HYDROLOGICAL PROCESSES
Hydrol. Process. **23**, 2987–2996 (2009)

(www.interscience.wiley.com) DOI: 10.1002/hyp.7418

Trace element and major ion concentrations and dynamics in glacier snow and melt: Eliot Glacier, Oregon Cascades

Sarah K. Fortner,* W. Berry Lyons, Andrew G. Fountain, Kathleen A. Welch and Natalie M. Kehrwald

The Ohio State University, Byrd Polar Research Center, Columbus, OH 43210, USA

Abstract:

We present concentrations of environmentally available (unfiltered acidified 2% v/v HNO_3) As, Cu, Cd, Pb, V, Sr, and major ions including Ca^{2+}, Cl^-, and $SO_4{}^{2-}$ in a July 2005 and a March 2006 shallow snow profile from the lower Eliot Glacier, Mount Hood, Oregon, and its proglacial stream, Eliot Creek. Low enrichment factors (EF) with respect to crustal averages suggests that in fresh March 2006 snow environmentally available elements are derived primarily from lithogenic sources. Soluble salts occurred in lower and less variable concentrations in July 2005 snow than March 2006. Conversely, environmentally available trace elements occurred in greater and more variable concentrations in July 2005 than March 2006 snow. Unlike major solutes, particulate-associated trace elements are not readily eluted during the melt season. Additionally, elevated surface concentrations suggest that they are likely added throughout the year via dry deposition. In a 1-h stream sampling, ratios of dissolved ($<0{\cdot}45$ μm) $V:Cl^-$, $Sr:Cl^-$, and $Cu:Cl^-$ are enriched in the Eliot Stream with respect to their environmentally available trace element to Cl^- ratios in Eliot Glacier snow, suggesting chemical weathering additions in the stream waters. Dissolved $Pb:Cl^-$ is depleted in the Eliot Stream with respect to the ratio of environmentally available Pb to Cl^- in snow, corresponding to greater adsorption onto particles at greater pH values. Copyright © 2009 John Wiley & Sons, Ltd.

KEY WORDS trace elements; glacial melt; Pacific northwest; dry deposition; snow chemistry

Received 6 September 2008; Accepted 16 June 2009

INTRODUCTION

Because glacier melt feeds downstream ecosystems, it is essential to characterize the geochemistry of snow and glacier melt. This is especially in true in regions like the Pacific Northwest where the timing and availability of glacier and snowmelt is dynamic. This paper begins to establish the relation between environmentally available elements in fresh and ablation glacier snow and dissolved elements in proglacial melt in the Oregon, Cascades at Eliot Glacier, Mount Hood (45° 22′N; 121° 42′W). This study is among the few studies that have compared concentration differences of trace and minor elements in both fresh and melting snow (Abrahams *et al.*, 1988; Mitchell *et al.*, 2001b; Mitchell *et al.*, 2006; Mitchell and Brown, 2007). This study includes an assessment of natural *versus* anthropogenic contributions of trace elements in fresh unaltered snow from a single snow event. The primary goal is to begin to quantify and compare trace element concentrations in a shallow snowpit collected from both fresh and ablation snow and in 10 discreet samples of proglacial stream water. Much more work is needed to characterize variation in trace element deposition and release from snow and proglacial melt over the course of a single year or multiple years. The Pacific Northwest is a unique Northern Hemisphere glacier site for new trace element studies given its high winter snow accumulation and long ablation/melt season (Mote, 2003).

Previous studies of snow chemistry in the Northern Hemisphere have largely focused on the deposition of natural and anthropogenic acids during the winter and their rapid elution during early spring melt (Brimblecombe *et al.*, 1986; Tranter *et al.*, 1987; Bales *et al.*, 1989; Williams and Melack, 1991). Yet, little is known about how concentrations and distributions of environmentally available trace and minor elements change throughout the melt season. Environmentally available (acidified 2% v/v HNO_3) concentrations of As, Cu, Cd, Pb, Sr, and V are derived from both dissolved and readily soluble particulate-associated trace elements. These elements were selected for their distinct behaviours. In oxygenated acidic stream conditions, oxyanion forming As and V are primarily associated with the particulate phase (Johannessen *et al.*, 2000). Conversely, Cu, Cd, Pb, and Sr occur mostly in the dissolved form (Astrom and Bjorklund, 1995; Bibby and Webster-Brown, 2006). Therefore, concentrations of environmentally available Cu, Cd, Pb, and Sr may be distinct from oxyanion-forming elements such as As and V in fresh *versus* ablations snow. These examinations build from a previous laboratory study on dissolved element concentrations in melting snow, which established that elevated concentrations of dissolved Cd and Mn are released in the first fraction of snowmelt (Abrahams *et al.*, 1988).

In addition to examining concentrations of environmentally available trace elements in fresh and ablation

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* Correspondence to: Sarah K. Fortner, The Ohio State University, Byrd Polar Research Center, 1090 Carmack Rd, Columbus, OH 43210, USA. E-mail: fortner.27@osu.edu

snow, a one-time sampling of dissolved ($<$0·45 μm) trace elements in the proglacial melt stream that drains the Eliot Glacier was conducted. The primary objective of these samples was to begin to assess the geochemical processing that occurs from glacial snow to melt as water : rock ratios increase. Concentrations of minor and trace elements in temperate glacial meltwater have been investigated in only the Swiss Alps and Yukon, Alaska (Brown *et al.*, 1998; Mitchell *et al.*, 2001a,b; USGS, 2003, 2005). Elemental concentrations in supraglacial meltwater are usually distinct from sub- and proglacial meltwater, where higher rock : water ratios exist (Tranter *et al.*, 1993; Hodgkins *et al.*, 1997; Brown *et al.*, 2001; Mitchell *et al.*, 2001b). At the Haut Glacier, d'Arolla, Switzerland, proglacial streams have elevated dissolved Al, Ti, Fe, Rb, Co, and Ni, with respect to world river-water averages, and these enrichments are attributed to silicate and sulfide mineral weathering of complex metamorphic rocks in the glaciated basin (Brown *et al.*, 1998; Mitchell *et al.*, 2001b). In the Swiss glacier meltwaters, the dissolved alkaline-earth elements Sr and Ba were an order of magnitude lower than the average stream and lake concentrations, likely reflecting the prevalence of silicate over carbonate weathering in the basin (Brown *et al.*, 1998).

CLIMATE AND SITE DESCRIPTION

Coastal regions in the Pacific Northwest (PNW) are characterized by their high precipitation. Regions of greatest annual precipitation include the western Oregon Cascades, with Mount Hood (3425 m) receiving over 500 cm annually with most occurring as snow (JISAO/SMA Climate Impacts Group, 1999). Most precipitation occurs between September and March, with high pressure keeping weather clear in the late spring and summer (JISAO/SMA Climate Impacts Group, 1999). Over the last century, temperatures in the PNW have warmed by an average of 0·8 °C, with precipitation increasing up to 40% (JISAO/SMA Climate Impacts Group, 1999). Mount Hood exceeds this average, having warmed almost 3 °C, with the greatest increase observed during the summer with temperatures increasing from 5·6 to 8·8 °C between 1902 and 2002 (Daly *et al.*, 1997). High winter precipitation rates coupled with rapid spring melt make Mount Hood an ideal location for an examination of the processing of environmentally available elements that occurs between fresh and ablation snow.

Mount Hood is an andesitic stratovolcano (Cribb and Barton, 1997) located 75 km southeast of Portland, a city of over 500 000 residents with over 2 million including its suburbs (Population Research Center PSU, 2005). Glaciers on Mount Hood are in disequilibrium and are rapidly losing volume and area. Between 1901 and 2001, these glaciers lost 31% of their area (Jackson and Fountain, 2007). Between 1901 and 2001, Eliot Glacier lost 775 m in length (Lillquist and Walker, 2006). Presently, Eliot Glacier is less than 1·6 km^2, 3·6 km long, and 800 m at its greatest width (Jackson, 2007) (Figure 1). The glacier response observed in the Cascades is consistent with worldwide loss of mountain glaciers (Dyurgerov and Meier, 2000).

Less glacial melt coupled with earlier snowmelt will affect agriculture and industries in the PNW. For example, Eliot Glacier meltwater flows into Eliot Creek, which is mostly diverted into holding ponds for summertime agricultural use (Lundstrom, 1992). The amount and timing of glacier melt affects the availability of Eliot Creek waters for agriculture as well as the amount of water that is discharged into the Hood River. Furthermore, the link

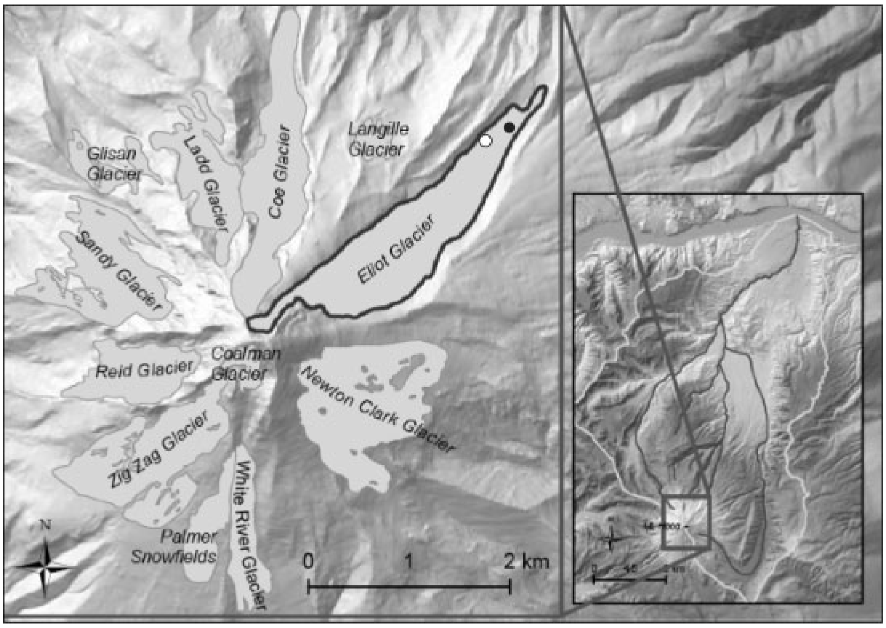

Figure 1. (modified from Jackson, 2007). Eliot Glacier Mount Hood, Oregon. July 2005 snow profile site indicated with a black circle. March 2006 snow profile site indicated with a white circle

between glacial melt and geochemistry need to be understood as it is unknown how downstream locations will be affected by diminishing glacial melt contributions (Hall and Fagre, 2003).

METHODS

Snow and melt samples were collected from Eliot Glacier, which is located on the northeastern flanks of Mount Hood (Figure 1). Thirty trace element and major ion samples were obtained in approximately 4–18-cm increments from two 1-m deep snowpits on 18 July 2005 and 11 March 2006 (Figure 1). In the July 2005, snow sampling increments were chosen above and below melt-refreeze areas that were too dense to sample using clean methods. Snowpits were not exactly in the same location given the low visibility of the sampling date (11 March) resulting in safety concerns. Yet, snowpit sites were selected in close proximity (~0·3 km) to each other. Sites were both above the tree line and with the same slope (<10°) and southeasterly aspect (Figure 1). These dates were selected to capture representative snow chemistry in the summer after most of the spring melt season occurred and during a fresh snow event. Ten meltwater samples for trace element and major ion analyses were collected at five sites within 0·5 km of each other on 19 July 2005 from the uppermost Eliot Stream, or less than 1 km from the terminus of Eliot Glacier.

LDPE Nalgene 60-ml bottles were used for both snow and stream water sample collection, as these have been effectively utilized in low-concentration snow and ice work (Barbante *et al.*, 1999a). Bottles for major ion and trace metal collection were rinsed three times with 18 MΩ deionized (DI) water to remove particulate matter and soaked overnight in DI water. Major ion bottles were later air-dried, capped, and stored in plastic bags. Trace element bottles were immersed in a 10% (v/v) Fisher trace-metal-grade HCl/DI covered bath for 1 week. Bottles were then rinsed three times with DI water and filled with 10% (v/v) Fisher trace-metal-grade HNO_3/DI water for a minimum of 1 week. Finally, bottles were rinsed three times with DI water and filled with 1% ultraclean Optima grade HNO_3/DI water and stored in plastic bags until transported. Bottles were transported in triple-bagged plastic bags after acid was removed, and utilized in the field within five days. Bottle cleaning methods were based on a proven trace-metal analytical method resulting in low blanks (Gardner and Carey, 2004).

Glacier meltwater trace-metal samples were collected in the field by first rinsing the bottles three times before collection and using 'clean hands, dirty hands' techniques (Fitzgerald, 1999). Sample gloves were changed between each collected sample. The 'dirty hands' person opened the two outermost plastic bags, while the 'clean hands' person opened the innermost plastic bag and took the sample, capped it, and returned the sample to the bag to be resealed in all three plastic bags. Clean hands, dirty hands techniques were also utilized during the snow sampling. During snow sampling, special precaution was taken to sample on the upwind side of the snowpit. The sample collection was accomplished by a team of two people wearing non-particulating Tyvek suits and Nitrile polyethelyne sampling gloves (Fitzgerald, 1999). After completing the sample collection for trace elements, major ion sampling was conducted. All snow and stream samples were shipped at on ice overnight to the Byrd Polar Research Center at The Ohio State University. The samples were then stored in the dark at 2 °C in their original bags. Glacier snow and ice samples are not typically filtered because it is easy to introduce contamination from filtration in low-concentration samples (Barbante *et al.*, 1999b).

Stream trace and major element samples were filtered using 0·45-μm pore size Nuclepore polycarbonate membrane filters and then acidified to 2% (v/v) using Optima HNO_3within 2 days of collection. Trace-metal stream samples were filtered using triple-acid-cleaned (10% HCl, 10% HNO_3, 1% Optima HNO_3) filter towers into clean bottles (Gardner and Carey, 2004). Major ion stream samples were filtered through nonacidified DI water-washed towers. Snow samples were shipped and acidified as described above but were not filtered. Because these acidified samples include dissolved colloidal metal as well as metal absorbed on particles, or dissolved from the particles, the subsequent concentrations are termed 'environmentally available' (Lyons *et al.*, 1983). One sample each of surface fresh snow, surface ablation snow, and stream was analysed for pH using a Beckman Coulter F200 pH meter. Major ion analyses were conducted using a Dionex-120 ion chromatograph (IC) with a sample loop of 400 μl for samples using methods outlined by Welch *et al.* (1996). A stock standard solution was created from single element standards, which were used to create seven calibration standards with a range bounding the sample concentrations (Welch *et al.*, 1996). Sample precision was typically better than 1% and never worse than 5% relative standard deviation (RSD). For stream samples, HCO_3^- was calculated by summing the cation equivalents (Ca^{2+}, K^+, Mg^{2+} Na^+) and subtracting the anion equivalents (Cl^-, NO_3^-, SO_4^{2-}, F^-) using the methods of Lyon *et al.* (1998).

A Thermo Finnigan Element 2 inductively coupled plasma sector-field mass spectrometer (ICP-SF-MS) was used for trace element analyses. External standards were run every three to four samples to correct for instrumental drift and to calculate precision. RSD values derived from three check standards repeated three to four times averaged 5%, and never exceeded 10%. Accuracy was better than 8% for all elements as determined by running certified reference material NWRI TM-RAIN 95, trace-metal fortified rainwater, between every six samples, including blanks.

Trace-element samples were handled and filtered entirely in a Class 100 laminar flow hood using Nitrile polyethelyne gloves. Certified concentrations of all measured trace elements gained through the addition of

Table I. Elements analysed based on best isotopic resolution, calibration curve success, and low spectral overlaps (Gabrielli *et al.*, 2006a)

Element (isotope)	ICP-MS resolution	Optima HNO_3 (pM)	HNO_3 additions (pM)	DL (pM)	DI blank	Method blank (pM)
As (75)	LR	270	0·3	90	<DL	880
Sr (86, 88)	LR	11	0·0	190	<DL	5400
Cd (111, 114)	LR	90	0·1	30	80	<DL
Pb (206, 207, 208)	LR	50	0·1	10	20	10
V (51)	MR	200	0·2	20	190	<DL
Cu (63)	MR	310	0·4	40	60	610

Optima HNO_3 certified trace metal concentrations and calculated HNO_3 metal additions in samples and blanks. Detection limits (DL) are calculated as 3 times the standard deviation of the instrument response to DI water. High DI water and method blanks are listed if above the detection limit. These values were subtracted from snow and stream samples respectively.

Optima nitric acid were far below the detection limits, and therefore insignificant in terms of their trace-metal contributions (Table I). Method blanks were collected by opening pre-cleaned bottles in the field, capping them, and transporting them back to the lab where they were filled with DI water and filtered and analysed in the same manner as the stream samples. This method blank allowed for any lab or filtration contamination to express itself. Method blanks were significantly higher than the instrument detection limit for most elements (Table I), and therefore we considered method blank to be the detection limit.

RESULTS

Surface snow pH values were 5·4 and 5·8 from the March and July samples respectively. Ca^{2+}, Cl$^-$ and SO$_4{}^{2-}$ concentrations in Eliot Glacier July 2005 and March 2006 snow are shown at depth (Figure 2). Note that all July 2005 major ion concentrations were below 1·4 μM, while in March 2006 Ca^{2+} ranged from 0·2 to 7·5 μM, Cl$^-$ ranged from 0·8 to 150 μM, and SO$_4{}^{2-}$ ranged from 0·2 to 15 μM. Unlike major ion concentrations, environmentally available element concentrations were typically lower in the March 2006 snow than the July 2005 snow (Figure 3). Cd was below the limit of detection in all samples except the top two samples in March snow, and is not compared. In the July 2005 snow, the greatest environmentally available element concentrations occurred at the surface and above an ice lens at 40 cm. Although the environmentally available element concentrations overall had greater mean concentrations in the July snow, there was substantial variation at depth. Throughout the July 2005 snow profile, As concentrations ranged from 0·2 to 2·1 nM, Cu ranged from <0·04 to 35 nM, Pb ranged from 0·23 to 10 nM, Sr ranged from 0·7 to 80 nM, and V ranged from <0·02 to 26 nM. The three Cu and V samples that were below detection limits occurred at the same sampling depths of 25, 33, and 92 cm.

In the March 2006 snow, the greatest environmentally available As, Cu, Pb, and V concentrations occurred at a depth of 15 cm. Similarly, the greatest Ca^{2+} and SO$_4{}^{2-}$ concentrations occurred at 15 cm (Figure 2). Concentrations of environmentally available Cu, Pb, and V were below detection in the 65–90-cm depth range (Figure 3). Because it snowed for several days prior to our March 2006 sampling, this snowpit likely only characterizes one or part of one snow event.

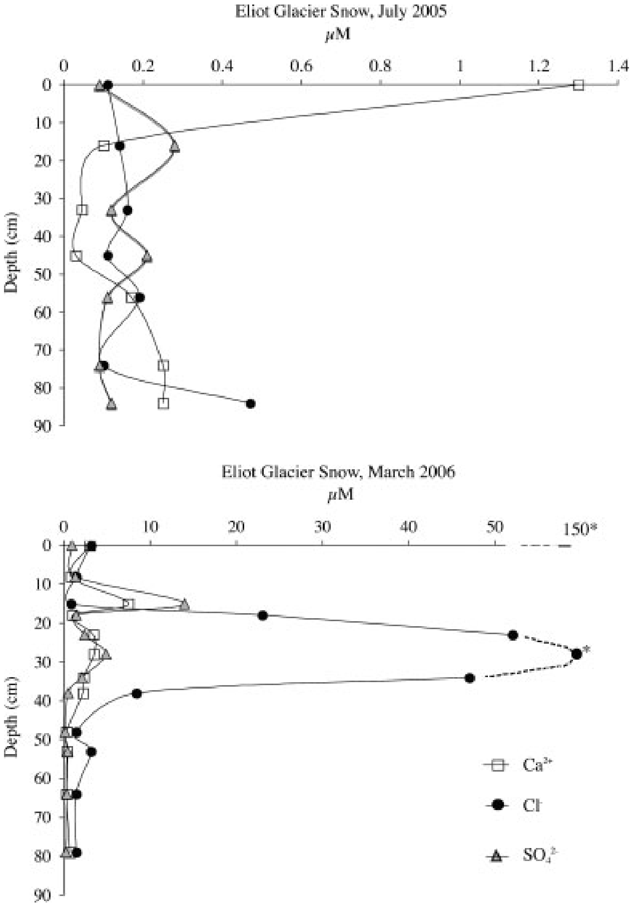

Figure 2. Ca^{2+}, Cl$^-$, and SO$_4{}^{2-}$ concentrations in μM at depth in Eliot Glacier snow sampled in July 2005 and March 2006. Note that the x-axis has distinct concentration ranges

Eliot Creek proglacial stream mean and median values are similar for all major ions with little variability during the sampling hour; for instance, the mean Ca^{2+} value was 44 μM and the median was 43 μM (Table II). The pH values in the stream were circum-neutral at 7·5. Relative stream cation abundances were in the

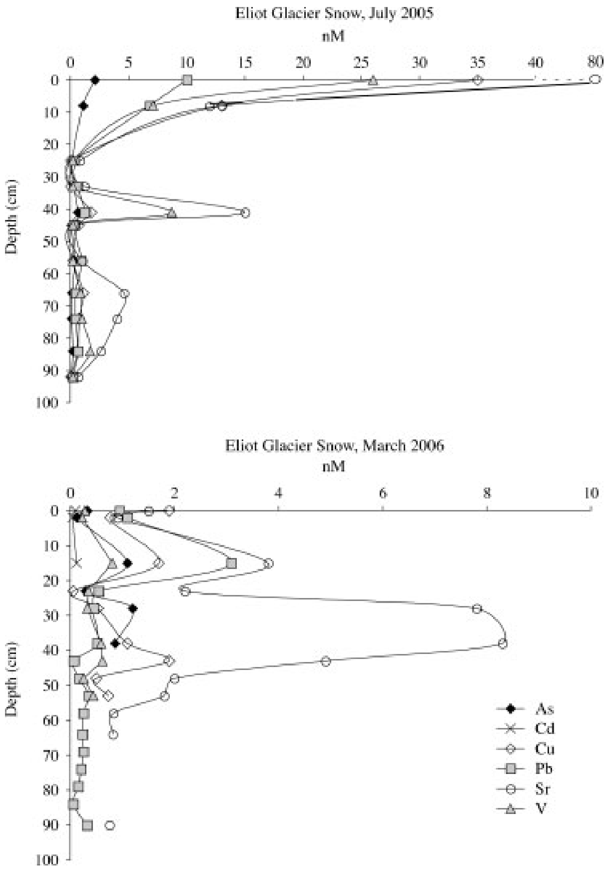

Figure 3. Environmentally available concentrations of As, Cd, Cu, Pb, Sr, and V in nM at depth in Eliot Glacier snow sampled in July 2005 and March 2006. Note that the *y*-axis has distinct concentration ranges

order $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$. Relative stream anion abundances were in the order $HCO_3^{-} > SO_4^{2-} > Cl^{-} >$. HCO_3^{-} concentrations were calculated by subtracting cation equivalent concentrations from anions, with a mean concentration of 110 μM (Table II). Proglacial stream trace element concentrations had similar mean and median values, except for As with a mean concentration of 1·4 nM and a median below the detection limit of 0·88 nM (Table II). Median Pb and Cd concentrations were also below detection. Mean V, Cu, and Sr concentrations were 20, 15, and 140 nM, respectively (Table II).

TRACE ELEMENT CONTRIBUTIONS TO ELIOT GLACIER MARCH 2006 SNOW

Marine contributions of ions and metals to glacier snow have been determined previously by comparing the ratio of an ion or element to Cl^{-} in the snow with the ratio of that same ion or element to Cl^{-} in seawater (Mayewski *et al.*, 1990). The percentage of non-marine contributions may be calculated as:

$$\%\text{non-Marine} = \left[\frac{[X]_{\text{snow}}}{[Cl^{-}]_{\text{snow}}} - \frac{[X]_{\text{ocean}}}{[Cl^{-}]_{\text{ocean}}}\right] \times 100 \quad (1)$$

where, $[X]_{\text{snow}}$ and $[Cl^{-}]_{\text{snow}}$ are the ion/element and chloride concentrations in the snow sample and $[X]_{\text{ocean}}$ and $[Cl^{-}]_{\text{ocean}}$ are the mean ion/element and chloride concentration in the ocean. This approach assumes that all the Cl^{-} present in the snow is from seasalt aerosol, which may lead to an overestimate of the marine contribution if there are additional sources of Cl^{-} to the snowpack.

The median Ca^{2+} in fresh snow from the Eliot Glacier is 96% non-marine origin (Ca^{2+}: Cl^{-} = 1·04). Marine-derived Cu, Cd, V, and Pb in all Northern Hemisphere snows, including Eliot Glacier, are negligible, or well below 1% of the total. Furthermore, the majority of Eliot Glacier fresh snow SO_4^{2-} was non-marine. The National Atmospheric Deposition Program SO_4^{2-} 2006 isopleth map shows that central western Oregon had among the lowest SO_4^{2-} concentrations (~0·2 mg/l) in the United States (NRSP-3, 2009).

Similar to calculating seasalt contributions by examining the ratio of an element to Cl^{-}, examining the ratio of an elements $[X]$ to S can be used to estimate volcanic contributions of trace metals to snow (Hinkley *et al.*, 1999; Mather *et al.*, 2003). Using this method, volcanic contributions were determined to be negligible, which is consistent with the absence of recent volcanic activity at Mount Hood whose last major eruption occurred more than 200 years ago (Crandell, 1980).

In the snow samples, lithogenic-derived trace element concentrations were calculated using upper continental crust (UCC) averages as an approximation for andesite-rich Mount Hood (Wedepohl, 1995). The EFs were calculated for both Eliot Glacier fresh and ablation snow

Table II. Eliot Glacier proglacial stream trace element (nM) and major ion (μM) concentrations during a high-melt afternoon

	nM					μM						
	As	Pb	V	Cu	Sr	Na^{+}	K^{+}	Mg^{2+}	Ca^{2+}	Cl^{-}	SO_4^{2-}	HCO_3^{-}
1 (2)	<0·88	<0·01	22	2·1	110	38	5·2	22	44	11	26	110
2 (2)	1·3	0·02	21	26	140	36	5·1	21	42	12	25	110
3 (2)	<0·88	0·04	20	23	130	37	5·2	21	42	11	25	110
4 (2)	2·9	<0·01	19	13	170	46	5·8	23	47	11	28	120
5 (2)	<0·88	<0·01	20	12	130	36	5·2	21	42	11	25	110
SDEV	0·88	<0·01	1·1	9·5	22	4·2	0·3	0·85	1·8	0·1	1·4	7·0
MEAN	1·4	0·02	20	15	140	39	5·3	21	43	11	25	110
MED	<0·88	<0·01	20	13	130	37	5·2	21	42	11	25	110

Sampling was among five locations within 500 m of each other. The average of (two) samples is given for each site in July 2005. Standard deviation, mean, and median concentrations are given excepting HCO_3^{-}, which was calculated by subtracting anions from cations. NO_3^{-} was always below detection (0·01 μM). Cd was below detection (<0·08 nM) in all but one sample (0·10 nM).

Table III. Enrichment Factor (EF) of Pb, Cu, and V in March 2006 Eliot Glacier snow

Eliot Glacier	Pb	Cu	V
EF Fresh Snow	1·4	0·6	0·1

Concentrations normalized to mean upper continental crust trace element concentrations (Wedepohl, 1995) and mean Oregon Cascade Ca^{2+} concentrations (McBirney, 1978)

using the equation below as previously used on alpine and polar snows (Wolff and Peel, 1985; Gabrielli *et al.*, 2006b).

$$\mathrm{EF} = \frac{[X]_{\mathrm{snow}}}{[Ca^{2+}]_{\mathrm{snow}}} \div \frac{[X]_{\mathrm{crust}}}{[Ca^{2+}]_{\mathrm{crust}}} \qquad (2)$$

where, $[X]_{\mathrm{snow}}$ and $[Ca^{2+}]_{\mathrm{snow}}$ are the element and calcium concentration in the snow samples and $[X]_{\mathrm{crust}}$ and $[Ca^{2+}]_{\mathrm{crust}}$ are the mean element and calcium concentration in the UC (Wedepohl, 1995). EFs are lower than crustal values for Cu and V (0·6, 0·1) and somewhat higher than crustal values for Pb (1·4) in the March 2006 snow (Table III). Because EFs are all within an order of magnitude of continental crust composition, environmentally available elemental concentrations are likely to be primarily derived from lithogenic sources.

POST-DEPOSITIONAL PROCESSING: TRACE ELEMENT VARIATION BETWEEN FRESH AND ABLATION SNOW

Unlike fresh March 2006 snow samples, July 2005 snow samples had undergone substantial melt since their original deposition. The post-depositional alteration of major and trace elements was evaluated with a non-parametric Mann–Whitney test comparing fresh and ablation snow (Table IV). There were significantly lower ($n = 7$, $p = 0{\cdot}001$) concentrations of $SO_4{}^{2-}$, $NO_3{}^{-}$, and Ca^{2+} in July 2005 compared to March 2006. This likely reflects the ongoing loss of soluble ions during early snowmelt (Brimblecombe *et al.*, 1986; Bales *et al.*, 1989). Interestingly Na^+, K^+, and Mg^{2+} were statistically similar between July 2005 and March 2006 snow, although median concentrations of these ions were lower in ablation snow (Table IV). This may be a result of the high winter accumulation rate generating dilute initial element concentrations. Throughout the March 2006 snow profile, the concentration of each major cation never exceeded 8 μM. Dilution of elements in winter snow has been observed at the most northern latitudes in the Italian Alps, attributed to higher snowfall (Gabrielli *et al.*, 2006b).

Major ion concentration ranges were greater in the March 2006 than July 2005 snow. Median March 2006 major ion concentrations represented an average of 38% of the arithmetic mean, while median July 2005 major ion concentrations represented an average of 58% of the arithmetic mean. This indicates that there is greater major ion variability in the March 2006 snow. July 2005 snow had undergone significant elution since original deposition, which likely lowered concentrations and dampened solute variability. Similarly, in the water-saturated Furtwangler Ice Core, Mt. Kilimanjaro, major soluble ions occurred at much lower concentrations than non-saturated cores from the mountain (Thompson *et al.*, 2002). Water saturation also created lower chemical variability throughout the ice core (Thompson *et al.*, 2002).

Table IV. Mann–Whitney ($\alpha = 0{\cdot}05$, $n = 11$) p-values for fresh (March 2006) and ablation snow (July 2005) collected from Mount Hood

Element	p-value	Median fresh snow (*Mean*) nM	Median ablation snow (*Mean*) nM
V	0·0287*	0·25 (0·32)	0·87 (4·2)
Cu	0·0338*	0·3 (0·6)	0·71 (4·8)
As	NA	BDL (>0·09)	0·20 (0·47)
Sr	0·0338*	1·2 (*2·3*)	2·6 (*9·0*)
Cd	NA	BDL (>0·03)	BDL (>0·03)
Pb	0·0574	0·28 (0·54)	0·60 (2·0)
Ion	**p-Value**	**Median fresh snow (*Mean*) μM**	**Median ablation snow (*Mean*) μM**
Ca^{2+}	0·001*	1·5 (2·0)	0·17 (0·30)
K^+	0·330	0·69 (1·9)	0·14 (0·18)
Mg^{2+}	0·384	0·75 (2·7)	0·12 (0·22)
Na^+	0·328	5·4 (25)	1·4 (2·1)
Cl^-	0·213	3·1 (24)	BDL (2·2)
$NO_3{}^-$	0·001*	0·43 (1·3)	BDL (0·07)
$SO_4{}^{2-}$	0·001*	1·1 (2·4)	0·12 (0·15)

Statistically significant differences between the fresh and ablation snow ($p \leq 0{\cdot}05$) are noted * and median and mean snow concentrations are included.

Unlike major elements, environmentally available trace elements occurred in greater concentrations in the July 2005 snow. V, Cu, and Sr were all statistically greater ($\alpha = 0{\cdot}05$, $n = 11$, $p \leq 0{\cdot}05$) in the July 2005 snow. Pb was slightly significantly higher in the ablation snow than in the fresh snow ($\alpha = 0{\cdot}05$, $n = 11$, $p = 0{\cdot}0574$). Arsenic concentrations changed from largely falling below detection limits in the fresh snow (<0·09 nM), to a median ablation snow concentration of 0·20 nM. The variability of environmentally available trace elements throughout the July 2005 snow profile was also greater than in the March 2006 profile. Median March 2006 environmentally available trace element concentrations represented an average of 80% of the arithmetic mean, with July trace element concentration medians only representing an average of 26%.

Particulates were much more visible throughout the snow profile and on the glacier surface during the July 2006 sampling than the March 2006 sampling, suggesting that large particles do not readily leave the glacier during ablation. Examinations of sub-micrometre soot and volcanic fall-out ash on Blue Glacier show that the fine soot is much more mobile than the >5-μm fall-out ash that remains on the glacier surface (Conway *et al.*, 1996). Similarly, drag-gravitational calculations suggest that particles larger than 6 μm are mobilized only when

DOI: 10.1002/hyp

flow is greater than 500 mm per day (Stenatakis and Tien, 1993).

Lack of dissolution may explain the overall greater concentrations of environmental elements in the ablation snow trace element concentrations. This is especially likely for environmentally available elements that remain particle-bound in oxygenated acidic waters including both As and V (Cullen and Reimer, 1989; Shiller and Mao, 2000). Yet, elements that typically desorb from particulates in oxygenated acidic waters (e.g. Cu and Pb) (Rauret *et al.*, 1988) also increased in ablation snow. Previous laboratory studies have shown that filtered trace elements are enriched in the early fraction of snow melt (Abrahams *et al.*, 1988). Filtered Cd and Pb were enriched by a mean factor of 3·91 and 2·48, respectively (Abrahams *et al.*, 1988). During early snowmelt, soluble acid concentrations are greatest (Tranter *et al.*, 1993) and likely facilitate greater dissolution of many trace elements. Finally, ongoing dry deposition may add new particles to the glacier surface given that less than 20% of the regional precipitation occurs during the ablation season (Lillquist and Walker, 2006). Particles added to the glacier after the acidic spring melt pulse may not dissolve as readily in the less acidic late-season conditions. The pH of July 2005 snow was greater (5·8) than that of March 2006 (5·4).

The greatest environmentally available trace element concentrations occurred in the July 2005 surface snow (Figure 3). While wet deposition results from atmospheric water particles, scavenging particulates within and while they condensate beneath clouds (e.g. form snow), dry deposition results from the transport of aerosols by turbulent air masses (Davidson, 1989; Cadle, 1991). The aerosols transported via dry deposition to the Eliot Glacier are not well known. Dry fallout of heavy metals, including Cu and Pb, often exceeds wet deposition and is especially related to human activity (Galloway *et al.*, 1982). However, dry deposition may not travel far from anthropogenic pollution sources. For example, dry deposition of smelter-derived elements to snowfall only exceeded wet deposition within a radius of 15 km in Quebec, Canada, while wet deposition dominated transport over longer distances (Telmer *et al.*, 2004). However, strong winds very likely contribute additional particulates to the surface of Eliot Glacier. In Oregon, strong winds occur with greater intensity at higher altitudes (Smith *et al.*, 2005).

Given the extent of post-depositional processing in Eliot Glacier ablation snow, it is difficult to discern natural from anthropogenic contributions. Non-ferrous metal production may deliver As and Cu to Eliot Glacier ablation snow because within the United States 200 tons of As and 112 tons of Cu are emitted annually (Pacyna and Pacyna, 2001). Almost one-third of all Cu mined, including slag and tailings, returns to the soil but typically nearer to urban areas such as landfills than to the remote regions from which it was mined (Graedel *et al.*, 2004). This suggests that the Cu concentrations in Eliot Glacier ablation snow may also result from the aeolian transport of contaminated soil (Georgopoulos *et al.*, 2001). Although the elevated V seen in the ablation snow may result from preferential retention of V in the snow compared with non-oxyanion-forming elements, V may also be introduced directly or indirectly from industrial activities, potentially including metal smelting and fossil-fuel burning (Pacyna and Pacyna, 2001) or the transport of contaminated dust.

ELEMENTAL CONCENTRATIONS IN ELIOT STREAM

Stream major cation concentrations measured from discreet 1-h sampling of Eliot Creek are distinct from the concentrations observed in both July 2005 and March 2006 snow. A ternary diagram with the relative percentage of $Na^+ + K^+$, Ca^{2+}, and Mg^{2+} for fresh and ablation snow and proglacial streams shows that the snow generally has a higher cationic abundance of $Na^+ + K^+$ and evolves to more Ca^{2+}-rich proglacial meltwaters (Figure 4). This is undoubtedly due to the preferential weathering of Ca-rich minerals observed within most glacier catchments as well as the likely loss of Na^+ during early snowmelt as noted (Tranter *et al.*, 1996, 2002; Brown *et al.*, 2001; Brown, 2002). Although seasonal trends are not examined, concentration differences do begin to illustrate the processing that occurs in glacial melt water once it is routed from the snowpack.

Sulfide minerals in andesite (Zimbelman *et al.*, 2005) may weather in the Eliot Stream, producing enrichments of $SO_4{}^{2-}$ (52 μM) with respect to other anions. $SO_4{}^{2-}$ is 59% of the total anion charge balance (% equivalents) in the bulk meltwater compared to 12% in ablation snow. Gains in $SO_4{}^{2-}$ may also reflect subglacial additions, as beneath the glacier weathering enhances both carbonation and sulfide weathering (Tranter *et al.*, 1993). Groundwater or hydrothermal springs may be another, although less likely, source of $SO_4{}^{2-}$ in the Eliot Stream. Several, but not all documented, Mount Hood region hot springs contain as much as 900 μM of $SO_4{}^{2-}$ (Mariner *et al.*, 2003). Our data suggest little to no hydrothermal input, with only minimal additions needed to elevate $SO_4{}^{2-}$ concentrations in the streams.

Like major ions, proglacial stream trace element concentrations appear to be related to processing en route than to their snow concentration. In natural waters, including glacial melt, Cl^- is conservative and will not increase or decrease in response to weathering, biological activity, and other processes (McKnight *et al.*, 1999). Therefore, other elements and ions can be normalized to Cl^- to determine how geochemical and biological processes such as weathering, adsorption, and biotic uptake affect them. For example, the ratio of dissolved Pb to Cl^- ($<1 \times 10^{-6}$) in the Eliot Stream is lower than the ratio of environmentally available Pb to Cl^- (9×10^{-5}) in fresh Eliot Glacier snow (Figure 5). Environmentally available V : Cl, Cu : Cl, and Sr : Cl in March 2006 snow ($8 \times 10^{-5}, 9 \times 10^{-5}, 4 \times 10^{-4}$) are 2 orders of magnitude

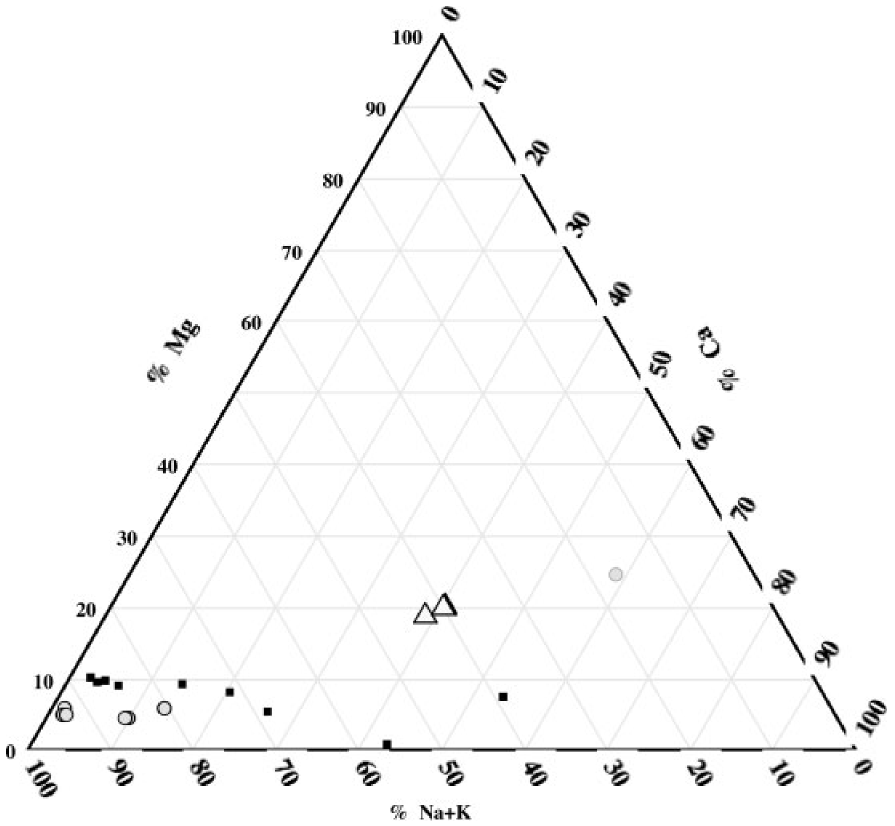

Figure 4. Molar cation percentages of Eliot Glacier March 2006 snow (squares), July 2005 snow (circles), and proglacial meltwater (triangles). Proglacial meltwater contains the highest percentage of Ca^{2+}, excepting a few July 2005 snow samples

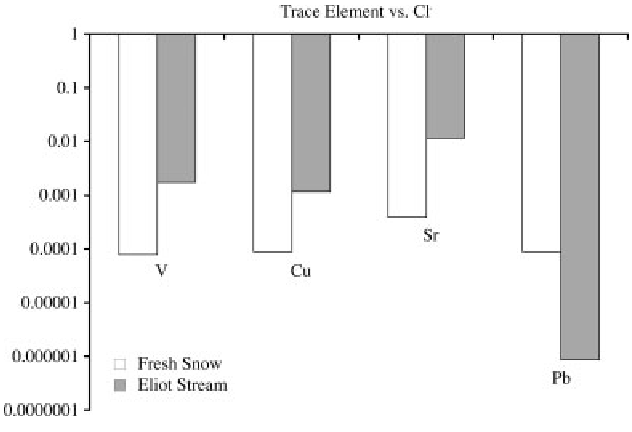

Figure 5. Environmentally available V, Cu, Sr, and Pb normalized to Cl^- in Eliot Glacier fresh snow, ablation snow, compared with dissolved ratios in Eliot Creek. Median snow and proglacial stream concentrations of As and Cd were below the detection limit

greater than dissolved ratios observed in Eliot Stream ($1{\cdot}8 \times 10^{-3}$, $1{\cdot}2 \times 10^{-3}$, $1{\cdot}2 \times 10^{-2}$). Although the environmentally available element concentrations were not measured in Eliot Creek, environmentally available concentrations of Cd, Cu, Pb, and Sr would likely be much greater than dissolved concentrations given that these elements are largely bound to particulates in basic waters and desorb with acidic conditions (Astrom and Bjorklund, 1995; Bibby and Webster-Brown, 2006). Hence, it is unclear whether environmentally available concentrations of Pb would increase or decrease in the proglacial stream. Pb does have a greater ability to absorb to soil particulate matter than other trace elements including Cu and Zn (Bibby and Webster-Brown, 2006). In the Eliot Creek, while Pb may or may not be released, dissolved Cu, Cd, and Sr are gained via rock-weathering in the sub- and proglacial environment. Furthermore, because dissolved As and V typically occur in similar concentrations in toxic basic waters, our results suggest V enrichments in Eliot Creek are also gained via weathering. Greater examination of speciation in glacier meltwater is needed to understand the ultimate fate of trace elements in glacier melt. These results show that the potentially toxic dissolved trace elements (Cu, Cd, and Pb) measured in proglacial melt are well below the United States Environmental Protection Agency (US-EPA) drinking water standards (U.S. EPA, 2004). Therefore, during the Oregon Cascades summer ablation season, glacier melt may act as a dilutant to downstream channels with greater anthropogenic element loads.

SUMMARY AND CONCLUSIONS

Environmentally available trace element concentrations occurred in greater median concentrations in a shallow ablation snow profile collected from Eliot Glacier in July 2005 than a nearby fresh snow profile collected in March 2006. Furthermore, concentrations of environmentally available elements had more variable concentrations in the ablation snow than in the fresh snow. While dissolved major solutes are rapidly leached, environmentally available trace elements likely do not as readily leave the glacier during melt and, or are added via dry deposition during the ablation season. March 2006 snow environmentally available trace element concentrations were further analysed to understand their source prior to post-depositional alteration. Crustal EFs suggest that As, Cu, Cd, Pb, Sr, and V are primarily derived from lithogenic sources.

Solute concentrations of all trace elements measured in the Eliot Stream and Glacier are well below drinking water standards, and pose no immediate threats to water quality. Trace element additions in the Eliot Stream, with respect to Eliot Glacier snow, are the result of chemical weathering additions with losses due to adsorption. Therefore, stream elemental concentrations bear little relation to snowpack concentrations. Future studies comparing seasonal variations in elemental fluxes in glacier-fed to nearby non-glacier-fed streams may best illustrate how the global retreat of glaciers will affect downstream water quality. Ongoing evaluation will be especially important to regions with high reliance on glacier melt for drinking water, agriculture, and ecosystem services.

ACKNOWLEDGEMENTS

We thank Jan Dougall, Dave Dranchak, Hiram Henry, Matt Hoffman, Keith Jackson, and Thomas Nylen for assisting with the sample collection. Thanks are also due to Dr. John Olesik and Anthony Lutton for their help with the ICP-SF-MS at the Ohio State Trace Element Research Laboratory (TERL). Partial funding for this research was provided by NSF Grant ANT-0423595.

REFERENCES

NRSP-3, National Atmospheric Deposition Program. 2009. Sulfate ion concentration, 2006. In *National Trends Network Offfice*, (ed). Illinois State Water Survey: Champaign.

Abrahams PW, Tranter M, Davies TD, Blackwood IL, Landsberger S. 1988. *Water, Air, and Soil Pollution* **37**: 255–271.

Astrom M, Bjorklund A. 1995. *Impact of Acid Sulfate Soils on Stream Water Geochemistry in Western Finland*. 163–170.

Bales RC, Davis RE, Stanley DA. 1989. *Water Resources Research* **25**: 1869–1877.

Barbante C, Cozzi G, Capodaglio G, Van de Velde K, Ferrari C, Boutron C, Cescon P. 1999a. *Journal of Analytical Atomic Spectrometry* **14**: 1433–1438.

Barbante C, Cozzi G, Capodaglio G, Van de Velde K, Ferrari C, Boutron C, Cescon P. 1999b. *Journal of Analytical Atomic Spectrometry* **14**: 1433.

Bibby RL, Webster-Brown JG. 2006. *Applied Geochemistry* **21**: 1135–1151.

Brimblecombe P, Tranter M, Tsiouris S, Davies TD, Vincent CE. 1986. *Modeling Snowmelt-Induced Processes*. IAHS; 283–295.

Brown GH. 2002. *Applied Geochemistry* **17**: 855–883.

Brown G, Fuge R, Kovar K, Tappeiner U, Peters NE, Craig RG. 1998. *Hydrology, Water Resources and Ecology in Headwaters*. IAHS-AISH: Merano, Italy.

Brown GH, Hubbard B, Seagren AG. 2001. *Hydrological Processes* **15**: 3487–3497.

Cadle SH. 1991. Dry deposition to snowpack. *Seasonal Snowpacks*. Springer-Verlag: Berlin.

Conway H, Gades A, Raymond CF. 1996. *Water Resources Research* **32**: 1713–1718.

Crandell DR. 1980. *U.S. Geological Survey Bulletin* **1492**: 81.

Cribb JW, Barton M. 1997. *Journal of Volcanology and Geothermal Research* **76**: 229–249.

Cullen WR, Reimer KJ. 1989. *Chemical Reviews* **89**: 713–764.

Daly C, Taylor G, Gibson W. 1997. The PRISM approach to mapping precipitation and temperature. In *10th Conference on Applied Climatology* (ed). American Meterological Society: Reno.

Davidson CI. 1989. Mechanisms of wet and dry deposition of atmospheric contaminants to snow surfaces. In *The Environmental Record in Glacier and Ice Sheets*. Oeschger H, Lanway CC (eds). John Wiley and Sons:New York.

Dyurgerov MB, Meier MF. 2000. *PNAS* **97**: 1406–1411.

Fitzgerald WF. 1999. Clean hands: clair patterson's crusade against environmental lead contamination. *Nova Science* 119–137.

Gabrielli P, Barbante C, Turetta C, Marteel A, Boutron CF, Cozzi G, Cairns W, Ferrari C, Cescon P. 2006a. *Analytical Chemistry* **78**: 1883–1889.

Gabrielli P, Cozzi G, Torcini S, Cescon P, Barbante C. 2006b. *Atmospheric Chemistry and Physics Discussions* **6**: 8781–8815.

Galloway JN, Thornton JD, Norton SA, Volchok HL, McLean RAN. 1982. *Atmospheric Environment (1967)* **16**: 1677–1700.

Gardner CB, Carey A. 2004. *Enviromental Science and Technology* **38**: 5319–5326.

Georgopoulos PG, Roy A, Yonone-Lioy MJ, Opiekun RE, Lioy PJ. 2001. *Journal of Toxicology and Environmental Health* **4**: 341–394.

Graedel TE, Van Beers D, Bertram M, Fuse K, Gordon RB, Gritsinin A, Kapur A, Klee RJ, Lifset RJ, Memon L, Rechberger H, Spatari S, Vexler D. 2004. *Environmental Science and Technology* **38**: 1242–1252.

Hall MP, Fagre DB. 2003. *Bioscience* **52**: 131–140.

Hinkley TK, Lamouthe PJ, Wilson SA, Finnegan DL, Gerlach TM. 1999. *Earth and Planetary Science Letters* **170**: 315–325.

Hodgkins R, Tranter M, Dowdeswell JA. 1997. *Hydrological Processes* **11**: 1813–1832.

Jackson K. 2007. *Spatial and Morphological Change of Eliot Glacier, Mount Hood, Oregon in Geography*. Portland State University: Portland; 124.

Jackson KM, Fountain AG. 2007. *Annals of Glaciology* **46**: 222–226.

JISAO/SMA Climate Impacts Group. 1999. *Impacts of Climate Variability and Change in the Pacific Northwest*. JISAO/SMA: Seattle; 109.

Johannessen M, Lyons WB, Graham EY, Welch KA. 2000. *Aquatic Geochemistry* **6**: 19–46.

Lillquist K, Walker K. 2006. *Arctic, Antarctic, and Alpine Research* **38**: 399–412.

Lundstrom SC. 1992. *The Budget and Effect of Supraglacial Debris on Eliot Glacier, Mt. Hood, Oregon*. Ph.D. dissertation, Boulder.

Lyons WB, Armstrong PB, Gaudette HE. 1983. *Marine Pollution Bulletin* **14**: 65–68.

Lyons WB, Welch A, Neumann K, Toxey JK, McArthur R, Williams C, McKnight DM, Moorhead D. 1998. Geochemical linkages among glaciers, streams and lakes within the Taylor Valley, Antarctica. In: *Ecosystem dynamics in a polar desert: The McMurdo Dry Valleys, Antarctica*. Priscu JC (ed)., American Geophysical Union (pub): 77–92.

Mariner RH, Evans WC, Presser TS, White LD. 2003. *Journal of Volcanology* **121**: 99–114.

Mather TA, Pyle DM, Oppenheimer C. 2003. *Volcanism and the Earth's Atmosphere Geophysical Monograph* **139**: 189–212.

Mayewski PA, Lyons WB, Spencer MJ, Twickler MS, Buck CF. 1990. *Nature* **346**: 554–556.

McBirney AR. 1978. *Annual Review of Earth and Planetary Sciences* **6**: 437–456.

McKnight DM, Niyogi DK, Alger AS, Bomblies A, Conovitz PA, Tate CM. 1999. *Bioscience* **49**: 985–995.

Mitchell A, Brown G, Fuge R. 2001a. *58th Eastern Snow Conference*. 11.

Mitchell A, Brown GH, Fuge R. 2001b. *Hydrological Processes* **15**: 3499–3524.

Mitchell A, Brown G, Fuge R. 2006. *Hydrological Processes* **20**: 877–897.

Mitchell AC, Brown GH. 2007. *Journal of Hydrology* **332**: 123–143.

Mote PW. 2003. *Geophysical Research Letters* **30**: 4.

Pacyna JM, Pacyna EG. 2001. *Environmental Review* **9**: 269–298.

Population Research Center. 2005. *Annual Oregon Population Report*. Portland State University, Proehl RS (ed): Portland.

Rauret G, Rubio R, Lopez-Sanchez JF, Cassassass E. 1988. *Water Research* **22**: 449.

Shiller AM, Mao L. 2000. *Chemical Geology* **165**: 13–22.

Smith RB, Barstad I, Bonneau L. 2005. *Journal of the Atmospheric Sciences* **62**: 177.

Stenatakis K, Tien C. 1993. *American Institute of Chemical Engineers* **39**: 1292–1302.

Telmer K, Bonham-Carter GF, Kliza DA, Hall GEM. 2004. *Geochimica et Cosmochimica Acta* **68**: 2961–2980.

Thompson L, Mosley-Thompson E, Davis M, Henderson KA, Brecher H, Zagorodnov V, Mashiotta T, Lin P-N, Mikhalenko V, Hardy D, Beer J. 2002. *Science* **298**: 589–593.

Tranter M, Brown GH, Raiswell R, Sharp M, Gurnell A. 1993. *Journal of Glaciology* **39**: 573–581.

Tranter M, Davies TD, Brimblecombe P, Vincent CE. 1987. *Water, Air, and Soil Pollution* **36**: 75–90.

Tranter M, Hodson AJ, Gurnell A. 1996. *Hydrological Processes* **10**: 541–556.

Tranter M, Sharp MJ, Brown GH, Hubbard BP, Willis IC. 2002. *Hydrological Processes* **16**: 959–993.

U.S. EPA. 2004. *2004 Edition of the Drinking Water Standards and Health Advisories*. Office of Water: 20.

USGS. 2003. *Water and Sediment Quality in the Yukon River Basin, Alaska, During Water Year 2001*. Schuster PF (ed). US Geological Survey Open File Report 03-0427. 120 p.

USGS. 2005. In *Water and Sediment Quality in the Yukon River Basin, Alaska, During Water Year 2002*. Schuster P (ed) US Geological Survey Open File Report 2005–1999. 82 p.

Wedepohl H. 1995. *Geochimica et Cosmochimica Acta* **59**: 1217–1232.

Welch KA, Lyons WB, Graham E, Neumann K, Thomas JM, Mikesell D. 1996. *Journal of Chromotography A* **739**: 257–263.

Williams MW, Melack JM. 1991. *Water Resources Research* **27**: 1575–1588.

Wolff E, Peel D. 1985. *Nature* **313**: 535–540.

Zimbelman DR, Rye RO, Breit GN. 2005. *Chemical Geology* **215**: 37–60.