INTRODUCTION

To determine the character and extent of possible changes in the chemistry of non-thermal ground waters in Yellowstone National Park that may have occurred as a result of the 1988 forest fires, a two-year program of sampling and analysis was begun in August, 1989. Samples from ground-water wells for which pre-fire chemical data could be obtained were selected for this study.

The influx of ground water into surface waters (as baseflow) presents a possible pathway for ash-derived components to impact surface waters in the Park. Data from a recent study of a silicic, non-carbonate aquifer system suggest even small amounts of ground water can significantly affect the chemical balance of dilute lake waters (Kenoyer and Bowser 1992a, 1992b). Because of the dilute nature of non-thermal waters in the Park and the unknown effects that the fire may have had on the solute content of the ground water, this study was commissioned by the National Park Service (NPS) to examine possible fire-induced changes in the chemistry of shallow ground-waters in the Park. Results of this study may allow the NPS to anticipate any future impact upon the chemistry of surface waters in Yellowstone, in addition to identifying any deleterious effects of the fire on quality of non-thermal ground water in the Park.

Due to the geochemical, biological and hydrological processes that modify infiltrating precipitation, it was anticipated that the impact of the forest fires on the chemistry of ground-water would be of lesser magnitude than the chemical and physical effects of fire on surface waters in the Park. Samples of soil water and ground water were collected and analyzed to evaluate the impact of the fires on the shallow, non-thermal ground waters in the Park. For detailed study sites and methodology see Runnells and Siders (1992).

RESEARCH OBJECTIVES

The main goal of this study was to define the chemistry, transport, and fate of dissolved components entering the ground water as a result of the forest fires of 1988. Specific tasks performed to achieve this objective include:

1. Determination of chemical and physical properties of the ground water by means of geochemical analyses performed in the field and in the laboratory.

2. Sampling and chemical analyses of soil water (i.e. water from the unsaturated zone).

3. Leaching of ash and soil samples and chemical analysis of the aqueous extracts and comparison of the chemistry of leachate to that of ground water and soil water.
(4) Comparison of the analytical results for the post-burn ground waters with the pre-fire data for samples collected from the same wells.

(5) Assessment of the transport and fate of ash-derived solubles and interpretation of possible water-rock interactions controlling the chemical composition of ground water, as determined by computer modeling of the analytical data. This analysis includes the use of several different geochemical modeling programs (WATEQB, Arikan 1988; PHREEQE, Parkhurst et al. 1980; MINTEQA2 v. 3.11, U.S. Environmental Protection Agency 1991; and NETPATH, Plummer et al. 1991).

CONDITIONS OF THE STUDY

Although the average annual precipitation is only about 38 to 76 cm throughout most of the park, the cool climate allows for abundant vegetation due to the lower rates of evapotranspiration. The years of 1987 and 1988 proved to be exceptionally dry, however, with snowpacks running less than 50 percent of normal. The combination of these deficient snowpacks and a long-term drought in the greater Yellowstone area resulted in extremely low moisture contents of trees and other vegetation, and set the stage for a summer of fires that ultimately burned 45 times more acreage in the Park than in any other recorded year (National Geographic 1988).

The forest fires of 1988, which affected nearly one million acres within Yellowstone National Park, have been described as "...the greatest ecological event in the history of the national parks..." (11/88, Yellowstone Today). The fires burned with variable intensities, forming a patchy mosaic of charred acreage contained within the burn perimeters.

The ecological effects of forest fires, as well as the periodicity and history of fires in Yellowstone, have been studied by a number of researchers. Romme and Despain (1989:17) summarized the results of their own research as well as those of others; they stated, in reference to the 1988 fires, that "These extremely large fires were primarily the result of extremely warm, dry and windy weather, coinciding with an extensive cover of highly flammable forests that had developed since the last extensive fires in the early 1700's."

HYPOTHESES TO BE TESTED

There are several possible scenarios describing the behavior of the forest-fire ash leachate, including: (1) the leachate reached the water table during the first period of ground-water recharge following the fires (i.e. during the summer of 1989) and was missed by this study, (2) the leachate was attenuated by dilution upon impact with the ground water, (3) the solutes were removed by sorption and/or precipitation as the leachate passed downward through the regolith, (4) the leachate has not yet reached the water table due to retardation of the solute ions as they interact with the substrate, and may still impact the ground-water chemistry, (5) the ash leachate never developed in the natural setting or never infiltrated (i.e. was removed in surface runoff).

Although none of these proposed events can be tested directly, data can be used to support or discount the likelihood of each scenario. A bromide tracer test was conducted in an effort to determine the amount of time necessary for snowmelt to reach the water table, thereby providing an estimation of the probable rate of downward migration of the ash leachate and indirect testing of the possible scenarios.

The null hypotheses tested in this study include: (1) large-scale forest fires do not change the chemistry of ground water, even in areas of dilute waters such as Yellowstone National Park, and, (2) chemistry of ground water does not change as a function of forest fire intensity.

DISCUSSION AND INTERPRETATION

The results of statistical and graphical analysis of the geochemical data, plus the results of geochemical computer modeling, indicate that the chemistry of non-thermal ground waters in Yellowstone has not been adversely affected by the 1988 forest fires. There is no evidence that the overall chemistry of the ground waters sampled for this investigation has changed due to factors directly attributable to the forest fires, however, there are indications of subtly changes in the behavior of some chemical and physical parameters.

The Biological Factor

Because biological activity plays a critical role in regulating the behavior and transport of water and

200
major ions, an ecosystem that has had all vegetation removed by intense burning may experience marked changes in the flux of water and major ions (Fahey and Knight 1986). Following the removal of forest vegetation, whether by logging or fire, there is a "reorganization phase" during which there is a loss of biotic regulation of the hydrologic and biogeochemical components of the ecosystem (Borman and Likens 1979). Other researchers have concluded that leaf area index (LAI) is a critical factor in nutrient retention in the snow-dominated lodgepole pine ecosystem, and that losses of limiting nutrients may occur after disturbances such as forest fire (Knight et al. 1985).

Nutrients "available" to plants are generally considered to be those ions that are dissolved in the soil water phase (Bidwell 1974). That is, only those nutrients present as solutes are available to plants, so experimental water-extraction of a soil (or ash) sample in the laboratory should indeed provide a measure of nutrient availability.

Nutrients in the ash are released and mobilized by precipitation, and it seems reasonable to expect that the less reactive and more mobile components of the dissolved salts (e.g., $\text{SO}_4$ and $\text{Cl}$) would be the first to show up in the ground water. However, none of the post-fire samples of ground water from the Grant Village site (severely burned) contained higher concentrations of either $\text{SO}_4$ or $\text{Cl}$; in fact, many post-fire samples actually had lower concentrations of these ions than did the pre-fire samples though not all at statistically significant levels.

Statistical Analysis and Significant Differences

Attempts to determine the statistical significance of differences between the pre-fire and post-fire data using the Student's $t$-tested led (erroneously) to the conclusion that there were many significant changes in the chemistry of the ground waters. However, there were no recognizable or interpretable patterns to these "differences," so a more rigorous and suitable statistical test was applied to the data.

Two-way ANOVA permits the determination of whether the variation between groups is larger than the variation within groups, by treating each group as a whole rather than as a collection of pairs. In doing so, results of the two-way ANOVA tests clearly indicate that the null hypothesis is sustained; that is, that the post-fire chemistry of ground water at the most severely burned site (Grant Village) is not significantly different from the pre-fire chemistry, when examining the site as a whole. There are, however, some significant differences when the statistical data for individual wells are studied.

At the Grant Village site, three of the five wells sampled showed statistically significant differences for as many as four dependent variables. These variables include: Ca, K, $\text{SO}_4$, and depth to water table, in wells GV-1, GV-6, and GV-10a. However, many of these differences resulted from a decrease in solute concentration ($\text{SO}_4$, $\text{Cl}$, K, Ca); exactly the opposite of what would be expected if, in fact, ash leachates impacted the chemistry of the ground water. In addition, the water table dropped in a number of wells, but only to a significant extent in two wells from the Grant Village site (GV-6 and GV-10a). One possible explanation for both of these observations is that reduced infiltration of precipitation - resulting in decreased recharge of the ground water - was due to the increased hydrophobicity of the burned soils.

Wildfires can cause increased hydrophobicity of soils due to the volatilization of soil organic matter by heating. The volatilized soil organics penetrate through soil pore space in a gaseous state and resolidify within the soil profile where temperatures are lower. The result is that soil particles are coated with a water-repellent organic layer that impedes infiltration of moisture into the soil profile. The formation of hydrophobic layers also causes increased runoff and a higher erosion potential (see DeBano et al. 1970 and 1976).

It is possible that the formation of a hydrophobic layer at the severely-burned Grant Village site contributed to the removal of ash and ash leachates in surface runoff, as well as to decreased ground-water recharge. The results of the statistical analysis would support such a scenario.

Lysimeters: Tracking the Ash-Derived Solutes

Because of the coarse texture of the soils (sand to sandy loam), we expected a fairly rapid downward migration of infiltrating solutions (ash leachate and snowmelt). Accordingly, lysimeters were installed at depths of 15, 30, 60, and 90 cm. Although analytical results gave some indication of a "solute maximum"
at the 30 to 60 cm depths, only a longer-term sampling program would provide sufficient data to draw more definitive conclusions about the presence (or absence) of a migrating solute front. The present results are inconclusive.

Bromide Tracer Test: Determining the Rate of Unsaturated Flow

In an effort to determine the amount of time necessary for infiltrating solutions to reach the water table, a solution of saturated KBr was released onto the ground surface at two of the four sites of groundwater sampling. Because the bromide ion behaves conservatively, it approximates the travel time of the solution and offers a minimum time for solute transport.

Unfortunately for this study, no bromide was recovered from ground-water samples collected throughout the summer and fall following the release of the KBr solution in June, 1991. This negative result strongly suggests that the rate of water movement in the unsaturated zone is no more than a few meters per year. Such a flow rate also suggests that infiltrating ash leachates have probably not yet reached the water table at many locations.

Collection of weekly grab samples for at least a year to two after the release of KBr solution during the period of snowmelt would probably be required to establish a breakthrough curve for the bromide, and provide an approximation of vertical flow rates in the unsaturated zone.

Mixing or Mineral Weathering?

To evaluate what the maximum possible impact of the mixing of ash and snowmelt might be (assuming no addition of solutes to the snowmelt other than those derived from ash leachate), simple calculations were performed to determine the mixing ratio of snowmelt ash leachate that would be required to produce the concentrations of ions measured in samples of post-fire ground water from Grant Village. Results of these calculations suggest that a mixing ratio of $> 99.4$ percent snowmelt with $< 0.6$ percent leachate would be required to give the $\text{SO}_4^{2-}$ concentrations observed in the post-fire samples. For $\text{Cl}^-$, the required amount of snowmelt ranges from 97.3 to 99.1 percent of the total mixture, whereas $\text{Na}$ requires only 61 to 83 percent of snowmelt mixed with 39 to 17 percent ash leachate. The proportion of snowmelt required to produce the concentration of dissolved $\text{SiO}_2$ measured in samples of ground water ranges from 74.0 to 91.3 percent mixed with 26.0 to 8.7 percent ash leachate. Clearly, there is no one mixture that can account for the concentrations of all components in the ground water.

In contrast to the mixing calculations above, models generated by NETPATH require only small amounts of ash leachate (less than one percent) in addition to dissolution/precipitation reactions. However, NETPATH could only model those components for which there was a realistic mineral phase. Because of this limitation, $\text{Cl}$ and $\text{NO}_3^-$ were not included in the NETPATH models; only $\text{Ca}$, $\text{Mg}$, $\text{K}$, $\text{Na}$, $\text{C}$, $\text{S}$, $\text{A}_1$, and $\text{Si}$ were modeled.

The apparent discrepancy between the hand calculations and the NETPATH models can be attributed to the possibility that some components have another source (other than ash leachate, snowmelt, or weathering of the specified minerals) that has not been included in the calculations. In the case of $\text{NO}_3^-$, mineralization by soil bacteria contribute to inorganic nitrate in solution, thereby minimizing the usefulness of $\text{NO}_3^-$ as a constraining variable in the calculations. Other sources, such as the indirect $\text{Cl}$ input from thermal waters or minor amounts of $\text{Cl}$ substitution in soil minerals like apatite, could also be responsible for the disparity. Chloride, which occurs in high concentrations in thermal waters (White et al. 1988), behaves conservatively and could travel farther than trace metals, which tend to be removed along the flow path by sorption or other physical processes. The occurrence of thermally-derived trace metals in the water samples would therefore indicate a more direct input of thermal waters mixing with the non-thermal, highly dilute ground waters examined for this study.

Because different mixing percentages are required to describe the concentrations of each solute in the ground water, it becomes apparent that simple mixing of different solutions (i.e. a percentage of pure snowmelt plus a percentage of ash leachate) cannot create a solution approximating the chemical composition measured in samples of post-fire ground water. Other sources of solutes or other processes are required to produce (simultaneously) the particular range of concentrations measured for all dissolved inorganic species.
Mass-balance (NETPATH) modeling indicated that mineral weathering (dissolution/precipitation reactions) by water of snowmelt composition can describe the transition in solute content from that of snowmelt to that of the ground water, without the necessity of mixing in any percentage of ash leachate (not considering chloride, which was not included in NETPATH modeling). The modeling, however, does not rule out the possibility of a combination of weathering and mixing (snow + ash) to produce the chemistry observed for the post-fire ground waters.

Overall, the results of mass-balance modeling indicate that weathering of a reasonable selection of minerals, added to snowmelt, can produce the observed ground-water compositions; with or without the addition of ash leachate. Therefore, the chemistry of the post-fire ground waters at the severely burned Grant Village site can be attributed to mineral weathering alone, or to a combination of mineral weathering and minor mixing of solutions, but not to mixing alone. The data, however, do not rule out the possibility that the leachates formed during wetting of the ash were subsequently diluted by mixing with additional snowmelt and by mixing with the dilute ground waters, or that the ash leachates were removed by surface runoff. In addition, the solute behavior seen in ground water at the severely burned site may be due to complete, though temporary, removal of the biotic component from the system, thereby altering the cycling of nutrients in this relatively infertile ecosystem.

Results of this study suggest that most of the soluble components in the ash were probably removed by surface runoff, rather than infiltrating directly into the ground waters. Increased hydrophobicity of the soils - a documented effect of forest fires - could have caused an increase in surface runoff, while decreasing the amount of infiltration and the accompanying ground-water recharge. The data presented here are consistent with such a scenario. However, infiltration of the leachates, combined with a low rate of flow through the unsaturated zone (i.e., leachates have not yet reached the water table), cannot be completely ruled out.

RECOMMENDATIONS FOR FUTURE STUDY

This study has determined the identity and quantity of water-soluble components contained in the forest-fire ash. In addition, likely scenarios for the transport and fate of the ash-derived solubles have been proposed. However, there are still a number of unknown items that could be the focus of future studies.

A systematic mass-balance study of burned and non-burned watersheds would provide additional details about the response of the lodgepole pine forest to forest fires. Such a study should include continuous analysis of rain and snow chemistry throughout the year. However, this amount of detail would require a daily to weekly sampling of precipitation, as well as some method of determining the amount of runoff, infiltration, and evaporation of this precipitation. In particular, more lysimeters and more bromide-tracer tests would be extremely useful in defining the rate of flow in the unsaturated zone. The study should be initiated immediately after a forest fire. Such a comprehensive investigation also points to the need for reliable baseline data; the importance of such data cannot be overstated.

A detailed characterization of soil mineralogy could provide additional data for the refinement of geochemical computer modeling. Collection of soils and soil parent-material from a deep profile, preferable extending to a depth below the water table, would be useful for verifying the mineralogy used in
modeling for the current study.

The high concentrations of NO₃ measured in the soil solution of a severely-burned site (Grant Village) are thought to result from a dramatic increase in the activity of nitrifying bacteria under post-fire conditions. It may be possible to test this by determining the isotopic composition of the NO₃ in solution. Microorganisms are known to fractionate C-isotopes, and can also fractionate ¹⁴N and ¹⁵N, thereby leaving an isotopic signature for biologically-fractionated nitrogen (Hem 1985).

Statistically significant changes in the chemistry of ground waters at the Fishing Bridge site are the result of impact from sewage effluent and are not related to the forest fires. However, this indication of impact on the ground-water chemistry by effluent from the sewage-treatment plant at the Fishing Bridge site may warrant further investigation. The degree of impact could be ascertained by sampling the adjacent surface waters in the Yellowstone River and measuring C¹ concentrations and conductivity, then comparing the results of these measurements with background values measured at an upstream locality.

*LITERATURE CITED*


U.S. Environmental Protection Agency. 1991. MINTEQA2, an equilibrium metal speciation model. EPA/600/3-91/0122, Environmental Research Laboratory, Athens, GA 30613.