INVESTIGATION OF THE IMPACT OF FOREST FIRES ON THE CHEMISTRY AND WATER QUALITY OF GROUND WATER IN YELLOWSTONE NATIONAL PARK

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Objectives

The objective of this research is to provide a detailed analysis and assessment of the impact of the 1988 forest fires on the chemistry and water quality of shallow ground water in Yellowstone National Park. Specific objectives for the first five months of this study (August through December, 1989) included: (1) review of existing data on the chemistry of ground water at selected sites in Yellowstone National Park, (2) selection of suitable sampling sites and initial rounds of sample collection and analysis, (3) continued literature search for comparable or complimentary studies, (4) establishment of professional contacts within the park, other universities, and within the U.S. Geological Survey.

Sampling sites for this investigation were selected on the basis of existing wells and pre-fire chemical data. Comparison of the analytical results for the post-burn waters with the pre-fire database will be made on a component by component basis (see Table 1 for a listing of parameters and components). Assessment of the sources, transport, and fates of dissolved components will be performed by means of geochemical computer modeling. We will use at least two standard geochemical models developed by the U.S. Geological Survey. These are PHREEQE (Parkhurst et al. 1980) and BALANCE (Parkhurst et al. 1982). Both of these programs were designed to model chemical reactions between ground water and minerals in the soils and bedrock.

A continuing search of the literature, including theses, journal articles, and other publications, has uncovered several studies of soil chemistry and surface water chemistry under post-fire conditions in areas far removed from Yellowstone. Some of the information contained in these publications may be instructive with regard to chemical trends

Table 1. List of components/parameters analyzed, type of sample container required, recommended holding times, and type of analysis employed. P = nalgene plastic bottle; G = amber glass; T = teflon cap; all containers cleaned to EPA specifications. F = filtered through 450 nm membrane filter. IC = ion chromatography; GFAA = graphite furnace atomic absorption spectroscopy; Flame AA = flame atomic absorption spectroscopy (air/acetylene unless otherwise specified); ICP = inductively-coupled plasma emission spectroscopy; DPP = differential pulse polarography; Colorimetry using Hach portable spectrophotometer and various methods. Redox potential (Eh) measured using platinum and calomel electrodes.

STANDARD SAMPLE COLLECTION AND TREATMENT PROCEDURES*

PARAMETER/ COMPONENT	TYPE OF CONTAINER	SAMPLE TREATMENT	RECOMMENDED HOLDING TIME	TYPE OF ANALYSIS
Alkalinity	P	F, 4°C	14 days	Titration
Conductivity	P		wellsite	Cond. meter
pH	P		wellsite	pH meter
Temperature	P		wellsite	Thermometer
Redox (Eh)	P		wellsite	Voltmeter
DOX	P		wellsite	Colorimetric
Fe^{+2}	P		wellsite	Colorimetric
DOC	G, T	F, 4°C	28 days	Colorimetric
SiO_2	P	F, 4°C	28 days	Colorimetric
Cl	P	F, 4°C	28 days	IC
F	P	F, 4°C	28 days	IC
NO_3	P	F, 4°C	2 days	Colorimetric, IC
NO2	P	F, 4°C	2 days	Colorimetric, IC
PO4	P	F, 4°C	2 days	Colorimetric, IC
Metals	P	F, pH 1.5	6 months	(see below)
As (total)				GFAA, ICP
As(III)				DPP
Pb				GFAA
Mn				GFAA, ICP
Fe (total)				GFAA, ICP, Colorimetric
Al				N2O/acetylene flame AA, ICP
Mg				Flame AA, ICP
Ca				Flame AA, ICP
Na				Flame AA, ICP
K				Flame AA, ICP

*Procedures from the following references: Standard Methods for the Examination of Water and Wastewater. 1989. National Handbook of Recommended Method for Water-data Acquisition, U.S.G.S., 1984.

or possible problems that may arise during the course of this study.

By interacting with other researchers, information complementary to, but outside the scope of this study, may be made available. We have arranged to work with Dr. Dan Norton, an analytical chemist with the U.S. Geological Survey, during the upcoming months. Dr. Norton has collected numerous ash, soil, and snow samples during his visits to Yellowstone for a different study. Ms. Siders will be analyzing these samples for Dr. Norton, using the facilities at both the University of Colorado and the laboratories of the U.S. Geological Survey in Denver.

Methods

Water samples have been, and will continue to be, collected at the selected sites in accordance with procedures outlined in the National Handbook of Recommended Methods for Water-Data Acquisition (Office of Water Data Coordination, USGS, August, 1984 update). Separate, one-liter bottles of water are collected for analysis of anions, cations, and nutrients. In addition, 250 mL samples are collected for analysis of dissolved organic carbon (DOC). All water samples are filtered through a 450 nm membrane filter at the field site, and cation samples are acidified to pH 1.5 or less, using concentrated ultrapure nitric acid. Samples for DOC, anions, and nutrients are immediately put on ice after collection, and kept refrigerated until analysis. Parameters measured in the field include pH, Eh (redox potential), water temperature, dissolved oxygen (DOX), dissolved ferric iron, total dissolved iron, and electrical conductivity.

Laboratory analyses employ a number of different analytical methods. Anions are being analyzed by ion chromatography and colorimetric methods. Cations are being analyzed by atomic absorption spectroscopy, colorimetric methods, and inductively coupled plasma emission spectroscopy (ICP). Table 1 summarizes the analytical methods used for each component, as well as the type of collection bottle, the methods of sample treatment and the recommended holding times.

Results

During the initial five months of this study, one reconnaissance trip and three sampling trips were made to Yellowstone. Samples were collected from selected wells at

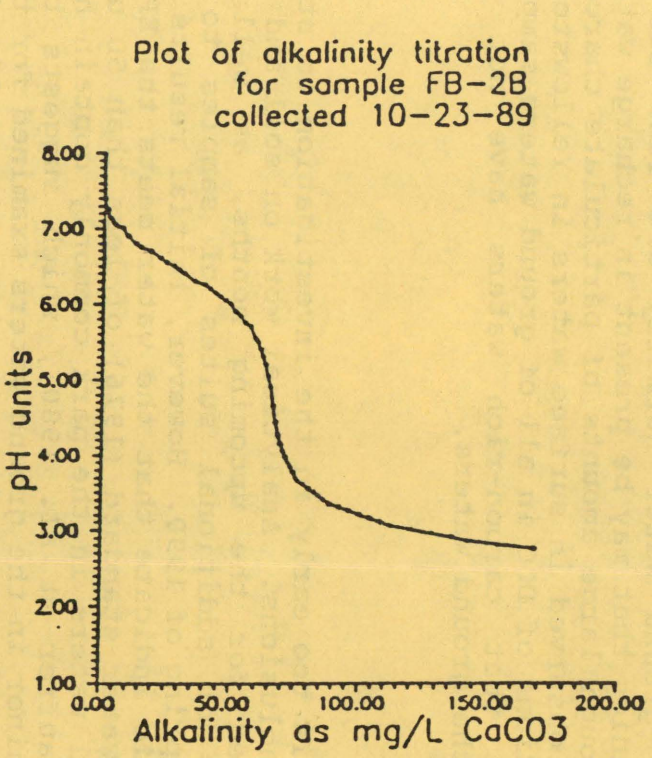
four sites in the park. These include: Grant Village (heavy burn), Old Faithful (moderate burn), Madison Junction (light to no burn), and Fishing Bridge (no burn). Samples were collected from 12 different wells and water table measurements were made for as many as 32 wells during each visit.

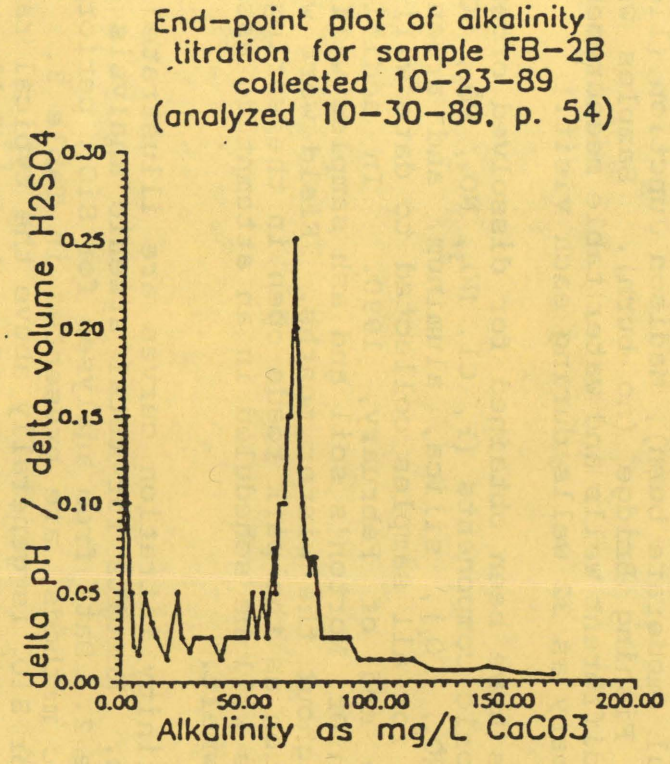
Analytical results have been obtained for dissolved organic carbon (DOC), anionic components (F, Cl, NO_3, NO_2, PO_4, SO_4), nutrients (NO_3, NO_2, PO_4), silica, aluminum, and arsenic. Complete analyses for all samples collected to date will be completed by the end of February, 1990. In addition, analytical work on Dr. Norton's soil and ash samples will be carried out throughout the winter months. Field work will resume again as soon as the park roads open in the spring of 1990. Early trips will be scheduled in an attempt to assess the effect of snowmelt.

Examples of alkalinity titration curves are illustrated in Figures 1a and 1b. Results for total arsenic analysis are presented in Table 2. Data from analyses for SiO_2, performed using colorimetric methods, are presented in Table 3. The range of values for SiO_2 is generally above the typical range for non-thermal ground water of 1 to 30 mg/L, but falls well below the concentrations of silica in some of the Park's thermal waters (Hem 1985). Dissolved organic carbon (DOC) values are shown in Table 4. The average concentration for DOC in rivers in Yellowstone is 5.75 mg/L (Hem 1985). The concentrations in ground water normally are less due to adsorption of organics that may be present in recharge waters (Hem 1985). Although large amounts of particulate charcoal and ash have been observed in surface waters in Yellowstone, the low concentrations of DOC in all of ground waters sampled to date indicate that carbon-rich waters have not yet infiltrated into the ground waters.

Conclusions

At this point it is too early in the investigation to state any definitive conclusions. Analytical work on soil and ash samples is planned for the upcoming months, as well as complete analysis of additional suites of samples to be collected in the spring of 1990. However, initial results for analysis of arsenic indicate that the water meets the EPA's Primary drinking water standard (1976) of less than 50 um/L (ppb) As. Thermal waters in the park commonly contain high levels of As (Stauffer et al. 1980), which suggests that thermal input is minor in the ground waters examined for this study. The elevated concentrations of SiO_2 are probably due





Figures 1a, 1b. Typical titration curves and derivative curves for alkalinity titrations. All titrations were done using normalized H_2SO_4. (NOTE: Error analysis not complete; no analytical uncertainties given in this preliminary report).

Table 2. Total arsenic concentrations as determined by graphite furnace atomic absorption spectroscopy (GFAA). Calibrated working range 3-50 ppb. All spikes 10 ppb; a spiked sample was run immediately after analysis for every sample. EPA requires spike recoveries between 85-115%; the few analyses falling outside this range are noted with an asterisk and were reanalyzed. (NOTE: Error analysis has not yet been done for these data, so only the value of standard deviation (SD) is given here). %RSD is a measure of the deviation of multiple analyses about the mean and is calculated as (SD/MEAN)*100 = %RSD. A variation (%RSD) of ≤ 10% is considered acceptable (Standard Methods, 1989), and is the case for all but one analysis. Accuracy checked by running standards as unknowns.

	ARSENIC ANALYSES			
SAMPLE	CONC.(ug/L)	SD(n=2)	%RSD	SPIKE RECOVERY(%)
FB-1a (8-29-89)	2.8	0.0	0.00	108
FB-1b (8-29-89)	2.3	0.2	9.56	109
FB-1 (9-10-89)	2.1	0.1	6.66	108
FB-2 (8-30-89)	2.6	0.4	13.85	114
Fb-2 (9-10-89)	3.0	0.1	3.33	115
FB-2b (10-23-89)	3.0	0.1	4.66	105
FB-2a (10-23-89)	2.6	0.1	5.38	110
GV-1 (9-8-89)	14.4	0.8	5.14	123*
GV-1 (9-9-89)	15.5	1.3	8.64	112
GV-5 (9-8-89)	7.1	0.1	1.40	107
GV-6 (9-11-89)	0.4	0.4	---	112
GV-6 (10-23-89)	0.5	0.5	---	104
GV-6b (10-23-89)	0.5	0.4	---	107
GV-10 (8-27-89)	6.6	0.1	1.51	116*
GV-10 (8-27-89)	7.2	0.4	5.83	114
GV-10 (10-23-89)	5.8	0.5	8.62	113
GV-10 (10-23-89)	5.6	0.3	5.00	113
Field Blank	0.3	0.2	---	104
STD 50 as unknown	51.2	0.4	0.82	
STD 25 as unknown	26.5	0.4	1.35	
STD 10 as unknown	10.2	0.3	2.74	
STD 5 as unknown	5.2	0.4	8.07	
STD 3 as unknown	2.9	0.2	7.58	
MJ-1 (8-28-89)	7.8	0.5	5.13	88-105
MJ-1 (9-9-89)	7.9	---	----	101
MJ-1 (10-24-89)	8.7	0.4	4.60	87-110
MJ-7 (9-9-89)	7.9	---	----	101
MJ-9 (9-10-89)	0.1	0.1	----	112
OF-1 (8-28-89)	8.7	0.4	4.60	93-99
OF-1 (9-10-89)	5.9	---	----	110
OF-1 (10-24-89)	6.1	---	----	109

Table 3. Silica analyses, with reported uncertainties equal to the standard deviation of triple or quadruple analyses. Analyzed using both silicomolybdate method and heteropoly blue method. Both methods adapted from Standard Methods by the Hach Co. %RSD is a measure of the deviation of multiple analyses about the mean value and is calculated as: (SD/MEAN)*100 = %RSD. Accuracy checked using USGS standards. The USGS standards have the following reported values: USGS M-94: X = 18.1, SD = 1.3; USGS M-6: X = 10.8, SD = 0.3, USGS M-98: X = 10.4, SD = 0.9; USGS M-108: X = 21.6, SD =1.5

SILICA ANALYSES			
SAMPLE	CONC. (mg/L)	SD	%RSD
MJ-1 (8-28-89)	80.3	0.2	0.25
MJ-7 (9-9-89)	62.3	0.0	0.00
MJ-9 (9-9-89)	84.4	0.2	0.24
OF-1 (8-28-89)	82.5	0.3	0.36
OF-1 (9-10-89)	82.2	0.3	0.36
OF-1 (10-24-89)	81.7	0.1	0.12
FB-1b (8-29-89)	43.7	0.1	0.23
FB-1a (8-29-89)	37.7	0.1	0.27
FB-1b (8-29-89)	43.2	0.0	0.00
FB-1b (8-29-89)	43.3	0.0	0.00
FB-1 (9-10-89)	42.8	0.0	0.00
FB-2 (8-30-89)	46.9	0.0	0.00
FB-2 (8-30-89)	45.8	0.1	0.22
FB-2a (10-23-89)	41.7	0.1	0.24
FB-2b (10-23-89)	46.4	0.2	0.37
FB-2b (10-23-89)	47.0	0.1	0.21
GV-1 (9-8-89)	33.9	0.0	0.00
GV-5 (9-8-89)	40.6	0.1	0.25
GV-6 (9-11-89)	35.0	0.2	0.59
GV-6 (9-11-89)	35.1	0.1	0.28
GV-6a (10-23-89)	38.2	0.2	0.52
Gv-6b (10-23-89)	37.2	0.3	0.81
GV-10 (8-27-89)	37.8	0.0	0.00
GV-10 (10-23-89)	40.4	0.1	0.25
USGS STD M-94	17.7	0.0	0.00
USGS STD M-94	17.5	0.0	0.00
USGS STD M-94	18.0	0.0	0.00
USGS STD M-6	10.4	0.1	0.96
USGS STD M-6	10.3	0.1	0.97
USGS STD M-98	10.3	0.1	0.97
USGS STD M-108	20.0	0.1	0.50
USGS STD M-108	21.0	0.1	0.48
Field Blank	0.1	0.0	0.00
Lab Blank	0.5	0.0	0.00

Table 4. Dissolved organic carbon (DOC) analyses for selected wells. Samples FB-2b, GV-6 and GV-10 were analyzed in duplicate. Analyzed using coulometric methods at Huffman Laboratories, Golden, CO.

DISSOLVED ORGANIC CARBON ANALYSES	
SAMPLE	DOC (mg/L)
FB-2a (10-23-89)	2.
FB-2b (10-23-89)	2., 2.
GV-1 (10-25-89)	3.
FB-1a (10-25-89)	2.
FB-1b (10-25-89)	2.
GV-5a (10-25-89)	3.
GV-5b (10-25-89)	3.
GV-6 (10-23-89)	1., 1.
GV-10 (10-23-89)	2., 2.
MJ-1 (10-24-89)	1.
MJ-7 (10-24-89)	2.
OF-1 (10-24-89)	<1.
Field Blank	<1.

in part to the silica-rich volcanic ash and rhyolitic rocks that comprise the substrate.

Avenues to be pursued in the upcoming year include installation of vacuum lysimeters at the study sites for collection of water from the unsaturated zone (i.e. above the water table). Also, during future sampling trips, more water table measurements will be made in order to better assess the direction of ground-water flow. Some work may also be performed with stable isotope analysis of both ground water and adjacent surface waters in order to estimate the percentage of surface flow versus infiltration and ground water recharge.

Literature Cited

Hem, J.D. 1985. Study and interpretation of the chemical characteristics of natural water. U.S. Geological Survey Water-Supply Paper 2254, 263 pp.

Office of Water Data Coordination. 1984. National Handbook of Recommended Methods for Water-data Acquisition. U.S. Geological Survey Water Resources Division.

Standard Methods for the Examination of Water And Wastewater. 1989. 17th edition, 1268 pp. American Public Health Association, Washington, D.C.

Staufer, R.E., E. A. Jenne, and J. W. Ball. 1980. Chemical studies of selected trace elements in hot-spring drainages of Yellowstone National Park: U.S. Geological Survey Professional Paper 1044-F, 20 pp.

U.S. Environmental Protection Agency. 1976. National interim primary drinking water regulations: EPA-570/9-76-003: Washington, D.C., EPA Office of Water Supply.