Hydrochemical evolution of Na-SO_4-Cl groundwaters in a cold, semi-arid region of southern Siberia

V.P. Parnachev · D. Banks · A.Y. Berezovsky
D. Garbe-Schönberg

Abstract The Shira region of Khakassia in southern Siberia exhibits many features governing the evolution of groundwater and surface-water chemistry that are common to other cold, semi-arid areas of the world: (1) a continental climate, (2) location in a rain shadow, (3) low density of surface-water drainage, (4) occurrence of saline lakes, and (5) occurrence of palaeo- and modern evaporite mineralisation. In lowland areas of Shira, the more saline groundwaters and lake waters have a sodium-sulphate (-chloride) composition. Results of thermodynamic modelling suggest that these evolve by a combination of silicate weathering and gypsum and halite dissolution, coupled with carbonate precipitation to remove calcium and bicarbonate ions. An approximately 1:1 sodium:sulphate ratio occurs even in groundwaters from non-evaporite-bearing aquifers. This may indicate the formation of secondary sodium sulphate evaporites (in or near saline lakes or in soil profiles where the water table is shallow), which are subsequently distributed throughout the study area by atmospheric transport. Several urban groundwaters are characterised by very high nitrate concentrations, conceivably derived from sewage/latrine leakage.

Résumé La région de Shira en Khakassia, dans le sud de la Sibérie, présente de nombreux phénomènes déterminant la chimie des eaux souterraines et des eaux de surface qui sont communs aux régions froides et semi-arides du monde : (1) un climat continental, (2) une localisation à l'abri des pluies, (3) un drainage de surface à faible densité, (4) la présence de lacs salés et (5) l'existence d'une minéralisation évaporitique ancienne et actuelle. Dans les zones déprimées de Shira, les eaux souterraines et lacustres les plus salées ont un faciès sulfaté (et chloruré) sodique. Les résultats de la modélisation thermodynamique laissent penser qu'elles ont évolué sous l'effet combiné de l'altération de silicates et de la dissolution de halite et de gypse, associées à la précipitation de carbonates, qui a soustrait les ions calcium et bicarbonate. Un rapport sensiblement 1:1 des ions sodium et sulfate existe même dans les eaux souterraines des aquifères ne possédant pas d'évaporites. Ceci peut indiquer la formation d'évaporites secondaires de sulfate de sodium (dans et près des lacs ou dans les profils de sols lorsque la nappe est proche de la surface), qui sont ensuite dispersées à travers la région étudiée par transport atmosphérique. Plusieurs nappes de zones urbaines sont caractérisées par de très fortes concentrations en nitrate, provenant certainement d'infiltrations d'eaux usées.

Resumen La región de Shira, en Khakassia (sur de Siberia), presenta muchas características en la química de sus aguas superficiales y subterráneas que son comunes a otras áreas frías y semiáridas en el mundo: (1) clima continental, (2) localización en una zona de sombra respecto a la precipitación, (3) baja densidad de drenaje para las aguas superficiales, (4) presencia de lagos salinos, y (5) mineralización de evaporitas. En las zonas más bajas de Shira, las aguas más salinas, subterráneas o de lagos, son sulfatado(-clorurado)-sódicas. Un modelo termodinámico sugiere que estas aguas se formaron por una combinación de la degradación de los silicatos y la disolución de yeso y halita, superpuesto a la precipitación de carbonatos, que eliminaron los iones calcio y bicarbonato. Incluso en las aguas subterráneas presentes en acuíferos no evaporíticos se registra una concentración iónica sodio/sulfato de 1:1. Esto puede indicar la formación de evaporitas

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V.P. Parnachev · A.Y. Berezovsky
Department of Dynamic Geology, Tomsk State University,
Lenina prospekt 36, Tomsk, 634050 Russia

D. Banks (✉)
Norges Geologiske Undersøkelse, Postboks 3006 Lade,
N-7002 Trondheim, Norway

D. Garbe-Schönberg
Geologisch-Paläontologisches Institut und Museum,
Christian-Albrechts-Universität zu Kiel, Olshausenstraße 40–60,
D-24118 Kiel, Germany

Present address:
D. Banks
Holymoor Consultancy, 86 Holymoor Road, Holymoorside,
Chesterfield, Derbyshire, S42 7DX, UK
Fax: +44-1246-568433
e-mail: david@holymoor.force9.co.uk

secundarias de sulfato de sodio (en o cerca de lagos salinos o en suelos con nivel freático subsuperficial), que se distribuyen a lo largo del área de estudio por transporte atmosférico. Las aguas subterráneas urbanas se caracterizan por muy altas concentraciones de nitrato, probablemente procedente de pérdidas en la red de saneamiento o en las letrinas.

Key words groundwater quality · hydrochemical modelling · salinisation · Siberia · semi-arid regions

Introduction

In 1989, a representative of the World Resources Institute in Washington, D.C., addressed the issue of the sustainability of semi-arid lands, noting that 16% of the world's population lives in the arid or semi-arid zones, which account for one-third of the earth's surface. He pointed to poor irrigation management and dry-land salinisation as key factors in land degradation in the Canadian prairies, the American Great Plains, and Western Australia (El-Ashry 1989). Noteworthy is the fact that, at the major international conference he was addressing, no paper considered the largest semi-arid region in the world: the steppes of southern Russia and central Asia, a region largely unknown to Western hydrogeologists.

Cold semi-arid areas possess important and unique hydrogeological and hydrochemical characteristics. The recharge, evolution, and discharge of groundwater systems are limited by the existence of a frozen soil layer for much of the year and the fact that potential recharge may be bound up as snow cover for long periods. The world's cold semi-arid regions are typically intracontinental and occur either in relatively stable shield regions, in rain-shadow areas, and/or in extensional tectonic depressions. Topography is often low and drainage basins may be partially or totally closed. Palaeoevaporite sequences are not uncommon. This combination of geological, geographical, and climatic factors often leads to salinisation of soils and groundwater (Salama et al. 1999). Sodium-sulphate-chloride groundwaters and lakes are typical; indeed, they often produce commercially exploitable mineral reserves, as in southern Siberia and the Canadian and American prairies (Harben and Bates 1990; Harben and Kuzvart 1996). The evolution of such waters remains poorly understood, however, and the Shira region of the Minusinsk Basin of northern Khakassia, one of Siberia's most popular spa resorts (Parnachev et al. 1997a, 1997b), provides an excellent laboratory to study them. The Minusinsk Basin is characterised by the following factors: (1) the geographical location and climate are extremely continental, far from the oceans and with very cold winters; (2) the basin lies in a rainshadow, and the climate is semi-arid; and (3) the basin represents a graben (rifting) environment, associated with alkaline magmatism, subsidence, poor surface-water drainage, and ancient palaeoevaporite sequences.

Objective

The initial objective of the study was to document, through a sampling program, the water quality of springs and wells in Precambrian and Palaeozoic aquifers in the Khakassian rift province. In particular, it was hoped to collect a groundwater-quality dataset from an alkaline igneous province in an area of extensional tectonics that could be compared with groundwater from similar tectonic settings elsewhere in the world (e.g., the Oslo Graben; Reimann et al. 1996; Morland et al. 1997). Thus, the relative importance of factors such as climate, land use, and glaciation history, relative to lithological factors, in controlling concentrations of health-related elements, such as uranium and fluoride (typically occurring at high concentrations in many granitic groundwaters), could be assessed. In reality, the small number of sampling points available in Khakassian granitoids largely negated this objective, although the few such samples revealed only modest concentrations of the health-related trace parameters (see below; Banks 1998; Banks et al. 1998d).

On receiving the analytical results, the most interesting aspect of the hydrochemistry appeared to be the presence of a Na-SO_4-Cl signature in most of the groundwaters. The objective of this paper is thus to elucidate the evolution of this signature in the 33 sampled groundwaters (and the lakes of the region, whose analyses have previously been published; see *Table 1*).

Study Area

Geology

Khakassia is a small republic of the Russian Federation, and is situated in the central part of the Altai-Sayan Mountain region in southern Siberia. Locations are show in *Figure 1*. The study area lies within the Minusinsk intermontane trough, bounded by the mountain areas of Kuznetsk-Alatau in the west, and the Western and Eastern Sayan mountains in the south and the east (all marked IX on the lower part of *Figure 1*). The trough itself, containing upper Palaeozoic sedimentary and volcanic rocks, is divided into four sub-basins (marked II on *Figure 1*, and named, from north to south, the Nazarovskaya, Chebakovo-Balakhtinskaya, Sydo-Eribinskaya and Yuzhno-Minusinskaya basins) by east–west ridges of Precambrian/lower Palaeozoic rocks (Luchitski 1960; Parnachev et al. 1992). The intervening ridges, marked III and VI on *Figure 1*, are offshoots of the Kuznetsk-Alatau and Eastern Sayan ranges. From a tectonic perspective, the Minusinsk Trough is an early Devonian palaeorift structure (Parnachev et al. 1996a).

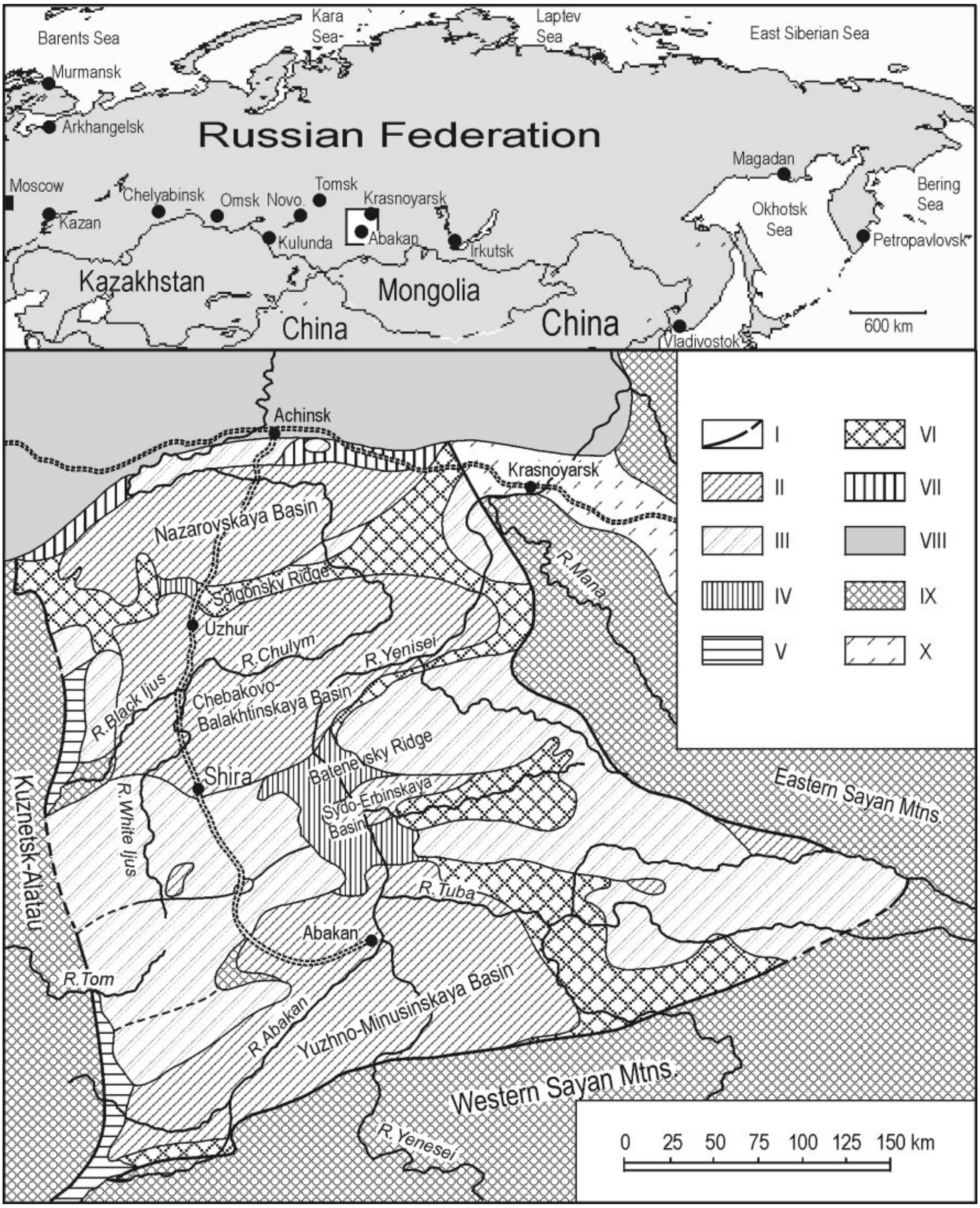


Figure 1 *Above* Northern Asia, showing location of the Khakassia region (*white square*). *Novo*. Novosibirsk. *Below* The Khakassia region, showing Shira in the Minusinsky intermontane trough within the Altai-Sayan mountain region, southern Siberia, Russia (after Luchitsky 1960). *I* Boundary of Minusinsk trough; *II* main Devonian sub-basins; *III* horst/ridge areas between sub-basins; *IV*, *V* depressions; *VI* horst/ridge area, beneath cover of Devonian volcanogenic rocks; *VII* horst/ridge area, beneath cover of Mesozoic (mainly Jurassic) deposits; *VIII* Chulimskaya synclinorium (Mesozoic sediments); *IX* pre-Devonian magmatic and metamorphic formations surrounding the Minusinsk trough (i.e., basement); *X* basement, beneath cover of mid-Palaeozoic sedimentary rocks

However, repeated phases of rifting activity occurred in Cambrian-Ordovician, early Devonian, and, most recently, Palaeogene-Quaternary (fault reactivation, volcanic activity) times. This study focuses on the region around the town of Shira, indicated in *Figure 2*.

The Shira region lies on the southern margin of the second (Chebakovo-Balakhtinskaya) sub-basin, which stretches from Shira to Uzhur (*Figure 1*), and which is bounded on the north and south by the Batenevsky and Solgonsky ridges. These ridges are composed, like the Kuznetsk-Alatau and Eastern Sayan mountain

Table 1 Chemical composition of six saline lakes and one fresh-water lake (Itkul) in the Shira region

Lake	Area (km^2)	Maximum depth (m)	Water composition. Kurlov formula (*M* mineralisation in g/L: major ions as % equivalents)	pH
Shira[a,b]	36	21.8	$M_{21.0}\ [SO4_{71}Cl_{21}HCO3_{4}/(Na+K)_{60}Mg_{38}]$	8.7 – 9.2
Byelyo[b]	75	48.2	$M_{8.7}\ [SO4_{57}Cl_{24}/(Na+K)_{58}Mg_{38}]$	8.9 – 9.2
Tus[b]	2.65	2.0	$M_{110}\ [SO4_{51}Cl_{46}(HCO3+CO3)_{3}/Mg_{49}\ (Na+K)_{48}Ca_{3}]$	8.3 – 8.4
Shunyet[b]	0.46	3.0	$M_{12.0}\ [Cl_{60}SO4_{33}/Mg_{56}(Na+K)_{41}]$	8.4
Utichye-1[a]	0.5	2.0	$M_{6}\ [SO4_{61}Cl_{22}/Na_{61}Mg_{37}]$	-
Utichye-3[a]	1.4	3.0	$M_{14.2}\ [SO4_{60}Cl_{36}/Na_{57}Mg_{26}]$	-
Itkul[b]	23	17	$M_{0.7}\ [(HCO3+CO3)_{74}SO4_{19}/Mg_{55}Na_{18}Ca_{16}]$	-

[a] Data after Parnachev et al. (1992)
[b] Data after Parnachev et al. (1997b)

ranges, of Precambrian and lower Palaeozoic formations, including volcanics, clastic and carbonate sedimentary rocks, and granitoids. These rocks are mapped in *Figure 2*, south of a line approximately passing through Shira town; the sedimentary sub-basin lies to the north. The sub-basin is essentially a large (250 × 100 km) synclinorium, infilled by Devonian and lower Carboniferous volcanic and sedimentary rocks, with a complex internal structure. The rocks are typically deposited in a continental, lagoonal, or shallow marine environment, and the lower and upper Devonian sequences (D_1 and D_3, respectively) are known to contain evaporite minerals, including gypsum and halite. The geology is described in more detail by Parnachev et al. (1996b, 1997b) and Banks et al. (1998d).

The modern structure of the sub-basins of the Minusinsk Trough is traversed by sub-latitudinal faults. The most recent displacements on these faults, accompanied by the formation of volcanic pipes, took place 28–78 Ma ago (Parnachev et al. 1996b).

Climate and Land Use

The climate is semi-arid: annual average rainfall is 312 mm at Shira; the ratio of rainfall to potential evaporation is 0.5–1.5 (Feshbach et al. 1995). At Shira, the majority of the rainfall occurs during June to September. The mean monthly temperature fluctuates between +20 and –20 °C, with a yearly mean of about 0 °C. The area is not permafrosted (Feshbach et al. 1995); it and the surrounding mountain areas were not extensively glaciated during the Weichselian (Nalivkin 1960). The semi-arid climate results in a low density of surface-water drainage, although the region lies on one of Siberia's major water divides, between the Ob' and Yenisei River basins.

The topography within the Chebakovo-Balakhtinskaya basin ranges from about 320 to 670 m and largely consists of hilly steppe, with dominant grass and low shrub vegetation and sparse trees. The land use ranges from open grassland and pasture used for free-range cattle herding to relatively low-intensity agriculture. The boundaries of the basin are formed by lower Palaeozoic and Precambrian outcrops (as much as 1300 m elevation), where a more taiga-like vegetation dominates. The Tuim granite complex, immediately south of Shira town (*Figure 2*), forms an area of intermediate hilly topography with low-to-medium-density woodland of mixed conifer and birch.

In Shira town, the land use is largely residential with some light-to-medium industry, including engineering. Mining and some smelting have historically occurred in the region for a variety of metals, including copper, molybdenum, and tungsten, dominantly associated with the granite complex. In fact, Sorsk, about 50 km SSE of Shira, is Russia's largest molybdenum mine. Full details of land use and climate are given in the atlas of Balakhchina et al. (1999).

Saline Lakes and Water Supply

The popularity of the Shira region of Khakassia as a holiday destination for Siberians is partly due to the abundance of lakes, both fresh and salt (Degermendzhi et al. 1996; Makarenko et al. 1999; Guznyaeva et al. 1999). Probably the most saline is Lake Tus, reported to have a mineralisation of more than 100 g/L. Other saline lakes are detailed in *Table 1*. The hydrochemical type of the lakes is variable, but the more saline are typically dominated by sodium sulphate-(chloride) hydrochemistry, as indicated by the Durov diagram in *Figure 3*. The saline lakes tend to be associated with Upper Devonian (D3) and Lower Devonian (D1) outcrops, which contain evaporite minerals and the more saline groundwaters.

The salinity of the lakes is further enhanced by a lack of surface-water through-flow and by high evaporation. In fact, the Devonian strata tend to occupy the lower-lying areas, with less rainfall and slightly higher summer temperatures than the pre-Devonian hilly terrain; these factors promote evaporative up-concentration of solutes (see Balakhchina et al. 1999). Modern evaporites (whose mineralogy is uncertain) form on the margins of several of the saline lakes. At Shira Spa (Kurort), on the banks of Lake Shira, min-

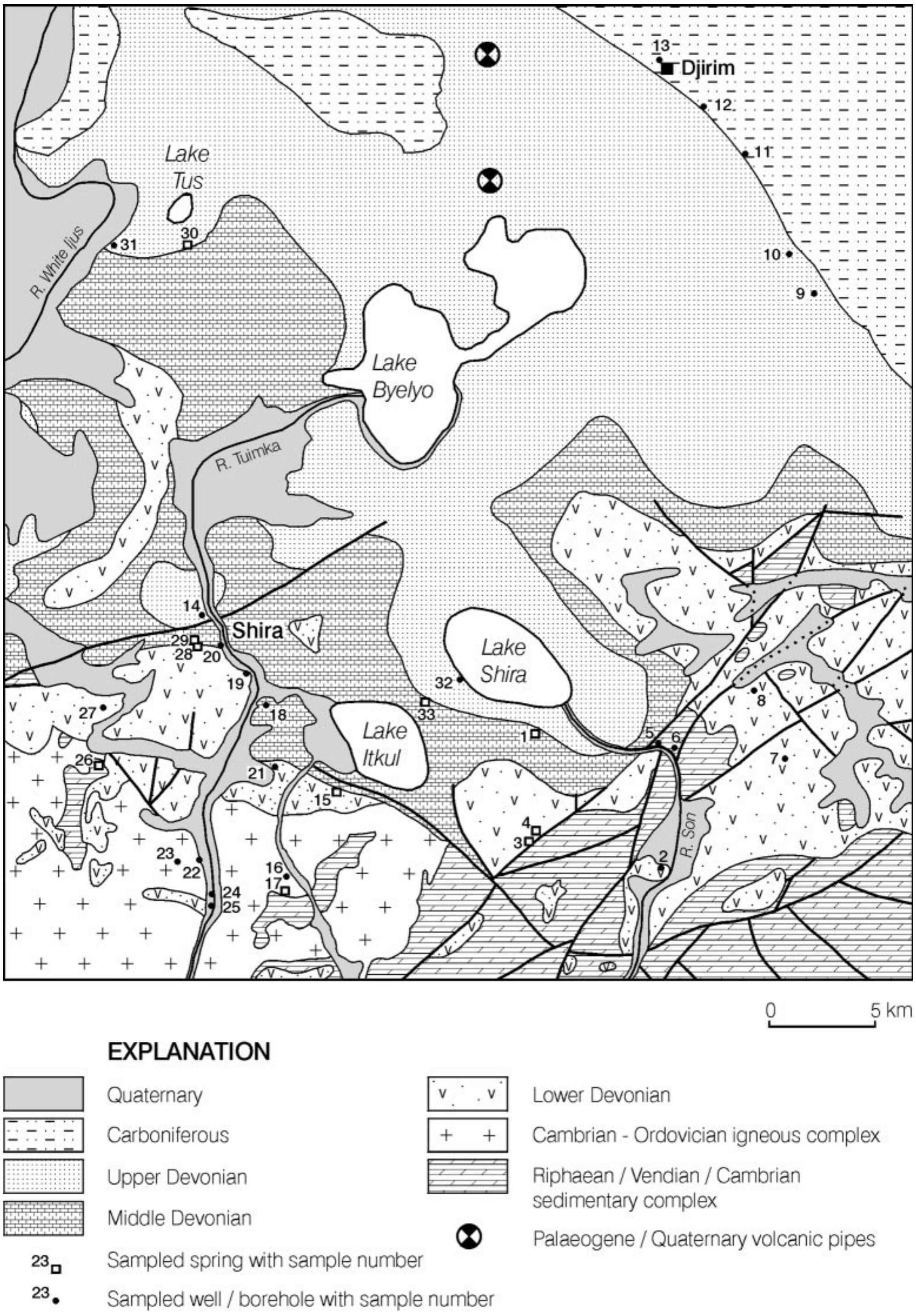


Figure 2 Geology and locations of sampled wells/boreholes and springs in the Shira district

eral water, whose composition is indicated in *Table 2* (sample 32), is also abstracted from a borehole, 100 m deep, that penetrates Upper Devonian rocks. Most fresh-water lakes occur on strata older than D3 without evaporite sequences. Lake Itkul, for example, on D2 carbonates, is the principal source of Shira town's water supply.

Na-SO$_4$-Cl Groundwaters in Cold, Semi-arid Regions

Existing literature suggests that a hydrochemical signature that is dominated by sodium sulphate is, to some extent, characteristic of cold, intracontinental, semi-arid regions. The evolution of this signature remains uncertain (Grossman 1968; Eugster and Hardie 1978; Eugster 1980; Hardie 1984; Harben and Kuzvart 1996), although large data sets compiled by

Table 2 Hydrochemistry of selected analytes in sampled groundwaters of the Shira region. Sample Xa30 is the Lake Tus spring. Xa32 is the Shira Kurort borehole. pH, temperature, and alkalinity were measured in the field; F, Cl, Br, NO_3, and SO_4 by ion chromatography; Si, Mg, Ca, Na, K, and Sr by ICP-AES; U and Tl by ICPMS. *S* spring, *B* borehole/well. All samples were field filtered and acidified, except sample Xa32UA, which was unfiltered but acidified

Sample Xa series	Rock code	Type	Depth (m)	pH	Temp. (°C)	Alk. (meq/L)	F (mg/L)	Cl (mg/L)	Br (mg/L)	NO_3 (mg/L)	SO_4 (mg/L)	Si (mg/L)	Mg (mg/L)	Ca (mg/L)	Na (mg/L)	K (mg/L)	Sr (mg/L)	Tl (μg/L)	U (μg/L)
1	D2(Q)	S	1.5	7.30	4.5	7.8	0.63	122	0.71	21.8	982	5.0	112	122	338	5.21	6.07	<0.03	7.5
2	D1	B	47	7.55	6.2	5.7	0.44	5.4	<0.1	7.3	58	6.1	27	63	34	<0.5	0.93	<0.03	6.4
3	D1	S	0	7.66	6.2	7.1	0.60	32	0.42	7.9	224	6.7	47	71	98	1.45	1.34	<0.03	9.5
4	D1	S	0	7.37	3.7	7.3	0.58	36	0.45	8.1	241	6.4	49	73	105	1.55	1.56	<0.03	9.7
5	V_C	B	100	7.60	7.5	6.9	0.30	38	0.30	82.1	127	4.1	63	57	65	2.52	0.76	<0.03	6.3
6	V_C	B	70	7.74	6.6	11.7	0.36	259	0.90	189	714	5.7	181	96	300	5.48	2.15	<0.03	13.2
7	D1	B	50	7.25	8.0	6.5	0.26	346	1.49	14.1	887	6.8	147	191	210	4.78	5.63	<0.03	8.3
8	D1	B	–	6.99	8.4	10.3	–	2970	14.3	<0.05	6250	5.9	1138	384	2240	8.99	8.32	<0.03	10.1
9	D3	B	350	7.75	7.5	5.0	0.11	131	0.47	112	632	3.9	70	84	212	2.99	7.14	<0.03	27.9
10	D3	B	–	7.46	4.4	6.1	0.32	6.1	<0.1	11.4	30	5.9	34	52	19	1.20	0.58	<0.03	3.7
11	C1	B	–	8.07	7.8	6.0	0.20	4.6	<0.1	9.1	39	7.7	29	36	48	<0.5	1.29	<0.03	11.0
12	C1	B	–	8.16	6.5	6.3	0.45	8.0	0.26	4.3	87	6.2	26	17	102	<0.5	1.75	<0.03	18.6
13	C1	B	–	8.03	6.7	10.0	0.92	118	0.53	28.7	563	4.8	42	26	423	1.15	1.84	0.07	16.3
14	D3/D2	B	–	7.49	6.8	6.8	0.51	71	0.27	17.9	91	5.4	42	87	39	2.92	1.79	<0.03	7.1
15	D1	S	0	7.50	3.5	5.2	0.57	20	<0.1	7.5	41	5.8	19	76	14	1.11	0.96	<0.03	6.4
16	C_O	B	32	7.50	3.9	5.4	0.93	14	<0.1	26.7	73	5.9	28	71	21	2.68	0.61	<0.03	5.7
17	C_O	S	0	7.76	4.9	4.9	0.64	1.7	<0.1	9.8	19	5.9	15	60	12	0.96	0.70	<0.03	16.1
18	D1	B	–	7.41	5.6	6.0	0.50	49	<0.1	56.7	60	7.1	29	94	25	1.93	1.28	<0.03	6.4
19	D1	B	10	7.38	3.5	6.4	0.48	52	<0.1	30.6	59	6.3	27	98	20	2.73	0.96	<0.03	5.2
20	D2	B	–	7.33	5.4	5.3	0.32	306	0.27	81.9	69	8.1	60	125	45	1.32	2.37	<0.03	9.6
21	D1	B	–	7.53	3.7	5.7	0.49	20	<0.1	16.0	47	5.7	20	85	12	3.05	0.80	<0.03	7.9
22	C_O	B	–	7.46	6.1	5.3	0.31	43	<0.1	7.0	44	6.4	16	86	18	2.47	0.67	<0.03	4.3
23	C_O	B	–	7.22	4.6	8.4	0.22	202	<0.1	76.7	40	5.4	51	194	17	6.64	1.20	<0.03	4.6
24	C_O+Q	B	19	7.35	3.3	5.2	0.38	23	<0.1	28.6	56	5.9	17	90	11	2.02	0.73	<0.03	6.9
25	C_O+Q	B	20	7.60	2.9	4.6	0.38	4.0	<0.1	15.1	15	6.0	11	66	6.4	1.49	0.46	<0.03	3.2
26	V_C	S	0	7.52	3.7	4.1	0.13	0.3	<0.1	2.2	7.2	5.0	13	54	2.7	1.00	0.23	<0.03	1.1
27	D1	B	–	7.62	3.6	3.7	0.20	0.8	<0.1	1.9	20	5.5	14	43	10	0.95	1.34	<0.03	5.6
28	D1	S	0	7.49	3.9	5.0	0.23	40	0.34	8.2	92	8.5	20	85	30	<0.5	1.33	<0.03	3.4
29	D2	S	0	7.38	4.0	6.4	0.25	11	<0.1	7.2	53	6.6	28	77	19	1.55	1.84	<0.03	5.1
30	D3	S	0	6.66	3.9	12.9	0.25	2850	7.64	<0.05	3230	6.5	686	467	1890	13.6	8.55	–	–
31	D3/D2+Q	B	–	7.98	5.5	5.6	1.08	34	0.30	60.6	118	3.4	43	28	82	3.66	2.72	<0.03	11.5
32	D3	B	100	7.55	4.8	3.4	<0.05	200	0.94	25.4	1530	3.5	73	150	450	3.16	4.48	<0.03	13.2
33	D2	S	0	7.50	4.3	8.3	1.07	31	0.33	0.20	405	3.9	63	47	181	5.94	7.54	0.06	5.8
32UA	D3	B	100	7.55	4.8	3.4	<0.05	199	0.92	24.3	1490	3.5	72	147	441	2.74	4.39	<0.03	13.1

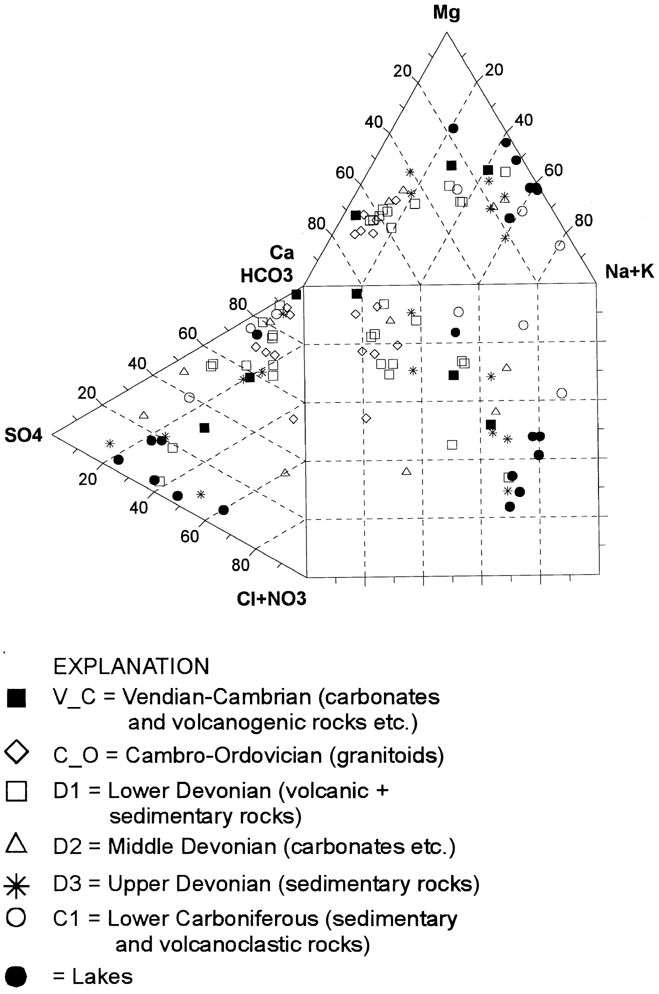


Figure 3 Durov diagram (based on milliequivalent proportions) illustrating main water types of sampled groundwaters and lake waters (from *Table 1*)

Russian geochemists (Bazilevich 1965; Shvartsev 1998) reveal trends in element concentrations that indicate possible evolutionary mechanisms.

The world's greatest reserves of natural sodium-sulphate evaporite minerals occur in the continental interiors of North America and Asia, in partially closed, poorly drained basins in semi-arid climates. In the plains of Alberta, Canada, extensive deposits of recent sodium sulphate evaporites were probably deposited from post-glacial saline lakes, where the crystallisation of mirabilite was promoted by periodic freezing of the lake water (Grossman 1968). The location of the deposits coincides with underlying evaporite-bearing upper Devonian sediments. The climate is not dissimilar to Siberia, and the area was probably partially hydraulically closed in post-glacial times, permitting evaporative concentration of saline groundwaters derived from Devonian strata in the lake basins (Grossman 1968).

Major deposits of sodium sulphate also occur in connection with saline lakes in North Dakota, Utah, and California (USA), in Transbaikal, and in several places in Kazakhstan and western Siberia, such as the Kulunda Steppe and the major deposit of Lake Kuchuk, near Novosibirsk. Lake Kuchuk covers 155 km^2, contains about 600 million tons of sodium sulphate, and precipitates 640,000 tons of mirabilite each winter (Harben and Bates 1990; Harben and Kuzvart 1996).

The Kara-Boghaz-Gol Gulf of the Caspian Sea is described (Anonymous 1957) as having a salinity of 28.5 g/L and precipitating mirabilite from a Na-Mg-SO_4-Cl solution in cycles that can be identified in cores. The history of the area suggests that the nature of the precipitate is highly sensitive to human interference and natural changes in salinity. Recent declines in water level and increases in salinity of the Gulf (from 16.4 g/L in 1897 to 28 g/L in 1941) resulted in the precipitation of halite in addition to mirabilite. Since 1941, water has been pumped to a salt factory where astrakhanite (blödite, $Na_2SO_4 \cdot MgSO_4 \cdot 7H_2O$), glauberite ($Na_2SO_4 \cdot CaSO_4$), epsomite ($MgSO_4 \cdot 7H_2O$), and halite were produced in evaporating basins, in addition to pure mirabilite. In 1947, the waters of the Gulf ceased to deposit mirabilite. This hydrochemical sensitivity suggests that saturation with respect to mirabilite and halite are achieved at rather similar stages in the water's evolution.

Some or all of the above-named sodium-sulphate provinces share similarities with the Minusinsk Trough area of Khakassia: (1) inland areas, far from the sea; (2) wholly or partially hydrologically and/or topographically closed basins with low surface-water through-flow; and (3) semi-arid or arid climate leading to: (a) a high potential for evaporative concentration of solutes in lake basins; and (b) the presence of evaporite-bearing formations at depth.

Field Techniques and Data Analysis

Groundwater samples (numbers Xa1–Xa33) were taken from 33 sources in the Shira region during August 16–21, 1996. Samples were taken from either bedrock groundwater springs or bedrock boreholes in regular use for water supply, in both rural and urban areas. Not all boreholes could be sampled directly at the well head; some samples were acquired from the header tank above the borehole, from a household tap fed by the borehole, or from a communal electric pump on a borehole-fed ring-main. In all cases, the tap was run for at least 5 min prior to sampling. pH and temperature of water were measured in the field using a Palintest Micro 900 pH meter, calibrated regularly against standard solutions of pH 7 and 10. Alkalinity was determined using an Aquamerck field titration kit, with indicator of end-point pH = 4.3, with an estimated accuracy of ± 0.2 meq/L. Duplicate determinations were carried out, and the mean value was used. Logistical constraints restricted sampling to a single 1×100-mL polyethene flask of groundwater, field-filtered at 0.45 μm with disposable Millipore "Millex" filters.

The samples were transported to Norway and about 10 mL of each sample was decanted for analysis at the Geological Survey of Norway (NGU) for the anions SO_4^{2-}, PO_4^{3-}, F^-, NO_3^-, Cl^-, Br^- and NO_2^- by ion chromatography (IC). The remaining 90 mL of sample was shipped to the University of Kiel, where it was acidified with concentrated ultrapure nitric acid in-flask and analysed for various trace elements by inductively coupled plasma mass spectrometry (ICPMS) techniques. The acidified samples were then returned to Norway for analysis on NGU's inductively coupled plasma atomic emission spectroscopy (ICPAES) equipment. Full methodological details and analytical results are provided by Banks et al. (1998d).

Samples were designated according to the most likely age and lithology of bedrock from which they were derived, listed from oldest to youngest (*Figure 2*):

- V-C = Vendian/Cambrian volcanogenic and carbonate sedimentary series.
- C-O = Cambrian/Ordovician igneous complex. Dominated by alkaline granitoid massifs.
- D1 = Lower Devonian. Interbedded volcanic and sedimentary rocks with some evaporite minerals.
- D2 = Middle Devonian. Carbonate-rich sedimentary rocks, including limestones and dolomites.
- D3 = Upper Devonian. Sedimentary sequence, dominated by an "Old Red Sandstone" facies, with numerous redbeds and evaporite-bearing units.
- C1 = Lower Carboniferous. Sandstones, siltstones, mudstones, limestones, and tuffites.

Four wells (numbers Xa8, Xa14, Xa20, and Xa31) are near lithological boundaries. For the purpose of statistical analysis, they are allocated to groups D1, D3, D2, and D3, respectively. Some wells, including Xa24 and Xa25, may also receive some input of groundwater from Quaternary deposits.

Groundwater Chemistry

Results

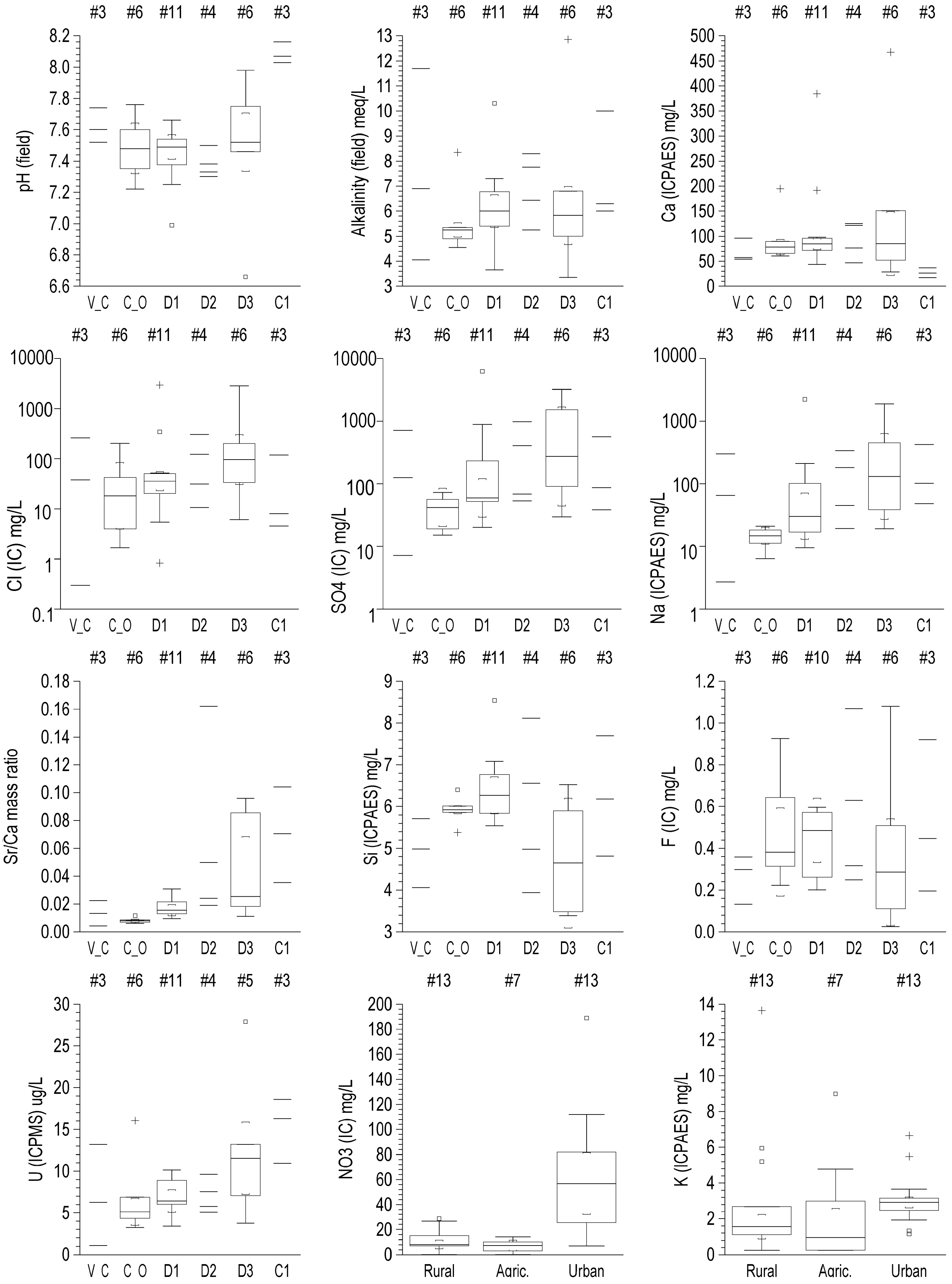
Temperatures of the sampled groundwaters typically range from 3–5 °C for springs; values are slightly higher for samples from some boreholes. These values approximately reflect annual average air temperature, possibly with a small additional geothermal and/or frictional heating component. The waters are of various hydrogeochemical types, as illustrated by the Durov diagram in *Figure 3*. The following features of the groundwater chemistry, indicated in *Figures 3*, *4*, and *5*, are of particular interest:

1. Even within the Devonian sedimentary aquifers, the waters are of various hydrochemical types, ranging from Ca-Mg-HCO_3, through Mg-SO_4 to Na-SO_4-Cl (*Figure 3*).
2. Chloride and sulphate have a high degree of covariance (*Figure 5*). The highest concentrations of both parameters are in samples from the D3 aquifers, with one particularly high outlier in D1 (*Figure 4*).
3. In the more saline groundwaters, Br/Cl mass ratios of about 0.0035 are typical; these are not shown here but are discussed by Parnachev et al. (1997a). This ratio is equivalent to the current average seawater ratio (Edmunds 1996).
4. Sodium and chloride also have a high degree of covariance (*Figure 5*), although in groundwaters of moderate salinity, an excess of sodium occurs.
5. Sodium and sulphate have a very high degree of correlation, even better than that of sodium with chloride (*Figure 5*), typically with a 1:1 meq ratio.
6. If, for example, chloride is taken as a conservative indicator of evolution of waters by evaporite dissolution and evapotranspirative concentration (*Figure 5*), direct linear relationships of sulphate and sodium with chloride exist. In contrast, both calcium and alkalinity have a very low rate of increase with chloride, whereas magnesium has an intermediate rate of increase.
7. The lowest median values for chloride and sulphate are generally in the groundwaters of the C-O igneous complex (*Figure 4*). These waters have low ionic content and are dominantly of calcium-bicarbonate type. Concentrations of U, F, Be, Tl, and Th are also modest compared with Norwegian granitoid groundwaters (Banks 1998).

Preliminary Interpretation

Even without the benefit of hydrochemical modeling, the above observations suggest key features of the hydrochemical evolution of the Khakassian groundwaters. These features could subsequently be tested in more rigorous models. The numerals below correspond to the observations in the previous section:

1. The Ca-Mg-HCO_3 waters within the Devonian aquifer complex probably reflect carbonate weathering in sedimentary sequences rich in dolomite. The predominance of Mg, $SO_4^=$, Na, and Cl^- in some groundwaters probably reflects the influence of evaporite minerals such as dolomite, gypsum, anhydrite, and halite.
2. The high covariance between chloride and sulphate suggests a common origin in evaporite minerals. Indeed, the geological sequences associated with the highest concentrations of these ions (D1 and D3) are those known to contain halite and gypsum mineralisation, although not all groundwaters in these formations are highly saline. The chloride and sulphate contents of the main Lake Tus spring (sample Xa30 from D3, 2850 mg/L Cl^- and 3230 mg/L SO_4^{2-}) suggest a considerably lower spring salinity than the lake water's reported salinity (>100 g/L). This discrepancy may be indica-


#3 #6 #11 #4 #6 #3
pH (field)
6.6 6.8 7.0 7.2 7.4 7.6 7.8 8.0 8.2
V_C C_O D1 D2 D3 C1
Alkalinity (field) meq/L
3 4 5 6 7 8 9 10 11 12 13
Ca (ICPAES) mg/L
0 50 100 150 200 250 300 350 400 450 500
Cl (IC) mg/L
0.1 1 10 100 1000 10000
SO4 (IC) mg/L
1 10 100 1000 10000
Na (ICPAES) mg/L
1 10 100 1000 10000
Sr/Ca mass ratio
0.00 0.02 0.04 0.06 0.08 0.10 0.12 0.14 0.16 0.18
Si (ICPAES) mg/L
3 4 5 6 7 8 9
#3 #6 #10 #4 #6 #3
F (IC) mg/L
0.0 0.2 0.4 0.6 0.8 1.0 1.2
#3 #6 #11 #4 #5 #3
U (ICPMS) ug/L
0 5 10 15 20 25 30
V C C O D1 D2 D3 C1
#13 #7 #13
NO3 (IC) mg/L
0 20 40 60 80 100 120 140 160 180 200
Rural Agric. Urban
K (ICPAES) mg/L
0 2 4 6 8 10 12 14

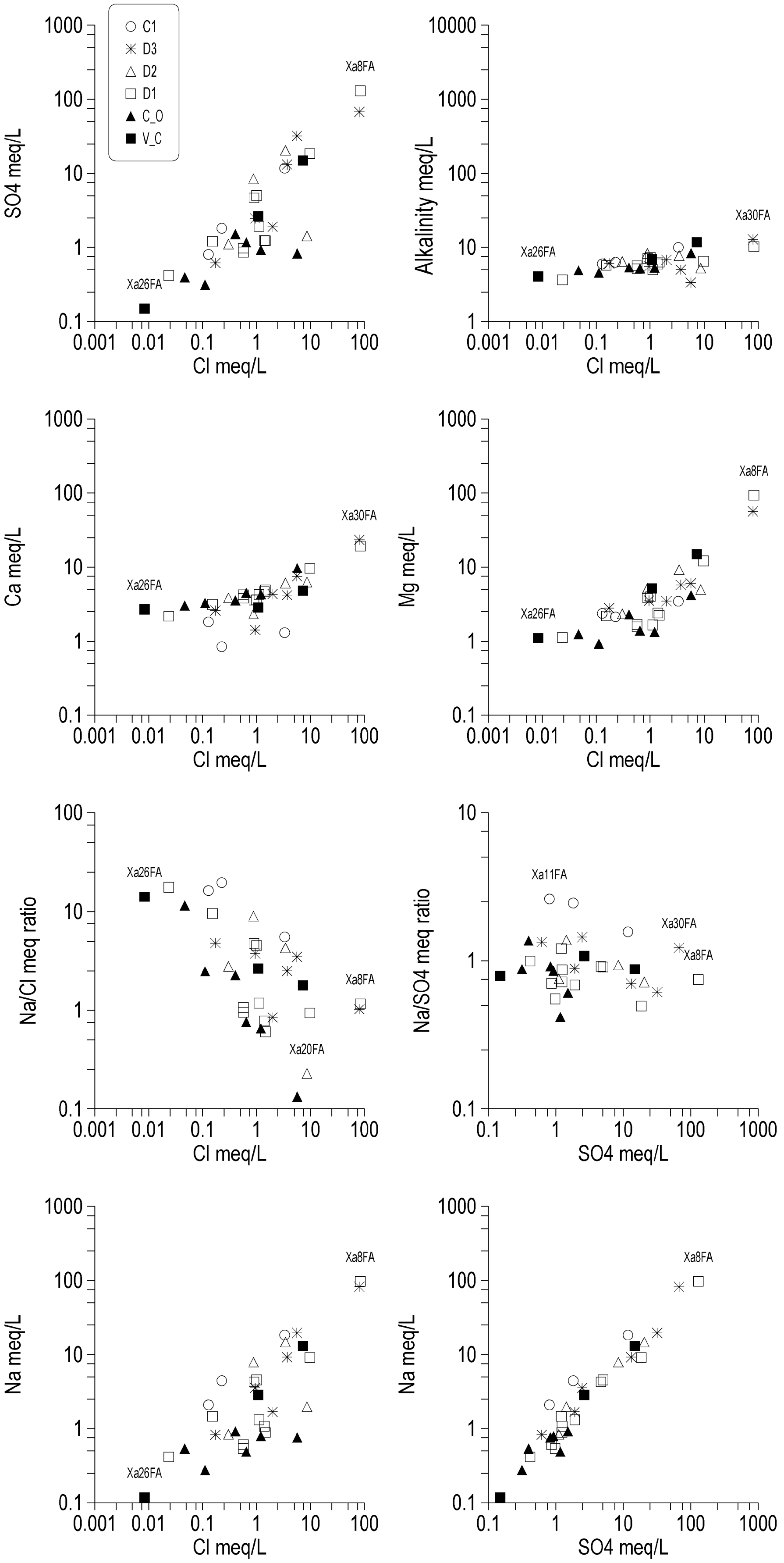


Figure 5 Plots illustrating dependence (1) of sulphate, alkalinity, calcium, magnesium, and sodium concentrations on chloride; and (2) of sodium concentrations on sulphate, for various lithologies. Labels refer to groundwater sample numbers Xa1–Xa33 (*FA* implies sample is field-filtered and acidified). Explanation of lithologies is given in the text and in *Figure 3*

◀
Figure 4 Relationships between selected hydrochemical parameters and (1) lithology and (2) surrounding land use (*two plots lower right*). Each box-plot represents all wells/springs associated with a given lithology/land-use category. # Number of samples; *box* shows interquartile range, with a *horizontal line* at median value. *Vertical bars* show extra-quartile data, excluding near and far outliers, shown as *squares* and *crosses*, respectively; *horizontal brackets* show 95% confidence interval around median value. Results below detection limit (for potassium, fluoride, and nitrate) are set to a value of half the detection limit for the purpose of this statistical presentation. Explanation of lithologies is given in the text and in *Figure 3*

tive of evaporative concentration in the lake itself, or of deeper, more saline sub-lacustrine springs.

3. The observed Br/Cl ratio in the saline waters is compatible with evaporite-derived brines.
4. The covariance between sodium and chloride suggests a possible common origin in halite. The sodium excess in several samples renders it necessary to invoke a secondary, non-halite source for sodium.
5. 6. It may be surmised from the proportional relationship of sulphate and sodium with chloride (*Figure 5*) that no sink exists for these species and that they accumulate and persist in the hydrosphere by similar mechanisms. In contrast, both calcium and alkalinity do not accumulate proportionally to chloride, and it is likely that calcite saturation imposes a limit on these solutes; this interpretation corresponds with the findings of hydrochemical modeling (see below). The somewhat higher rate of increase of magnesium with chloride than calcium suggests that dolomite/epsomite/magnesite saturation is not such a strict limiting factor as calcite saturation is for calcium. Indeed, results of subsequent hydrochemical modeling (see below) indicate that, although dolomite saturation commonly occurs, supersaturation is apparent at higher salinities, suggesting a kinetic obstacle to dolomite precipitation.
7. The low concentrations of chloride and sulphate in the granitoid groundwaters reflect a lack of mineralogical sources for these solutes. Several authors, including Banks et al. (1998c), recognise that atmospheric sources may be important for these ions in shallow Scandinavian granitic groundwaters. The calcium bicarbonate facies; the low ionic content; and the modest pH, alkalinity, Na/Ca and Sr/Ca ratios, and trace element contents all suggest that these groundwaters have not progressed as far along a silicate rock–water interaction pathway as, for example, shallow granitic groundwaters in Norway (Banks et al. 1995a, 1995b; Reimann et al. 1996; Banks et al. 1998a, 1998b, 1998c). Several explanations for this difference are possible: (1) the presence of higher granite permeability and the depletion of some key mineral phases in the zone of active groundwater circulation, due to a history of prolonged sub-aerial weathering without extensive recent glacial scouring (Banks et al. 1998a); (2) sampled wells and springs are typically of shallower depth than those boreholes sampled in Norwegian granites; and (3) admixture with water from overlying Quaternary deposits.

Thermodynamic Modeling

The thermodynamic model MINTEQA2 (US EPA 1991) was chosen, on the basis of its comprehensive database of evaporite minerals, to calculate saturation indices for a range of relevant mineral phases for the majority of groundwaters and the water of Lake Itkul. Activity coefficients were calculated using the Davies algorithm, which is valid up to ionic strengths of 0.5. The most saline groundwaters (samples Xa8 and Xa30, with ionic strengths of about 0.2) and the saline lake waters (all waters except Lake Itkul) were similarly modeled using the code PHRQPITZ (Plummer et al. 1988), which is specially designed for modeling brines using Pitzer's ion-pairing methods. In fact, deviations between PHRQPITZ and MINTEQA2 were minor, even for the most saline Khakassian groundwaters. In all simulations, only major cations and anions were input, and no redox chemistry (e.g., for sulphur) was considered.

The modeling results are presented in *Figure 6* where mineral saturation indices are plotted against chloride, which is taken as a conservative tracer of evaporite (i.e., halite) dissolution during groundwater evolution. Given that the samples modeled come from very different aquifer systems and lithologies in the same area, the samples do not represent a true groundwater evolutionary pathway. Nevertheless, *Figure 6* indicates the following:

1. Calcite saturation is achieved at an early stage of groundwater evolution, followed by dolomite saturation. Most groundwaters are approximately saturated with respect to these two phases.
2. Gypsum saturation is achieved only in the most saline waters.
3. Most waters are significantly undersaturated with respect to mirabilite and halite, although saturation with respect to mirabilite is achieved in the most saline waters, at approximately the same "stage" as gypsum.
4. Halite is less saturated in most waters than mirabilite, although the degree of saturation progresses largely in parallel, thereby providing a plausible explanation of the sensitivity of the waters of Kara-Boghaz-Gol to halite or mirabilite precipitation (see above).
5. At salinities greater than 10 mg/L Cl, a slight trend exists of decreasing groundwater pH with increasing chloride salinity. The saline lakes have pH values that are higher than the pH of the groundwaters, although these lake-water pH values are obtained from the literature (*Table 1*), rather than measured in the field as part of this study.
6. The most saline waters, especially the lake waters, are typically oversaturated with respect to dolomite and, to a lesser degree, with respect to calcite. This result may be related to evaporative concentration of waters in discharge or lake basins and may reflect kinetic limitations in mineral precipitation.

These observations, in particular the linear increase of sodium and sulphate concentrations with chloride, suggest that the Na-SO_4-Cl hydrochemical signature of the saline waters can be explained by: (1) the dissolution of palaeoevaporite minerals (halite, gypsum, dolomite) to provide Ca, Na, Mg, Cl^-, and SO_4^{2-} to the

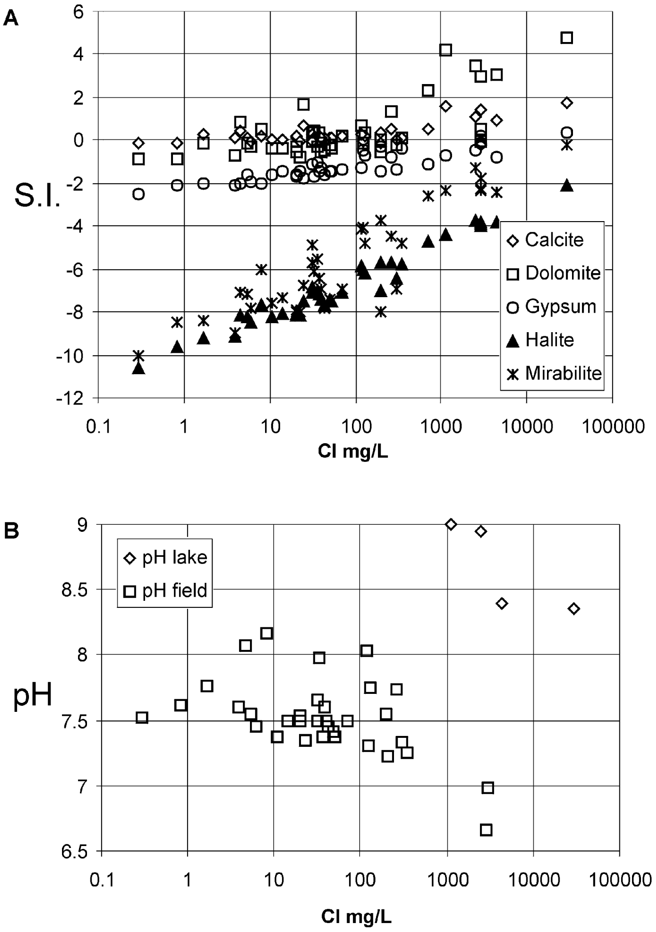


Figure 6 Relationships between **A** calculated mineral saturation indices (*S.I.*) and chloride, using MINTEQA2 (or PHRQPITZ for the most saline waters); and **B** pH and chloride. Data for sampled groundwaters are derived from actual analytical data from this study, whereas lake-water data are derived from literature and reproduced in *Table 1*

solution; and (2) the removal of Ca and, to a lesser extent, Mg by calcite and dolomite precipitation, leaving Na, Cl^-, and SO_4^{2-} in solution. The precipitation of the carbonate phases also generates protons:

$$Ca^{2+} + HCO_3^- = CaCO_3 + H^+ \tag{1}$$

providing a possible explanation for the observed pH decline with increasing salinity.

Simulation of Groundwater Chemical Evolution

Model Version I

To test whether this descriptive model is a realistic possibility, the code PHREEQC (Parkhurst 1995) was utilised. The code was chosen due to the possibilities for stepwise irreversible dissolution and precipitation of selected mineral phases not afforded by older codes such as PHRQPITZ. The PHREEQC code uses a modified Debye-Huckel activity algorithm which, it is claimed, is appropriate to ionic strengths approaching seawater, and for sodium chloride solutions in excess of this. The PHREEQC code was run using the MINTEQA2 thermodynamic database, which contains the appropriate evaporite phases. The modelling exercise must be regarded as a feasibility study rather than an attempt to simulate the real data set, which is derived from a variety of aquifers containing differing mineral assemblages, grain sizes, etc. The initial solution of pure water of temperature 4 °C was subject at each step to the following:

1. The irreversible dissolution of a given number of millimoles of the following minerals: halite, dolomite, calcite, and gypsum. The model was run such that the ionic strength did not exceed 0.5.
2. Equilibration with a partial CO_2 pressure of $10^{-2.5}$ atm, which is plausible for soil gas in southern Siberia, according to the map reproduced by Appelo and Postma (1996), in an open CO_2 system. The reaction of CO_2 with the carbonate phases provides bicarbonate alkalinity to the system.
3. Precipitation of any of the following phases if, and when, they become oversaturated, to such an extent as to restore them to saturation: mirabilite, *natron*, *thenardite*, *thermonatrite*, calcite, *anhydrite*, *magnesite*, dolomite, gypsum and halite. In fact, the phases in italics were irrelevant to the calculations, because they were always less saturated than phases such as mirabilite, gypsum, and dolomite.

During the early stages of the evolution of the model, the concentrations of Na, Cl^-, and SO_4^{2-} are controlled by the relative amounts of gypsum and halite dissolved at each step. Calcite rapidly becomes saturated, followed by dolomite, as occurs in the real data (*Figure 6*). However, gypsum achieves saturation far too early in the model; it precipitates and removes sulphate from the solution, promoting a residual Na-Cl brine. To overcome this, a non-calcium-associated source of alkalinity (i.e., essentially a sodium bicarbonate solution) was required in order to remove additional calcium by calcite precipitation, delaying the onset of gypsum saturation:

$$\begin{aligned} &Na^+ + HCO_3^- + CaSO_4 \cdot 2H_2O = \\ &Na^+ + SO_4^{2-} + CaCO_3 + H^+ + 2H_2O \end{aligned} \tag{2}$$

Model Version II

Version II of the model included the additional irreversible dissolution of albite, although, in reality, the effective addition of sodium bicarbonate could have been achieved by dissolution of various alkaline silicate mineral phases, or by ion exchange of Ca for Na. For example, Harben and Kuzvart (1996) suggest ion exchange between gypsum and alkali silicates as a mechanism for sodium sulphate formation, which is tantamount to the reaction in Eq. (2).

Version II is supported by the real data, where an excess of sodium over chloride often occurs, which cannot be ascribed to halite dissolution. Precipitation of albite was not permitted, as it was regarded as kinetically too slow compared with the other reactions occurring. Precipitation of chalcedony, when oversaturated, was permitted to maintain dissolved silicon levels at the relatively constant observed concentrations.

Sources of sodium bicarbonate alkalinity could be:

1. Internal: weathering of feldspars within the Devonian sedimentary rocks, or ion-exchange reactions.
2. External: derived from weathering of sodic silicates (e.g., feldspars) in the alkaline igneous rocks fringing the basin and transported to the Devonian system by inter-aquifer flow or even by surface waters.
3. External: derived from the Carboniferous aquifer system, which (*Figure 4*) appears to be dominated by high-pH sodium bicarbonate waters, possibly derived from ion exchange on the zeolite minerals commonly observed in the tuffite strata of the system.

Figure 7 shows one possible result of the modeling exercise, although several solutions are plausible, depending on ratios of evaporite minerals added. The result was derived by the dissolution of 2 units of halite, 1 of gypsum, 0.5 of calcite, 2 of dolomite, and 2 of albite per step, in an open CO_2 system of partial pressure $10^{-2.5}$ atm. The system was allowed to precipitate oversaturated quantities of permitted minerals (see above) at each step. Forty steps comprising units of 0.0625 mmol were followed by 39 steps of unit size 2.5 mmol. Thus, in total, 0.2 mol of halite, 0.1 of gypsum, 0.05 of calcite, 0.2 of dolomite, and 0.2 of albite were added. The final ionic strength is 0.47. The result shown demonstrates that sodium-sulphate-chloride waters may evolve by relatively simple evolutionary pathways. The main drawback of the model is that, although it permits higher concentrations of magnesium than calcium, it does not yield the elevated magnesium concentrations observed in several of the real saline waters. This difference is probably related to the observation (see above) that many of the most saline waters are oversaturated with respect to dolomite, a feature not permitted by the model.

The model predicts that gypsum and mirabilite will eventually become saturated at chloride concentrations in excess of 10,000 mg/L, which agrees well with real data (*Figure 6*). One might expect to observe these mineral phases in and around the most saline lakes, where freezing may promote mirabilite precipitation (Grossman 1968). The minerals may also be expected in soils where the water table is near the surface and evapotranspirative concentration of solutions can occur. Salama et al. (1999) note that formation of soluble sodium salts often occurs in the topmost soil layers in semi-arid Alberta, while soil solutions are dominated by sodium sulphate. This observation provides a tentative mechanism for an intriguing feature of the hydrochemistry of northern Khakassia, namely the presence of a ubiquitous approximately 1 : 1 meq sodium : sulphate ratio, even in non-evaporite-bearing lithologies (*Figure 5*).

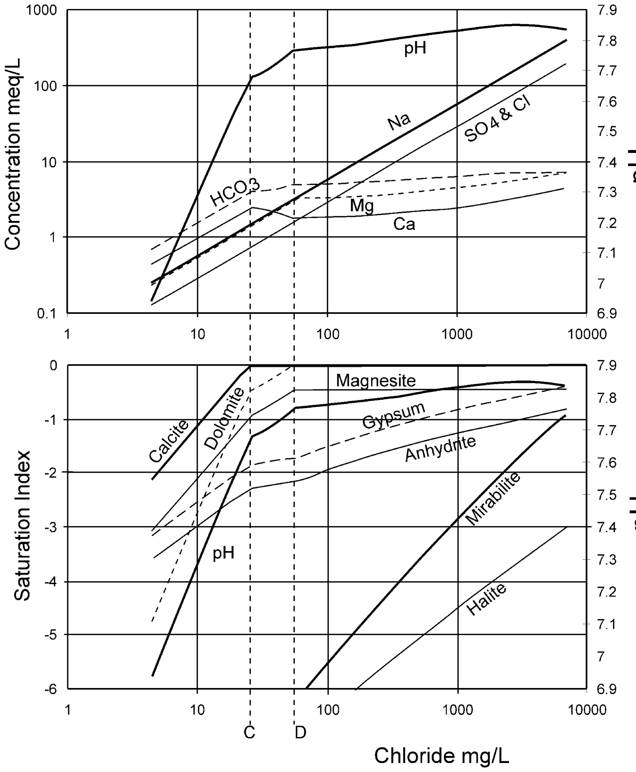


Figure 7 Simulated (PHREEQC) evolution of mineral saturation indices and ion concentrations in water (see text). *Vertical lines* represent calcite (*C*) and dolomite (*D*) saturation

Aeolian Redistribution of Sodium Sulphate Signature to Non-Evaporite-Bearing Aquifers

The Cambro-Ordovician granitoids do not contain evaporite minerals and are topographically higher than the Devonian strata, thus preventing any direct inflow of evaporite-derived waters or brines. One would thus expect to observe a completely different hydrochemical signature in granitic groundwaters. To a large extent, this is observed (see above and *Figures 3*, *4*, and *5*).

However, water–rock interaction is not the only source of solutes to a groundwater system. In maritime regions, sea salts become incorporated into aerosols and are transported inland via wind and thence by wet or dry precipitation to soils and waters. Marine ions (e.g., sodium and chloride) thus exhibit concentration gradients inland from the coast, in soils, groundwater, and streamwater in, for example, Norway (Banks et al. 1998c; Reimann et al. 1999). In extreme inland climates, where a marine influence is negligible, salts and aerosols from soil dust and saline lakes exert a similar role on the composition of precipitation (e.g., in Australia; Salama et al. 1999).

Evaporite minerals such as mirabilite are hypothesised to accumulate in topsoil, soil water, and lakeside evaporites in semi-arid areas such as Alberta or southern Siberia. One would thus expect such minerals to be redistributed throughout the hydrosphere in small concentrations by their atmospheric mobilisation as aerosols, via wet or dry deposition.

In many of the Khakassian aquifers, such an atmospheric signature would be swamped by dissolution of in situ palaeoevaporites. Intriguingly, however, even in groundwaters of the Cambro-Ordovician granitoid complex, an approximately 1:1 sodium:sulphate milliequivalent ratio is observed (*Figure 5*). A plausible explanation for this is the atmospheric transport of sodium-sulphate-(chloride)-dominated aerosols from the Devonian outcrop to the granitoid complex, thence to be incorporated into recharge water from wet or dry fallout. The concentrations of sodium, sulphate, and chloride in the granitoid aquifers (a few tens of milligrams per litre; *Figure 4*) are similar to the chloride concentrations in siliceous aquifers in Norway and Britain, which have been ascribed to marine aerosols (Banks et al. 1998a, 1998c).

This explanation raises some interesting postulates: if a non-marine, non-anthropogenic (presumably geogenic) component of sulphate dominates precipitation and the hydrosphere in Khakassia, could the same also be true in Europe? Do some of the solutes in so-called acid-rain have a geogenic origin (sulphate) or even an origin in wind-blown dust from fertilised arable land (NO_3^- or NH_4^+)?

Anthropogenic Influence on Hydrochemistry

The focus of this paper is principally on natural hydrochemical evolution pathways, but evidence also exists of human influence. The various groundwater sources are divided into rural, agricultural (including cattle station), and urban land-use categories in *Figure 4*. Groundwaters from rural and agricultural sources have concentrations of nitrate of <45 mg/L, which is the Russian GOST (i.e., State) drinking-water limit (Kirjukhin et al. 1993). The median urban concentration is about 57 mg/L, with a maximum of 189 mg/L in Vlasyevo town supply (sample Xa6). Such a level is regarded as being potentially hazardous for young children. A similar pattern exists for potassium, with urban groundwater sources yielding the highest concentrations (Banks et al. 1998d). Thus, in general, urban sources should be invoked for the worst instances of nitrate contamination. The most likely source is sewage or leaking latrines (Lagerstedt et al. 1994), although other sources such as refuse tips may contribute. The results of this study suggest that a microbiological investigation of urban groundwater sources in Khakassia should be a high-priority activity. Significant sanitation-related nitrate and microbiological contamination of village groundwater supplies may be a general issue throughout many parts of the former Soviet Union, as indicated by similar findings in Moldova (Melian et al. 1999).

Conclusions

The compositions of the more saline groundwaters and lake waters from the Devonian aquifer complex of the Shira region are typically of sodium sulphate(-chloride) type. This signature is postulated to be characteristic for inland, semi-arid, partially closed drainage basins, particularly where a long history of extensional tectonic activity has resulted in the deposition of palaeoevaporite sequences. The signature is probably derived from the dissolution of halite, gypsum (and dolomite) mineral phases from the Devonian strata, coupled with a non-calcium source of alkalinity (sodium bicarbonate derived from silicate weathering or ion exchange), which is necessary to promote calcite precipitation and suppress gypsum saturation.

Evaporite-derived saline groundwaters feed lake systems, where further evaporative concentration may occur. Salinities of more than 100 g/L occur in the most saline lake (Lake Tus).

An approximately 1:1 meq sodium : sulphate ratio is present even in non-evaporite-bearing aquifers (granitoids) and may pervade the entire hydrological cycle. This occurrence is probably related to the secondary formation of sodium sulphate evaporite minerals at saline lakes and in topsoils, followed by their dispersion throughout the region's soils and water via windblown dust and precipitation. A program of soil and precipitation sampling would be required to confirm this.

In urban areas in the Shira region, groundwater nitrate concentrations often exceed drinking-water norms, suggesting possible contamination from latrines or sewage.

Acknowledgments The suggestion that some contribution to the composition of "acid rain" may come from geogenic or soil sources is that of Clemens Reimann, Geological Survey of Norway (NGU). NGU's unstinting enthusiasm and willingness to send one of their hydrogeologists to Siberia is appreciated, as is the hard work of Bård Søberg, Egil Kvam, and colleagues of the NGU lab. The referees' comments from Alan Dutton and Mel Gascoyne were of great assistance, as were discussions with Prof. S.L. Shvartsev, Dr. N.A. Makarenko, Dr. Y.M. Dutova, Dr. D.S. Pokrovsky (Tomsk) and Prof. Romeo Eftimi (Tirana). Thanks also to Valya Vilnina, Boris Ilyukhin, Oleg Skornyakov, Andrei Zverev, Igor Seryodkin, Olga Karnachuk, Sergei Parnachev, and colleagues for their hospitality in Tomsk and to the local authorities of Shira region for assistance in correcting a visa.

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