

Springs of Virginia Revisited: A Comparative Analysis of the Current and Historical Water-Quality Data

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ABSTRACT

Physicochemical analyses of 31 springs in Virginia, previously sampled in 1928, were compared with current (post-1952) data collected at identical sites. This study examined the potential long-term trends in the physical and chemical constituents of spring waters. Water-quality variability (within-spring variation), expressed as the percent coefficient of variation (% CV), over the study period was relatively high for nitrate, sodium, sulfate, and chloride ions, averaging 70, 57, 42, and 40% CV respectively, but moderate for calcium, hardness, bicarbonate, and dissolved solids, averaging 22, 19, 18, and 15% CV, respectively. Variation in water temperatures was minor, averaging less than three percent CV. Spring discharge fluctuated considerably, ranging from three to 95% CV and averaging 37% CV. Although the chemical content of most springs examined has remained relatively consistent for more than 60 years, increasing concentrations of nitrate, chloride, and total dissolved solids in some springs indicated a modest degree of pollution, perhaps resulting from surface contaminant infiltration. No notable trend in sodium and sulfate concentrations (pollution) was evident.

INTRODUCTION

Springs are immensely important aquatic resources because they afford a reliable source of high quality ground water at a relatively constant temperature and flow. As the public need for water escalates, springs represent a dependable and increasingly valuable supply of water, particularly during drought conditions. Springs are being tapped for domestic (drinking, bathing, and cleaning), commercial (brewing, distilleries, and bottled mineral water), agricultural (crop irrigation, livestock watering, and fish hatcheries), industrial (mining, manufacturing, and hydropower), and recreational purposes (fishing, swimming, and boating). Springs

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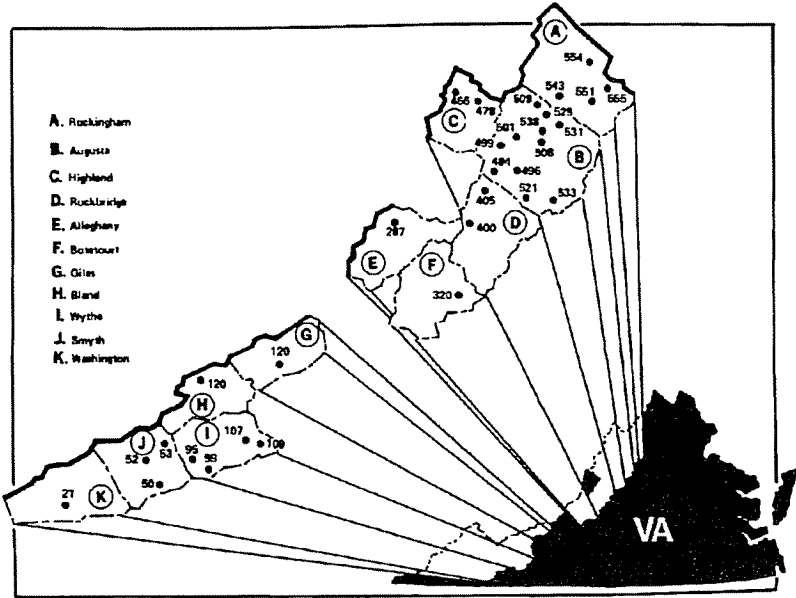


FIGURE 1. Locations of Virginia springs (n = 31) used for water quality comparisons between the 1928 survey and more recent (post-1952) surveys.

often provide the only flow (base flow) to rivers and streams during periods of extreme drought.

Although surface water supplies more than half of the 5.6 billion gallons used daily by Virginians, ground water supplies the water needs of 41 percent of Virginia's 5.3 million residents, and public water-supply systems in 64 of the 95 counties rely on aquifers to provide more than half of their domestic drinking water needs (Weigmann and Kroehler, 1988). Nearly one-third of the average 27 million gallons of water used per day for irrigation of Virginia's crops is ground water (USGS, 1985).

Despite its multiple benefits, ground water in Virginia is increasingly threatened by a variety of chemical and biological pollutants (Weigmann and Kroehler, 1988). Toxic waste in the form of pesticides, heavy metals, acids, petroleum products (gasoline, motor oil, diesel fuel), fertilizers, and a multitude of other familiar, but harmful, chemicals leach from underground storage tanks, mining sites, industrial waste lagoons and dumps, and municipal landfills daily. Pathogenic bacteria, viruses, and nutrients from livestock wastes, human sewage, and decaying animals seep into spring and ground water as drainage from barnyards, feedlots, outhouses, and septic systems.

A major pathway by which surface contaminants reach ground water is through sinkholes. These crater-like depressions are characteristic of areas underlain by limestone such as the Valley and Ridge Province of Virginia. Each sinkhole is a potential, direct channel for polluted water to infiltrate into the aquifer. The traditional but mindless use of sinkholes as rural dumps and disposal sites for dead livestock, domestic waste, household cleaning supplies, pesticide containers, old painting materials, and other hazardous chemicals and refuse intensifies the problem and increases the probability of ground-water degradation. Slifer (1987)

TABLE 1. Location of Virginia springs monitored by Collins *et al.* (1930) and used for comparative trend analysis in this study.

Spring No.	Location Latitude Longitude		Spring Name	County	Topographic Map (USGS 7.5 minute)
21	36,38,25	82,06,06	Percy Preston	Washington	Wyndale
50	36,46,27	81,25,05	Kessling	Smyth	Atkins
52	36,51,27	81,25,05	Arnold	Smyth	Atkins
53	36,51,33	81,23,55	Atkins	Smyth	Atkins
86	37,09,00	81,10,30	Walker	Bland	Rocky Gap
99	36,48,00	81,10,57	Seven	Wythe	Speedwell
95	36,52,03	81,16,15	Neff-Kutz	Wythe	Cedar Springs
107	36,55,58	80,54,06	Harkrader-West	Wythe	Max Meadows
109	36,55,50	80,53,47	Harkrader	Wythe	Max Meadows
120	37,15,42	80,41,21	T.B. Francis	Giles	Pearisburg
287	37,52,09	79,55,59	Falling	Alleghany	Covington
320	37,35,54	79,40,46	Karnes	Botetourt	Buchanan
400	37,50,53	79,28,37	Big	Rockbridge	Lexington
405	38,00,027	9,31,49	Warm	Rockbridge	Green Valley
466	38,21,46	79,37,48	Mackey	Highland	Mustoe
478	38,20,15	79,26,04	Stuart	Highland	McDowell
494	38,06,33	79,18,39	Augusta White	Augusta	Augusta Springs
496	38,04,18	79,14,57	Cochran	Augusta	Greenville
499	38,12,20	79,10,03	Cave	Augusta	Churchville
501	38,05,33	79,10,45	J.J. Bowman	Augusta	Greenville
504	38,20,40	79,05,02	Blue Hole	Augusta	Parnassus
508	38,12,24	79,02,12	Berry Farm	Augusta	Staunton
521	37,59,29	79,12,20	Broadhead	Augusta	Vesuvius
529	38,16,49	78,59,18	Seawright	Augusta	Mount Sidney
531	38,18,25	78,55,23	Weyers Cave	Augusta	Mount Sidney
533	38,03,14	78,55,54	Koiner #1	Augusta	Waynesboro West
538	38,03,32	78,53,35	Baker	Augusta	Waynesboro West
543	38,24,30	79,02,57	Patterson	Rockingham	Briery Branch
551	38,24,02	78,50,12	Massanetta	Rockingham	Harrisonburg
554	38,32,33	78,45,54	Lacey	Rockingham	Broadway
555	38,26,09	79,37,13	Bear Lithia	Rockingham	ElktonEast

identified 73 illegal dumps, many in limestone sinkholes interconnected to ground water, in Rockbridge County, Virginia, where wells and springs supply water for half of the 16,000 residents. This problem is pervasive throughout Virginia, particularly in the limestone valleys where sinkholes offer convenient pits for solid- and liquid-waste disposal.

The physical and chemical characteristics of spring waters reflect the quality of ground water and mirror chemical conditions in aquifers feeding the rivers and streams in the Commonwealth. They provide a convenient window through which

to examine long-term trends in ground water quality. An early survey in 1928 (Collins *et al.*, 1930) provided the location and some water-quality conditions for 566 springs in Virginia. This early account afforded a unique 60-year historical benchmark for a comparative analysis of physical and chemical conditions in selected springs in the Commonwealth. This paper summarizes alterations in physicochemical conditions for 31 selected springs for which sufficient historical and current water-quality data were available.

METHODS

Water quality data from the 31 Virginia springs (Figure 1) in the current (post-1952) analysis were collected from the unpublished records of the Virginia Water Control Board (VWCB), Virginia Department of Health (VDH), Virginia Department of Game and Inland Fisheries (VDGIF), U.S. Geological Survey (USGS), U.S. Environmental Protection Agency (EPA), Virginia Tech Department of Fisheries, Virginia Cooperative Extension Service, and private owners (see Table 1). Recent physicochemical data (Table 2) were compared directly to that collected in a 1928 survey (Collins *et al.*, 1930).

The data in Table 2 represent values measured over a time period of 60 years, during which analytical procedures, sampling protocol, and sample preservation techniques varied significantly. No attempts have been made to compare the field or laboratory methods employed, some of which are unknown. The current data undoubtedly are more accurate than the earlier measurements because of advancements in analytical technology since 1928. Because seasonal variation in spring discharge and water quality generally was minor, comparisons among years of data collected at identical sites was assumed valid for trend analysis.

Much of the recent data on springs in the Shenandoah Valley of Virginia were collected as part of a spring monitoring program instituted by the Valley Regional Office (Sterrett, 1989 personal communication). This monitoring effort consists of semi-annual collections of 16 selected springs (six of which correspond to those measured by Collins *et al.*, 1930). Field measurements of discharge, water temperature, and pH were made on site; chemical analyses were conducted by the Virginia Division of Consolidated Laboratories in Richmond, Virginia, using standard methods. All available existing data were compiled and compared with that collected in 1928 by Collins *et al.*, (1930). For many other springs surveyed by Collins *et al.* (1930) recent, comparable water-quality samples have not been collected or analyzed to date. We have, however, initiated a more comprehensive survey to locate and collect water samples from other springs located by Collins *et al.* (1930) in order to expand our comparative analysis beyond the 31 springs described herein. Variability of current physicochemical measurements within springs was expressed as the coefficient of variation ($100 \times \text{standard deviation}/\text{mean}$). These estimates include temporal and seasonal variability and that variability resulting from measurement error within springs through time.

The major chemical parameters considered were calcium, bicarbonate, chloride, sulfate, sodium, hardness, and nitrate-nitrogen concentrations. Minor elements such as iron and fluoride, though monitored, generally were present in trace or undetectable concentrations, too low for valid comparisons. Total dissolved solids, one of the most important parameters used to measure water quality

deterioration (Sherrard *et al.*, 1988), served as a useful general index of the mineral content (salinity) of springs. Physical variables included spring discharge and water temperatures.

RESULTS AND DISCUSSION

Physical Measurements

Discharges of the 31 Virginia springs (160 observations) ranged from 0.1 to 15.6 cubic feet second (cfs) or 50 to 7,000 gallons per minute (gpm); the majority (67 percent) of the springs discharged over 1,000 gpm (Table 2). Comparisons between historic and current data indicated a general pattern of decrease in discharge rates for most (68 percent) of the springs examined. Variability in discharge within-springs over the study period (comparison of historic and current records) expressed as percent coefficient of variation (% CV), was high, ranging from 3 to 95% CV, and averaging 37% CV. Maximum fluctuation in discharge recorded for a single spring over the study period was 9.6 cfs (4,283 gpm) for spring 320.

Collins *et al.* (1930) reported the largest spring in Virginia was Woolwine Spring. Located four miles east of Newbern, Pulaski County, near the New River, this spring flow (the only measurement available) was recorded at 23 cfs (10,300 gpm) in 1928 (Table 3). Unfortunately, this spring was submerged by the construction of Claytor Lake reservoir in 1938. More recent surveys (Sterrett, 1988, personal communication) have identified and characterized other equally large-volume springs in Northwestern Virginia such as Coursey Springs (11.8 to 25.9 cfs) and Mackey Spring (4.3 to 28.6 cfs), neither of which were sampled in the early survey by Collins *et al.* (1928). Single flow measurements, sometimes estimates, were reported for each spring by Collins *et al.* (1930). The relatively high coefficient of variation calculated for many of the springs examined and the limited number of long-term flow observations per spring suggest that significantly lower or higher flows than those reported may occur.

Meinzer (1923) classified springs according to their average discharge from a magnitude 1 for flows over 44,900 gpm (100 cfs) to a magnitude 8 for those less than 0.25 gpm. Based on this scale, Virginia has no known first magnitude springs, but does contain at least 13 springs of the second magnitude. The size of the surface opening and that of the underground aquifer, and the associated water pressure largely determine the amount of discharge, which can range from a small trickle to that of a large stream. Most springs flow at a relatively constant rate throughout the year, but those at high elevations with limited aquifers or those receiving surface-water inflows can display wide-ranging flow regimes. Intermittent springs (impermanent, temporary ones) flow only during periods of high rainfall when the water table rises to intersect the land surface or when a spring receives all of its recharge from direct surface infiltration. A wide variety of other factors, notably geological characteristics, recharge area, average annual precipitation, and topography, are important determinants of spring flows.

Most spring waters have a relatively uniform temperature regime, varying only a few degrees throughout the year. The temperature of the 31 Virginia springs monitored in this study ranged from 10 to 19 C, and averaged 12.7 C (Table 2), which approximates the mean annual air temperature in Virginia. Thermal variability within springs through time was relatively minor, averaging less than 3%

CV, about 1 C. Small, shallow springs or those subject to surface-water inflows can exhibit widely fluctuating water temperatures. Maximum within-spring variation over the study period was 8 C recorded for spring 287. Spring water from deep aquifers tends to have higher water temperatures because of geothermal heating. In general the rate of temperature increase with depth is 1 C per 30.5 m (Reeves, 1935). None of the 31 springs examined in this study were designated as thermal (warm or hot) springs.

Chemical Constituents

The calcium content of the 31 Virginia springs (160 analyses) ranged from 1 to 138 mg/l; the majority (65 percent) had concentrations below 50 mg/l (Table 2). Mean within-spring variability in calcium levels between historical and current records was moderate, averaging 22% CV or less than 10 mg/l for the majority (71 percent) of springs. The highest within spring variation in mean calcium concentration was 38 mg/l for spring number 287. The proportion of springs exhibiting a decrease in calcium levels (48 percent) was similar to that showing an increase (58 percent).

Calcium is one of the most abundant elements in the soil, a major constituent in ground water, and a primary contributor of water hardness. Calcium concentrations in ground water generally range from 10 to 100 mg/l (Davis and DeWiest, 1966; Weigmann and Kroehler, 1988). Collins *et al.* (1930) reported minimum-maximum calcium concentrations for 566 Virginia springs as 1 and 400 mg/l for Spout Spring and Sweet Chalybeate Spring, Alleghany County, respectively (Table 3). In adjacent states, levels ranged from 0 to 943 mg/l in 130 West Virginia springs (McColloch, 1986) and from 0 to 119 mg/l in 196 Pennsylvania springs (Flippo, 1974).

Sodium concentrations ranged from 0 to 27 mg/l for the 31 Virginia springs monitored (Table 2). Variability in sodium levels within-springs over sampling dates was substantial, averaging 57 percent. Nearly one-half of the springs studied exhibited CV values of 50 percent or greater. With the exception of nitrate, sodium showed the greatest within-spring variation of all elements considered. Maximum within-spring fluctuation of sodium was 24 mg/l for spring number 287. No significant long term trend in sodium levels was apparent; 32 percent of the springs exhibited decreased levels and 19 percent showed increased levels through time. In the 1928 survey by Collins *et al.* (1930) minimum-maximum sodium levels for 566 Virginia springs were 3 and 206 mg/l for Hall Spring, Lee County and Mineral Spring, Botetourt County, respectively (Collins *et al.*, 1930). Prior to development of reliable flame spectrochemical methods used today for sodium determinations, concentrations frequently were estimated by ionic balance to avoid complex and costly analysis (Hem, 1970). It appears likely that sodium levels estimated in the early 1928 survey may not be representative (overestimated) or comparable to those of later studies that were determined using more sophisticated procedures.

Sodium levels in ground waters in the United States can range from 1 to 1,000 mg/l (Fortescue, 1980). The sodium content of 161 analyses of West Virginia spring water ranged from 0.2 to 2,402 mg/l (McColloch, 1986) and from 0 to 40 mg/l in a survey of Pennsylvania springs (Flippo, 1974). The Virginia Ground Water Standard for sodium is 270 mg/l (Virginia Water Control Board, 1986).

TABLE 2. Comparative physicochemical analyses of spring water in Virginia collected during the 1928 survey (Collins *et al.*, 1930) and periodically between 1952 and 1989. Mean values and coefficient of variation (CV) are presented for multiple sampling dates (N); all chemical analyses are expressed in mg/l.

CHEMICAL ANALYSES (mg/l)												
Spring no.	Date (mo/yr)	N	Flow (gpm)	Temp. (C)	TDS	HCO ₃	Hardness	Ca	Na	SO ₄	NO ₃ -N	Cl
21	8/28	1	1140	13	209	216	171	56	15	3.0	2.3	0.2
	11/52	1	224(95)	--	212(1)	250(10)	210(14)	52(5)	1(124)	5.8(45)	2.5(6)	0.8(85)
50	7/28	1	1700	12	80	92	66	66	19	14	6.0	0.2 0.1
	11/54	1	851(47)	--	96(8)	110(13)	93(24)	21(7)	1(123)	2.5(58)	2.6(121)	1.4(122)
52	8/28	1	620	12	73	82	70	22	--	3.0	0.1	0.3
	1981-87	4	--	--	99(13)	73(7)	88(23)	25(32)	1(10)	2.0(15)	0.6(66)	1.0(10)
53	8/28	1	890	10	34	36	26	6	--	2.0	0.2	0.6
	1975-85	3	--	--	59(37)	42(38)	47(23)	1(80)	1(33)	2.0(40)	0.2(50)	1.0(20)
86	7/28	1	1250	15	60	63	40	16	8	5.0	0.0	--
	4/86	1	--	--	24(61)	24(63)	2	1(44)	--	--	1.6(72)	0.2 0.5
95	7/28	1	2140	12	113	126	108	40(41)	<5	4.0	1.1	--
	1976-79	3	956(54)	--	111(4)	125(4)	104(4)	22	1(7)	4.1(49)	1.4(21)	5.0(2)
99	7/28	1	170	--	59	178	64	20	--	3.0	0.4	0.7
	6/65	1	60(68)	11	81(22)	91(45)	76(12)	17(5)	1	1.0(71)	0.2(47)	0.8(9)
107	7/28	1	2500	13	141	162	111	28	12	3.0	0.4	0.2
	1976-79	12	2200(9)	12(2)	116(18)	137(23)	123(8)	25(8)	1(50)	2.2(90)	0.2(95)	2.0(5)
109	7/28	1	2250	13	115	134	93	26	9	2.0	0.3	0.4
	1976-79	12	2649(12)	12(2)	112(14)	132(6)	120(2)	23(9)	1(33)	1.9(53)	0.2(50)	2.0(35)
120	7/28	1	700	12	300	342	250	60	19	5.0	4.2	0.0
	1976-79	3	365(26)	12(2)	251(14)	303(6)	256(17)	54(6)	1(20)	5.0(1)	5.2(2)	0.2

CHEMICAL ANALYSES (mg/l) Cont.

Spring no.	Date (mo/yr)	N	Flow (gpm)	Temp. (C)	TDS	HCO ₃	Hardness	Ca	Na	SO ₄	NO ₃ -N	Cl
287	2/28	1	7000	18	386	220	272	100	27	140.0	2.9	0.5
	1975-76	2	3940(40)	14(6)	--	282(2)	--	138(51)	3(23)	239.0(37)	1.9(36)	2.5(5)
320	2/28	1	6000	11	99	113	86	36	7	1.9	6.0	0.8
	1952-68	4	1717(77)	12(4)	136(10)	148(13)	128(1)	42(9)	1	6.0(1)	1.4(21)	1.3(46)
400	2/28	1	4500	14	184	193	152	56	10	12.0	3.3	1.0
	1984-87	10	2189(18)	13(4)	209(3)	174(4)	187(4)	61(7)	16(69)	10.0(90)	0.6(83)	3.9(6)
405	3/28	1	800	17	101	115	94	24	--	3.0	0.3	0.2
	1984-87	1	215(27)	--	111(7)	106(6)	110(11)	35(26)	1	3.0(0)	0.1(71)	0.0
466	8/28	1	5200	8	67	76	58	24	--	2.0	0.3	5.0
	1982-87	10	4286(83)	9(3)	83(18)	65(17)	70(20)	27(15)	9(59)	3.0(38)	0.3(1)	1.6(75)
478	2/28	1	4500	13	117	127	102	36	5	6.0	1.4	0.5
	1952-68	3	1031(23)	13(0)	122(2)	133(5)	116(4)	35(26)	1(94)	5.6(35)	1.4(42)	1.0(20)
494	2/28	1	300	7	79	86	66	24	--	2.0	2.4	0.6
	5/87	1	50(17)	--	122(30)	61(24)	96(26)	24(0)	5	5.0(61)	1.3(84)	--
496	2/28	1	1180	13	175	193	164	60	--	4.0	5.2	0.8
	5/81	1	1000(8)	--	181(2)	151(17)	160(2)	42(25)	8	3.0(20)	1.6(75)	0.0
499	2/28	1	2000	9	65	69	56	18	3	4.0	1.0	0.6
	9/81	1	2280(9)	--	134(49)	119(38)	124(53)	34(44)	9(71)	5.6(24)	0.5(47)	2.0(71)
501	2/28	1	500	12	101	217	177	64	--	2.0	4.1	0.0
	6/85	1	--	13(3)	181(40)	165(19)	170(3)	39(34)	7(57)	1.0(47)	1.1(82)	0.0

CHEMICAL ANALYSES (mg/l) Cont.

Spring no.	Date (mo/yr)	N	Flow (gpm)	Temp. (C)	TDS	HCO ₃	Hardness	Ca	Na	SO ₄	NO ₃ -N	Cl
504	2/28	1	2000	11	36	40	28	7	3	1.0	0.4	0.3
	5/81	1	1770(11)	--	85(57)	53(20)	58(49)	14(47)	2(28)	5.0(94)	0.2(47)	0.0
508	2/28	1	1000	14	310	360	339	75	--	3.0	3.6	0.6
	1963-75	5	1330(20)	16(2)	293(1)	283(2)	268(29)	51(35)	2(50)	2.3(2)	2.8(57)	1.4(71)
521	2/28	1	150	12	237	249	187	68	13	4.0	8.0	0.9
	9/81	1	646(88)	--	217(4)	191(19)	201(1)	49(2)	14(10)	3.0(66)	1.4(10)	0.5(20)
529	2/28	1	1200	15	305	344	292	45	--	6.0	5.0	0.8
	1976-81	2	--	14(1)	305(1)	266(1)	295(14)	65(9)	2(50)	6.0(10)	1.5(13)	0.6(50)
531	2/28	1	2000	17	330	334	306	50	13	4.0	4.0	0.9
	1971-88	4	1910(3)	17(0)	305(1)	274(2)	246(43)	57(56)	14(10)	3.4(56)	2.7(51)	0.5(50)
533	2/28	1	1800	12	95	99	88	24	--	8.0	0.4	0.6
	1970-88	3	1552(10)	14(5)	105(8)	81(5)	93(4)	24(4)	2(90)	7.0(71)	1.8(95)	1.7(58)
538	2/28	1	5300	12	47	58	50	10	--	2.0	0.3	0.5
	7/85	1	3000(39)	13(1)	75(23)	57(1)	20(60)	13(18)	3	2.8(24)	0.4(20)	--
543	2/28	1	4000	11	164	186	138	32	9	1.0	4.5	0.7
	1981-88	11	3759(4)	11(7)	64(29)	37(51)	45(42)	12(67)	4(90)	6.5(30)	0.7(43)	1.8(39)
551	2/28	1	400	15	206	342	250	--	17	3.0	4.4	0.5
	2/88	1	133(71)	14(1)	310(29)	300(9)	307(15)	66	4(88)	5.3(39)	1.5(70)	--
554	2/28	1	4000	13	270	292	243	100	7	10.0	6.9	1.7
	1962-88	10	2748(46)	13(7)	301(9)	244(8)	252(13)	79(11)	13(92)	17.0(29)	4.3(69)	10.0(50)
555	5/28	2	1000	13	80	86	63	24	6	5.0	0.5	0.3
	1962--89	15	895(58)	13(9)	99(12)	85(8)	87(10)	20(15)	7(71)	3.0(33)	0.3(95)	1.7(4)

TABLE 3. Maximum values for chemical constituents in Virginia springs monitored in 1928 by Collins *et al.* (1930).

Parameter	Maximum (mg/l)	Spring number	Spring Name	County
Ca	400	258	Sweet Chalybeate	Alleghany
HCO ₃	777	258	Sweet Chalybeate	Alleghany
Na	206	311	Mineral	Botetourt
Cl	106	316	Daggers	Botetourt
SO ₄	2500	208	Alleghany	Montgomery
NO ₃ -N	20	148	Vaughan	Pulaski
Hardness	1886	314	Blue Ridge	Botetourt
TDS	2541	314	Blue Ridge	Botetourt

Sulfate (SO₄) concentrations in this study ranged from 1 to 239 mg/l (Table 2). One particular spring, Falling Spring, Alleghany County, showed very high values, but the majority (94 percent) had total levels less than 10 mg/l. Sulfate levels varied considerably through time, averaging 42% CV. Nearly one-half of the springs monitored displayed CVs greater than 50 percent. No distinct long-term trend in sulfate concentrations was evident; 29 percent of the springs examined reflected small increases between dates and 35 percent showed decreasing levels. Collins *et al.* (1930) found sulfate levels in Virginia springs from 1 to 2,500 mg/l for spring numbers 379 and 208 (Reagon Spring, Rockbridge County; Alleghany Spring, Montgomery County, respectively). The sulfate content from 199 analyses of West Virginia spring waters ranged from 1.2 to 4,377 mg/l (McColloch, 1986), and that of Pennsylvania springs was 0.8 to 1,764 mg/l (Flippo, 1974).

Sulfate, a major constituent of ground water in the United States, is found at levels ranging from 0.2 to 100,000 mg/l (Davis and DeWiest, 1966). High sulfate concentrations may arise from erosion of iron-sulfide associated with deposits of coal and shale. The recommended EPA maximum safe limit for sulfate in drinking water is 250 mg/l nationwide (Viessman and Hammer, 1985). Although no sulfate standard has been established for ground water in Virginia (Sterrett, 1989, personal communication), the Virginia Secondary Maximum Contaminant Level (SMCL) for sulfate in drinking water is 250 mg/l. Hydrogen sulfide gas is very toxic to aquatic life; the EPA chronic criterion for the protection of aquatic life is 2 μg/l of hydrogen sulfide. Ground water low in sulfate generally contains little or no sulfide (Hem, 1970).

Nitrate concentrations ranged from 0 to 8.0 mg/l. Nitrate exhibited the greatest within-spring variability over the study period of any of the chemical constituents examined, averaging 70% CV. The maximum fluctuation was 5.6 mg/l nitrate-nitrogen. A clear pattern of increasing concentrations through time was apparent for many (39 percent) of the springs; 12 percent showed decreases, and the rest remained unchanged when the 1929 and current measurements were compared. Increasing nitrate levels in springs suggest possible contamination of ground water from the soil percolation of agricultural fertilizers, livestock wastes, and leakage from septic systems.

Nitrate is a secondary constituent of ground water in the U.S. and typically ranges in concentration from 0.01 to 10 mg/l. Collins *et al.* (1930) found nitrate levels in Virginia springs ranged from 0 to 20 mg/l. The nitrate content of 194 analyses of West Virginia spring water ranged from 0 to 171 mg/l (McColloch, 1986), and that of Pennsylvania springs from 0.3 to 48 mg/l (Flippo, 1974).

Nitrate-nitrogen results from the oxidation of organic compounds (amino acids, proteins). The presence of nitrate in spring water may indicate pollution from fertilizers, animal wastes, septic systems, and other organic matter. Nitrate is a fertilizer that stimulates the growth of noxious algae that can cause undesirable taste and odor problems in drinking-water supplies. The Maximum Contaminant Level (MCL) approved for health by the EPA is 10 mg/l nitrate-nitrogen (Viessman and Hammer, 1985), which is also the MCL for drinking water in Virginia (Virginia Health Department, 1982). The standard for nitrate in ground water in Virginia is variable and dependent on the physiographic province. In the Coastal Plain, Piedmont, Blue Ridge, and Valley and Ridge provinces the standard is 5 mg/l $\text{NO}_3\text{-N}$, whereas it is 0.5 mg/l $\text{NO}_3\text{-N}$ in the Cumberland Plateau (Virginia Water Control Board, 1986). Values in excess of the MCL may result in methemoglobinemia in infants. Non-ionized ammonia (NH_3) and nitrite concentrations at low pH levels can be toxic to fish life.

Chloride levels ranged from 0 to 10 mg/l, and a majority of the springs (58 percent) exhibited elevated levels in the recent monitoring when compared to the historic data (Table 2). Variability in chloride levels within-springs through time was substantial, averaging 40% CV.

Chloride typically is present in ground water at low concentrations, usually less than 30 mg/l (Davis and DeWiest, 1966). Collins *et al.* (1930) found chloride levels for Virginia springs to be between 0.1 and 105 mg/l for Scott spring (number 45), Smyth County, and Dagers Spring (number 316), Botetourt County, respectively. Chloride content of 387 analyses of West Virginia spring water revealed levels ranging from 0 to 4,017 mg/l (McColloch, 1986), and that of Pennsylvania springs from 0 to 87 mg/l (Flippo, 1974). High chloride levels occur in marine shales or evaporite deposits, though anthropogenic sources such as highway-department applications or storage piles of road salt can contaminate ground water (McColloch, 1986). The Secondary Maximum Contaminant Level for chloride in drinking water in Virginia is 250 mg/l (Virginia Department of Health 1982).

Bicarbonate alkalinities in this study ranged from 24 to 342 mg/l (Table 2). Alkalinities generally were lower in recent (post-1952) sampling in a majority (68 percent) of the springs examined. Variability of bicarbonate alkalinity within-springs during the study period was low, averaging only 15% CV. The maximum fluctuation in alkalinity for a single spring was 149 mg/l.

Primary sources of bicarbonate and carbonate ions in ground water are from the solution of carbonate rocks and carbon dioxide in the soil and atmosphere. Water temperature and pH relationships largely regulate the concentrations in solution in ground water. The bicarbonate content of ground water frequently ranges between 10 and 800 mg/l (Davis and DeWiest, 1966). Collins *et al.* (1930) reported bicarbonate alkalinity values for Virginia springs from 2 to 777 mg/l (Spout Spring, Alleghany County; Sweet Chalybeate Spring, Alleghany County, respectively). Bicarbonate alkalinity content of 143 analyses of West Virginia spring

water ranged from 0 to 715 mg/l (McColloch, 1986), while that of 175 Pennsylvania springs ranged from 14 to 348 mg/l (Flippo, 1974). Bicarbonate and carbonate alkalinity significantly contribute to the buffering capacity of ground and surface waters.

Hardness values ranged from 21 to 339 mg/l (Table 2). Hardness values generally increased through time in the majority (77 percent) of the springs examined. Variability in water hardness within-springs over time was relatively minor, averaging 19% CV. Maximum fluctuation in hardness over the study period for a spring was 93 mg/l.

Although calcium and magnesium ions are the principal contributors to hardness, other metal cations including iron, manganese, copper, and barium are included in this measure. Classification of water on the basis of hardness values is as follows: soft waters, 0-60 mg/l; moderately hard, 61-120 mg/l; hard, 121-180 mg/l; very hard, greater than 180 mg/l (Hem, 1970). According to this model, Virginia spring water in this study ranged from soft to very hard; 29 percent were very hard, 48 percent were moderately hard, and 12 percent were soft. Total calcium and magnesium hardness values above 100 mg/l generally are objectionable for domestic uses. In spring waters, calcium-magnesium hardness is often a function of the turnover time of ground water and, therefore, is inversely related to discharge (Flippo, 1974). This relationship was not apparent in the present study, perhaps because our sample size of 31 springs was too limited. Collins *et al.* (1930) reported that hardness values in Virginia spring water between 1.8 and 1,886 mg/l (Dodge Spring, Augusta County; Blue Ridge Spring, Botetourt County, respectively). McColloch (1986) found total hardness levels in 306 analyses of West Virginia springs to range from 3 to 923 mg/l.

Total dissolved solids (TDS) ranged from 24 to 386 mg/l. TDS levels increased through time in the majority (81 percent) of the springs surveyed. Variability in TDS within-springs through time was low, averaging 18% CV. Maximum fluctuation in TDS values for any spring observed during the study was 104 mg/l, although variability for most springs generally was less than 20 mg/l.

TDS, includes all solid substances in solution, but excludes suspended sediments, colloids, and dissolved gasses (Davis and DeWiest, 1966; Sherrard *et al.*, 1988). TDS levels are calculated by gravimetric measurement of the residue following evaporation of a specific quantity of water at 130 C or 180 C (APHA, 1985) or by calculation of the major ionic concentrations. The maximum recommended TDS concentration in drinking water is 500 mg/l (Viesmann and Hammer, 1985). The Secondary Maximum Contaminant Level for TDS in Virginia is 500 mg/l (Virginia Department of Health, 1982). Values from the 1928 survey were estimated by ionic balance calculations, whereas current (post-1952) measurements were by the gravimetric method. Standard classification of water by USGS on the basis of total dissolved solid levels is as follows: slightly saline, 1,000-3,000 mg/l; moderately saline, 3,000-10,000 mg/l; very saline, 10,000-35,000 mg/l; and briny, >35,000 mg/l (Hem, 1970). According to this scale, all Virginia springs exhibited relatively low TDS and salinity levels. In comparison, total dissolved solids of 135 analyses of West Virginia spring waters ranged from 14 to 4,585 mg/l (McColloch, 1986) and from 10 to 2,565 mg/l in Pennsylvania spring waters (Flippo, 1974).

Low iron content (< 0.1 mg/l), typical of most springs sampled, is a desirable drinking water characteristic. Water from certain areas in Virginia, particularly in the southwest where acidic water may promote the solution and transport of high levels of iron which is distasteful and undesirable. The high carbonate conditions evident in spring waters promote the precipitation of ferrous carbonate resulting in low iron levels. Water containing iron concentrations greater than 0.3 mg/l may stain laundry or plumbing fixtures and impart an unpleasant taste. On exposure to air, water containing higher levels than 1 mg/l becomes turbid with reddish ferric compounds via oxidation. Collins *et al.* (1930) used air exposure to visually test for iron. A concentration of 0.3 mg/l is the federal MCL approved for drinking water and ground water (Viessman and Hammer, 1985) and a Virginia Ground Water Standard (Virginia Water Control Board, 1986).

CONCLUSION

It is important to emphasize that the physical and chemical values reported for springs in the 1928 survey (Collins *et al.*, 1930) and in recent monitoring programs were single-point measurements, sometimes estimates, in time (daily, seasonally) and space (spring location). They may or may not have been representative of mean annual conditions of a spring or aquifer. Although springs generally exhibit a uniformity in physicochemical conditions throughout the year, we have no evidence to document stability within years for any springs monitored.

The physical and chemical constituents of spring water reflect a general trend in the quality of ground water in the Valley and Ridge Province of Virginia. Comparisons of historical water-quality data with current measurements offer a unique window through which to view long-term trends of water quality in the aquifer area. This method provides a relatively convenient and economic method for identifying potential contamination of ground water, and springs can serve as additional monitoring sites to supplement data from test wells. Water quality variability (within-spring variation), expressed as the percent coefficient of variation (% CV), over the study period was relatively high for nitrate, sodium, sulfate, and chloride ions, averaging 70, 57, 42, and 40% CV respectively, but moderate for calcium, hardness, bicarbonate, and dissolved solids, averaging 22, 19, 18, and 15% CV, respectively. Variation in water temperatures was minor, averaging less than three percent CV. Spring discharge fluctuated considerably, ranging from three to 95% CV and averaging 37% CV. Although the chemical content of most springs examined has remained relatively consistent for more than 60 years, increasing concentrations of nitrate, chloride, and total dissolved solids in some springs indicated a modest degree of pollution, perhaps resulting from surface contaminant infiltration. Distinguishing local surface water contamination of a spring from pervasive pollution of the entire aquifer is one problem associated with the use of springs or wells as water-quality monitoring sites.

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LITERATURE CITED

- Collins, W. D., M. D. Foster, F. Reeves, and R. P. Meacham. 1930. Springs of Virginia. 55 pages. Virginia Commission on Conservation and Development, Water Resources and Power Division, Bulletin No. 1, University of Virginia, Charlottesville, Virginia.
- Davis, S. N., and R. J. M. DeWiest, 1966. Hydrogeology. 463 pages. John Wiley & Sons, Inc., New York.
- Flippo, H. N., Jr. 1974. Springs of Pennsylvania. 46 pages. U.S. Geological Survey, Water Resources Bulletin No. 10, Harrisburg, Pennsylvania.
- Fortescue, J. A. C. 1980. Environmental Geochemistry. 347 pages. Springer-Verlag, New York.
- Hem J. D. 1970. Study and Interpretation of the Chemical Characteristics of Natural Water. 363 pages. U.S.G.S. Water Supply Paper 1473. Washington, DC.
- McColloch, J. S. 1986. Springs of West Virginia. 493 pages. West Virginia Geological and Economic Survey, Mont Chateau Research Center, Morgantown, West Virginia.
- Meinzer, O. E. 1923. Outline of Ground-Water Hydrology. 71 pages. U.S. Geological Survey Water Supply Paper 494. U.S.G.S., Washington, DC.
- Reeves, F. 1932. Thermal Springs of Virginia. 56 pages. Virginia Commission on Conservation and Development, Virginia Geological Survey, Bulletin 35. Charlottesville, Virginia.
- Sherrard, J. H., D. R. Moore, and T. A. Dillaha. 1987. Total Dissolved Solids: Determination, Sources, Effects, and Removal. J. of Environmental Ed. 18:19-24.
- Slifer, D. 1987. Rockbridge's Illegal Dumps. 9 pages. Focus on Water. No 2. Virginia Water Resources Research Center, Virginia Tech, Blacksburg, Virginia.
- U.S. Geological Survey. 1985. National Water Summary 1984 -- Hydrologic Events, Selected Water Quality Trends and Ground Water Resources. 467 pages. U.S.G.S. Water Supply Paper 2275, Government Printing Office, Washington, DC.
- U.S. Public Health Association. 1985. Standard Methods for the Examination of Water and Wastewater. American Public Health Association, Washington, DC. 1268 pages.
- Viessman W., Jr., and M. J. Hammer. 1985. Water Supply and Pollution control. 797 pages. Harper and Row Publishers, New York.
- Virginia Water Control Board. 1986. Water Quality Standards. 129 pages. Virginia Water Control Board, Publication No. RB-2-86. Richmond, Virginia.
- Virginia Department of Health. 1982. Waterworks Regulations. Virginia Department of Health, Richmond, Virginia.
- Weigmann, D. L. and C. J. Kroehler. 1988. Threats to Virginia's Groundwater. 45 pages. Virginia Water Resources Research Center, Virginia Tech, Blacksburg, Virginia.