form; Bio-Rad Laboratories) at a rate of  $5 \text{ mL min}^{-1}$ . The anion exchange resins containing the nitrate were stored at  $4^\circ\text{C}$  in darkness until further processing in the Isotope Science Laboratory at the University of Calgary, Alberta, Canada. Nitrate was eluted and converted to  $\text{AgNO}_3$  using a procedure published by Silva et al. (2000) with modifications described by Mayer et al. (2002). Approximately 1 L of water was collected for determination of nitrogen isotope ratios of ammonium (for January 2002 samples only). Samples were filtered and processed based on the techniques described in Lehmann et al. (2001) and Velinsky et al. (1989). Nitrogen isotope ratios of nitrate and ammonium are given in the usual  $\delta$  notation:

$$\delta^{15}\text{N} (\text{‰}) = \left[ \frac{(^{15}\text{N}/^{14}\text{N})_{\text{sample}}}{(^{15}\text{N}/^{14}\text{N})_{\text{standard}}} - 1 \right] \times 1000 \quad [1a]$$

where  $^{15}\text{N}/^{14}\text{N}$  is the isotope ratio in the sample and in atmospheric  $\text{N}_2$  (used as the reference standard), respectively. Nitrogen isotope ratios were determined on  $\text{N}_2$  after thermal decomposition of the sample material in an elemental analyzer (NA 1500; Carlo Erba, Milan, Italy) and subsequent continuous-flow isotope ratio mass spectrometry (IRMS). The  $\delta^{15}\text{N}$  values for all samples were calibrated against international reference materials (IAEA N1 and N2). The reproducibility of nitrate and ammonium extraction, gas preparation, and mass spectrometric measurement was better than  $\pm 0.3\text{‰}$  for all  $\delta^{15}\text{N}$  determinations.

Measurements of oxygen isotope ratios in nitrate were conducted on CO gas after pyrolysis of  $\text{AgNO}_3$  in a Finnigan MAT TC/EA (Thermo Electron, Bremen, Germany) at  $1350^\circ\text{C}$  and subsequent continuous-flow IRMS. Results are expressed in the usual  $\delta$  notation:

$$\delta^{18}\text{O} (\text{NO}_3) (\text{‰}) = \left[ \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} - 1 \right] \times 1000 \quad [1b]$$

Accuracy and precision of the measurements were assured by repeated analyses of laboratory internal and international reference materials such as IAEA-NO-3, which had a mean  $\delta^{18}\text{O} (\text{NO}_3)$  value of  $+23.0 \pm 0.7\text{‰}$  ( $n = 12$ ). The reproducibility of nitrate extraction, gas preparation, and mass spectrometric measurement was found to be better than  $\pm 0.8\text{‰}$  for  $\delta^{18}\text{O} (\text{NO}_3)$ , as determined by duplicate analyses.

## RESULTS AND DISCUSSION

Our study shows that the Lower Jordan River contains high concentrations of nitrate, nitrite, and ammonium (Fig. 2 and Table 2). Figure 2a reveals that the highest ammonium concentrations are at the source of the river. Ammonium concentrations then decrease along the river flow (Segments N1 and N2, Fig. 1), between Dalhamiya (Site 6) and Nave Ur (Site 11). The Bitania sewage effluent (Site 1) and the Saline Water Carrier

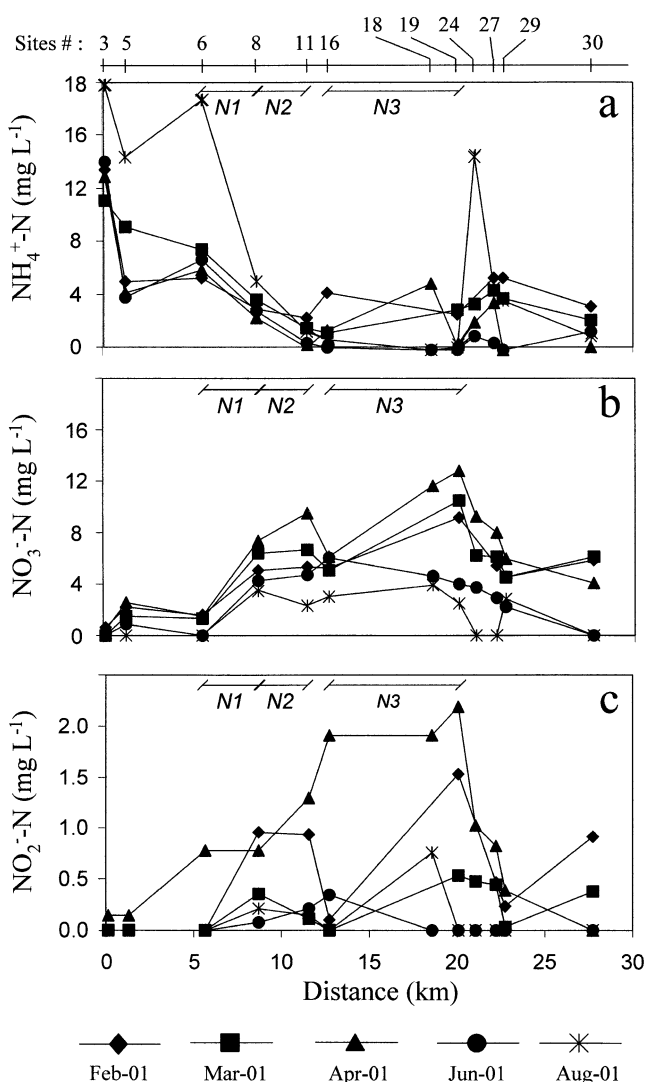


Fig. 2. Ammonium (a), nitrate (b), and nitrite (c) concentrations in the river water versus aerial distance from Alumot dam (Table 1). River segments are drawn schematically along the flow (N1, N2, and N3). Site numbers are shown at the top.

**Table 2. Flow rate, concentration of chloride, sulfate, ammonium, nitrate, nitrite, total N, total organic carbon, and  $\delta^{15}\text{N}$  values of ammonium and nitrate at different river sites and segments.**

Date	$Q^\dagger$	$\text{Cl}^-$	$\text{SO}_4^{2-}$	$\text{mg L}^{-1}$			Total N	TOC $^\ddagger$	$\delta^{15}\text{N}^\S$
	$\text{L s}^{-1}$			$\text{NH}_4^+-\text{N}$	$\text{NO}_3^--\text{N}$	$\text{NO}_2^--\text{N}$			
<b>Dalhamiya bridge (Site 6; N1 input segment)</b>									
Feb. 2001	671	1983	250	5.4	1.6	0.0	22	11	9.1
Mar. 2001	921	1950	220	7.5	1.3	0.0	21	11	NA
Apr. 2001	757	2140	230	6.0	1.5	0.8	–	9	2.2
June 2001	659	2100	198	6.8	0.1	0.0	57	13	4.5
Aug. 2001	676	2097	190	18.7	0.1	0.0	89	10	–0.1
Jan. 2002	–	1959	240	54.0	0.1	0	–	–	15.8 $\ $ /9.7
<b>Gesher (Site 8; N1 output and N2 input segments)#</b>									
Feb. 2001	671	1941	275	3.1	5.1	1.0	23	13	16.2
Mar. 2001	921	2160	270	3.7	6.4	0.4	14	9	6.0
Apr. 2001	757	2225	260	2.4	7.4	0.8	5	8	6.4
June 2001	659	2177	224	2.9	4.3	0.1	13	13	12.1
Aug. 2001	676	2195	220	5.1	3.5	0.2	10	9	4.3
Jan. 2002	–	1994	276	1.0	4.7	1.2	–	–	39.7 $\ $ /12.8
<b>Nave Ur north (Site 11; N2 output segment)</b>									
Feb. 2001	839	1890	372	2.4	5.3	0.9	10	10	15.7
Mar. 2001	995	2040	410	1.7	6.7	0.1	32	10	8.6
Apr. 2001	862	2120	370	0.2	9.6	1.3	9	8	16.5
June 2001	1087	2056	317	0.5	4.7	0.2	15	12	19.3
Aug. 2001	808	2240	300	1.4	2.3	0.1	4	15	10.7
Jan. 2002	–	1872	400	0.6	4.3	0.6	–	–	25.5 $\ $ /14.7
<b>Nave Ur south (Site 16; N3 input segment)<math>\dagger\dagger</math></b>									
Feb. 2001	759	1599	380	4.3	5.3	0.1	24	9	15.4
Mar. 2001	819	1850	390	1.3	5.0	0.0	7	11	14.3
Apr. 2001	747	1635	370	1.4	6.1	1.9	85	7	12.7
June 2001	825	1755	359	0.2	6.1	0.4	7	138	17.3
Aug. 2001	480	1965	330	0.7	3.0	0.0	58	9	17.0
<b>Hamadiya south (Site 19; N3 output segment)<math>\dagger\dagger\dagger</math></b>									
Feb. 2001	1109	1493	460	2.6	9.1	1.5	18	10	16.4
Mar. 2001	984	1700	490	3.0	10.5	0.5	23	11	14.0
Apr. 2001	787	1690	475	0.3	12.8	2.2	12	10	14.0
June 2001	1073	1806	433	0.0	4.0	0.0	4	15	19.5
Aug. 2001	480	1724	370	0.2	2.5	0.0	2	11	21.3

$^\dagger$  Flow rate was measured by Holtzman (2003).

$^\ddagger$  Total organic carbon.

$^\S$  All measured  $\delta^{15}\text{N}$  values represent  $\delta^{15}\text{N}$  ( $\text{NO}_3^-$ ) unless otherwise specified.

$\|$   $\delta^{15}\text{N}$  ( $\text{NH}_4^+$ ) values. All samples were processed according to Velinsky et al. (1989).

# Flow rate in Gesher was measured upstream from the pumping station, and thus, equals Dalhamiya flow rate.

$\dagger\dagger$  Flow rate in Nave Ur south was measured downstream from pumping stations of Nave Ur north and south and includes the El-Arab stream discharge.

$\dagger\dagger\dagger$  Flow rate in Hamadiya south was measured downstream from pumping stations of Hamadiya north and south.

(Site 2) are the main contributors of ammonium and organic N to the river system (Table 3). Our analysis shows that the Bitania inflow contains 50 to 194 mg N  $\text{L}^{-1}$  of total nitrogen, mostly as ammonium ( $\geq 50\%$  of total N) and TOC of 75 to 187 mg C  $\text{L}^{-1}$ . The pH values along the river were around 8 and water temperature varied between 20 and 30°C. The range of dissolved oxygen along Segments N1, N2, and N3 was 3 to 6 mg  $\text{L}^{-1}$ , with little variation as a function of depth within the water column. The ammonium concentrations found in Bitania (49 to 82 mg N  $\text{L}^{-1}$ ; Table 3) are similar to those of poorly treated sewage water (Feigin et al., 1991, p. 28, 62). Despite mixing with the Saline Water Carrier, high ammonium concentrations varying between 11 and 12 mg N  $\text{L}^{-1}$  were measured at the starting point of the river (at Alumot, Site 3, downstream from the mixing location of Bitania and the Saline Water Carrier). Figures 2b and 2c show that the concentrations of nitrate and nitrite increased along the three river segments and that nitrate concentrations in February through April were generally higher than those in the summer months of June and August.

We conducted mass-balance calculations along three

segments: Dalhamiya to Gesher (N1), Gesher to Nave Ur (N2), and Nave Ur to Hamadiya (N3). In most cases, the known monitored nitrate fluxes from the surface tributaries were insufficient to explain the variations of nitrate concentrations observed along the river (Table 3). For example, in April 2001, the nitrate concentration in Canal 81 (Site 9) was similar to that in the Jordan River, but nitrate concentrations continued to rise after the confluence (Fig. 2b). In March 2001, the nitrate concentration in Canal 81 was higher than that in the Jordan River (Table 3), but no change of nitrate concentrations was observed in the river. Similarly, the high nitrite concentrations measured along the river cannot be explained by surface inflows (Fig. 2c).

## Isotopic Compositions

### Data Description

Figures 2 and 3 and Tables 2 and 3 show that most of the variations in the concentrations of nitrogen compounds and in their isotopic compositions occur along Segments N1 and N2. While nitrate concentration in-

**Table 3.** Flow rate, concentration of chloride, sulfate, ammonium, nitrate, nitrite, total N, total organic carbon, and  $\delta^{15}\text{N}$  values of ammonium and nitrate as measured at the river tributaries.

Date	$Q^\dagger$ L s <sup>-1</sup>	Cl <sup>-</sup>	SO <sub>4</sub> <sup>2-</sup>	NH <sub>4</sub> <sup>+</sup> -N	NO <sub>3</sub> <sup>-</sup> -N	NO <sub>2</sub> <sup>-</sup> -N	Total N	TOC‡	$\delta^{15}\text{N}\S$
		mg L <sup>-1</sup>					mg C L <sup>-1</sup>		%
<b>Bitania (Site 1)</b>									
Feb. 2001	300¶	442	96	49.5	0.0	0.0	49	75	NA#
Mar. 2001	300¶	245	95	58.2	0.0	0.0	71	107	NA
Apr. 2001	300¶	474	88	82.0	0.9	0.0	–	91	8.3††/2.2
June 2001	300¶	–	–	80.0	1.4	0.6	129	187	9.4††/2.1
Aug. 2001	300¶	467	85	74.5	1.0	1.0	194	148	8.1††/3.2
Jan. 2002	300¶	–	–	6.5	2.3	1.0	–	–	-5.1
<b>Saline Water Carrier (Site 2)</b>									
Feb. 2001	600¶	2765	180	11.1	0.6	0.0	22	12	5.2
Mar. 2001	600¶	2210	165	5.1	0.0	0.0	17	14	NA
Apr. 2001	600¶	2395	173	2.5	2.9	0.0	30	9	4.3
June 2001	600¶	2000	146	5.3	0.1	0.0	10	12	8.1
Aug. 2001	600¶	2464	170	6.1	1.4	0.0	77	10	NA
Jan. 2002	600¶	2003	155	0.2	5.7	0.0	–	–	10.9††/11.3
<b>Yavneal stream (Site 4)</b>									
Feb. 2001	60–100¶	247	95	0.0	12.5	0.0	22	4	4.5
Mar. 2001	60–100¶	245	95	0.5	11.6	0.0	–	5	4.6
Apr. 2001	60–100¶	235	97	0.0	10.2	0.0	10	6	4.8
June 2001	60–100¶	233	100	0.0	10.0	0.0	62	6	5.5
Aug. 2001	60–100¶	211	97	0.2	16.3	0.0	6	5	5.0
<b>Yarmouk River (Site 7; N1 surface tributary segment)</b>									
Feb. 2001	0	823	515	0.5	5.6	0.0	5	6	11.7
Mar. 2001	0	1330	853	0.3	4.4	0.0	9	6	15.5
Apr. 2001	0	1240	815	0.0	4.0	0.0	7	7	14.7
June 2001	0	1546	1083	0.0	4.1	0.0	20	13	17.2
Aug. 2001	0	3083	2390	0.0	5.0	0.0	78	10	16.7
Jan. 2002	–	1100	680	0.1	5.6	0.0	–	–	12.2
<b>Canal 81 (Site 9; N2 surface tributary segment)</b>									
Feb. 2001	68	–	–	–	–	–	–	–	–
Mar. 2001	155	1940	260	2.7	8.8	0.6	11	14	12.0
Apr. 2001	122	1890	520	1.0	7.5	1.1	7	16	NA
June 2001	79	1700	502	0	1.5	0.0	6	20	12.4
Aug. 2001	9	2883	246	1.0	1.0	0.0	8	28	4.8
<b>Canal 78 (Site 10; N2 surface tributary segment)</b>									
Feb. 2001	31	–	–	–	–	–	–	–	–
Mar. 2001	21	1905	1250	0.6	3.3	0.0	11	14	13.4
Apr. 2001	44	1910	1050	0	1.3	0.0	3	9	13.3
June 2001	222	2221	405	1.0	0.7	0.0	7	17	NA
Aug. 2001	5	2560	422	3.7	0	0.0	6	12	NA
<b>Harod stream (Site 23)</b>									
Feb. 2001	260	1545	193	5.5	2.6	0.0	11	10	7.7
Mar. 2001	260	1750	180	7.3	2.1	0.0	16	15	9.6
Apr. 2001	260	1700	185	5.9	2.2	0.0	20	8	8.9
June 2001	260	1578	203	1.5	2.1	0.0	5	13	11.3
Aug. 2001	260	1636	180	15.8	1.3	0.0	2	22	3.0

† Flow rate was measured by Holtzman (2003).

‡ Total organic carbon.

§ All measured  $\delta^{15}\text{N}$  values represent  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) unless otherwise specified.

¶ Flow rate represents an average based on the Israeli Hydrological Service measurements. The Saline Water Carrier discharges  $20 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ , Bitania discharges  $10 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ , and Yavneal stream discharges  $2\text{--}3 \times 10^6 \text{ m}^3 \text{ yr}^{-1}$ .

# Not available.

††  $\delta^{15}\text{N}$  ( $\text{NH}_4$ ) values. All samples were processed according to Velinsky et al. (1989), except from Bitania samples, which were processed according to a procedure described by Lehmann et al. (2001).

creases (Fig. 2b), ammonium decreases (Fig. 2a), and both  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) and  $\delta^{15}\text{N}$  ( $\text{NH}_4$ ) values increase (Fig. 3a). Figure 3a shows that the source waters of the Lower Jordan River (Site 3) are characterized by  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values of 0 to 6‰ and  $\delta^{15}\text{N}$  ( $\text{NH}_4$ ) values of 10 to 16‰. Whereas the Bitania effluent (Site 1) has low  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values (approximately 3‰) and relatively high  $\delta^{15}\text{N}$  ( $\text{NH}_4$ ) values (approximately 9‰), the Saline Water Carrier (Site 2) is characterized by higher  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values (11.3‰) and a similar  $\delta^{15}\text{N}$  ( $\text{NH}_4$ ) value (10.9‰). The river  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values increased initially along Segment N1 (from a range of 2–9‰ to 4–16‰), and then further downstream along N2 to values between 9 and

20‰. Downstream from N2,  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values remain high and almost constant. The  $\delta^{15}\text{N}$  ( $\text{NH}_4$ ) values increased markedly from 15.8‰ at 1.3 km to nearly 40‰ at 8.5 km. Figure 3b shows that  $\delta^{18}\text{O}$  ( $\text{NO}_3$ ) values were generally lower than 13‰ and, for the most part, did not vary much with distance. Such oxygen isotope compositions are typical for nitrate derived from nitrification processes in manure, sewage, or soils (Mayer et al., 2002).

### Nitrification

The process of nitrification often proceeds with isotopic fractionation (e.g., Mariotti et al., 1981) with the

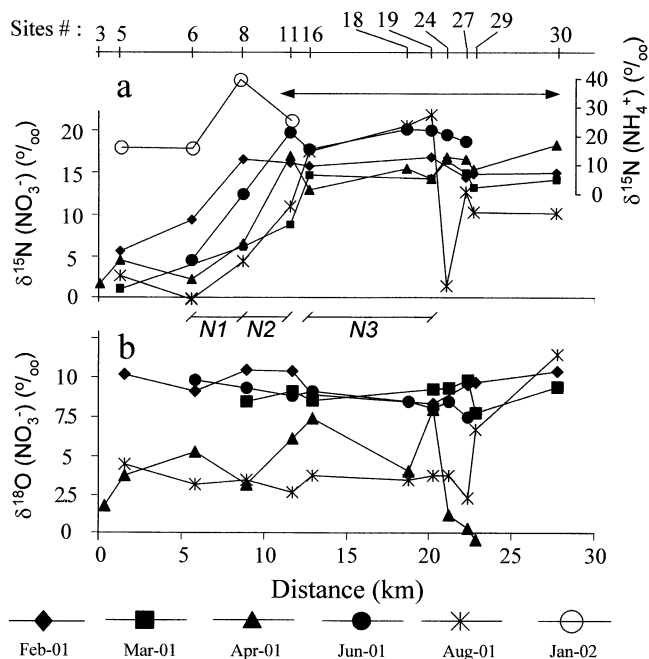


Fig. 3. Values of  $\delta^{15}\text{N}(\text{NO}_3^-)$ ,  $\delta^{15}\text{N}(\text{NH}_4^+)$ , and  $\delta^{18}\text{O}(\text{NO}_3^-)$  along the river as a function of time and distance from Alumot dam.

light isotope  $^{14}\text{N}$  preferentially accumulating in nitrate, leaving the remaining ammonium enriched in  $^{15}\text{N}$  (Kendall, 1998; Shearer and Kohl, 1986; Nadelhoffer and Fry, 1994). If this process progressively continues in a closed system,  $\delta^{15}\text{N}$  values of the nitrate will approach those of the initial ammonium (Rayleigh distillation in a closed system). Our data suggest that the increase of  $\delta^{15}\text{N}$  values in the riverine nitrate is due to nitrification of ammonium characterized by high  $\delta^{15}\text{N}$  values. These high  $\delta^{15}\text{N}(\text{NH}_4^+)$  values are typically associated with isotopic enrichment due to nitrification and due to fractionation caused by gaseous losses such as volatilization (Kendall, 1998; Heaton, 1986). The  $\delta^{15}\text{N}$  values of ammonium in the source waters (Table 3) and in the river (Fig. 3a, Table 2) varied between 8 and 11‰ in the former to 16 and 40‰ in the latter. The nitrification of this ammonium can generate nitrate with  $\delta^{15}\text{N}$  values between 8 and 40‰, hence providing a feasible explanation for the increasing  $\delta^{15}\text{N}$  values of riverine nitrate in Segments N1 and N2. It was also observed that in co-existing nitrate and ammonium, the ammonium  $\delta^{15}\text{N}$  composition was consistently more enriched. Indeed, the most enriched  $\delta^{15}\text{N}(\text{NH}_4^+)$  values were found in samples with the lowest ammonium concentration, consistent with the Rayleigh distillation process. In fact, we observed the highest  $\delta^{15}\text{N}(\text{NH}_4^+)$  value where the ammonium concentration was at its lowest level (see Table 2).

The variations in ammonium and nitrate concentrations and nitrogen isotope ratios along the river (as shown in Fig. 2a and 2b) support our mechanistic explanation that nitrification is a predominant process along Segments N1 and N2. However, along Segment N3 downstream from Site 11 (and to some extent along Segment N2), the concentration of ammonium is often too low to provide a complete explanation for the con-

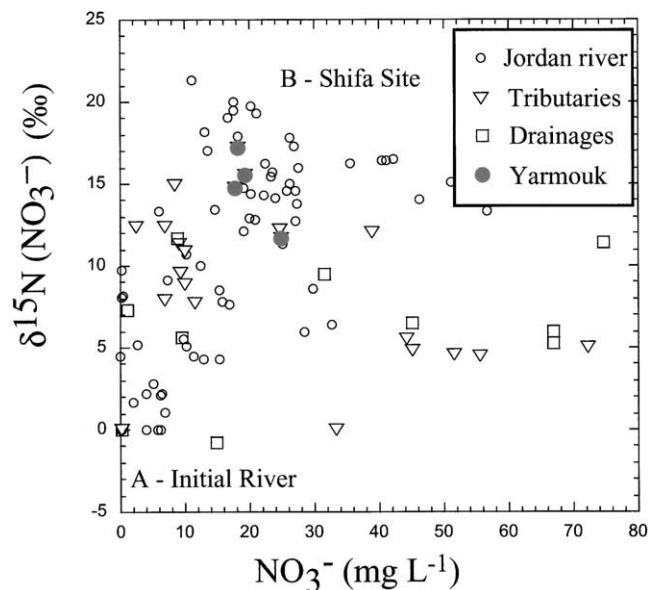


Fig. 4. The  $\delta^{15}\text{N}(\text{NO}_3^-)$  values in the Jordan River, the Yarmouk River, and other inflows versus nitrate concentrations. Data are based on all sampling dates.

tinuous increase of nitrate and the high  $\delta^{15}\text{N}(\text{NO}_3^-)$  values. This indicates that in addition to nitrification, mixing processes influence the river nitrate concentration and its isotopic values.

### Mixing

We previously showed (Shavit et al., 2002; Holtzman, 2003; Farber et al., 2004) that the chemistry of the Lower Jordan River is influenced by a nonpoint water source. The gradual decrease in chloride concentration and the sharp rise in sulfate concentration (Tables 2 and 3) were attributed to the discharge of a nonpoint source. This nonpoint source enters the river through the local shallow aquifer, which is influenced by agricultural return flows. Following our observation that the geochemical signature of water from the Yarmouk River (Site 7, Fig. 1) is consistent with the chemical modifications observed along the Lower Jordan River (Farber et al., 2004), it was suggested to consider the Yarmouk water as a possible analog of the Jordan River nonpoint source.

Figure 4 shows the  $\delta^{15}\text{N}(\text{NO}_3^-)$  values versus nitrate concentration as measured in the Jordan River, in the Yarmouk River, and in other possible inflows (recall that the discharge of these other inflows is too small to significantly affect the river). Many of the river samples follow a general mixing line between the river source (Point A) and the Jordan River water near Shifa (point B, downstream). The Yarmouk samples, which are found along this line, are characterized by higher nitrate concentrations and higher  $\delta^{15}\text{N}(\text{NO}_3^-)$  values than those of the river source waters. However, they have lower nitrate concentrations and lower  $\delta^{15}\text{N}(\text{NO}_3^-)$  values than the Jordan River water at Shifa (Point B). This demonstrates that, although mixing provides a possible explanation for the trend shown in Fig. 4, it is not the only mechanism. We therefore suggest that a combination of mixing (between river water and the nonpoint source)

and in-stream nitrification of  $^{15}\text{N}$ -enriched ammonium provides the best explanation for the trends shown in Fig. 4.

### Denitrification

Although denitrification in natural systems may provide an explanation for increasing  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values (Kendall, 1998; Kellman and Hillaire-Marcel, 1998), our results are not consistent with possible water column denitrification, since nitrate concentrations should decrease rather than increase concomitantly with  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) (Fig. 4). Moreover, during microbial denitrification, both  $^{14}\text{N}$  and  $^{16}\text{O}$  are preferentially metabolized, causing an enrichment of the heavy isotopes  $^{15}\text{N}$  and  $^{18}\text{O}$  in the residual nitrate (Kendall, 1998; Mariotti et al., 1981). Our results show, however, no correlation between  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) and  $\delta^{18}\text{O}$  ( $\text{NO}_3$ ) values. In addition, the field measurements show that dissolved oxygen was always above  $2 \text{ mg L}^{-1}$  across the whole vertical profile of the water column. High oxygen concentrations eliminate the possibility of denitrification in the water column but provide no indication about denitrification in the river sediments.

### Other Possible Nitrogen Transformations

Mineralization generates ammonium at the source of the Jordan River. Its role along other river segments varies as a function of organic nitrogen content and environmental conditions such as temperature, pH, and dissolved oxygen.

Nitrogen losses to the gas phase may affect the nitrogen concentration in the river. It is also known that rivers with high N concentration release significant amounts of  $\text{N}_2\text{O}$  into the atmosphere through nitrification and denitrification (McMahon and Dennehy, 1999; Cole and Caraco, 2001), and therefore,  $\text{N}_2\text{O}$  emissions should not be disregarded. Freney et al. (1983) showed that the equilibrium ratio of ammonia to ammonium is about 1:10 when the pH is around 8. As this is the pH we have measured along the Jordan River, losses due to ammonia volatilization are likely to occur. The volatilization of ammonia from the river water, which is already isotopically enriched due to nitrification, results in further isotope enrichment of the remaining ammonium because of the fractionation associated with the volatilization process.

### Nitrogen Mass Balance

Interpretation of the geochemical and isotopic data revealed that mixing and nitrification are the most significant processes affecting nitrogen compounds in the water column of the Lower Jordan River, and that mineralization and gaseous losses (e.g.,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$  or  $\text{N}_2$ ) should also be considered. In the following, we use the transport equation to delineate and quantify the mechanisms that govern the nitrogen budget in the Lower Jordan River. Since the influx of water from nonpoint sources is not uniformly distributed, solutions were obtained separately for each river segment.

The following steady-state transport equations provide a first approximation for the concentration of ammonium (A) and nitrate + nitrite (N) in the river water:

$$-V \frac{\partial C^A}{\partial x} - \Gamma + \alpha + \beta^A = 0 \quad [2]$$

$$-V \frac{\partial C^N}{\partial x} - \Gamma + \beta^N = 0 \quad [3]$$

where  $V$  is the mean river velocity ( $\text{m d}^{-1}$ ),  $C^A$  and  $C^N$  are the concentrations of ammonium and nitrate + nitrite ( $\text{mg N m}^{-3}$ ),  $\Gamma$  is the net rate of ammonium consumption (and nitrate production) by nitrification ( $\text{mg N m}^{-3} \text{ d}^{-1}$ ),  $\alpha$  is the average rate of net ammonium production (mineralization minus total gaseous losses), and  $\beta^A$  and  $\beta^N$  represent the inflow of ammonium and nitrate + nitrite dissolved in water of the nonpoint source (SI units). The inflow term,  $\beta$ , represents the subsurface contribution, which was identified by Farber et al. (2004) and quantitatively estimated by Holtzman (2003). Where necessary, flows from canals and streams were lumped into the segment input and output. The inflow term,  $\beta$ , is equal to the product of the nonpoint source total discharge,  $Q_j$ , and the concentration of ammonium or nitrate + nitrite,  $C_j$ , per unit volume. Hence,  $\beta = Q_j C_j / AL$ , where  $L$  is the segment length and  $A$  is the average cross-sectional area of the river. Note that the chemical composition of water from the nonpoint source is the end result of the complex transformations that occur along its flow path from its sources to the river. The effect of evapotranspiration is small (Holtzman, 2003) and was therefore neglected.

Nitrification in shallow streams (0.06–3 m) with low mean velocities (approximately  $0.1 \text{ m s}^{-1}$ ) and continuous loads of unoxidized nitrogen is commonly described by a first-order reaction model (McCutcheon, 1987). Since these are the characteristics of the Lower Jordan River,  $\Gamma$  was expressed as:

$$\Gamma = k_A C^A \quad [4]$$

where  $k_A$  is a rate constant ( $\text{d}^{-1}$ ).

Holtzman (2003) obtained detailed water and solute mass balances for the three river segments. When including all known inputs and pumping rates and assuring a nearly steady state condition, the additional nonpoint water source was quantified. It was shown that the river mean velocity under steady state conditions increases with distance due to the nonpoint water source. Assuming a uniform distribution of the nonpoint water source within each segment,  $V$  is approximated as:

$$V(x) = \frac{Q_{\text{in}}}{A} + \frac{Q_j x}{A L} \quad [5]$$

where  $Q_{\text{in}}$  ( $\text{m}^3 \text{ s}^{-1}$ ) is the river discharge at the segment input and  $Q_j$  is the nonpoint source discharge.

### Segment N1

Our measurements show that the discharge of the nonpoint source along Segment N1 is less than 10% of the river discharge, and therefore negligible (Holtzman,



**Table 4. Calculated values of the nitrification rate constant,  $k_A$ .**

Date	$k_A$
	$d^{-1}$
Feb. 2001	0.36
Mar. 2001	0.46
Apr. 2001	0.68
June 2001	0.30
Aug. 2001	0.10

2003). Segment N1 is a special case, as, in addition to the negligible nonpoint source, no significant tributaries exist. As indicated above, the direct inflow from the Yarmouk River is zero (Table 3). Given  $\beta^A = \beta^N = 0$ , the analytical solutions of Eq. [2] and [3] for Segment N1 are:

$$C^A(x) = \frac{\alpha}{k_A} - \left( \frac{\alpha}{k_A} - C_{in}^A \right) \exp(-k_A x/V) \quad [6]$$

$$C^N(x) = C_{in}^N + C_{in}^A - \frac{\alpha}{k_A} + \frac{\alpha}{V} x + \left( \frac{\alpha}{k_A} - C_{in}^A \right) \exp(-k_A x/V) \quad [7]$$

where  $C_{in}^A$  and  $C_{in}^N$  are the ammonium and nitrate + nitrite concentrations at Dalhamiya (Site 6), and the flux,  $V$ , is constant and equal to the flow rate at Dalhamiya (Table 2) divided by the mean cross-sectional area. The rate constant,  $k_A$ , was calculated by solving implicitly Eq. [6], where  $\alpha$  was obtained by combining Eq. [6] and [7] and using the concentration boundary condition,  $C_{out}^A$  and  $C_{out}^N$ , at the segment exit (Gesher, Site 8), according to:

$$\alpha = \frac{V}{L} [(C_{out}^A + C_{out}^N) - (C_{in}^A + C_{in}^N)] \quad [8]$$

Table 4 lists the calculated nitrification rate constants,  $k_A$ , for the respective sampling months. Its average value is  $0.38 \pm 0.21 d^{-1}$  ( $n = 5$ ). The analytical solution is sensitive to the average cross-sectional area; the reported results were obtained for an averaged cross-sectional area of  $30 m^2$ . Higher cross-sectional areas reduce the value of  $k_A$  and vice versa. The results shown in Table 4 are within the range of values found in other polluted riverine systems such as the Chattahoochee River (Stamer, 1979; Miller and Jennings, 1979), Peachtree Creek, and sewage effluent water (McCutcheon, 1987), which yielded  $k_A$  values in the range of 0.25 to  $0.5 d^{-1}$ .

The rate of nitrate production by nitrification,  $\Gamma$ , was calculated for the N1 segment using Eq. [4] and [6]. As shown in Table 5, both  $\Gamma$  and  $\alpha$  values are positive (except for  $\alpha$  in August 2001). These results show that nitrification is the predominant process responsible for the increasing nitrate concentrations in the Lower Jordan River along Segment N1. The negative  $\alpha$  value in August may indicate that gaseous losses became dominant.

### Segments N2 and N3

The results of Holtzman (2003) show that the water flux from the nonpoint source along N2 is significant.

**Table 5. Calculated values of average rate of net ammonium production (mineralization minus total gaseous losses) ( $\alpha$ ), net rate of ammonium consumption (and nitrate production) by nitrification ( $\Gamma$ ), and inflow of nitrate + nitrite dissolved in water of the nonpoint source ( $\beta^N$ ) for Segments N1, N2, and N3.**

Date	$\alpha$	$\Gamma$	$\beta^N$
	$mg N m^{-3} d^{-1}$		
	<u>N1†</u>		
Feb. 2001	709	1449	–
Mar. 2001	752	2431	–
Apr. 2001	836	3234	–
June 2001	127	1360	–
Aug. 2001	–3245	1168	–
	<u>N2‡</u>		
Feb. 2001	–213	974	–811
Mar. 2001	–3710	1173	–322
Apr. 2001	–4861	1165	5173
June 2001	–3572	467	2818
	<u>N3§</u>		
Feb. 2001	136	1177	2072
Mar. 2001	2006	1062	2354
Apr. 2001	–85	482	3247
Aug. 2001	–139	42	–228

† Length and cross-sectional area of Segment N1 are 6000 m and  $30 m^2$ , respectively.

‡ Length and cross-sectional area of Segment N2 are 2250 m and  $15 m^2$ , respectively.

§ Length and cross-sectional area of Segment N3 are 14 500 m and  $10 m^2$ , respectively.

The concentration of sulfate, which was nearly constant along Segment N1 (Table 2), increased along Segment N2. Sulfate is considered a conservative ion under the oxidative conditions of the river (Lindsay, 1979, p. 281–297; Cortecci et al., 2002). The calculation of the discharge from the nonpoint source was determined based on the assumption of mixing between two water bodies (e.g., Herczeg and Edmunds, 1999), and that the sulfate concentration of the nonpoint source is identical to that of the Yarmouk River, Site 7. The calculation revealed that the discharge of the nonpoint source water into the river was 30, 22, 6, 21, and 27% of the total river flow (measured at Nave Ur north, Site 11) during February, March, April, June, and August 2001, respectively.

The analytical solutions of Eq. [2] and [3] for N2 and N3 assume that the nitrification rate coefficient,  $k_A$ , is the same as the coefficient found in N1. This assumption seems justified because environmental conditions such as temperature, pH, and dissolved oxygen are uniform along these river segments. The ammonium concentrations in the surface tributaries were low or zero at all times (Table 3). Since ammonium is considered immobile in soils, we assumed that  $\beta^A$  is zero. Using these assumptions, the longitudinal distribution of ammonium is:

$$C^A(x) = \frac{\alpha}{k_A} - \left( \frac{\alpha}{k_A} - C_{in}^A \right) \left( \frac{Q_j}{LQ_{in}} x + 1 \right)^{-k_A AL/Q_j} \quad [9]$$

The average rate of net ammonium production (mineralization minus gaseous losses) is:

$$\alpha = k_A [C_{out}^A - \gamma(L)C_{in}^A] / (1 - \gamma(L)) \quad [10]$$

where:

$$\gamma(L) = (Q_j/Q_{in} + 1)^{-k_A AL/Q} \quad [11]$$

Note that the formulation of Eq. [9–11] was simplified by excluding the surface contribution of Tributaries 9 and 10. The flow rate and concentrations measured at the segment outlet (Site 11) were modified to include the influence of Tributaries 9 and 10 as if they have joined the river at the segment exit.

A solution of Eq. [3] provides an estimate of the input of nitrate + nitrite through the nonpoint water source,  $\beta^N$ :

$$\beta^N = \frac{Q_j}{AL \ln(Q_j/Q_{in} + 1)} [(C_{out}^N - C_{in}^N) - I] \quad [12]$$

where the integral  $I$  is solved numerically using  $V(x)$  and  $C^A(x)$  given by Eq. [5] and Eq. [9]:

$$I = \int_{x=0}^L k_A C^A(x)/V(x) dx \quad [13]$$

Table 5 shows that the rate of nitrification,  $\Gamma$ , in N2 is positive, but lower than in N1. This is consistent with the trends in ammonium and nitrate concentrations as presented in Fig. 2a and 2b, showing that the ammonium concentration is lower than in N1 and that the variations in ammonium and nitrate concentrations along N2 are more gradual. This suggests that nitrification rates are decreasing with increasing distance from the sewage source and decreasing concentrations of ammonium.

Positive  $\beta^N$  values were obtained only for water samples collected in April and June 2001 (Table 5) and enabled us to calculate the nitrate + nitrite concentrations of the nonpoint source, which were 48.4 and 6.7 mg N L<sup>-1</sup>, respectively. These values are higher than that in the Yarmouk River (4 mg N L<sup>-1</sup>, Table 3). Extensive irrigation and fertilization is typical in the agricultural fields in the vicinity of the Lower Jordan River toward the end of the rainy season (around April). The high nitrate + nitrite concentrations in the subsurface water source in April may result from agricultural return flows originating from the fields adjacent to the river. Year 2001 was a dry year. As a result, the irrigation quota was significantly curtailed and field cultivation during the summer was reduced. The relatively low nitrate concentration in the subsurface water source in June may reflect these changes. Unexpected negative  $\beta^N$  values were determined for water samples obtained in February and March 2001. As shown in Fig. 2, the longitudinal variations in both ammonium and nitrate concentrations are minor along N2. Such small variations increase the uncertainty level of our calculation. The almost constant  $\delta^{15}\text{N}$  values of riverine nitrate in February and March 2001 shown in Fig. 3a support the finding that the nitrate concentration in the subsurface source was low during these two months. A mass balance calculation was not performed for August samples due to the observed decrease in nitrate concentrations along N2 (Fig. 2b). Finally,  $\alpha$  values for N2 were negative for all survey dates. This probably indicates that gaseous losses of N compounds were significant. As mentioned before, gaseous losses of ammonium via volatilization are accompanied by nitrogen isotope fractionation and result in increasing  $\delta^{15}\text{N}$  values in the remaining aqueous  $\text{NH}_4^+$ . This, in turn,

increases  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values by nitrification of the  $^{15}\text{N}$ -enriched  $\text{NH}_4^+$ .

The contribution of water from the nonpoint source along Segment N3, between Nave Ur south (Site 16) and Hamadiya south (Site 19), is higher than in any other river segment (Holtzman, 2003). The discharge of the nonpoint source is approximately 40 to 60% of the total river flow with the exception of June 2001, when it was only 10%. Concentration changes of the inorganic N forms show a trend different from N1 and N2 with increasing nitrate concentrations while ammonium concentrations remained generally low (Fig. 2a and 2b). The  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values were nearly constant.

As shown in Fig. 1, Segment N3 receives water from several canals. However, during all sampling campaigns, these canals delivered a small or negligible discharge into the river and were therefore excluded from the mass balance calculation. The ammonium flux from the nonpoint source,  $\beta^A$ , was considered zero. Table 5 shows that  $\Gamma$  values were smaller than in N1, indicating that the net contribution of nitrification is less dominant along this segment. The  $\beta^N$  values for N3 were positive during February, March, and April. Calculated nitrate + nitrite concentrations of the nonpoint source were 5.2, 14.3, and 16.8 mg N L<sup>-1</sup>, respectively. These values are within the concentration range found in several tributaries and drainages and are assumed to represent agricultural return flows. The  $\Gamma$  and  $\beta^N$  values indicate that the increasing nitrate concentrations are predominantly caused by infiltration of water from the external nonpoint source. The elevated and almost constant  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values along N3 indicate that the nitrate in this water source is enriched in  $^{15}\text{N}$ , an interpretation that is consistent with the high  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) values found for the Yarmouk River water and other agricultural return flows. Mass balance calculations for June were not obtained due to the observed decrease in nitrate concentrations (Fig. 2b) and the low subsurface flux. The insignificant changes in the riverine nitrate concentrations (Fig. 2b) and the limited agricultural activity in the summer explain the nearly zero  $\beta^N$  for samples obtained in August 2001.

## CONCLUSIONS

This study combined physical, chemical, and isotopic analyses with analytical solutions of the transport equation to determine the sources and transformations of nitrogen compounds along the northern part of the Lower Jordan River. Interpretation of the chemical and isotopic data identified the predominant N transformation processes, which were then quantified by the analytical solutions.

Chemical and isotopic analyses of the river water show that while nitrate concentration increases, ammonium decreases, and both  $\delta^{15}\text{N}$  ( $\text{NO}_3$ ) and  $\delta^{15}\text{N}$  ( $\text{NH}_4$ ) values increase. This indicates that nitrification was an important process in the upper 12 km of the river, resulting in a decrease in ammonium and an increase of nitrate concentrations. It was found that the increase of  $\delta^{15}\text{N}$  values of the riverine nitrate is mainly due to

nitrification of ammonium characterized by high  $\delta^{15}\text{N}$  values. Further downstream, nitrification rates decreased and the river nitrogen budget was predominantly influenced by infiltration of water from nonpoint ground water sources that are primarily composed of agricultural return flows.

The analytical solutions of the transport equation provided an estimate of the nitrification rate constants along Segment N1. Applying these constants in the other two segments reveals that nitrification is higher in N1, where ammonium concentration is highest, than in N2 and N3. Similar to the results of the isotopic analyses, the calculations show that nitrate increase in the river along Segments N2 and N3 is predominantly by mixing of the river water with water from the nonpoint source. The analytical solution provided an estimate for the concentrations of nitrate in the nonpoint source. These concentrations are similar to those measured in water samples from agricultural drainages in the region. Finally,  $\alpha$  values (mineralization minus total gaseous losses) for N2 were negative for all survey dates. This indicates that gaseous losses of N compounds were significant. Gaseous losses of ammonium via volatilization are accompanied by nitrogen isotope fractionation and result in increasing  $\delta^{15}\text{N}$  values in the remaining aqueous  $\text{NH}_4^+$ . This, in turn, may increase  $\delta^{15}\text{N}$  ( $\text{NO}_3^-$ ) values resulting from nitrification of the  $^{15}\text{N}$ -enriched  $\text{NH}_4^+$ .

The transformation of ammonium to nitrate and nitrite has important management implications. The Lower Jordan River is used primarily as source water for fishponds, which are sensitive to high contents of nitrite. The results of our study indicate that even if sewage will be eliminated from flowing to the Lower Jordan River (i.e., implication of the peace treaty between Israel and Jordan), the nitrogen content of the Lower Jordan River is expected to be high due to influx of nitrate-rich shallow ground water derived from agricultural activities in the vicinity of the river.

#### ACKNOWLEDGMENTS

The study was supported by the U.S. Agency for International Development, the Middle East Regional Cooperation program (MERC Project TA-MOU-01-M22-043), the Grand Water Research Institute (Technion), and the Technion, Haifa, Israel. We also thank ECO Jordan, the Israeli Agricultural ministry, and the Nature Protection Authority in Israel for their logistic support.

#### REFERENCES

- Cole, J.J., and N.F. Caraco. 2001. Emissions of nitrous oxide ( $\text{N}_2\text{O}$ ) from a tidal, freshwater river, the Hudson River, New York. *Environ. Sci. Technol.* 35:991–996.
- Cortecci, G., E. Dinelli, A. Bencini, A. Adorni-Braccesi, and G. La Ruffa. 2002. Natural and anthropogenic  $\text{SO}_4$  sources in the Arno river catchment, northern Tuscany, Italy: A chemical and isotopic reconnaissance. *Appl. Geochem.* 17:79–92.
- Curtis, E.J.C., K. Durrant, and M.M.I. Harman. 1975. Nitrification in rivers in the Trent basin. *Water Res.* 9:255–268.
- Eaton, A.D., L.S. Clesceri, and A.E. Greenberg. (ed.) 1995. Standard methods for the examination of water and wastewater. 19th ed. Am. Public Health Assoc., Washington, DC.
- Efrat, E. 1996. The land of Israel—Physical, settlement and regional geography. Tel-Aviv Univ., Tel-Aviv, Israel.
- Farber, E., A. Vengosh, I. Gavrieli, A. Marie, T.D. Bullen, B. Mayer, R. Holtzman, M. Segal, and U. Shavit. 2004. Hydrochemistry and isotope geochemistry of the Lower Jordan River: Constraints for the origin and mechanisms of salinization. *Geochim. Cosmochim. Acta* 68:1989–2006.
- Feigin, A., I. Ravina, and J. Shalhevet. 1991. Irrigation with treated sewage effluents. Springer-Verlag, Berlin.
- Freney, J.R., J.R. Simpson, and O.T. Denmead. 1983. Volatilization of ammonia. p. 1–33. In J.R. Freney and J.R. Simpson (ed.) *Gaseous loss of nitrogen from plant-soil systems*. Kluwer, Boston.
- Governments of Israel and Jordan. 1994. Israel–Jordan Peace Treaty. Annex II, water related matters (Online). Available at [www.israel.org/mfa/go.asp?MFAH00pc0](http://www.israel.org/mfa/go.asp?MFAH00pc0) (verified 4 Mar. 2004). Governments of Israel and Jordan.
- Heaton, T.H.E. 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. *Chem. Geol.* 59:87–102.
- Herczeg, A.L., and W.M. Edmunds. 1999. Inorganic ions as tracers. p. 31–71. In P.G. Cook and A.L. Herczeg (ed.) *Environmental tracers in subsurface hydrology*. Kluwer, Boston.
- Hof, F.C. 1998. Dividing the Yarmouk's waters: Jordan's treaties with Syria and Israel. *Water Policy* 1:81–94.
- Holtzman, R. 2003. Water quality and quantities along the Jordan River—Salinization sources and mechanisms. (In Hebrew; tables, figures, and references in English.) M.Sc. thesis. Technion, Haifa, Israel.
- Jansson, S.L., and J. Persson. 1982. Mineralization and Immobilization of soil nitrogen. p. 229–230. In F.J. Stevenson (ed.) *Nitrogen in agricultural soils*. ASA, Madison, WI.
- Jones, J.G. 1985. Denitrification in freshwaters. p. 225–239. In H.L. Golterman (ed.) *Denitrification in the nitrogen cycle*. Plenum, New York.
- Kellman, L., and C. Hillaire-Marcel. 1998. Nitrate cycling in streams: Using natural abundance of  $\text{NO}_3^-$ - $\delta^{15}\text{N}$  to measure in-situ denitrification. *Biogeochemistry* 43:273–292.
- Kendall, C. 1998. Tracing nitrogen sources and cycling in catchments. p. 534–569. In C. Kendall and J.J. McDonnell (ed.) *Isotope tracers in catchment hydrology*. Elsevier, Amsterdam.
- Lehmann, M.F., S.M. Bemasconi, and J.A. McKenzie. 2001. A method for the extraction of ammonium from freshwaters for nitrogen isotope analysis. *Anal. Chem.* 73:4717–4721.
- Lindsay, L.W. 1979. *Chemical equilibria in soils*. Wiley-Interscience, New York.
- Mariotti, A., J.C. Germon, P. Hubert, P. Kaiser, R. Letolle, A. Tardieux, and P. Tardieux. 1981. Experimental determination of nitrogen kinetic isotope fractionation: Some principles, illustration for the denitrification and nitrification processes. *Plant Soil* 62:413–430.
- Master, Y., R.J. Laughlin, U. Shavit, R.J. Stevens, and A. Shavit. 2003. The effect of secondary effluent irrigation on gaseous nitrogen losses. *J. Environ. Qual.* 32:1204–1211.
- Mayer, B., E.W. Boyer, C. Goodale, N.A. Jaworski, N. van Breemen, R.W. Howarth, S. Seitzinger, G. Billen, K. Lajtha, K. Nadelhoffer, D. Van Dam, L.J. Hetling, M. Nosal, and K. Paustian. 2002. Sources of nitrate in rivers draining sixteen watersheds in the northeastern U.S.: Isotopic constraints. *Biogeochemistry* 57:171–197.
- McCutcheon, S. 1987. Laboratory and instream nitrification rates for selected streams. *J. Environ. Eng.* 113:628–646.
- McMahon, P.B., and K.F. Dennehy. 1999.  $\text{N}_2\text{O}$  emissions from a nitrogen-enriched river. *Environ. Sci. Technol.* 33:21–25.
- Miller, J.E., and M.E. Jennings. 1979. Modeling nitrogen, oxygen, Chattahoochee River, GA. *J. Environ. Eng.* 105:641–653.
- Nadelhoffer, K.J., and B. Fry. 1994. Nitrogen isotope studies in forest ecosystems. p. 22–36. In K. Lajtha and R.H. Michener (ed.) *Stable isotopes in ecology and environmental science*. Blackwell Sci. Publ., Oxford.
- Nelson, D.W. 1982. Gaseous losses of nitrogen other than through denitrification. p. 327–344. In F.J. Stevenson (ed.) *Nitrogen in agricultural soils*. ASA, Madison, WI.
- Pauer, J.J., and M.T. Auer. 2000. Nitrification in the water column and sediment of a hypereutrophic lake and adjoining river system. *Water Res.* 34:1247–1254.
- Peterson, B.J., W.M. Wollheim, P.J. Mulholland, J.R. Webster, J.L. Meyer, J.L. Tank, E. Martí, W.B. Bowden, H.M. Valett, A.E. Hershey, W.H. McDowell, W.K. Dodds, S.K. Hamilton, S. Gregory,

- and D.D. Morrall. 2001. Control of nitrogen export from watersheds by headwater streams. *Science* (Washington, DC) 292:86–90.
- Sain, P., J.B. Robinson, W.N. Stammers, N.K. Kaushik, and H.R. Whiteley. 1977. A laboratory study on the role of stream sediment in nitrogen loss from water. *J. Environ. Qual.* 6:274–278.
- Salameh, E. 1996. Water quality degradation in Jordan: Impacts on environment, economy and future generations resources base. Royal Soc. for the Conservation of Nature and Friedrich Ebert Stiftung, Amman, Jordan.
- Salameh, E., and H. Naser. 1999. Does the actual drop in Dead Sea level reflect the development of water resources within its drainage basin. *Acta Hydrochim. Hydrobiol.* 27:5–11.
- Seitzinger, S.P., R.V. Styles, E. Boyer, R.B. Alexander, G. Billen, R. Howarth, B. Mayer, and N. van Breemen. 2002. Nitrogen retention in rivers: Model development and application to watersheds in the eastern U.S.A. *Biogeochemistry* 57:199–237.
- Shavit, U., R. Holtzman, M. Segal, A. Vengosh, E. Farber, I. Gavrieli, T.M. Bullen, and ECO-Research Team. 2002. Water sources and quality along the Lower Jordan River, regional study. p. 127–148. *In* H. Rubin, H.P. Nachtnebel, J. Furst, and U. Shamir (ed.) *Water resources quality—Preserving the quality of our water resources*. Springer-Verlag, Berlin.
- Shearer, G., and D. Kohl. 1986.  $N_2$  fixation in field settings, estimations based on natural  $^{15}N$  abundance. *Aust. J. Plant Physiol.* 13:699–757.
- Silva, S.R., C. Kendall, D.H. Wilkison, A.C. Ziegler, C.C.Y. Chang, and R.J. Avanzino. 2000. A new method for collection of nitrate from fresh water and the analysis of nitrogen and oxygen isotope ratios. *J. Hydrol. (Amsterdam)* 228:22–36.
- Stamer, J.K. 1979. Magnitudes, nature, and effects of point and non-point discharges in the Chattahoochee River basin. USGS Water Supply Paper 2059. U.S. Gov. Print. Office, Washington, DC.
- Thomas, R.L., R.W. Sheard, and J.R. Moyer. 1967. Comparison of conventional and automated procedures for nitrogen, phosphorous, and potassium analysis of plant material using a single digestion. *Agron. J.* 59:240–243.
- Velinsky, D., J.R. Pennock, J.H. Sharp, A. Cifuentes, and M.L. Fogel. 1989. Determination of the isotopic composition of ammonium nitrogen at the natural abundance level from estuarine waters. *Mar. Chem.* 26:351–361.