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2009-2010 PROJECTS

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Faculty: Cameron Davidson (Carleton College), Karl Wirth (Macalester College), Tim White (Penn State University) Students: Lenny Ancuta, Jordan Epstein, Nathan Evenson, Samantha Falcon, Alexander Gonzalez, Tiffany Henderson, Conor McNally, *Julia Nave, Maria Princen*

COLORADO – INTERDISCIPLINARY STUDIES IN THE CRITICAL ZONE, BOULDER CREEK CATCHMENT, FRONT RANGE, COLORADO.

Faculty: David Dethier (Williams) Students: Elizabeth Dengler, Evan Riddle, James Trotta

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Faculty: Holli Frey (Union) and Kathryn Szramek (Drake U.)

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Faculty: Connie Soja (Colgate), Paul Myrow (Colorado College), Jeff Over (SUNY-Geneseo), Chuluun Minjin (Mongolian University of *Science and Technology)*

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Faculty: Greg Wiles (The College of Wooster), Tom Lowell, (U. Cincinnati), Ed Berg (Kenai National Wildlife Refuge, Soldotna AK) *Students: Alena Giesche, Jessa Moser, Terry Workman*

SVALBARD - HOLOCENE AND MODERN CLIMATE CHANGE IN THE HIGH ARCTIC, SVALBARD, NORWAY.

Faculty: Al Werner (Mount Holyoke College), Steve Roof (Hampshire College), Mike Retelle (Bates College) Students: Travis Brown, Chris Coleman, Franklin Dekker, Jacalyn Gorczynski, Alice Nelson, Alexander Nereson, David Vallencourt

UNALASKA - LATE CENOZOIC VOLCANISM IN THE ALEUTIAN ARC: EXAMINING THE PRE-HOLOCENE RECORD ON UNALASKA ISLAND, AK.

Faculty: Kirsten Nicolaysen (Whitman College) and Rick Hazlett (Pomona College) Students: Adam Curry, Allison Goldberg, Lauren Idleman, Allan Lerner, Max Siegrist, Clare Tochilin

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Keck Geology Consortium: Projects 2009-2010 Short Contributions – OREGON

WEATHERING OF A VOLCANIC LANDSCAPE: THE GEOCHEMISTRY OF THE DESCHUTES RIVER WATERSHED, CENTRAL OREGON.

Project Faculty: *HOLLI FREY*, Union College & *KATHRYN SZRAMEK*, Drake University

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LIVIA CAPALDI: Oberlin College Research Advisor: Steven Wojtal

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MATTHEW HARWARD: University of North Carolina at Charlotte Research Advisor: Dr. Martha C. Eppes

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MATTHEW KISSANE: Union College Research Advisor: Holli Frey

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ASHLEY MELENDEZ: California State University, Fullerton Research Advisor: Brandon Browne

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JULIA SCHWARZ: Carleton College Research Advisor: Cameron Davidson

ALKALINITY AND DISSOLVED ORGANIC CARBON IN SURFACE WATERS OF THE DESCHUTES DRAINAGE BASIN, OREGON

LAUREN WERCKENTHIEN: DePauw University Research Advisor: Dr. James G. Mills, Jr.

Funding provided by: Keck Geology Consortium Member Institutions and NSF (NSF-REU: 0648782)

Keck Geology Consortium Franklin & Marshall College PO Box 3003, Lancaster Pa, 17603 Keckgeology.org

ALKALINITY AND DISSOLVED ORGANIC CARBON IN SURFACE WATERS OF THE DESCHUTES DRAINAGE BASIN, OREGON

LAUREN WERCKENTHIEN

DePauw University Research Advisor: Dr. James G. Mills, Jr.

INTRODUCTION

Weathering of silicate rock has a large impact on the carbon cycle within drainage basins. In aqueous systems, carbon can occur in organic and/or inorganic forms. The most common form of inorganic carbon in natural water is $HCO₃$ ⁻ (Langmuir, 1997). The weathering of silicate rock results in the formation of HCO_3^- due to consumption of atmospheric CO_2 (as per the equations below) (Berner, 1995):

$$
2 CO_{2} + 3 H_{2}O + CaSiO_{3} \rightarrow
$$

\n
$$
Ca^{2+} + 2 HCO_{3} + H_{4}SiO_{4}
$$

\n
$$
2 CO_{2} + 3 H_{2}O + MgSiO_{3} \rightarrow
$$

\n
$$
Mg^{2+} + 2 HCO_{3} + H_{4}SiO_{4}
$$

The resulting bicarbonate ions are then transported by streams back to the oceanic reservoir. Many researchers have shown that this HCO_{3}^{-} combined with $Ca²⁺$ can form ca-carbonate within the oceans. This acts as a geologic sink for atmospheric CO_2 . (Kump et al., 2000) Weathering rates therefore have a significant impact on global atmospheric CO₂ changes (Gaillardet et al., 1999). Weathering rates can be dependent on various factors, including continental land area, lithology, mountain uplift, climate and vegetation (Berner, 1995).

Dissolved organic carbon (DOC) is also a key component of the carbon cycle. The ability of DOC to transport different elements and its ability to facilitate mineral weathering makes it a significant geochemical compound for study, for example, iron is transported in association with DOC (Vestin et al., 2008; Björkvald et al., 2008). Concentrations of DOC vary by aquatic environment. Generally,

groundwater has a lower concentration of DOC, because it is a food source for heterotrophic microbes, and, contains less decayed organic material. Streams have a larger concentration of DOC due to the larger contribution of plant material, marsh and bog waters have extremely high DOC levels (15-30 mg/l), rivers have lower DOC levels (5 mg/l), and precipitation has DOC levels of less than one mg/l (Eby, 2004). Previous studies have shown that at periods of high river discharge DOC concentrations increase (Björkvald et al., 2008).

This study seeks to examine how mineral weathering relates to the short-term carbon cycle by analyzing DOC and elemental data from stream and spring samples within the Deschutes River basin in Central Oregon.

The Deschutes drainage basin in central Oregon covers approximately 27,195 km² (U.S.G.S. NWIS, July 2009). The basin drains the eastern side of the Cascade Mountains in Oregon and flows north into the Columbia River. Land use and vegetative cover in the basin consists primarily of managed forest and minor cropland with bedrock consisting primarily of Tertiary and Quaternary volcanics. The months of June and July are wetter than August, and, the eastern-most region of the basin receives less precipitation (and has higher rates of evapotranspiration) than the western-most region (2000-2008, 208.59 cm and 1861.89 cm respectively) (NADP/NTN, US Bureau of Reclamation: Agri-Met). Other notable features within the basin are the Three Sisters Volcanoes, which are active and located on the western edge of the basin and Newberry Volcano, which is located in the south-central part of the basin.

METHODOLOGY

51 streams and 14 springs within the Deschutes River Watershed were sampled between June 24 and July 6, 2009 and 25 streams were again sampled between August 11 and 13th, 2009. Water sampling sites were chosen for three primary reasons; accessibility of sample sites, sampling the drainage of various lithologies in the basin, and sampling streams above and below tributaries. Water samples were collected in 30 ml high-density polyethylene bottles for alkalinity (HCO₃), ion chromatography (IC), and inductively coupled plasma mass spectroscopy (ICP-MS). The ICP-MS samples were preserved by the addition of nitric acid.

A basin-wide subset of the sample sites were utilized for collecting DOC samples (Fig. 1). The DOC samples were filtered with 0.45-micron nylon filters into glass boston round bottles (hydrochloric acid

was added to drive off dissolved inorganic carbon). Alkalinity was measured using the Gran titration method (Gran et al., 1981). The samples were within the error of the measurement.

GIS maps are used to show sampling locations and concentrations of alkalinity and DOC spatially throughout the basin using the geology to make potential geochemical correlations (Figs. 1, 2). Stream and lake files are from Census 2000 TIGER/ Line Data. The geologic map shapefile is from The USGS's Mineral Resources On-Line Spatial Data. All other files are from the National Atlas.

RESULTS

90 values of alkalinity were collected throughout the basin, 65 of which were sampled in late June through early July 2009 (0.07 to 6.68 meq/l); the remaining 25 were sampled in August 2009 (0.07 to 6.88 meq/l)(Fig. 2; Table 1). All 86 samples were

Figure 1. Dissolved Organic Carbon concentrations for springs and streams in the Deschutes Basin, Oregon. The base map shows general geologic units across the basin.

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also analyzed for Fe, Mg, Na, K, Ca, Cl, and SO_4 (Table 1).

62 water samples for DOC were collected and analyzed, 37 of which were sampled in late June through early July 2009 (0.68 to 8.94 mg/l); the remaining 25 were sampled in August 2009 (0.637 to 11.1 mg/ l)(Fig. 1; Table 1).

DISCUSSION

Alkalinity

Alkalinity concentrations were divided into four groups based on natural breaks in the data: low (less than 0.44 meq/l), moderately low (0.44-0.85 meq/l), moderately high (0.86-2.0 meq/l) and high (greater than 2.0 meq/l) (Table 1). Only six of the total 65 sampling locations are in the high alkalinity group. All six of these sampling locations occur in the northern and eastern part of the basin with the exception of one site, Paulina Creek, which is located

in south-central part of the basin. The proximity of Paulina Creek to Newberry Volcano may be contributing to the high alkalinity value through interaction with volcanic rock.

Three hypotheses are proposed to explain the higher alkalinity values on the north and eastern side of the basin. First, the rocks on the northern and eastern region of the basin are generally older than those in the rest of the basin. The sampling sites with high alkalinities on the northeastern and eastern region of the basin are in most cases passing through rock of Paleocene to Early Oligocene age (some Late Triassic, Miocene and Pliocene rocks also occur here). On the western side of the basin the sample sites are draining rock of mostly Pleistocene to Holocene age. The older rock is most likely more weathered than the younger rock, which may be contributing to the range in alkalinity values. During the rock weathering process atmospheric CO₂ is consumed and is converted in the surface waters to dissolved HCO_3^- (Berner, 1995). Secondly, the rock in the northern

Figure 2. Alkalinity concentrations for springs and streams in the Deschutes Basin, Oregon. The base map shows general geologic units across the basin.

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 Table 1. Geochemical data for springs and streams in the Deschutes Basin, Oregon.

Figure 3. Geochemical correlation of alkalinity and Dissolved Organic Carbon with Fe, Mg, K, and Cl for springs and streams in the Deschutes Basin, Oregon.

and eastern parts of the basin are not of the same lithology as in the rest of the basin. A large portion of the sampling sites occur along the Little Deschutes

River which starts in the southwestern part of the basin and travels through a large region of Pleistocene clay and mud (yellowish-gray color section on

Figure 2). On the eastern side of the basin the rocks are mostly andesite, dacite and basalt. The range of composition and age of the rocks within the basin could result in different weathering rates and therefore different alkalinities. Thirdly, the eastern-most region of the basin receives the least precipitation and undergoes higher rates of evapotranspiration than the rest of the basin (NADP/NTN, US Bureau of Reclamation: AgriMet). To further test this third hypothesis, discharge data for streams in the eastern and western region of the basin could be determined and water samples could be analyzed for elemental concentrations. Looking at the elemental data to discharge ratios could provide further insight into this hypothesis.

There were 18 sampling locations that were sampled in late June and early July 2009 and sampled again in August 2009. Of these 18 sites, five of the samples had significant increases in alkalinity and 13 had significant decreases in alkalinity. These variations appear to be random across the basin, which implies that local changes are occurring to cause this temporal variation in data values.

Dissolved Organic Carbon (DOC)

DOC concentrations were divided into four groups based on natural breaks in the data: low (less than 1.49 mg/l), moderately low (1.49-2.72 mg/l), moderately high (2.73-4.67 mg/l) and high (greater than 4.67 mg/l). After reviewing Google Earth™ and GIS maps (which accounts for land use, geology and geographic location in the basin), the sample sites with moderately high and high DOC values, are controlled by marshy areas, decaying vegetation and/or agriculture. For example, a sample site located along the South Fork of the Crooked River, in the eastern part of the basin has the highest DOC value of all samples $(7/3/09 = 8.94 \text{ mg} / \text{l}; 8/12/09 =$ 11.1 mg/l). There is heavy agriculture upstream of the sampling location and near the sampling location itself. In addition, there is a hay facility just upstream of the sample site. At the facility there is a barn with effluent fluid coming out of it (which can be seen on Google Earth™). This heavy agriculture and the presence of effluent fluid may contribute to

the high DOC value at this sampling location. The South Fork of the Crooked River (which connects to the North Fork of the Crooked River) also has a high DOC (7/3/09 = 5.87 mg/l). This may also be due to agricultural inputs from the North Fork of the Crooked River. The Crooked River was sampled a few miles downstream from this confluence and it also had a high DOC $(7/3/09 = 5.68 \text{ mg/l})$ but the concentration is lower than that of the South Fork and North Fork of the Crooked River. At another sampling point located along the Little Deschutes River in the southwest corner of the basin was very swampy with a lot of vegetation and fallen logs; this can account for the high DOC level $(6/30/09 = 7.38)$ mg/l).

The sample sites with lower DOC values tend to be in areas with less vegetation. For example, a site along Snow Creek had low DOC levels (6/28/09 = 0.727 mg/l). Water at this site originates as snow melt and travels through poorly vegetated lava flows. Many of the sampling sites with low DOC levels were located near the Three Sisters Volcanoes or were in sparsely vegetated areas.

The majority of the springs have low to moderately low DOC values except for three springs sampled on the northeastern side of the basin, a spring next to a logging area and two springs in a marshy area.

There were 12 sampling locations that were sampled in late June and early July 2009 and sampled again in August 2009. Of these 12 sites, four of the samples had significant increases in DOC, seven had significant decreases in DOC and one remained fairly constant. These variations appear to be random across the basin. A preliminary hypothesis would suggest that localized precipitation is flushing the DOC from the system creating increases in DOC concentration and in areas with little to no precipitation, the DOC concentration decreases.

Geochemical Correlation of Alkalinity and DOC to Other Elements

There is a positive correlation between alkalinity and Fe, Cl, SO_4 , Na, K, Ca and Mg, other elements such

as Al and Si show weak to no correlation with alkalinity (Fig. 3). In Figure 3a, there is a small range of alkalinity values; however, around 100 ppm Fe there is a large spread of alkalinity values. In Figures 3b and 3c, correlation of higher alkalinity with higher Mg and K values is used to suggest that the waters in the northern and eastern region of the basin have different residence times which may affect water/ rock interaction times, weathering and evaporation rates. Na and Ca data mimic the Mg and K data trends (Figs. 3a, 3b). Two parallel data trends for alkalinity vs. Cl in Figure 3d are interpreted to be the result of different, unidentified geochemical processes/sources affecting the waters. The data points on the higher Cl concentration trend are from the Crooked River and the South Fork of the Crooked River. The lower Cl concentration trend is from Paulina Creek, Bandit Spring, and Ochoco Creek (Table 1). SO_4 data mimic the Cl data trends (Fig. 3d).

There is a positive correlation between DOC and Fe, Cl, SO_4 , Na and K, other elements, such as Al, Ca, Mg and Si show weak to no correlation with DOC. Figure 3e shows a positive correlation between Fe and DOC as noted in other studies and a weaker positive correlation with Mg (Fig. 3f) (e.g. Björkvald et al., 2008; pers. comm., 2010, Szramek). In Figure 3g, K (and Na) and DOC show a weak positive correlation. Two parallel data trends for DOC vs. Cl in Figure 3h are interpreted to be the result of climatic differences within the basin. The data points on the higher Cl concentration trend are from the Crooked River and South Fork of the Crooked River. The lower Cl concentration trend is from the North Fork of the Crooked River and two locations in the southwestern region of the basin. Although precipitation across the basin has similar Cl concentrations (June-August 2008; 0.080 to 1.02 ppm), increased evaporation in the northern and eastern portion of the basin may contribute to the higher Cl values in water samples from this region (NADP/NTN). During precipitation events flushing of DOC and Cl most likely occurs. SO_4 data mimic the Cl data trends (Fig. 3h).

CONCLUSIONS

Alkalinity and DOC concentrations most likely vary across the Deschutes basin in response to changes in land use, geology and climatic variation. Higher alkalinity concentrations in the northern and eastern parts of the Deschutes Basin are most likely due to the presence of older, more weathered volcanic rock as compared to other parts of the basin. Additionally, the drier climate in the eastern part of the basin may lead to higher evaporation rates causing enhanced alkalinity values in samples from this region. Random temporal variations in alkalinity values from June to August also occur throughout the basin but the cause is unknown.

High DOC concentrations in the basin are located near marshy areas and areas where there is decaying vegetation and/or agriculture. Areas of low DOC concentrations occur where there is less vegetation and/or snow melt, such as recent lava flows near the Three Sisters Volcanoes. Temporal variations in DOC concentrations within the basin are most likely due to localized variations in precipitation. General geochemical correlation of alkalinity and DOC with various elements is probably related to weathering rates, climatic variation, and geochemical processes.

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