

Annual Geochemical Dynamics of a Spring-Fed Stream in an Arid Climate

Tracy J. Lund*, Everett Shock*^, Panjai Prapaipong*

* School of Earth and Space Exploration, Arizona State University, Tempe, AZ 85287

^Department of Chemistry and Biochemistry, Arizona State University, Tempe, AZ 85287



Questions and Hypotheses:

While studies have analyzed major ion composition in streams at different time scales (Parker et al., 2007; Miller & Drever, 1977) and nutrient loads in rural and urban arid streams (Martí et al., 1997; Jones et al., 1996) over different time scales and in response to weather events, little work has been done to learn about long-term, seasonal trends of trace elements in perennial, minimally-managed, semi-arid streams.

Our goals for this project were two-fold:

- Measure major and trace elements in a minimally anthropogenically-impacted (i.e. rural and minimally diverted) stream in central Arizona to investigate long-term and storm-driven chemical trends. These trends could then be extrapolated over a broader scope to encompass other watersheds in the Mogollon Rim region.
- Compare chemical trends in the style of Miller & Drever (1977) to determine what roles the essentially bi-modal precipitation scheme has on stream chemistry overall.

To effectively accomplish these goals, we asked ourselves the following questions:

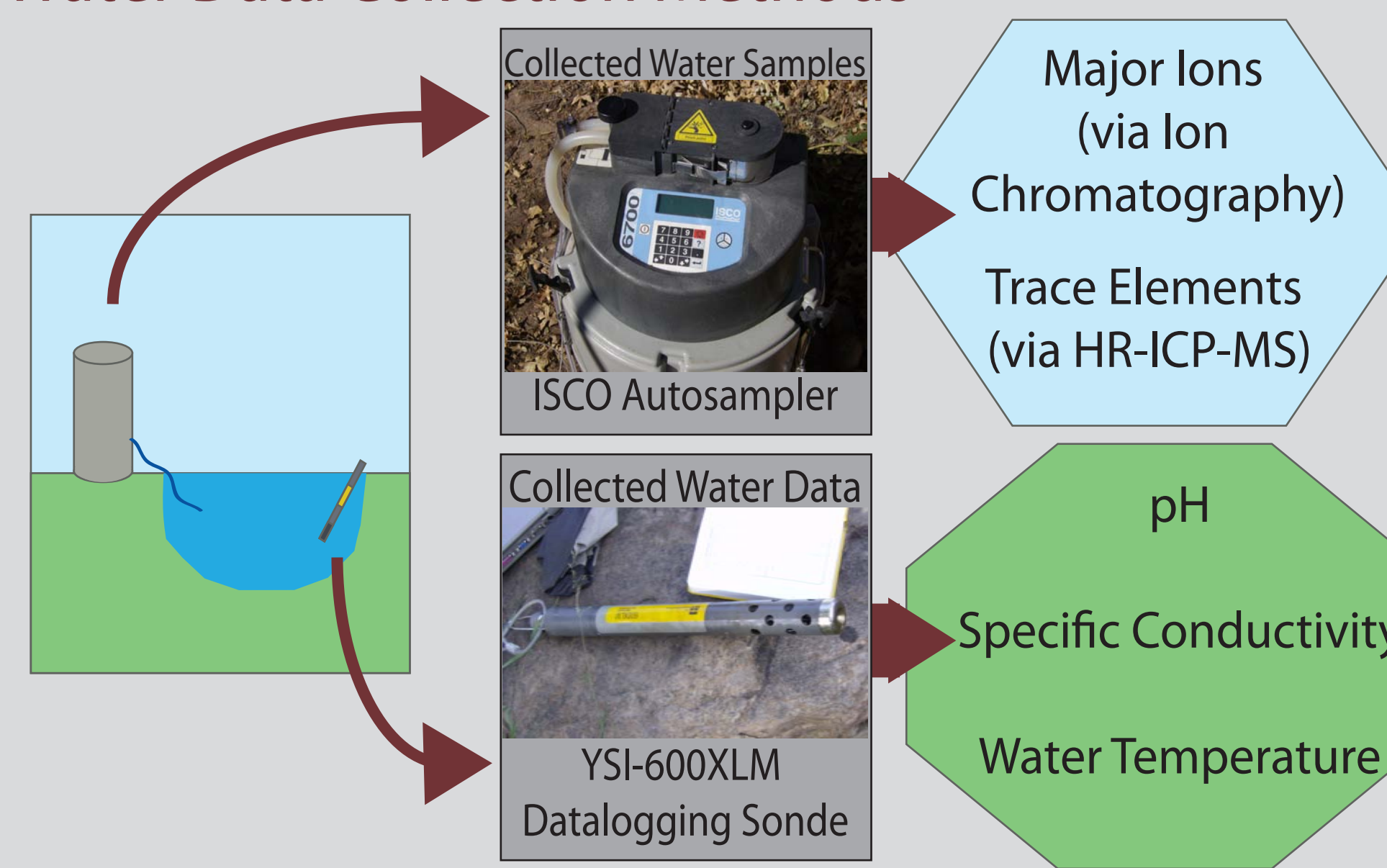
How does water chemistry change as a function of time and seasonal changes?

Hypothesis: Snowmelt, precipitation and other surface inputs should alter the main spring water chemistry as these types of events occur. Each of these events may also contribute their own chemical "markers" that will increase and decrease as inputs from those sources increase or decrease.

How do precipitation events alter elemental concentrations, pH and conductivity?

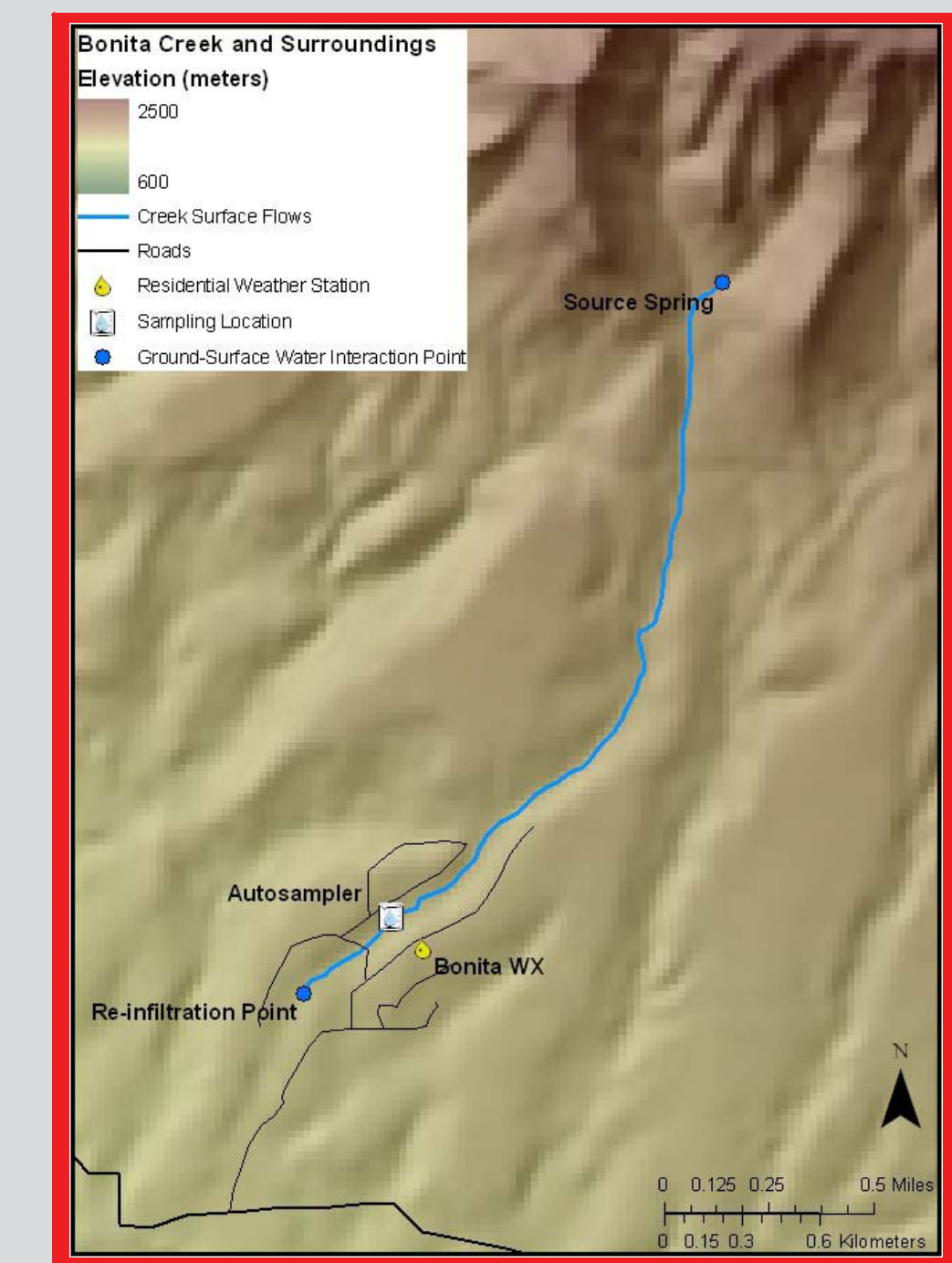
Hypothesis: Spring water-derived elemental signals should be overwhelmed during and immediately after rainfall events as surficial flows are at peak volume.

Water Data Collection Methods



Study Location

Bonita Creek is a spring-fed perennial stream flowing southward from the base of the Mogollon Rim escarpment about 12 miles northeast of Payson, Arizona. The creek emerges from within or immediately above a limestone unit (the Fort Apache limestone unit, as described by Blakey and Knapp, 1989; see Photo 2) within the Pennsylvanian-Permian Supai Group and flows overlaid through the Tonto National Forest for about 2 miles before entering the community of Bonita Creek (Photo 1), which diverts a small amount of surface flow for household use for homes on the east side of the Creek. The majority of flow continues for approximately 0.5 mile before re-infiltrating as groundwater near the concealed contact between the Supai and Pennsylvanian Naco Formation. Groundwater flows from Bonita Creek presumably re-emerge within the Verde River watershed, a major water source for the Phoenix metro area.



The watershed is a thriving, burn-scarred ecosystem of manzanita, ferns and grasses, with some small stands of ponderosa clustered primarily around the creek itself. Evidence of the Dude Fire of 1990 is widespread, with a vast amount of charred stumps still present throughout the area some 20 years later. See Photos 1-4 for more details on this fire.

Weather Data Collection

Climatological and meteorological conditions for the Mogollon Rim area were collected from several different sources, including local residents via Weather Underground and the USDA National Resource Conservation Service. Weather trends were used to lend context to the collected and measured geochemical data, as events do have a profound impact on water chemistry through dilution and concentration of species (Rose, 2003; Miller & Drever, 1977).



Figure 2. Close-up detail of regional map near the study site. The two USDA-NRCS sites are each 10.1 miles from the autosampler site at Bonita Creek.

Weather Data Site Descriptions

Bonita - real-time temperature and water precipitation measurements at Bonita Creek as provided by resident Dave Kelly. The station is about 0.25 miles away from the autosampler. This station does not accurately measure snow so precipitation amounts during the winter season are not dependable for either rain or snow data.

Baker Butte and Promontory - US Department of Agriculture Natural Resource Conservation Service weather observation sites featuring daily temperature, rainfall and snow (measured in inches of snow-water equivalent or SWE) measurements in a nationwide network. These are the two closest sites to the study area at about 10 miles away.

Seasonal vs. Event-Driven Chemical Changes

As shown in Figure 3, major shifts in dissolved elemental chemistry, as shown by the specific conductivity plot, correlate well with major meteorological events. The first month of the study period is marked by significant reduction in snowpack at both SNOTEL sites, which beautifully lines up with the observed dip in conductivity. This correlation indicates that the melting snowpack in the upper reaches of the Bonita Creek watershed is diluting the major ion concentration imparted by the source spring. This hypothesis is supported by the subsequent increase in conductivity seen from spring through late fall, a period affected only by sparse rainfall events or the summer Arizona Monsoon pattern. Once significant snowpack amounts accumulate again in late-December, conductivity falls dramatically to nearly the same values seen at the beginning of the study period.

The summer monsoon period also has an effect on conductivity although not as great and only for discrete, very short periods, likely due to the short duration of these discrete rainfall events relative to melting snowpack conditions seen through the winter. Chemical effects from two rainfall events—July 12 and August 10, 2008—were captured to compare rainfall event-driven chemical changes with seasonal chemical dynamics. Figure 5 shows the July 12 event.

Figure 4 shows the full study period minus all data and samples that were collected less than 18 hours after a Bonita Creek rainfall event. The 18 hour criteria was generated from close observation of data trends following the July 12 and August 10 events, i.e. post-event concentrations resume near pre-event levels for all but one or two elements. The elements shown here are a small sampling of the nearly 60 major and trace elements included in our analyses and are showcased here because of the data trends observed throughout the study period.

Certain trends are clearly shown in the seasonal data. Calcium, magnesium and strontium—all +2 ions in solution—all exhibit very similar concentration increases to the conductivity data, which makes sense as calcium is the most concentrated, readily-measurable major ion in solution. Uranium—and arsenic to a certain extent—exhibits somewhat similar behavior, with the lowest measured concentrations occurring during snowmelt periods. Major +1 ions in solution, like potassium, chloride and sodium (not shown here), show comparatively little change over the course of the year, but do exhibit a small slump during snowmelt times. Because of these apparent decreases during snowmelt, all of the aforementioned elements are likely coming from the source spring, which is undergoing dilution during those periods. Dissolved iron appears, on the surface, to at least partially resemble precipitation patterns but may also represent colloidal iron flocculation in collected samples that could occur before filtration. Neodymium—as well as some transition metals and other rare-earth metals—exhibits a strongly anti-correlative signature in relation to calcium, with maximum concentrations occurring during snowmelt periods.

Figure 5 shows the same elements during and after a Monsoon storm on July 12, 2008. The rain event is documented on top, with elemental concentrations plotted as a function of time below. Note the abrupt trend shift in strontium, which shows strong seasonal correlation with calcium, but is actually strongly anti-correlative during this event. This would seem to suggest a secondary strontium source being washed into solution from somewhere on the surface, either from soil or some exposed high-concentration strontium-salt layer within the Supai Group, which does contain some evaporite salt deposit strata (Blakey & Knapp, 1989). Also note the very different responses of chloride and potassium, which exhibit similar behavior seasonally. All other elements shown here behave similarly to observed seasonal trends.

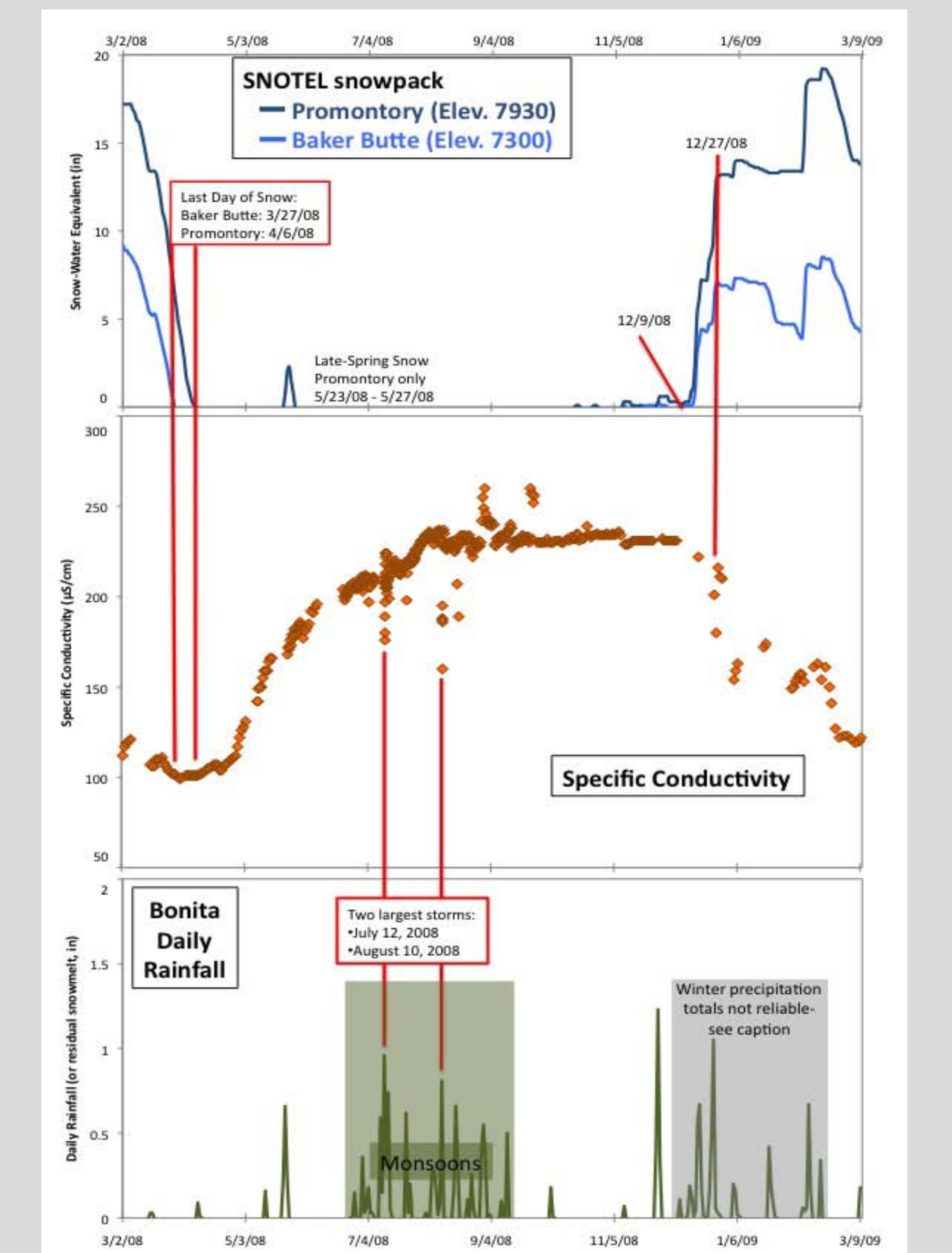


Figure 3. Regional snowpack at USDA-NRCS SNOTEL sites (top, in inches of snow-water equivalent) and local residential rainfall measurements (bottom, in inches, courtesy of Dave Kelly) compared with specific conductivity measurements (bottom, in µS/cm) from the YSI-600XLM installed in Bonita Creek for the full study period. Note that rain measurements for the Bonita Creek residential site are not reliable due to the inability of the installed weather equipment to accurately measure snow.

Figure 4. Measured concentrations of a few of the major and trace elements measured for this project for the full study period. Purple data points represent major elements and are measured in mmol/kg, while aquamarine data points represent trace elements and are in µmol/kg. Data was plotted in this way to accommodate the 1000-fold concentration differences between major and trace elements. Error bars are standard deviation of multiple sample measurements.

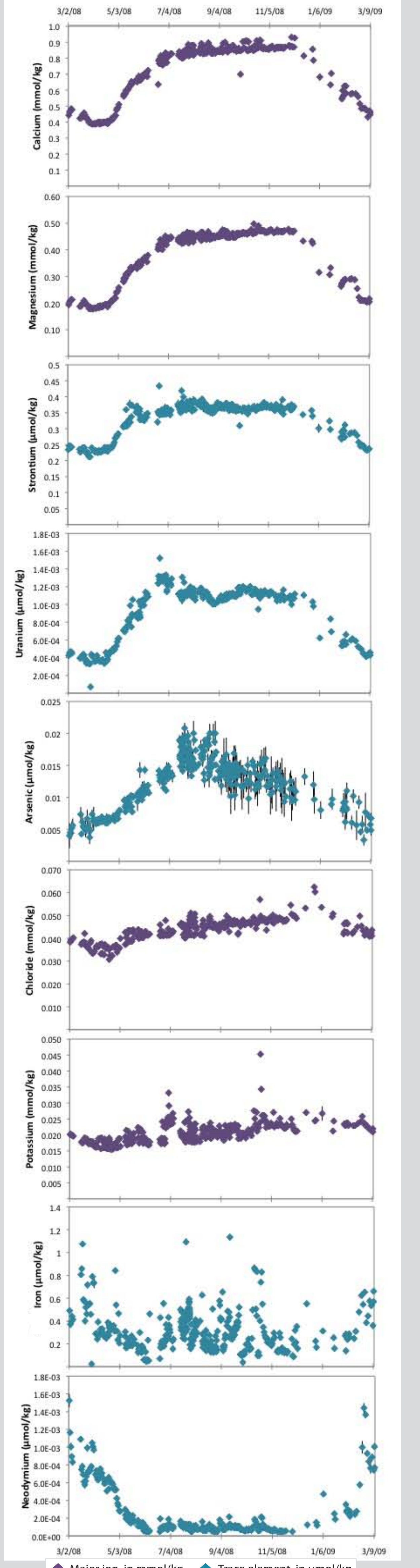


Figure 5. Elemental concentration changes as a function of time in relation to a documented rainfall event (Bonita site data). Purple data points represent major elements and are measured in mmol/kg, while aquamarine data points represent trace elements and are in µmol/kg. Error represents standard deviation of multiple measurements.

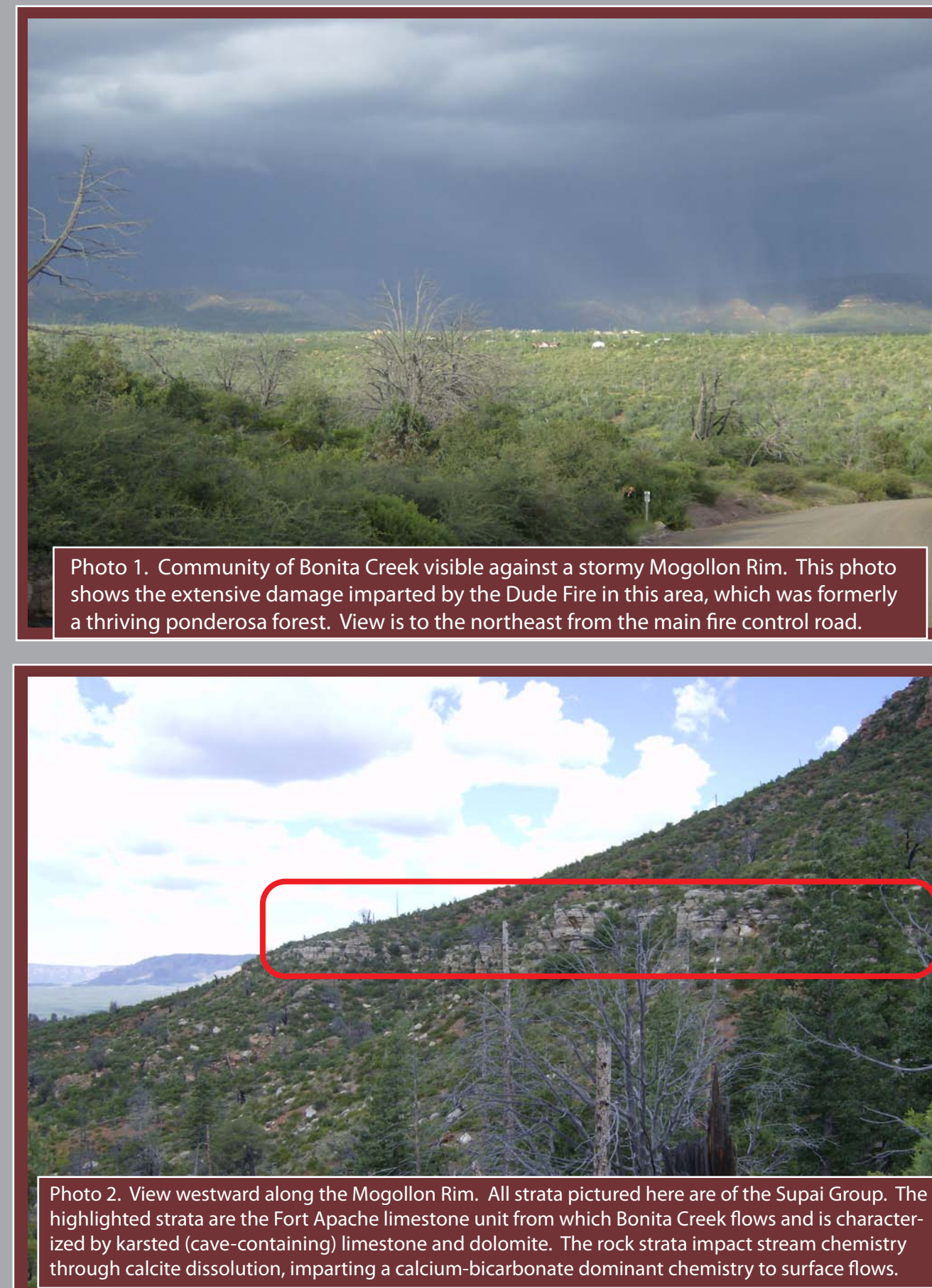


Photo 1. Community of Bonita Creek visible against a stormy Mogollon Rim. This photo shows the extensive damage imparted by the Dude Fire in this area, which was formerly a thriving ponderosa forest. View is to the northeast from the main fire control road.

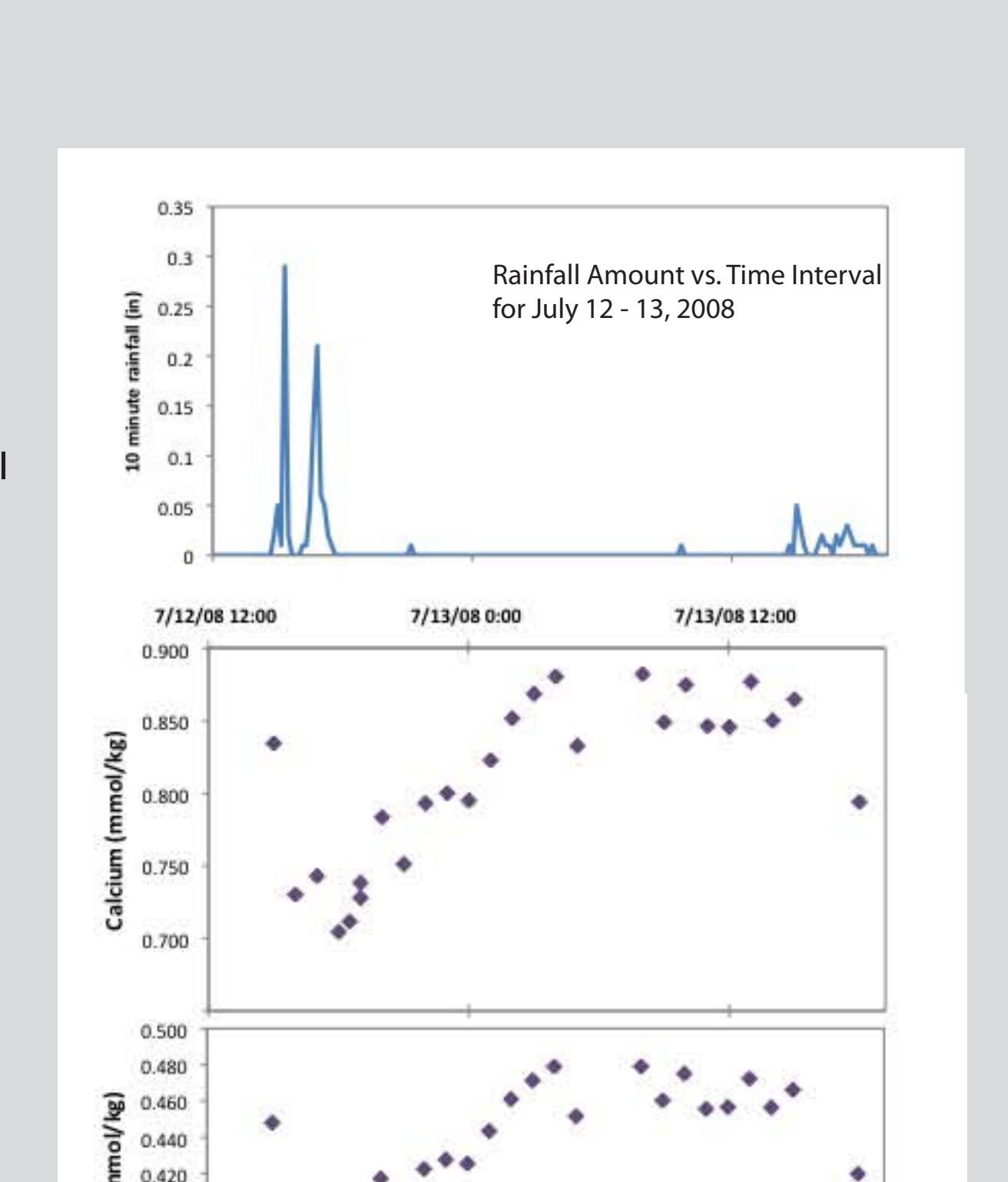


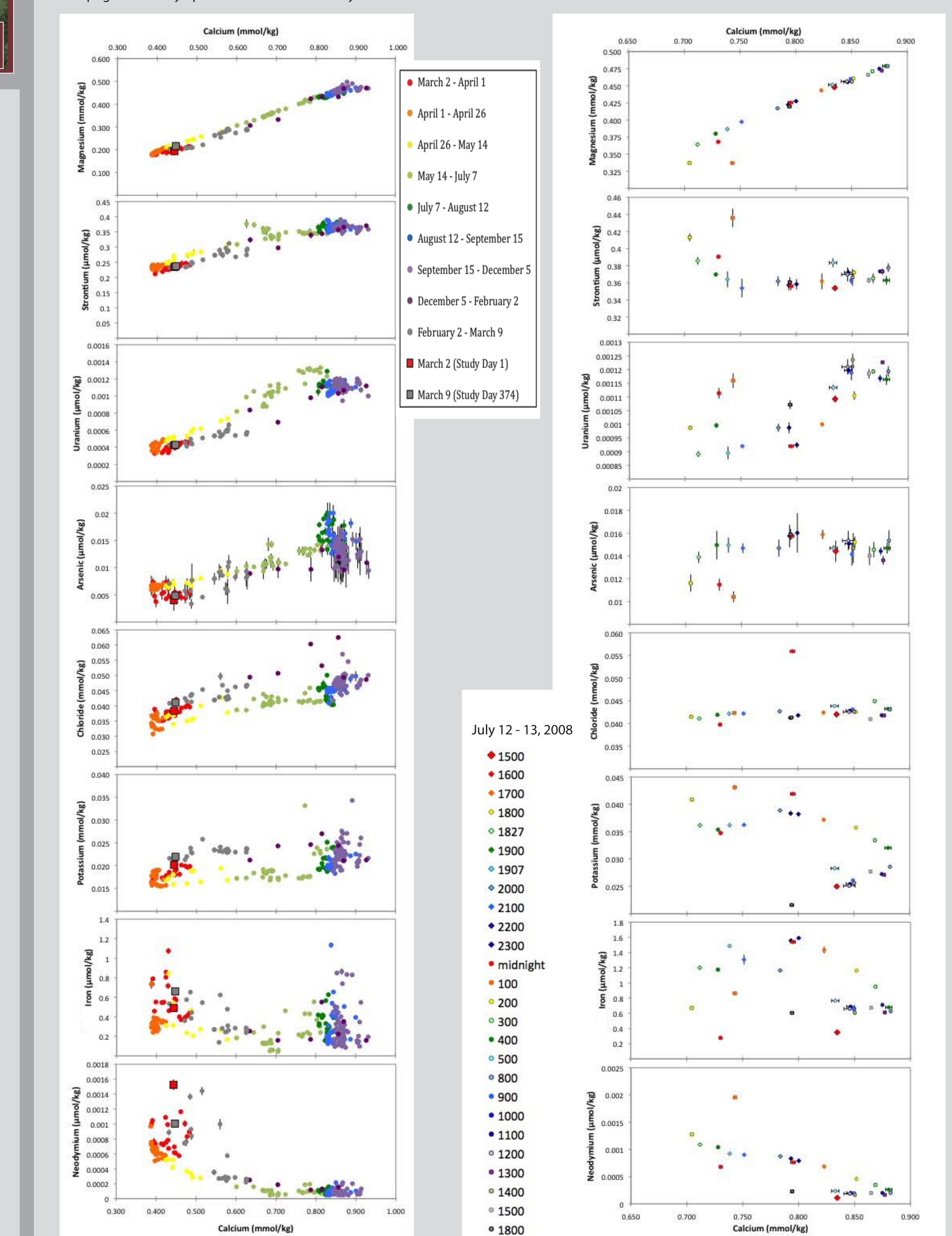
Photo 2. View westward along the Mogollon Rim. All strata pictured here are of the Supai Group. The highlighted strata are the Fort Apache limestone unit from which Bonita Creek flows and is characterized by laminated (lime-containing) limestone and dolomite. The rock strata impact stream chemistry through calcite dissolution, imparting a calcium-sulfate-bearing dominant chemistry to surface flows.

Data Trend Plotting for Source Correlation

When using data visualization techniques suggested in Rose (2003), Miller & Drever (1977) and others to determine the relationships between two chemical or hydrologic parameters or elemental concentrations, important details—sources of elements, mixing of waters of chemically different water sources, system input complexity, hysteresis trends—become easier to see. To that end, hysteresis trends of the elements of interest have been plotted against calcium on both seasonal and event-response scales in Figures 6 and 7. Seasonal data are plotted in monthly date groups that were determined by subtle changes in slope for plotted seasonal calcium data, as seen in the top of Figure 4. The data were then sorted and data points for samples collected in the afternoon between 12:00 and 5:00 pm were then plotted. The figure tend to favor a mixing trend between two chemically different sources, with markedly higher calcium concentrations in the summer and lower calcium concentrations during the winter, as limestone dissolution within the source rock is the dominating geochemical driver until snowmelt dilutes the spring water in the winter and early spring. Other elements plotted against calcium are also traceable as coming from the same source or from an alternate source depending on the overall slope trend of the data, with elements either correlative (positive slope) or anti-correlative (negative slope), respectively.

Event-driven data from July 12 - 13, 2008 are shown in Figure 7. Event data plotted for calcium vs. magnesium resembles seasonal dynamics, but calcium vs. strontium exhibits widely different behavior and is at least partially anti-correlative (negative slope). Calcium vs. uranium is strongly correlative, but data point trends are opposite between seasonal and event data, with uranium being depleted relative to calcium seasonally and enriched relative to calcium after precipitation. Calcium vs. arsenic shows an interesting departure from mid summer to late fall, when calcium continues to increase while arsenic concentrations start to fall. Calcium vs. arsenic after a precipitation event shows almost no correlation except during the rainfall event itself. Calcium vs. chloride (and sodium, not pictured here) concentrations show a somewhat correlative trend seasonally but during and after rainfall chloride concentrations remain unchanged. Calcium vs. potassium looks similar to calcium vs. chloride on a seasonal scale, but during and after rainfall trends follow a figure-8 pattern. Calcium vs. total iron shows a loose interpretation of the two end member system seasonally but the two elements are somewhat anti-correlative, while rainfall seems to cause chaos to ensue. Calcium vs. neodymium (as well as some transition metals and most rare-earth elements) show strong anti-correlative trends that are similar regardless of the time scale.

Differences in chemical dynamics between these two timescales seem to indicate that while a two end-member mixing scenario can explain seasonal changes in water chemistry, other factors seem to be impacting chemistry on precipitation-event scales. It is unclear what exactly is causing these fluctuations, but possible causes may be flushing of leaf and trunk surfaces by through-falling rain, dissolution of salts from soils, some heretofore unknown anthropogenic activity upstream or some factor as yet unknown.



Figures 6 and 7. Calcium plotted versus various elements of interest for the full study period and for during and immediately after a rainfall event on July 12, 2008. Sample dates and times are listed in each separate key.

Summary

- Seasonally, snowmelt has a profound impact on Bonita Creek, with source spring-derived elements diluted to between 25 and 50% of maximum concentrations during drier seasons. This activity creates what appears to be a two end-member mixing line between source spring water and snowmelt water when most major ions are plotted against each other.
- While seasonal trends appear to be fairly consist among elements of similar solution species (i.e. alkaline earth metals from source rocks including calcium, magnesium and strontium all have +2 charge in solution, chemically similar rare earth elements flushing through simultaneously by snowmelt), precipitation events appear to impart other chemical dynamics to the system.
- Further comparison of the two rainfall events may suggest an answer as to the auxiliary sources of strontium and a few other elements (not pictured here) that exhibit trends vastly dissimilar to seasonal trends.

Acknowledgements

The student author would like to thank Loma and Bill Glausinger, Dave Kelley, Hilairy Hartnett, Steven Semken, Jeff Havig, Xiaoding Zhuo and many other friends and colleagues for their insights and support. Thanks also to Michael Strobel from the USDA National Resource Conservation Service for his insights on the SNOTEL network. Funding for this project was provided by the Central Arizona-Phoenix Long-Term Ecological Research Summer Graduate Fellowship for Summer 2009.

References

Miller W.R. and Drever J.J. (1977) Water chemistry of a stream following a storm, Abasco mountains, Wyoming. *Geochimica et Cosmochimica Acta* 41, 1693-1702.
 Miller W.R. and Drever J.J. (1977) Chemical weathering and related controls on surface water chemistry in the Abasco Mountains, Wyoming. *Geochimica et Cosmochimica Acta* 41, 1693-1702.
 Parker S.R., Gammons C.H., Poulsen S.R. and DeGrandpre M.D. (2007) Diel variations in stream chemistry and isotopic composition of dissolved inorganic carbon, upper Clark Fork River, Montana, USA. *Applied Geochemistry* 22, 1329-1343.
 Martí E., Grimm N.B. and Fisher S.G. (1997) Pre- and post-flood retention efficiency of nitrogen in a Sonoran Desert stream. *Journal of the North American Benthological Society* 16, 805-819.
 Jones J.B., Fisher S.G. and Grimm N.B. (1996) A long-term perspective of dissolved organic carbon transport in Syncrude Creek, Arizona, USA. *Hydrobiologia* 317, 183-188.
 Blakey R.C. and Knapp R. (1989) Pennsylvanian and Permian geology of Arizona. In Jenney J.P. and Reynolds S.J., eds. *Geologic evolution of Arizona*: Tucson, Arizona Geological Society Digest 17, 313-347.
 Rose A.D. (2003) Comparative solute-discharge hysteresis analysis for an urbanized and a control basin in the Georgia (USA) Piedmont. *Journal of Hydrology* 284, 45-56.

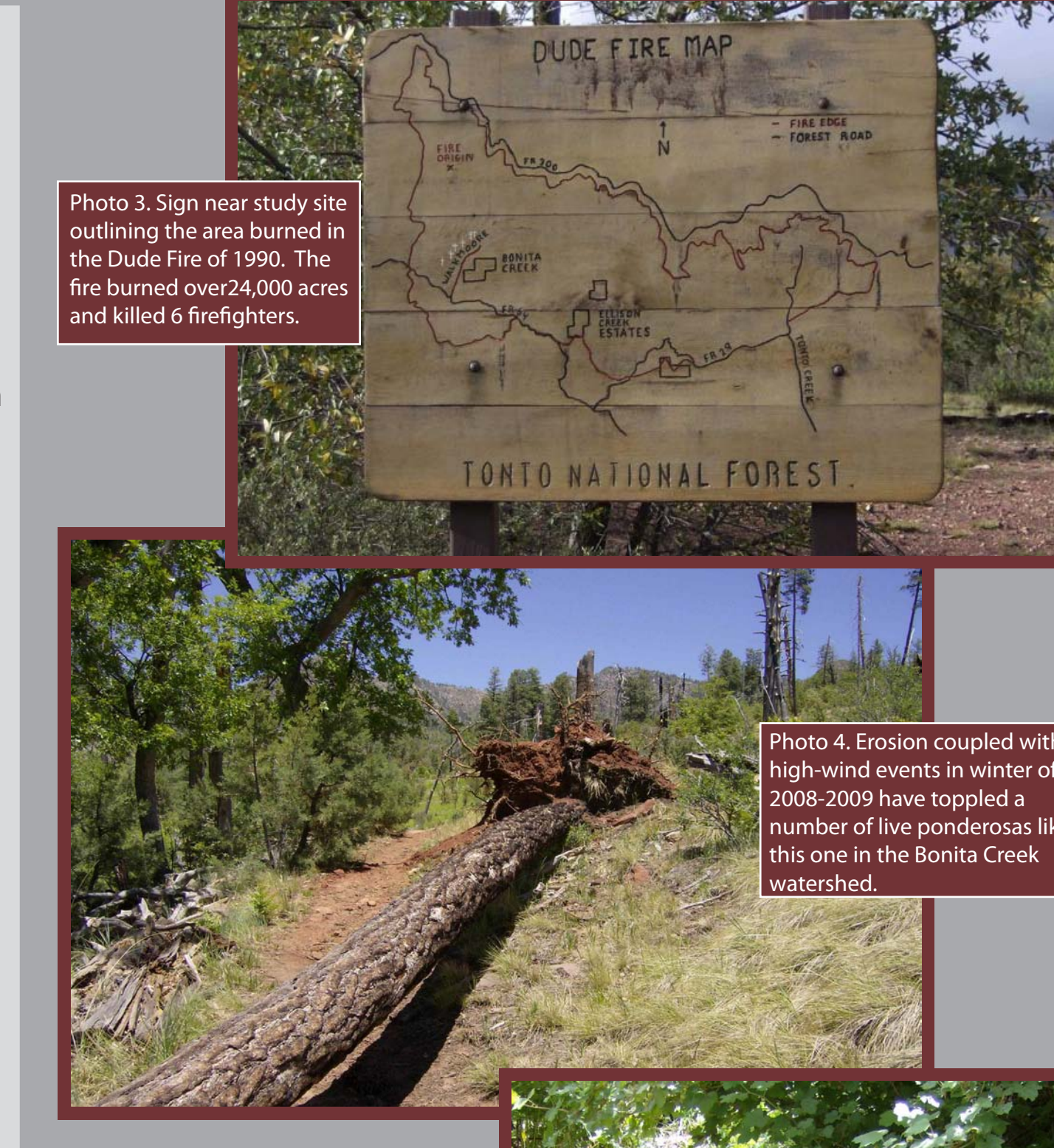


Photo 3. Sign near study site outlining the area burned in the Dude Fire of 1990. The fire burned over 24,000 acres and killed 6 firefighters.

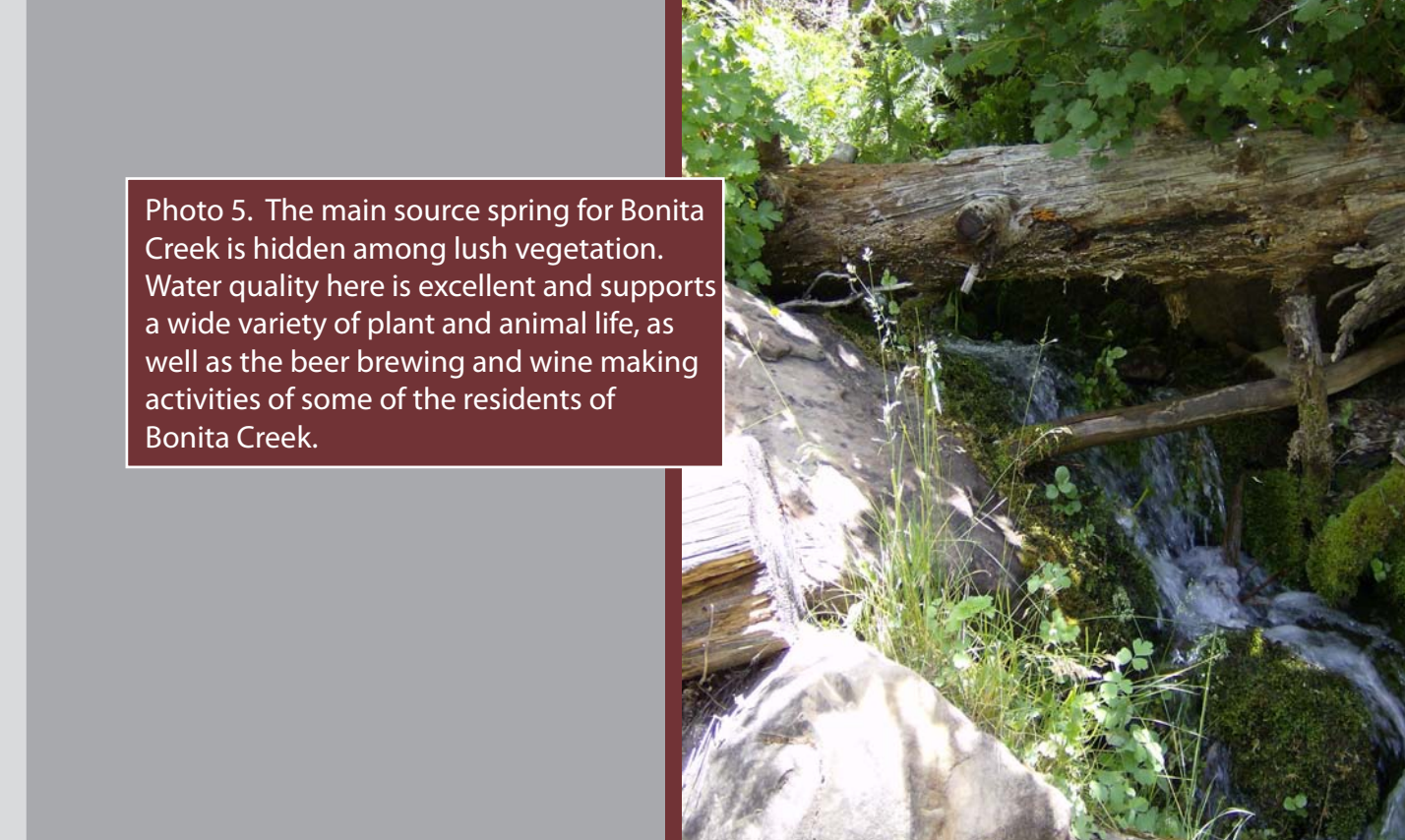


Photo 4. Erosion coupled with high-wind events in winter of 2008-2009 have toppled the number of live ponderosa like this one in the Bonita Creek watershed.



Photo 5. The main source spring for Bonita Creek is hidden among lush vegetation. Water quality here is excellent and supports a wide variety of plant and animal life, as well as the beer brewing and wine making activities of some of the residents of Bonita Creek.



Photo 6. The main water sampling area on July 12, 2008. The creek was 1.0 meters wide. The boulders circled in this photo are the same as those circled in the sequence of photos below. Note the very clear flow as well.



Photo 7. Sampling area on July 12, 2008 immediately post-storm. Note the very turbid flow over the boulder pile. Overall monsoonal precipitation events only increase discharge and turbidity for a very short period (18-24 hours before returning pre-event levels).

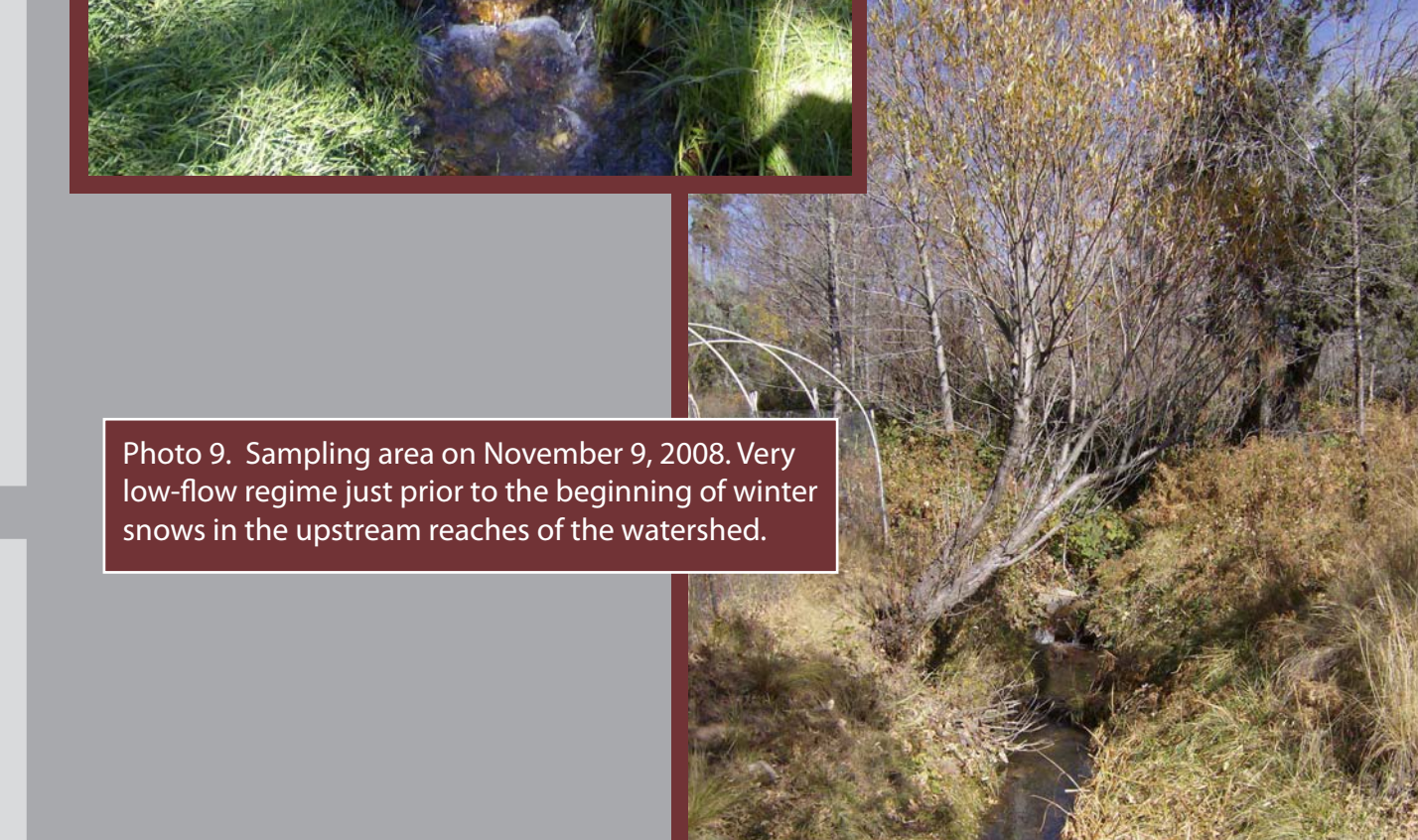


Photo 8. The sampling area on September 5, 2008. The stream is entering a low-flow regime by this time and is 0.93 meters wide at this point.



Photo 9. Sampling area on November 9, 2008. Very low-flow regime just prior to the beginning of winter snows in the upstream reaches of the watershed.



Photo 10. Sampling area on January 19, 2009. Note the blue-gray turbid quality to the creek. Flows have swollen the creek back to a width of 4.3 inches (1.10 meters) wide.