
Chlorine-36 in groundwater of the United States: empirical data

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Abstract Natural production of the radionuclide chlorine-36 (^{36}Cl) has provided a valuable tracer for groundwater studies. The nuclear industry, especially the testing of thermonuclear weapons, has also produced large amounts of ^{36}Cl that can be detected in many samples of groundwater. In order to be most useful in hydrologic studies, the natural production prior to 1952 should be distinguished from more recent artificial sources. The object of this study was to reconstruct the probable preanthropogenic levels of ^{36}Cl in groundwater in the United States. Although significant local variations exist, they are superimposed on a broad regional pattern of $^{36}\text{Cl}/\text{Cl}$ ratios in the United States. Owing to the influence of atmospherically transported ocean salt, natural ratios of $^{36}\text{Cl}/\text{total Cl}$ are lowest near the coast and increase to a maximum in the central Rocky Mountains of the United States.

Résumé La production naturelle du radionucléide chlore-36 (^{36}Cl) fournit un intéressant traceur pour l'étude des eaux souterraines. L'industrie nucléaire, en particulier les essais de bombes thermonucléaires, a également produit de grandes quantités de ^{36}Cl qui a pu être détecté dans de nombreux échantillons d'eau souterraine. Afin d'en améliorer l'usage dans les études hydrologiques, la production naturelle avant 1952 doit être distinguée des sources artificielles plus récentes. L'objectif de cette étude a été la reconstruction des niveaux probables de ^{36}Cl dans les eaux souterraines des États-Unis, avant la production anthropique du ^{36}Cl . Bien qu'il existe des variations locales signi-

ficatives, elles se surimposent à un canevas régional de rapports $^{36}\text{Cl}/\text{Cl}$ dans les États-Unis. Du fait de l'influence du sel océanique transporté dans l'atmosphère, les rapports naturels de $^{36}\text{Cl}/\text{Cl}$ total sont plus faibles près de la côte et augmentent jusqu'à un maximum dans les Montagnes Rocheuses centrales des États-Unis.

Resumen La producción natural del radionucleido cloro-36 (^{36}Cl) representa un trazador valioso para estudios de hidrogeología. La industria nuclear, sobretudo por los ensayos con armas nucleares, también ha producido grandes cantidades de ^{36}Cl que pueden ser detectadas en muchas muestras de aguas subterráneas. Para que sean lo más útiles posible en estudios hidrológicos, la producción natural anterior al año 1952 debe ser diferenciada de la procedente de fuentes artificiales más recientes. El objeto de este estudio era la reconstrucción de los niveles probables de ^{36}Cl en las aguas subterráneas de los Estados Unidos de América con anterioridad a las aportaciones de origen antrópico. Aunque existen variaciones locales significativas, éstas se superponen a un extenso patrón regional de la relación $^{36}\text{Cl}/\text{Cl}$ en el país. Debido a la influencia de la sal transportada en los aerosoles marinos, las proporciones naturales de $^{36}\text{Cl}/\text{Cl}$ total son menores cerca de la costa, y alcanzan su máximo en el centro de las Montañas Rocosas.

Keywords Radioactive isotopes · Chlorine-36 · Chloride/bromide ratios

Introduction

Chlorine-36 (^{36}Cl) has emerged recently as a useful tracer in groundwater studies (Bentley and Davis 1982; Fabryka-Martin et al. 1987a; Cecil et al. 2000; Phillips 2000). Natural production of this radionuclide, which has a half-life of 301,000 years, takes place in the deep subsurface through thermal neutron capture (Kuhn et al. 1984) on the stable nuclide chlorine-35 (^{35}Cl), at and near the land surface by spallation and neutron capture related to secondary cosmic particle bombardment, and by cosmic particle interaction with atmospheric gases, particularly argon (Phillips 2000). Commonly, rapidly circulating groundwater is dominated by ^{36}Cl that has primarily an atmospheric origin. Contrarily, groundwater that is almost static is dominated by ^{36}Cl of thermal neu-

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Table 1 Chlorine-36/chlorine ratios, previously published as well as unpublished work of others

Sample no.	State	Nearest city	Cl ⁻ (mg/L)	NO ₃ (mg/L)	Number in cluster	³⁶ Cl/Cl ratio ^a	³ H TU	¹⁴ C % mod.	Comments	References
1	Arizona	Tuba City	1.3	–	10	840	–	2.7	See also Davis et al. (2000)	Lopes and Hoffmann (1997)
2	Arizona	St. David	–	–	1	400	–	–	–	Bentley et al. (1986)
3	Arizona	Tucson	–	–	3	330	–	–	–	Bentley et al. (1986)
4	Arkansas	Wynne	3.2	<0.5	3	205	–	–	–	Davis et al. (1998a)
5	Colorado	Pritchett	2.6	<0.02	10	1,102	0.1	–	–	A. Macfarlane (personal communication, Dec. 2000)
6	Florida	Sebring	8.1	1.8	1	45	0.1	–	110 km from Atlantic shore	Davis et al. (1998a)
7	Florida	Jacksonville	5.6	–	47	38	–	2.9	44 km from Atlantic shore	G.G. Phelps (personal communication, Sept. 2000)
8	Georgia	Perry	1.7	0.54	1	156	<0.1	77	–	Davis et al. (1998a)
9	Georgia	Avera	1.7	<0.5	1	97	0.04	86	–	Davis et al. (1998a)
10	Indiana	West Lafayette	1.6	–	3	400	–	–	–	Vogt et al. (1993)
11	Indiana	Fort Wayne	1.65	3.2	5	166	<0.1	–	–	Davis et al. (2000)
12	Kansas	Garden City	6.2	0.5	1	623	–0.02	6.4	–	Dutton (1994)
13	Maryland	Lexington Park	2.2	–	8	150	0.06	–	Well at coast	Purdy et al. (1996)
14	Maryland	Waldorf	0.8	–	8	251	–	–	Well about 55 km from coast	Purdy et al. (1996)
15	Minnesota	Minneapolis	0.69	<0.3	12	657	<0.9	36.1	–	Davis et al. (2000)
16	Mississippi	Hattiesburg	2.2	4.5	3	50	<0.1	–	–	Davis et al. (1998a)
17	Missouri	Bloomfield	5.0	–	7	272	–	48	–	J. Van Brahana (personal communication, 1994)
18	Nevada	Las Vegas	7.0	–	1	505	–	–	–	Fabryka-Martin et al. (1996)
19	North Dakota	Oakes	0.62	1.2	5	838	–	–	–	Davis et al. (2000)
20	Oklahoma	Oklahoma City	5.5	0.99	3	300	–	–	–	Davis et al. (1998a)
21	South Carolina	Aiken	1.5	–	28	98	–	–	–	Beasley et al. (1992)
22	Tennessee	Paris	1.8	–	6	184	–	24.6	–	J. Van Brahana (personal communication, 1994)
23	Texas	Pleasanton	33	–	6	64	–	–	–	Bentley and Davis (1982)
24	Wyoming	Cheyenne	3.2	2.2	4	1,393	–	3.1	–	Dutton (1994)

^a (Number of atoms of ³⁶Cl/total number of atoms of Cl)×10¹⁵

tron origin (Bentley and Davis 1982; Fabryka-Martin et al. 1987b; Fabryka-Martin 1988; Andrews et al. 1989; Lehmann et al. 1991; Phillips 2000). For the purpose of this study, ³⁶Cl will be considered that is presently in groundwater but probably originated in the atmosphere.

The most significant artificial source of ³⁶Cl was the activation of ³⁵Cl in seawater by the high flux of neutrons from weapons testing of fusion devices in the western Pacific starting in late 1952 and extending through mid-1958. Measurable fallout from these tests continued for about 10 years beyond 1958 (Phillips 2000). However, Scheffel et al. (1999) have presented evidence that suggests that resuspension of ³⁶Cl may have produced measurable fallout of artificially produced ³⁶Cl as late as 1996.

On a purely local scale, anomalous concentrations of ³⁶Cl have been found near two major nuclear installations in the United States (Beasley et al. 1992, 1993;

Cecil et al. 1992). These anomalies undoubtedly are related directly to the operation of nuclear reactors.

Data given in this paper were collected for a general study of the ³⁶Cl content of groundwater in the 48 contiguous states in the United States. A previous report produced during this research discussed the difficulties of determining the preanthropogenic concentrations of ³⁶Cl in the hydrosphere (Davis et al. 1998a). Other reports generated by this project have described ³⁶Cl in spring water (Davis et al. 2001) as well as ³⁶Cl in water having very low concentrations of chloride (Davis et al. 2000). Preliminary accounts of the work have been presented by Moysey et al. (1999) and Davis et al. (1999). A listing of almost all chemical data, as well as an extensive discussion of the data, has been included in an M.Sc. thesis by Moysey (1999).

The objective of the work was to reconstruct the preanthropogenic content of ³⁶Cl in groundwater recharge and to

Table 2 Chlorine-36/chlorine ratios in soil leachates and pack-rat middens

	Sample no.	State	Nearest city	³⁶ Cl/Cl ratio ^a	References
	25	Idaho	Arco	290	Cecil et al. (1992)
	26	Nevada	Wadsworth	720	Plummer et al. (1997)
^a (Number of atoms of ³⁶ Cl/total number of atoms of Cl)×10 ¹⁵	27	Nevada	Alamo	675	Plummer et al. (1997)
	28	Nevada	Beatty	515	Plummer et al. (1997)
^b Mean of minimum (708) and maximum (1,070) ratios reported. All ratios were not reported by authors	29	Nevada	Pahrump	550	Plummer et al. (1997)
	30	Nevada	Pahrump	500	Norris et al. (1985)
	31	New Mexico	Las Cruces	465	Phillips et al. (1988)
^c Mean of minimum (690) and maximum (914) ratios reported. All ratios were not reported by authors	32	New Mexico	Socorro	720	Phillips et al. (1988)
	33	Texas	El Paso	460	Scanlon et al. (1990)
	34	Washington	Richland	889 ^b	Murphy et al. (1996)
	35	Washington	Richland	802 ^c	Prych and Sharma (1994)

provide an improved baseline for studies utilizing ³⁶Cl. An important assumption is that the ³⁶Cl content of actively circulating groundwater prior to 1952 is related directly to the original and natural ³⁶Cl content in the recharge water.

Analytical results have been divided into three categories in order to facilitate discussion. The first category includes samples with ³⁶Cl indicative of preanthropogenic levels in groundwater (Tables 1, 2, and 3). The second category includes water samples having ³⁶Cl that is in concentrations far below preanthropogenic levels (Table 4). These suggest that chloride in the water has been isolated from the surface for hundreds of thousands of years, or longer. The third category includes results of soil and water analyses that show ³⁶Cl values which were increased by radioactive fallout from testing of nuclear weapons in the Pacific (Tables 5 and 6). Importantly, the history of the chloride may be much different than the history of the water. For example, rapidly circulating groundwater can dissolve bedded rock salt that has been isolated from the surface for tens of millions of years; thus, the water would be young and the chloride in that water would be old from the standpoint of prior cycling in the atmosphere. Contrariwise, a small amount of weapons fallout of ³⁶Cl, if mixed with old water, can give the false impression that all the water is very young.

Chlorine-36 Units

The ratio of the number of ³⁶Cl atoms to total atoms of chlorine present in water is not affected significantly by evaporation of the water unless chlorine is removed or added to the water during the evaporation process. Because of this, ³⁶Cl values are reported in this paper as a ratio rather than a concentration. The actual concentration of ³⁶Cl atoms is very small, so the common convention of multiplying the very small ratio by 10¹⁵ is used. The resultant ratio, (³⁶Cl/total Cl)×10¹⁵, will be simply referred to as the ³⁶Cl/Cl ratio in this paper unless specified otherwise. If the chloride concentration in the water sample is known, the concentration of atoms of ³⁶Cl per liter of water can be calculated by the following simple relationship:

Concentration of ³⁶Cl (atoms per liter)=1.699×10⁴×B×R, where B is the concentration of chloride in mg/L and R is the (³⁶Cl/total Cl)×10¹⁵ ratio.

For practical purposes, the assumption is made that all of the chlorine in the water is in the form of the monovalent anion, chloride (Cl⁻). For potable water unaffected by human activity, this assumption appears to be reasonable (Feth 1981; Hem 1985).

Collection and Analysis of Samples

The sampling program was designed to: (1) achieve a wide geographic coverage of the United States, (2) study primarily ³⁶Cl in water unaffected by human activity, and (3) assess the local variability of ³⁶Cl concentrations in samples from groups of wells in the same general region. Groundwater samples were collected from a total of 183 wells and springs throughout the United States.

Sample volumes ranged from 30 ml for δ¹⁸O and δD analyses to 3.79 L (1 gallon) for analysis of ³⁶Cl. All bottles were thoroughly cleaned then rinsed with distilled water in the laboratory. Prior to filling each bottle in the field, water from the well or spring was used to rinse the bottle three times. Electrical conductivity and pH were measured in the field. Filled bottles were sealed in the field and kept cool and in the dark in the laboratory until analyses were completed. Nitrate NO₃⁻ was determined at the University of Arizona. Detection limit was 0.3 mg/L with a precision of ±10%. Chloride and bromide concentrations were determined at the Los Alamos National Laboratory using a customized Dionex 2000 ion chromatography system with a conductivity detector. All samples were filtered prior to analysis using a 0.2-μm nylon filter. Detection limits were 4 ppb bromide and 0.1 ppm chloride with precisions better than ±5%.

Measurements of the ³⁶Cl/Cl ratio were performed at the AMS facility in the PRIME Lab at Purdue University (Elmore and Phillips 1987); however, samples were prepared for target loading at the University of Arizona. An AgNO₃ solution was added to the samples to precipitate AgCl that was subsequently purified by dissolving it with NH₄OH, adding Ba(NO₃)₂ to precipitate unwanted sulfur as BaSO₄, neutralizing with HNO₃, and finally reprecipitating the AgCl with AgNO₃ for target preparation. A carrier was added to samples that contained very small concentrations of chloride.

Table 3 Chlorine-36/chlorine ratios in groundwater samples, from present study

Sample no.	State	Lat. (deg./min. N)	Long. (deg./min W)	Nearest city	Cl ⁻ (mg/L)	Cl ⁻ /Br ⁻ mass ratio	NO ₃ (mg/L)	³⁶ Cl/ ³⁵ Cl ratio ^a	Error ±	Tritium TU	¹⁴ C % mod.	Total in cluster	Acceptable number in cluster	Collected (month/year)	Remarks
36	Alabama	31/58	85/01	Troy	2.83	175	<0.3	99.9	5.4	<0.1	4.2	7	6	5/98	Municipal supply well
37	Alabama	32/58	87/38	Greensboro	1.44	97	<0.3	122	13	<0.1	-	8	4	5/98	Municipal supply well
38	Arizona	32/11	110/50	Tucson	4.64	102	3.7	373	15	-	73	10	5	9/99	Municipal supply well
39	Arizona	31/53	110/12	Benson	3.52	93	3.1	364	16	-	24	1	1	3/97	Flowing well
40	California	39/10	120/07	Tahoe City	0.62	194	<0.3	1,257	73	-	-	5	2	6/97	See text
41	California	36/43	119/35	Fresno	6.12	194	4.9	224	10	-	83	3	1	6/97	USGS test hole
42	Colorado	39/00	104/44	Denver	1.12	51	<0.3	1,672	58	-	2.1	4	4	6/97	-
43	Idaho	44/05	111/26	Ashton	3.07	168	<0.3	133	45	<1.0	47	4	1	5/97	Deep well, flowing, hot
44	Iowa	42/07	93/32	Ames	0.52	51	<0.3	473	86	<0.7	46	6	3	7/98	Test flow, flowing
45	Montana	48/12	114/04	Kalispell	0.47	59	<0.3	1,180	76	0.3	4.4	8	8	6/98	Private well
46	Ohio	40/03	83/47	Urbana	1.84	141	3.2	165	8	-	-	6	1	10/97	See discussion in text
47	Oregon	44/19	121/24	Bend	2.95	128	2.5	641	21	-	-	5	4	6/97	Private well
48	Oregon	44/45	122/55	Corvallis	1.78	191	1.8	289	15	-	74	7	6	6/97	Private well
49	South Dakota	44/41	103/51	Belle Fourche	0.86	80.6	1.1	1,190	130	-	-	3	2	10/95	Municipal supply well
50	Utah	37/11	113/30	St. George	4.81	136	0.9	359	17	-	-	5	2	5/97	See text
51	Washington	45/43	121/32	White Salmon	2.12	287	<0.3	33.6	37.5	-	57.7	1	1	6/97	See text
52	West Virginia	39/37	78/13	Martinsburg	2.04	100	<0.3	385	18	<0.9 ^b	-	3	3	6/96	Spring water
53	Wisconsin	43/07	89/30	Madison	0.66	57	<0.3	368	215	0.9 ^b	62	4	1	8/98	Municipal supply
54	Wyoming	43/50	104/11	Newcastle	1.37	84	1.0	1,095	46	-	-	2	2	9/97	Municipal supply

^a (Number of ³⁶Cl atoms/total number of atoms of Cl)×10¹⁵^b Analyses at the University of Arizona

Table 4 Chlorine-36/chlorine ratios in samples from present study containing old chloride

Sample no.	State	Lat. (deg./min. N)	Long. (deg./min. W)	Cl ⁻ (mg/L)	Cl ⁻ /Br ⁻ mass ratio	³⁶ Cl/Cl ^a measured	Error ^a ±	³⁶ Cl/Cl ^{a,b} expected from Fig. 1	NO ₃ (mg/L)	Remarks
55	Florida	29/04	81/34	233	274	4.5	5.4	50	0.7	Alexander Spring, carbonate-rock aquifer
56	North Dakota	45/59	97/50	34.2	282	62	31	830	3.0	Test hole drawing water from Pleistocene sediments just above Cretaceous shale
57	New York	43/00	73/51	646	92	15.3	2.4	500	<6.0	Old Iron Spring, actually a well drilled for mineral water. Aquifer is Paleozoic sedimentary rocks
58	New York	43/05	73/46	489	98	8.7	3.1	500	<6.0	Old Red Spring, actually a well drilled for mineral water. Aquifer is Paleozoic sedimentary rocks
59	New York	43/04	73/47	2,112	101	7.4	3.2	500	<6.0	Hathorn Spring, actually a well drilled for mineral water. Aquifer is Paleozoic sedimentary rocks
60	Oregon	45/15	123/08	29,138	647	6.0	5.3	250	<0.3	Aquifer unknown, probably sedimentary rocks
61	Washington	45/43	121/32	2.12	287	33.6	37.5	850	<0.3	Aquifer is basalt
62	Indiana	40/57	85/14	29.7	2,700	12.6	2.9	450	4.15	Aquifer is glacial sand. Shallow test hole (6.2 m). ³ H=16 TU ^c
63	Alabama	32/32	87/50	106	108	7.1	1.9	100	<0.3	Aquifer is Cretaceous sandstone. ³ H<1.0 TU
64	Minnesota	44/57	93/05	35.2	203	13.0	1.4	650	<0.3	Aquifer is Cambrian and Precambrian sandstone. ¹⁴ C % modern = 1.7 ^d
65	Minnesota	45/05	93/16	30.8	227	15.4	1.5	650	<0.3	Aquifer is Cambrian and Precambrian sandstone. ¹⁴ C % modern = 17.4 ^d

^a (Number of ³⁶Cl atoms/total number of Cl atoms)×10¹⁵

^b Expected ratio is the preanthropogenic ratio estimated from Fig. 1

^c Tritium analysis from Ferguson (1992)

^d ¹⁴C analyses from Lively et al. (1992)

The extraction of inorganic carbon and preparation of targets for ¹⁴C analysis at the University of Arizona was a two-stage process. First, CO₂ was degassed from the water sample by adding H₃PO₄ (phosphoric acid). After purification, the carbon in the gas was reduced to graphite and loaded into the target cups for AMS analysis. Results of the Arizona analyses are accurate to ±0.5% modern ¹⁴C. Unless specified otherwise, ¹⁴C analyses reported in Tables 3, 4, and 5 were completed at the University of Arizona. Details of target preparation for both ³⁶Cl and ¹⁴C analyses are given by Moysey (1999). Most of the analyses reported in Tables 3, 4, and 5 for ³H were provided by the US Geological Survey. Reported accuracy is ±0.1 TU. Analyses completed at the University of Arizona are reported with an accuracy of ±0.5 TU. A complete listing of these analyses, together with all other analyses, is given by Moysey (1999).

Selection of Chlorine-36 Data Used to Construct Figure 1

Although an effort was made to collect water that was neither affected by human activity nor by the natural addition of small amounts of subsurface brine, only

about 50% of the water samples met the criteria used to select ³⁶Cl/Cl ratios for the preanthropogenic values (Fig. 1). These criteria are given below.

1. Results of analyses of water containing more than 10 mg/L of chloride were not used. Higher concentrations commonly have components of industrial or agricultural sources of chloride or natural sources not related to meteoric origins (Davis et al. 2000).
2. Radionuclides of obvious human origin must be absent from the groundwater sample. Analyses containing more than 2 tritium units (1 TU equals 10¹⁸ stable H atoms per ³H atom) and more than 86% of modern ¹⁴C likely reflect some anthropogenic contributions (Davis and Murphy 1987). Analyses with ³⁶Cl/Cl ratios greater than 2,000 also likely reflect anthropogenic contributions of ³⁶Cl. This limit is discussed in subsequent parts of this paper.
3. Chloride/bromide mass ratios should be less than 260. Higher ratios commonly indicate chloride from other than atmospheric origin (Davis et al. 1998b).
4. Analyses with nitrate concentrations greater than 5 mg/L were not used. Higher values are commonly produced by human or animal waste as well as agricultural fertilizers (Feth 1966; Hem 1985).

Table 5 Chlorine-36/chlorine ratios in samples from present study containing bomb fallout

Sample no.	State	Lat. (deg./min. N)	Long. (deg./min. W)	³ H TU	¹⁴ C % mod.	Cl ⁻ (mg/L)	NO ₃ (mg/L)	³⁶ Cl/Cl ^a measured	Error ^a ±	³⁶ Cl/Cl ^{a,b} expected from Fig. 1	Cl ⁻ /Br ⁻ mass ratio	Remarks
66	Florida	30/24	84/15	5.5	44	4.19	0.7	377	75	50	165	Near the coast
67	North Dakota	45/59	97/50	–	–	1.42	<0.3	6,660	160	830	67	Shallow well
68	South Dakota	43/31	103/23	12.9	60	2.10	1.4	3,027	59	1,200	71	Artesian well, carbonate-rock aquifer
69	Utah	41/52	111/37	–	–	1.13	<0.3	2,360	90	800	192	Spring from carbonate-rock aquifer, Ricks Spring
70	Idaho	44/30	111/19	14	–	1.68	0.7	5,275	127	550	311	Shallow well
71	Idaho	44.15	111.27	11.6	102	0.83	<0.3	12,796	512	550	97	Shallow well
72	Colorado	39/09	103/03	–	–	4.96	30.3	8,270	20	1,000	85	Irrigation well
73	Arizona	33/49	109/08	–	80	3.12	<0.3	5,790	216	650	48	Community supply well
74	Arizona	32/15	110/54	–	102	6.55	–	1,770	20	400	161	Municipal supply well
L7	Nebraska	41/05	100/38	–	–	0.86	–	11,858	584	850	29	Leachate from Peorian loess, Wisconsinan age; see Table 6

^a (Number of ³⁶Cl atoms/total number of Cl atoms)×10¹⁵

^b Expected ratio is the preanthropogenic ratio estimated from Fig. 1

Table 6 Chlorine-36/chlorine ratios in leachate from Wisconsinan loess in southwestern Nebraska

Sample no.	Stratigraphic unit	Depth below land surface (m)	Moisture (% by weight)	³⁶ Cl/Cl ratio in leachate ^a	Error ±
L1	Peorian	18.3	7.4	2,720	154
L2	Brady soil	0.7	6.6	1,610	78
L3	Peorian	1.5	6.1	2,634	199
L4	Peorian	2.3	4.5	8,880	422
L5	Peorian	6.1	9.1	853	52
L6	Bignell	2.1	3.7	11,960	714
L7	Brady soil	3.2	5.0	11,858	584
L8	Peorian	5.2	6.7	10,570	591
L9	Brady soil	3.2	6.9	10,260	373
L10	Bignell	2.4	8.7	889	52

^a (Number of atoms of ³⁶Cl/total number of atoms of Cl)×10¹

- Data from most springs were not used. Analyses of all springs sampled reflect mixed sources and human influence with the exception of Berkeley Springs, West Virginia, where nitrate was below detection (0.3 mg/L), ³H was below 0.9 TU, and Cl/Br was in the normal range (Davis et al. 2001).
- Where a cluster of wells was sampled, the ³⁶Cl/Cl ratio of water that was used was from the single well that conformed to the above criteria and had the lowest chloride concentration. The assumption was made that, of the cluster analyses, the lowest chloride concentration would be the nearest in composition to the original precipitation.

Preanthropogenic Chlorine-36 in Groundwater Recharge

General Range of Values

When the foregoing criteria are used to select preanthropogenic ³⁶Cl/Cl ratios of groundwater samples, the

range of the ratios is from 38 to 1,672 (Figure 1). In comparison, other studies have shown ranges of ³⁶Cl/Cl ratios of 20 to 640 (Bentley and Davis 1982), 100 to 1,600 (Hainsworth 1994), and 100 to 1,500 (Phillips 2000). Although the broad continental patterns presented in all these studies are somewhat similar, there are differences in important details.

Regional Trends

Chlorine-36/chlorine ratios used to construct isopleths in Figure 1 come from past studies (Tables 1 and 2) and from the present research (Table 3). Lack of data in a number of the publications cited prevented the selection criteria from being applied uniformly to data shown in Table 1. For ratios of ³⁶Cl/Cl from leachates of soil samples and pack-rat middens, values of preanthropogenic ratios given by the researchers listed in Table 2 were assumed to be correct. The general process of interpreting soil leachates is given by Phillips et al. (1988).

Fig. 1 Preanthropogenic $^{36}\text{Cl}/\text{Cl}$ ratios in groundwater of the United States based on empirical data

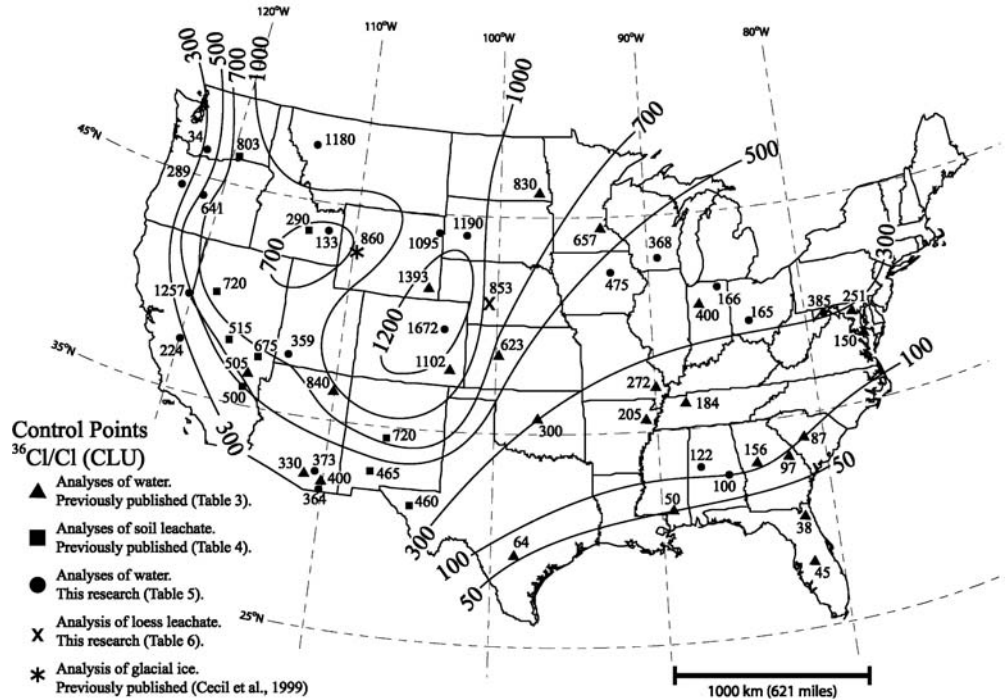


Table 7 Points on Fig. 1 that do not conform to the pattern of the isopleths

Sample no.	State	Ratio ^a shown in Fig. 1	Expected ratio (approximate)	Possible reasons for the anomaly
62	California	1,257	600	Some bomb fallout
64	Colorado	1,672	1,400	Water may have been recharged more than 10,000 years ago during a time of increased cosmogenic production (Plummer et al. 1997)
65	Idaho	133	800	Very old chloride mixing with younger water. Well is 915 m deep
32	Indiana	166	400	Chloride leached from fluid inclusions within grains of glacial outwash. (see discussion by Davis et al. 2000)
68	Ohio	165	350	Human influence. Road salt and/or agricultural chemicals. See discussion in text
72	Utah	359	800	Possible dissolution of dry fallout from desert playas
73	Washington	34	500	Very old chloride mixing with younger water. Well is 200 m deep

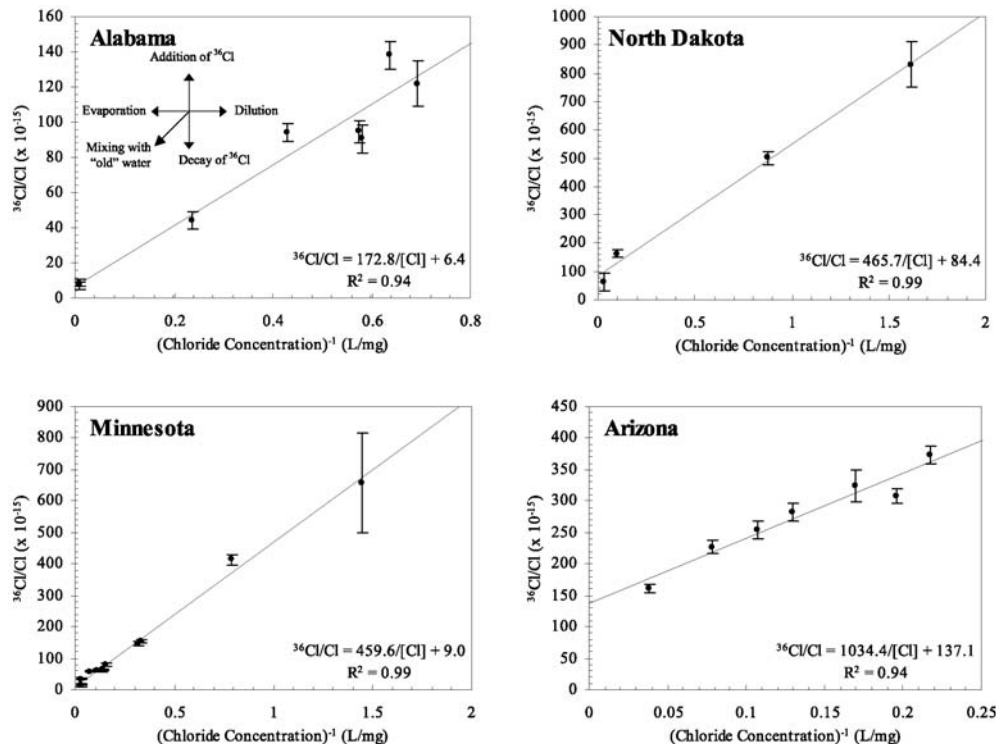
^a (Number of atoms of ^{36}Cl /total number of atoms of Cl) $\times 10^{15}$

Three salient features seen on Fig. 1 deserve comment. First, the most prominent feature is the trend of increasing $^{36}\text{Cl}/\text{Cl}$ ratios as the distance from the oceans increases. As a consequence, isopleths tend to follow the general trend of chloride delivered by precipitation (National Atmospheric Deposition Program 1999). Second, the gradient of values is much steeper in the Pacific states than elsewhere. Third, and lastly, a prominent eastward bulge is seen in southern Idaho, northern Utah, and western Wyoming. This bulge of lower ratios may be a reflection of a significant secondary airborne source of stable chloride from the Bonneville Salt Flats, Utah, and nearby playas. Four $^{36}\text{Cl}/\text{Cl}$ ratios reported for the Great Salt Lake, Utah, and the Bonneville Salt Flats ranged from 23 ± 6 – 31 ± 6 (Phillips et al. 1995), which is sufficiently low to account for the bulge.

Sample Clusters and Local Variations

Out of 55 $^{36}\text{Cl}/\text{Cl}$ ratios plotted on Fig. 1, seven met the selection criteria but do not conform to the pattern presented. Reasons for these departures are largely speculative. In addition to the comments on Table 7, two points in particular can be given a more complete explanation. The data from Ohio are particularly troublesome. Six different shallow (14–31 m deep) wells were sampled in the area. Half of the samples had more than 5.0 mg/L nitrate. Three of the samples had Cl/Br ratios greater than 260, and all but one well had been sampled for tritium. Concentrations of tritium in water from these wells all exceeded 3.6 TU (Cheng 1996). The single well without analyses for tritium passed all the other selection criteria. This well is plotted in Fig. 1. However, the probability is high that the water from this well also contains significant amounts of tritium. The entire area is low

Fig. 2 Regression curves for a mixing model between meteoric water and more saline "older" water from the subsurface having a lower $^{36}\text{Cl}/\text{Cl}$. These groundwater samples were collected from aquifer systems in *Alabama* (Cretaceous Eutaw sandstone; Cook 1993), *North Dakota* (late Pleistocene sand; Bluemle 1979), *Minnesota* (early Cambrian and late Precambrian sandstone; Lively et al. 1992), and *Arizona* (late Pliocene and early Pleistocene sand and gravel in a desert basin; Davidson 1973). The five radiating arrows shown on the Alabama graph represent different processes that can change chloride and $^{36}\text{Cl}/\text{Cl}$ ratios of water samples (Davis et al. 1998b; Moyses 1999)



lying and collects runoff from roads and farmland. Therefore, the $^{36}\text{Cl}/\text{Cl}$ ratio of 165 here (sample 46, Table 3) is not considered reliable.

Four wells were sampled near Madison, Wisconsin. Only one analysis (sample 53, Table 3) out of the four was useful for Fig. 1 owing to high concentrations of nitrate and tritium as well as high Cl/Br ratios in the other three samples. The large error (± 215 in the $^{36}\text{Cl}/\text{Cl}$ ratio) in the analyses for the single well allows a broad assumption of possible values at this point.

In contrast with the clusters in Ohio and Wisconsin, half of the ten Tucson, Arizona, samples met the established criteria and provided useful values that range from 254 ± 14 – 373 ± 15 . Only the value from the analysis with the lowest chloride is plotted in Fig. 1 (sample 38, Table 3). Eight wells that were sampled in eastern Alabama provided an even better success rate. Here, all except one of the eight wells sampled yielded values within the selection guidelines for preanthropogenic groundwater. These ranged from 59 ± 6 – 156 ± 8 . Only one of these ratios, which was from the well with the lowest chloride concentration (sample 36, Table 3), is plotted in Fig. 1.

A well-defined relationship is commonly observed to exist between chloride concentrations and the $^{36}\text{Cl}/\text{Cl}$ ratios in water samples from a given region (Fig. 2; Davis et al. 2000). One of the several mechanisms shown by arrows in Fig. 2 is subsurface mixing between sources of water having different ^{36}Cl ratios and chloride concentrations. The simplest example of such a system is binary mixing. In this case, the resulting measured ^{36}Cl ratio

(R_{meas}) is a mixture of contributions from each of two end members:

$$R_{\text{meas}} = \frac{{}^{36}\text{Cl}_{\text{meas}}}{\text{Cl}_{\text{meas}}} = \frac{{}^{36}\text{Cl}_1 + {}^{36}\text{Cl}_2}{\text{Cl}_{\text{meas}}} \\ = \frac{R_1 \text{Cl}_1 + R_2 (\text{Cl}_{\text{meas}} - \text{Cl}_1)}{\text{Cl}_{\text{meas}}} = \frac{(R_1 - R_2) \text{Cl}_1}{\text{Cl}_{\text{meas}}} + R_2 \quad (1)$$

where ${}^{36}\text{Cl}_{\text{meas}}$ and Cl_{meas} are the total number of atoms of ^{36}Cl and chloride, respectively, that would be measured in the mixture, ${}^{36}\text{Cl}_1$ and Cl_1 are the number of atoms of ^{36}Cl and chloride, respectively, for the first end member, and ${}^{36}\text{Cl}_2$ and $(\text{Cl}_{\text{meas}} - \text{Cl}_1)$ are the same for the second end member. This mixing relation results in a linear relationship between the observed ^{36}Cl ratio and inverse chloride concentration for any group of samples derived from such a system, i.e.:

$$R_{\text{meas}} = \frac{a}{\text{Cl}_{\text{meas}}} + b \quad (2)$$

where a and b are slope and intercept parameters.

Figure 2 shows inverse chloride concentration vs. $^{36}\text{Cl}/\text{Cl}$ ratio for groups of samples collected from hydrogeologic systems located in Alabama, North Dakota, Minnesota, and Arizona. In all four cases, a binary mixing model fits the data very well. It is also evident from Fig. 2 that other processes, such as the decay of ^{36}Cl or mixing with chloride-free water, cannot explain the observed data. In the current study, no attempt was made to use the mixing model to infer the meteoric $^{36}\text{Cl}/\text{Cl}$ ratio for each site, but rather the model was used as a tool to

eliminate unlikely processes as possible hypotheses for explaining the data.

Old Chloride in Groundwater

The half-life of ^{36}Cl is long enough so that atmospherically generated ^{36}Cl will require more than 2 million years to effectively disappear in a closed system. Subsurface production, however, will generate some ^{36}Cl (Bentley et al. 1986; Fabryka-Martin 1988; Lehmann et al. 1993; Cecil et al. 1999; Phillips 2000). Although the $^{36}\text{Cl}/\text{Cl}$ ratio of water from uranium ore deposits can exceed 40,000 (Cornett et al. 1996; Fabryka-Martin et al. 1987b), equilibrium values in rocks of average composition are generally in the range of 5 to 50 (Lehmann et al. 1991). As a consequence, measurable amounts of ^{36}Cl will be found in almost all natural materials, but high ratios in deep confined aquifers are rare. On the low end of the scale, in contrast with uranium ore deposits, seawater and some salt from salt domes can contain ^{36}Cl at or below limits of detection, that is, a $^{36}\text{Cl}/\text{Cl}$ ratio of about 1.0 (Phillips 2000).

In addition to seawater and evaporite deposits, numerous other natural chloride sources appear old from the standpoint of the low $^{36}\text{Cl}/\text{Cl}$ ratio. Ancient formation water, fluid inclusions, and saline water from compacting clay and shale are examples of such sources.

Within a limited region, say with an area of 100 km², $^{36}\text{Cl}/\text{Cl}$ ratios can vary from less than 10 to more than 10,000. The higher values are commonly associated with tritium concentrations of more than 6 TU and other unequivocal indications of young groundwater affected by bomb fallout. The lower values may be explained by the presence of old chlorine having very little ^{36}Cl owing to isolation from the atmosphere for many half-lives of the radionuclide. In the present study, this old chlorine was probably from ancient water in Florida, North Dakota, Oregon, and Minnesota (samples 55, 56, 60, and 64, Table 4). However, in other areas, such as Indiana (sample 62, Table 4), contamination by deicing salt, chlorine in fertilizers, industrial effluents, and many other sources of old chloride, which are ultimately from the mining of subsurface salt deposits, accounts for low $^{36}\text{Cl}/\text{Cl}$ ratios.

Data in Table 4 show a number of samples that have $^{36}\text{Cl}/\text{Cl}$ ratios which are well below the reconstructed meteoric input value for that region (Fig. 1). All except sample 61 have chloride concentrations in excess of 29 mg/L, suggesting a nonmeteoric origin for at least some of the chloride (Davis et al. 2000). The low ^{36}Cl concentrations may also suggest long-term isolation, generally in excess of 10⁶ years, of the chloride from its original atmospherically produced ^{36}Cl concentration. In the case of sample 62 (Table 4), a high concentration of tritium and significant amounts of nitrate, together with the shallow depth of the test hole, suggest strongly that the chloride is anthropogenic and its low $^{36}\text{Cl}/\text{Cl}$ ratio is inherited from the original source of the chloride.

Sample 63 (Table 4), from a confined Cretaceous aquifer in Alabama, could have chloride that has a low $^{36}\text{Cl}/\text{Cl}$ ratio owing to long-term isolation that would allow radioactive decay within the aquifer. The origin of the chloride in sample 63, however, is puzzling. The Cl/Br ratio of sample 63 (Table 4) is similar to ratios found in atmospherically derived water in the region. Ion filtration might explain the concentration of Cl^- , Br^- , and ^{36}Cl . Despite the fact that the $^{36}\text{Cl}/\text{Cl}$ ratio is low, the higher Cl^- concentration more than compensates for the lower ratio. Consequently, the absolute concentration of ^{36}Cl is higher than that in other groundwater in the region. The remaining samples in Table 4 appear to have mixed sources as evidenced by some high Cl/Br mass ratios as well as high chloride concentrations.

Chlorine-36 from Weapons-Testing Fallout

The earliest study of ^{36}Cl in meteoric water was made at the Brookhaven National Laboratory on Long Island, New York, (Schaeffer et al. 1960). Peak concentrations of 1.83×10^6 atoms/ml were attributed to testing of fusion weapons in the Pacific. This translates to a $^{36}\text{Cl}/\text{Cl}$ ratio of 127,000. Although this ratio was an order of magnitude greater than the highest ratio measured for the present study, the Brookhaven sample was collected in September 1957, at the height of the weapons testing in the Pacific and before natural mixing processes reduced the peak concentration of ^{36}Cl .

Weapons testing in the western Pacific during the period from late 1952–1958 produced a worldwide fallout of ^{36}Cl that is seen clearly in analyses of water from many wells. In order to show the general range of values to be expected, the results of several analyses are given in Table 5. Although analyses for tritium, also from weapons testing, have not been made for all samples collected, wherever unusually high concentrations of ^{36}Cl are present the water is either from a shallow well or tritium values are unusually high (above 2 TU).

All of the $^{36}\text{Cl}/\text{Cl}$ ratios in Table 5 exceed the expected natural background values (Fig. 1) by a factor of at least 2.5.

Chlorine-36 in Wisconsinan Loess

Ten samples of late Pleistocene loess were collected from the vicinity of North Platte, Nebraska. Eight of the samples (L1 through L8, Table 6) came from a fresh face in a large borrow pit. The other two samples (L9 and L10, Table 6) were from the vertical face of a rapidly eroding bluff. The expectation was that moisture in the loess would migrate more or less vertically downward with a velocity so slow that at depths of a few meters the soil water would be below the depth of penetration of bomb-pulse ^{36}Cl . As can be seen from ratios obtained in leachates that are listed in Table 6, some bomb-pulse ^{36}Cl evidently did penetrate to a depth of at least 18.3 m.

Several ratios in excess of 2,500 suggest a rather rapid and highly irregular penetration of ^{36}Cl with nonvertical migration being probable. This type of water movement in loess is compatible with observations made by Williams and Allman (1969) in the Palouse loess in Idaho and Washington.

For the purpose of reconstructing preanthropogenic ratios in atmospheric precipitation, the lowest ratio shown in Table 6 (sample L5), that is, the $^{36}\text{Cl}/\text{Cl}$ ratio of 853, has been selected. Although tenuous, this assumption is based on the fact that all of the loess is in an area of recharge and is less than about 50,000 years old (Maat and Johnson 1996), so any leachable chloride would have been introduced by infiltrating precipitation at a later date. Also, the value of 853 is reasonably close to the expected regional value shown by Hainsworth (1994), Moysey (1999), and Bentley and Davis (1982) as well as values shown in Fig. 1.

Discussion and Conclusions

The most important factor that controls the regional distribution of the $^{36}\text{Cl}/\text{Cl}$ ratio appears to be the amount of sea salt (oceanic salt) that mixes with atmospherically derived ^{36}Cl . It has been long known (Jackson 1905; Eriksson 1960; Baldwin 1971) that wet and dry fallout of oceanic salts decreases rapidly inland from the coast. Inasmuch as the $^{36}\text{Cl}/\text{Cl}$ ratio is below the level of detection in oceanic salt, the effect is one of dilution of the naturally produced ^{36}Cl that takes place in the atmosphere. This explains the large regional variation of the ratio from less than 50 in Florida to more than 1,200 in the central Rocky Mountains in the western United States (Fig. 1).

Theoretical calculations and some measurements show a latitudinal effect on the ^{36}Cl concentration in precipitation with maximum natural concentrations between 35°N and 45°N (Bentley et al. 1986; Phillips 2000). Data in this report lack the coverage necessary to show any such effect (Moysey 1999).

One of the initial hydrogeologic interests in ^{36}Cl was the fact that its long half-life provided a promise of dating old groundwater beyond the range of ^{14}C dating, which is about 50,000 years (Davis and Murphy 1987). Dating using ^{36}Cl has proved feasible for water from a few confined aquifers with well-defined regional circulation (summarized by Phillips 2000). The problems encountered in dating, however, are numerous. Among other things, the initial value of the ^{36}Cl concentration to be assumed in the radioactive decay calculations is of fundamental importance (Davis et al. 1998a). The present work, nevertheless, suggests that almost all clusters of wells that have been sampled have variations in $^{36}\text{Cl}/\text{Cl}$ ratios that are caused primarily by addition of dead Cl (Fig. 2). This would make the choice of an initial value quite arbitrary without a means to estimate the amount of dilution of the chloride. This problem is considered in detail by Torgersen and Phillips (1993). Analyses for

bromide can also provide some help with the dilution problem (Davis et al. 1998b; Davis et al. 2000).

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References

- Andrews JN, Davis SN, Fabryka-Martin JT, Fontes JC, Lehmann, BE, Loosli HH, Michelot JL, Moser H, Smith B, Wolf M (1989) The in situ production of radioisotopes in rock matrices with particular reference to the Stripa granite. *Geochim Cosmochim Acta* 53(8):1803–1815
- Baldwin AD (1971) Contribution of atmospheric chloride in water from selected coastal streams of central California. *Water Resour Res* 7(4):1007–1012
- Beasley TM, Elmore D, Kubik PW, Sharma P (1992) Chlorine-36 releases from the Savannah River Site nuclear fuel reprocessing facilities. *Ground Water* 30(4):539–548
- Beasley TM, Cecil LD, Sharma P, Kubik PW, Fehn U, Mann LJ, Gove HE (1993) Chlorine-36 in the Snake River Plain aquifer at the Idaho National Engineering Laboratory: origin and implications. *Ground Water* 31(2):302–310
- Bentley HW, Davis SN (1982) Applications of AMS to hydrology. In: Kutschera W (ed) Symposium on accelerator mass spectrometry. Argonne National Laboratory, ANL/PHY-81-1, pp 193–227
- Bentley HW, Phillips FM, Davis SN (1986) Chlorine-36 in the terrestrial environment. In: Fritz P, Fontes JC (eds) Handbook of environmental isotope geochemistry vol 2, part B. Elsevier, Amsterdam, pp 427–480
- Bluemle JP (1979) Geology of Ransom and Sargent counties, North Dakota. *North Dakota Geol Survey Bulletin* 59, part 1
- Cecil LD, Beasley TM, Pittman JR, Michel RL, Kubik PW, Sharma P, Fehn U, Gove HE (1992) Water infiltration rates in the unsaturated zone at the Idaho National Engineering Laboratory estimated from chlorine-36 and tritium profiles and neutron logging. In: Kharaka YF, Maest AS (eds) Water-rock interaction vol 1. AA Balkema, Rotterdam, pp 709–714
- Cecil LD, Vogt S, Frape SK, Davis SN, Cottrell GL, Sharma P (1999) Chlorine-36 in water, snow, and mid-latitude glacial ice of North America: meteoric and weapons-test production in the vicinity of the Idaho National Engineering and Environmental Laboratory, Idaho. *US Geol Survey, Water Resources Investigation Report* 99-4037, 27 pp
- Cecil LD, Welhan JA, Green JR, Frape SK, Sudicky ER (2000) Use of chlorine-36 to determine regional-scale aquifer dispersivity, eastern Snake River Plain aquifer, Idaho/USA. *Nucl Instrum Methods Phys Res B* 172:679–687
- Cheng S (1996) Isotopic tracing of the source water for Cedar Bog in west-central Ohio, USA. *J Hydrol* 186:31–42
- Cook MR (1993) The Eutaw aquifer in Alabama. *Geol Surv Alabama Bull* 156:105 pp
- Cornett RJ, Cramer J, Andrews HR, Chant LA, Davies W, Greiner BF, Imahori Y, Koslowsky V, McKay J, Milton GM, Milton JCD (1996) In situ production of ^{36}Cl in uranium ore: a hydrogeological assessment tool. *Water Resour Res* 32(6):1511–1518
- Davidson ES (1973) Geohydrology and water resources of the Tucson basin, Arizona. *US Geol Survey Water-Supply Paper* 1939-E, 81 pp

- Davis SN, Murphy EM (1987) Dating ground water and the evaluation of repositories for radioactive waste. US Nuclear Regulatory Commission, NUREG/CR-4912, 181 pp
- Davis SN, Cecil LD, Zreda M, Sharma P (1998a) Chlorine-36 and the initial value problem. *Hydrogeol J* 6(1):1004–1014
- Davis SN, Whittemore DO, Fabryka-Martin JT (1998b) Uses of chloride/bromide ratios in studies of potable water. *Ground Water* 36(2):338–350
- Davis SN, Cecil LD, Zreda M, Moysey S (1999) Chlorine-36, bromide, and the origin of spring water. *Geol Soc Am Abstr Programs* 31(7):A330
- Davis SN, Fabryka-Martin JT, Wolfsberg L, Moysey S, Shaver R, Alexander EC Jr, Krothe N (2000) Chlorine-36 in ground water containing low chloride concentrations. *Ground Water* 38(6):912–921
- Davis SN, Cecil LD, Zreda M, Moysey S (2001) Chlorine-36, bromide, and the origin of spring water. *Chem Geol* 179(1):3–16
- Dutton AR (1994) Sources and ages of ground water in unconfined and confined aquifers beneath the U.S. High Plains. Special Report to the U.S. Geological Survey, Texas Bureau of Economic Geology, Austin, Texas, 43 pp
- Elmore D, Phillips FM (1987) Accelerator mass spectrometry for measurement of long-lived radioisotopes. *Science* 236:543–550
- Eriksson E (1960) The yearly circulation of chloride and sulfur in nature, meteorological, geochemical, and pedological implications, part II. *Tellus* 12:63–109
- Fabryka-Martin JT (1988) Production of radionuclides in the earth and their hydrogeologic significance, with emphasis on chlorine-36 and iodine-129. PhD, University of Arizona, 400 pp
- Fabryka-Martin JT, Davis SN, Elmore D (1987a) Applications of ^{129}I and ^{36}Cl to hydrology. *Nucl Instrum Methods Phys Res B* 29:361–371
- Fabryka-Martin JT, Davis SN, Wirt L, Elmore D, Kubik PW (1987b) Comparison of theoretical and measured deep subsurface production of chlorine-36. *Geol Soc Am Abstr Programs* 19(7):658
- Fabryka-Martin JT, Dixon PR, Levy S, Liu B, Turin HJ, Wolfsberg AV (1996) Summary report of chlorine-36 studies: systematic sampling for chlorine-36 in the Exploratory Studies Facility, Yucca Mountain Characterization Project Milestone Report 3783AD, Los Alamos National Laboratory, 61 pp
- Ferguson VR (1992) Hydrogeology and hydrogeochemistry of fine-grained glacial till, northeastern Indiana. MSc Thesis, Indiana University, 75 pp
- Feth JH (1966) Nitrogen compounds in natural water – a review. *Water Resour Res* 2(1):41–58
- Feth JH (1981) Chloride in natural continental water – a review. US Geol Survey Water-Supply Paper 276, 30 pp
- Hainsworth LJ (1994) Spatial and temporal variations in chlorine-36 deposition in the northern United States. PhD, University of Maryland, 215 pp
- Hem JD (1985) Study and interpretation of the chemical characteristics of natural water. US Geol Survey Water-Supply Paper 2254, 3rd edn
- Jackson DD (1905) The normal distribution of chlorine in the natural waters of New York and New England. US Geol Survey Water-Supply Paper 144
- Kuhn MW, Davis SN, Bentley HW, Zito R (1984) Measurements of thermal neutrons in the subsurface. *Geophys Res Lett* 11(6):607–610
- Lehmann BE, Loosli HH, Balderer W, Fontes JC, Michelot JL, Soreau (1991) Chlorine-36. In: Applied isotope hydrogeology – a case study in northern Switzerland. *Studies in environmental science* 43. Elsevier, Amsterdam, pp 250–265
- Lehmann BE, Davis SN, Fabryka-Martin JT (1993) Atmospheric and subsurface sources of stable and radioactive nuclides used for groundwater dating. *Water Resour Res* 29(7):2027–2040
- Lively RS, Jameson R, Alexander EC Jr, Morey GB (1992) Radium in the Mt. Simon-Hinckley aquifer, east-central and southeastern Minnesota. Minnesota Geol Survey Information Circular 36, 58 pp
- Lopes TJ, Hoffmann JP (1997) Geochemical analyses of ground-water ages, recharge rates, and hydraulic conductivity of the N aquifer, Black Mesa Area, Arizona. US Geol Survey Water-Resources Investigations Report 96–4190, 42 pp
- Maat PB, Johnson WC (1996) Thermoluminescence and new C-14 age estimates for late Quaternary loesses in southwestern Nebraska. *Geomorphology* 17(1–3):115–128
- Moysey S (1999) Meteoric ^{36}Cl in the contiguous United States. MSc Thesis, University of Arizona, 163 pp
- Moysey S, Davis SN, Zreda M (1999) A preliminary report on the distribution and variability of chlorine-36 in groundwater across the United States. *Am Geophys Union Trans (Abstr)* 80(17):S139
- Murphy EM, Ginn TR, Phillips JL (1996) Geochemical estimates of paleorecharge in the Pasco Basin: evaluation of the chloride mass balance technique. *Water Resour Res* 32(9):2853–2868
- National Atmospheric Deposition Program/National Trends Network (1999) Chloride precipitation map. NADP Program Office, Illinois State Water Survey, 2204 Griffith Drive, Champaign, IL 61820
- Norris AE, Wolfsberg K, Gifford SK (1985) ^{36}Cl measurements of the unsaturated zone flux at Yucca Mountain. Preprint LA-UR-85–2408, Los Alamos National Laboratory, 9 pp
- Phillips FM (2000) Chlorine-36. In: Cook PG, Herczeg AL (eds) *Environmental tracers in subsurface hydrology*. Kluwer, Boston, pp 229–348
- Phillips FM, Mattick JL, Duval TA, Elmore D, Kubick PW (1988) Chlorine-36 and tritium from nuclear-weapons fallout as tracers for long-term liquid and vapor movement in desert soils. *Water Resour Res* 24:1877–1891
- Phillips FM, Rogers DB, Dreiss SJ, Jannik NO, Elmore D (1995) Chlorine-36 in Great Basin waters: revisited. *Water Resour Res* 31(12):3195–3204
- Plummer MA, Phillips FM, Fabryka-Martin JT, Turin HJ, Wigand PE, Sharma P (1997) Chlorine-36 in fossil rat urine: an archive of cosmogenic nuclide deposition during the past 40,000 years. *Science* 277:538–541
- Prych EA, Sharma P (1994) Estimating deep-percolation rates at the DOE Hanford Site, Washington. 1993 Annual Report, PRIME Lab, Purdue University, pp 17–18
- Purdy CB, Helz GR, Mignerey AC, Kubik PW, Elmore D, Sharma P, Hemmick T (1996) Aquia aquifer dissolved Cl^- and $^{36}\text{Cl}/\text{Cl}$: implications for flow velocities. *Water Resour Res* 32(5):1163–1171
- Scanlon BR, Kubik PW, Sharma P, Richter BC, Gove HE (1990) Bomb chlorine-36 analysis in the characterization of unsaturated flow at a proposed radioactive waste disposal facility, Chihuahuan Desert, Texas. *Nucl Instrum Methods Phys Res B* 52:489–492
- Schaeffer OA, Thompson SO, Lark NL (1960) Chlorine-36 radioactivity in rain. *J Geophys Res* 65:4013–4016
- Scheffel C, Blinov A, Massonet S, Sachsenhauser H, Stan-Sion C, Beer J, Synal HA, Kubik PW, Kaba M, Nolte E (1999) ^{36}Cl in modern atmospheric precipitation. *Geophys Res Lett* 26(10):1401–1404
- Torgersen T, Phillips FM (1993) Reply to “Comment on chlorine 36 dating of very old groundwater, 3. Further results on the Great Artesian Basin, Australia by T. Torgersen et al.” by JN Andrews and JC Fontes. *Water Resour Res* 29:1875–1877
- Vogt S, Elmore D, Fritz SJ (1993) ^{36}Cl in shallow, perched aquifers from central Indiana. Report PL9309, PRIME Lab, Purdue University, 14 pp
- Williams RE, Allman DW (1969) Factors affecting infiltration and recharge in a loess covered basin. *J Hydrol* 8:265–281