Major solutes, metals, and alkylated aromatic compounds in high-latitude maritime snowpacks near the trans-Alaska pipeline terminal, Valdez, Alaska

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Abstract
The chemical constituents within a snowpack can provide information about the atmosphere
through which the snow was deposited. Valdez is located in south-central Alaska and has a
high-latitude maritime climate, with annual snowfall typically exceeding 8 m within the city
limits. Valdez is also the termination point of the trans-Alaska pipeline system, where tankers
are loaded with crude oil from the North Slope of Alaska. Integrated samples of the top 1 m of
snow were collected at seven sites near Valdez and analyzed for major solutes, lead, and
alkylated aromatic compounds, in particular benzene, toluene, ethylbenzene, and xylene
(BTEX). For comparison, sites were also sampled near Juneau, Alaska, which has a similar
climate but no petroleum transport infrastructure. Major solute chemistry at all sites was
dominated by chloride and was consistent with a marine air mass source of ions in precipitation.
Sulfate levels in Valdez were typically on the order of 10 μeq l^{-1} and significantly higher than
found in Juneau snow. Other major solute levels were low in Valdez and Juneau. Lead levels
were below detection limits for all sites, with the exception of trace concentrations
(<0.4 μg l^{-1}) reported at two Valdez locations. Alkylated organics were present at all Valdez
locations, at levels similar to those documented previously in urban locations. No alkylated
organics were detected in Juneau snowpacks.

Keywords: snow chemistry, nutrients, volatile organic compounds, Alaska

1. Introduction

Snow mediates the transfer of particulates and gases between the atmosphere and landscape (Jones *et al* 1993). The majority of the volume of a seasonal snowpack consists of air, which is readily exchanged with the atmosphere (Dominé and Shepson 2002) by diffusion and ventilation, processes that may be impeded by layers of low gas permeability (Kuhn 2001).

Once deposited and incorporated into a snowpack, nonvolatile solutes are subject to redistribution by water vapor fluxes that change with depth (Dominé and Shepson 2002) and can also become concentrated in melt–freeze events during the winter season (Johannessen and Henriksen 1978). Thus, physical properties of a snowpack can influence the infiltration of atmospheric gases as well as the transport of solutes so that knowledge of snowpack stratigraphy and solute content can provide useful information about meteorological conditions and can help predict solute release to a watershed during spring melt.

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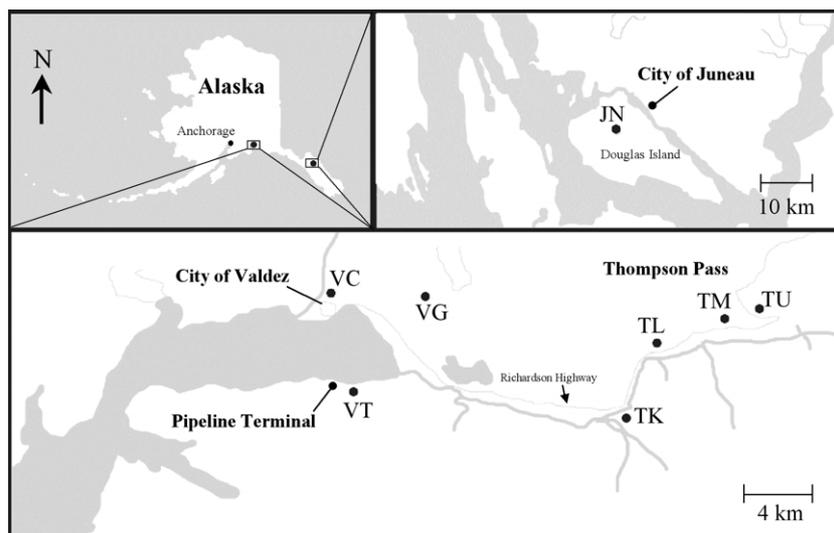
Figure 1. Location of sampling sites in Juneau and Valdez, Alaska. Juneau sites (JN) were collocated on Douglas Island. The Valdez set includes the city side of Port Valdez (VC), the pipeline terminal side of Port Valdez (VT), and the approximate midpoint between the local airport and the Valdez Glacier (VG). The Thompson Pass set includes Keystone Canyon (TK), lower Thompson Pass (TL), mid Thompson Pass (TM), and upper Thompson Pass (UT).

Major solutes (e.g. sulfate, nitrate) deposited from the atmosphere in snow can be used to characterize the extent of urban or agricultural impacts and may indicate how watershed hydrochemistry is being affected by atmospheric deposition. Past studies have used major solute analyses to examine effects of industrial centers on snowpacks that feed glaciers (Williams *et al* 1992), the impact of recreational vehicles on snow chemistry (Ingersoll *et al* 1997), and the meteorological and chemical dynamics of a seasonally snow-covered watershed (Williams and Melack 1991). In several studies, snowpack concentrations of metals have been studied as indicators of atmospheric pollution. For example, lead has been investigated in snowpacks in urban environments and high-altitude areas to examine impacts of atmospheric pollution on local, regional, and global scales (Elik 2002, Schwikowski *et al* 2004).

Unlike major solutes and metals, studies of snowpack concentrations of volatile organic compounds (VOCs), of which alkylated aromatics are a subset, are extremely limited. In the atmosphere, VOCs contribute to various environmental issues. VOCs can accumulate and persist in terrestrial and aquatic environments (Hester and Harrison 1995) and can contaminate drinking water supplies (Czuczwa *et al* 1988). Atmospheric VOCs are traditionally linked to urban environments, where incomplete combustion and fuel vaporization associated with motor vehicles are cited as a dominant source of VOC emissions (Wayne 2000, Hester and Harrison 1995). Roth *et al* 2004 (and references therein) describe a variety of mechanisms by which VOCs may be incorporated into snow. In addition to scavenging processes, attention has been given to the atmospheric transport, attenuation, and health hazards of VOCs in the environment (e.g. Zhao *et al* 2004, Kang *et al* 2004, Gramatica *et al* 2004). It has been suggested that meteorological parameters such as temperature, relative humidity, and wind direction and speed strongly influence the dispersion and transport of VOCs in the atmosphere (Lin *et al* 2004).

Valdez, Alaska is the termination point of the trans-Alaska pipeline where oil tankers are loaded with oil from the North Slope. Alkylated aromatics, including benzene, toluene, ethylbenzene, and xylenes, collectively known as BTEX, are emitted from the pipeline terminal (Cohen 1992). Previous research has documented elevated ambient air concentrations of benzene (range = 0.76–9.50 ppbv; Cohen 1992) and toluene (range = 0.61–7.14 ppbv; Cohen 1992) at the pipeline terminal and within the city of Valdez. For comparison, in urban Guangzhou, China atmospheric levels of benzene averaged 14 ppbv and toluene averaged 21.2 ppbv (Zhao *et al* 2004). The extent to which these compounds are scavenged and deposited in watersheds around Valdez is not known.

The purpose of this study was to (1) establish baseline measurements of major solutes in snowpacks in the Valdez region, (2) to determine if quantifiable levels of atmospheric pollutant species traditionally associated with industrial activities (lead and alkylated aromatics) could be found in snowpacks of Valdez, and (3) to investigate the relationship between proximity to the trans-Alaska pipeline and the chemical content of the seasonal snowpack around Valdez.

2. Experimental details

2.1. Site description

Valdez (pop. ∼4200) is located at the head of Prince William sound in south-central Alaska, approximately 225 km east of Anchorage (figure 1). Valdez has a high-latitude maritime climate with mean annual temperature of 3.2 °C and annual average precipitation of 1.6 m. Valdez is surrounded by the Chugach National Forest and highly glaciated Chugach Mountains, ranging in elevation from sea level to 815 m at

Thompson Pass and up to 4016 m, at Mt Marcus Baker. Maximum snowfall occurs during the late winter, at which time prevailing winds are from the east-northeast.

Snow samples were collected at seven sites around Valdez during a four-day period in March of 2004. Sites were accessed along the local road system and were located greater than 100 m from roadway. These sites were subdivided into two sets, Valdez (V) and Thompson Pass (T). The three Valdez set sites were located in and around Port Valdez, all within 12 km of the pipeline terminal (table 1): on the city side of the port (VC), the pipeline terminal side of the port (VT), and at the approximate midpoint between the local airport and Valdez Glacier (VG) (figure 1). The elevations of the Valdez sites ranged from 76 to 183 m and the distance from the pipeline terminal (d.p.t.) ranged from 6 to 12 km (table 1). The four Thompson Pass sites were located along an elevation gradient on Thompson Pass and included: the southern end of Keystone Canyon (TK), the northern end of Keystone Canyon near lower Thompson Pass (TL), and at middle (TM) and upper (TU) Thompson Pass (figure 1). The Thompson Pass sites ranged in elevation from 90 to 820 m (table 1). The distance from the pipeline terminal of the Thompson Pass sites was 24–37 km (table 1).

For comparison, snowpacks were also sampled at three locations on Douglas Island near Juneau, Alaska. Snowpack chemistry varied little between these sites, thus sample results were averaged from the three locations and presented as a single Juneau site (JN; figure 1). Juneau (pop. ∼30 000) is located in southeast Alaska and has a similar high-latitude maritime climate with a mean annual temperature of 4.8 °C and annual average precipitation of 1.4 m. The elevation of sample sites in Juneau was 550 m (table 1). These Juneau sites represent a pristine control as they are not subject to any significant industrial emissions. However, similar to Valdez sites, the Juneau sites were located less than 1 km from a road, which services the Eaglecrest Ski Area on Douglas Island.

2.2. Snowpack sampling

At each sample site a snowpit was dug to a minimum depth of 1 m, with the exception of VG where total snow depth was less than 1 m. Total snow depth was measured using a snow probe at the face of the pit wall. Snow temperature and density were measured at 10 cm increments vertically in the face of the pit wall. Due to relatively constant density near the bottom of the snowpits, density for snow below the pit depth was estimated as the mean of the lowest four density measurements within each snowpit. Total snow water equivalent (SWE) at each site was estimated as

$$\mathrm{SWE} = \frac{\rho_{\mathrm{snow}}}{\rho_{\mathrm{water}}} D$$

where ρ_{snow} is the average density of the snowpack, ρ_{water} is the density of liquid water, and D is the depth of the snowpack. Key stratigraphic observations in the snowpacks were also recorded (e.g. grain size, bonding, ice layers, etc).

At each site, triplicate samples of snow were collected 50 cm behind the wall of each snowpit using pre-washed 1 m

Table 1. Sample set designation, approximate elevation and distance from pipeline terminal (d.p.t.) of snow sampling sites in Valdez and Juneau, AK.

Sites	Elevation (m)	d.p.t. (km)
Valdez set		
VC	183	6
VT	76	2
VG	76	12
Thompson Pass set		
TK	91	24
TL	152	28
TM	381	35
TU	823	37
Juneau		
JN	550	n/a

PVC (polyvinyl chloride) cores and immediately transferred to new polyethylene bags for transport to the laboratory following the protocol of Williams *et al* (1992). Samples were melted, transferred to small bottles taking care to minimize air in the headspace, and stored at <5 °C until analysis. All chemical analyses were completed within two weeks of sample collection. All solute concentrations represent the integrated upper 1 m of the snowpack. Surface snow, deposited within 48 h of sampling, was also collected at JN.

Laboratory blanks were prepared by running distilled water through the cores, sample collection bags, and transfer containers.

2.3. Chemical analysis

Three snow samples from each site were analyzed for chloride, nitrate, and sulfate using ion chromatography (DX-500 ion chromatography system with conductivity detection) with a CO_3^-/HCO_3 buffer system and chemical ion suppression. Concentrations of cations (Na^+, NH_4^+, K^+, and Ca^{2+}) were analyzed using the same instrument with 30 mM sulfuric acid eluent and chemical ion suppression.

Total organic carbon (TOC) and total nitrogen (TN) were determined by high temperature combustion with a Shimadzu TOC-V/CSH with a TNM-1 attachment. Organic nitrogen (ON) was calculated as TN minus inorganic nitrogen (NH_4^+ + NO_3^- + NO_2^-).

Lead was analyzed by graphite furnace atomic absorption (GFAA) spectrometry (Solaar M Series spectrometer, $\lambda = 283.3$). Minimum limit of detection was calculated as 0.08 μg l^{-1} by taking the average signal from blanks summed with twice the standard deviation. Laboratory blanks were prepared with quartz distilled water. Quantification was carried out by comparison to standard solutions via the Solaar software package.

Alkylated aromatics (i.e. BTEX) were identified and quantified on a GC/MS (Varian Chromapack CP-3800 gas chromatograph, Saturn 2000 mass spectrometer, RTX-624 Restek column, 60 m × 0.25 mm × 1.4 μm) using purge and

trap sample introduction. Minimum limit of detection was determined from at the 90% confidence interval from a method similar to that set forth by the US Environmental Protection Agency for water quality standards, where the standard deviation was taken from low standards and multiplied by the appropriate *t*-value for the level of confidence and degrees of freedom. These values were estimated to be 0.5 μg l^{-1} for ethylbenzene, 0.9 μg l^{-1} for *m*/*p*-xylene, 0.3 μg l^{-1} for *o*-xylene, 0.5 for 1,3,5-trimethylbenzene, and 0.7 for 1,2,4-trimethylbenzene. Laboratory blanks were prepared from double distilled water purged with nitrogen. Quantification was carried out by comparison to standard solutions via the Saturn 2000 software package. Standards were run prior to each analysis and an internal standard of 1,2-dichloroethane was used quantify transfer onto GC column, and showed variation less than about 5%.

3. Results and discussion

3.1. Snowpack characteristics

Average winter air temperature 2003–4 in Valdez was −4 °C through time of sampling. Average snowpack temperatures around Valdez ranged from −3 to −8 °C (table 2), indicating that seasonal melt had not begun. In Juneau, mean snowpack temperature was close to 0 °C, indicating that the snowpack was nearly isothermal. Snowpack temperature can be used as an indicator of the onset of seasonal melt in which surface-tension forces govern the initial rate of downward transport of water. When these forces are overcome, meltwater along with its dissolved load begins to seep downwards in the snowpack (Waldner *et al* 2004). The below freezing snow temperatures and low snow water content at our sites suggested that spring snowmelt and its associated loss of solutes had not begun in Valdez or Juneau at the time of sampling.

3.2. Snowpack solutes

Snowpack chloride concentrations at the Valdez and Juneau sites ranged from 22.3 to 29.5 μeq l^{-1}, with the exception of TL, which had a concentration of 43.7 μeq l^{-1} (table 3). These levels were up to six times higher than snowpack concentrations reported in more continental areas of the northern hemisphere (e.g. Wake *et al* 1992, Jones *et al* 1993). Snowpack concentrations of sodium ranged from 3.3 and 12.1 μeq l^{-1}, with the exception of TL, which had a sodium concentration of 29.8 μeq l^{-1} (table 3).

The average Na$^+$:Cl$^-$ ratio in Valdez was 0.36 ($\sigma = 0.17$) and 0.44 in Juneau. The Na$^+$:Cl$^-$ ratio was 0.61 in new JN surface layer snow. Sea salt has a Na$^+$:Cl$^-$ ratio of 0.85, which can be used to determine marine inputs of chemicals to snowpacks. For snowpacks in Asia, Wake *et al* (1990) reported a range of ratios from 0.98 to 1.2 as indicative of a marine air mass source, over two times the ratio found in the present study. Preferential loss of ions has been reported for continental snowpacks where, with the exception of chloride, a loss of most major ions (including Na$^+$) was observed (Jefferies and Snyder 1981). Analogous behavior in the study

Table 2. Physical snowpack characteristics at sample locations in Valdez and Juneau Alaska including: total depth of snow, total snow water equivalent (SWE), the percentage of total SWE sampled, and mean snowpack temperature (MST).

Site	Total snow depth (m)	Total SWE (m)	% of SWE sampled	MST (°C)
Valdez set				
VC	1.70	0.605	56	−4
VT	2.02	0.674	47	−4
VG	0.87	0.303	56	−3
Thompson Pass set				
TK	2.06	0.882	45	−5
TL	1.35	0.473	73	−4
TM	2.30	0.958	42	−6
TU	2.63	0.985	35	−8
Juneau				
JN	1.60	0.628	55	0

site snowpacks would produce lower Na$^+$:Cl$^-$ ratios. Thus, while it is likely that relatively warmer and more humid marine air is the source of snow in both Valdez and Juneau, it is not completely clear from Na$^+$ and Cl$^-$ analyses.

An evaluation of sulfate levels provides a more compelling picture of snow origin for the Valdez and Juneau study sites. At TK, the snowpack concentration of sulfate was 17.8 μeq l^{-1} while the remaining Valdez study sites had sulfate concentrations ranging from 8.6 to 11.0 μeq l^{-1} (table 3). Average sulfate levels at the Juneau sites were 0.5 μeq l^{-1}. The SO$_4^{2-}$:Na$^+$ ratios ranged between 0.66 and 4.8 in Valdez snowpacks. In Juneau the SO$_4^{2-}$:Na$^+$ ratio was 0.25 and similar to the ratio in bulk seawater (0.252; Norman *et al* 1999) supporting a marine air mass source of precipitation at this site. If we assume a similar case for Valdez on the grounds that the Na$^+$:Cl$^-$ ratios between Valdez and Juneau are similar, then the significantly higher Valdez SO$_4^{2-}$:Na$^+$ ratios suggest a substantial non-sea-salt source of sulfate in Valdez, one that is presumably independent of marine aerosols. Snowpack concentrations of sulfate greater than 16 μeq l^{-1} have been reported in areas subject to heavy industrial input (e.g. coal burning) (Wake *et al* 1992) and motor vehicle emissions (Ingersoll *et al* 1997).

Concentrations of base cations (K$^+$, Mg^{2+}, Ca^{2+}), nitrogen species (NH$_4^+$ and NO$_3^-$) and TOC in all snowpacks were relatively low (table 3) and similar to levels reported for pristine snowpacks in other geographic regions (e.g. Williams *et al* 1992, Douglas and Sturm 2004). There was no significant relationship between concentrations of snowpack solutes and either sample site elevation or sample site distance from the pipeline terminal.

3.3. Snowpack metals

Lead was detected only in snowpacks at TK and TL sites in Valdez although concentrations were less than 0.4 μg l^{-1} (data not shown). Lead levels were below detection limits in JN samples and blanks. In snow of north-western

Table 3. Average concentrations of major solutes in snowpacks near Valdez and Juneau Alaska including: chloride, sulfate, nitrate, sodium, ammonium, potassium, magnesium, calcium, organic nitrogen, and total organic carbon. Numbers in parenthesis indicate the standard deviation of the average of three integrated snow cores at each location. Dash (—) indicates concentration below instrument detection limits.

Site	Cl^- ($\mu eq\,l^{-1}$)	SO_4^{2-} ($\mu eq\,l^{-1}$)	NO_3^- ($\mu eq\,l^{-1}$)	Na^+ ($\mu eq\,l^{-1}$)	NH_4^+ ($\mu eq\,l^{-1}$)	K^+ ($\mu eq\,l^{-1}$)	Mg^{2+} ($\mu eq\,l^{-1}$)	Ca^{2+} ($\mu eq\,l^{-1}$)	TOC ($\mu g\,l^{-1}$)
					Valdez set				
VC	25.9 (3.0)	11.0 (2.0)	0.8 (0.7)	8.5 (0.1)	1.0 (0.2)	0.5 (0.2)	1.2 (0.03)	2.2 (0.8)	103
VT	25.9 (0.6)	11.0 (0.2)	1.2 (0.07)	10.3 (0.4)	0.4 (0.7)	0.5 (0.1)	0.8 (0.01)	1.2 (0.2)	40
VG	24.1 (2.0)	10.0 (0.5)	0.5 (0.08)	7.7 (1.0)	1.3 (0.4)	0.3 (0.05)	0.6 (0.2)	1.4 (0.3)	82
					Thompson Pass set				
TK	29.5 (0.3)	17.8 (0.5)	0.7 (0.07)	12.1 (0.5)	0.4 (0.5)	3.4 (0.7)	3.2 (0.6)	—	104
TL	43.7 (4.0)	9.4 (1.0)	0.7 (0.2)	29.8 (5.4)	—	0.5 (0.07)	2.8 (0.6)	3.2 (1.0)	136
TM	22.3 (0.6)	8.6 (0.4)	0.4 (0.5)	3.8 (0.7)	0.6 (0.2)	0.5 (0.3)	0.2 (0.02)	1.0 (0.5)	140
TU	25.7 (4.0)	9.6 (2.0)	0.4 (0.6)	5.5 (0.7)	0.1 (0.2)	0.5 (0.1)	0.2 (0.2)	1.2 (0.3)	120
					Juneau				
JN	26.4 (2.0)	0.5 (1.0)	0.4 (0.3)	11.5 (1.8)	—	0.4 (0.3)	1.0 (0.2)	1.7 (0.9)	41

Table 4. Average concentrations of alkylated aromatic compounds in snow samples: ethylbenzene, *meta/para*-xylene, *ortho*-xylene, 1,3,5-trimethylbenzene (TMB), and 1,2,4-TMB. Dash (—) indicates species not detected.

Site	Ethylbenzene ($\mu g\,l^{-1}$)	m/p-xylene ($\mu g\,l^{-1}$)	o-xylene ($\mu g\,l^{-1}$)	1,3,5-TMB ($\mu g\,l^{-1}$)	1,2,4-TMB ($\mu g\,l^{-1}$)	Total ($\mu g\,l^{-1}$)
			Valdez set			
VC	1.0	3.0	1.1	—	0.4	5.5
VT	1.1	3.2	1.3	—	1.1	6.7
VG	1.1	3.1	1.2	0.4	1.2	7.0
			Thompson Pass set			
TK	1.1	3.3	1.2	0.8	1.3	7.7
TL	1.1	3.3	1.2	—	1.1	6.7
TM	1.1	3.3	1.2	—	1.1	6.8
TU	1.0	3.0	0.4	—	—	4.3
			Juneau			
JN	—	—	—	—	—	—

Alaska, mid-March concentrations of lead ranged from 0.26 to 0.60 $\mu g\,l^{-1}$ (Douglas and Sturm 2004), similar to concentrations found at the two sites in Valdez. Lead has been used to chronicle urban pollution events by its accumulation in urban snow (Elik 2002), as well as to trace historical contamination in snow and ice (Schwikowski *et al* 2004, Shotyk *et al* 2005). Combustion of leaded and low-leaded gasoline is the primary source for atmospheric inputs of lead (Pacyna and Pacyna 2001). Natural contributions of lead to snow (e.g. soil) are minor (Schwikowski *et al* 2004, Shotyk *et al* 2005). In Valdez, lead in snowpacks was concentrated along the Thompson Pass highway in Keystone Canyon suggesting a local source rather than a regional/global source.

3.4. Snowpack alkylated aromatic compounds

Total concentrations of alkylated aromatics (AA_{Total} = [ethylbenzene] + [m- and p-xylene] + [o-xylene] + [1, 3, 5 -trimethylbenzene] + [1, 2, 4-trimethylbenzene]) in Valdez snowpacks ranged 4.3 to 7.7 $\mu g\,l^{-1}$, with the lowest concentrations consistently found at the highest elevation site (TU) (table 4). Three of the analytes were found at all Valdez sampling sites; ethylbenzene concentrations ranged from 1.0 to 1.1 $\mu g\,l^{-1}$; the sum of m- and p-xylene, which typically co-elute and were quantified collectively, ranged from 3.0 to 3.3 $\mu g\,l^{-1}$; o-xylene was found at levels between 0.4 and 1.3 $\mu g\,l^{-1}$. Concentrations of 1,3,5-trimethylbenzene (TMB) ranged from 0.8 and 0.4 $\mu g\,l^{-1}$ but only at sites TK and VG while 1,2,4-TMB concentrations ranged from 0.4 to
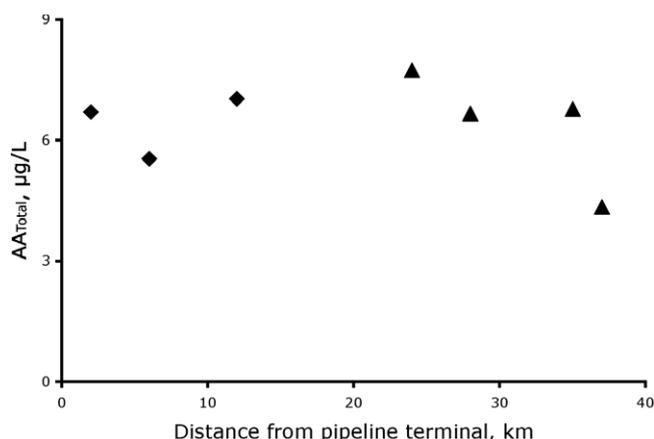
Figure 2. Concentration of total alkylated aromatics (AA$_{Total}$) with respect to sample site distance from the pipeline terminal in Valdez. The Valdez sites are shown as diamonds and the Thompson Pass sites are shown as triangles.

Table 5. Total snow depth loading of alkylated aromatic compounds at sites in Valdez, Alaska. Alkylated aromatics were not detected in the snowpack around Juneau, Alaska.

Site	Total depth loading (g ha^{-1})
Valdez set	
VC	33.5
VT	45.2
VG	21.3
Thompson Pass set	
TK	68.2
TL	31.5
TM	64.8
TU	42.7
Juneau	
JN	—

1.3 μg l^{-1} with levels at site TU below the detection limit (table 4). These concentrations are similar in magnitude to concentrations reported by Czuczwa *et al* (1988) for an urban location in Dubendorf, Switzerland where concentrations of ethylbenzene in winter snow ranged from 0.13 to 2.7 μg l^{-1}, *m*- and *p*-xylenes between 0.17 and 7.4 μg l^{-1}, *o*-xylene between 0.067 and 1.5 μg l^{-1}, and 1,2,4-TMB between 0.027 and 1.3 μg l^{-1}. Czuczwa *et al* (1988) found that concentrations of alkylbenzenes were higher in snow and winter rain than in rain in the autumn, spring and summer months. The concentrations measured in this study were found in overwinter snow accumulation and represent elevated alkylated aromatic concentrations in precipitation for Valdez. Alkylated organics were not detected in Juneau snowpacks.

Potential sources of the alkylated aromatics found at the Valdez study site were assessed by considering their spatial variations in concentration. The variation in concentrations of ethylbenzene and *m*- and *p*-xylene was relatively small, varying by less than 10% between sites (table 4). The concentrations of other alkylated aromatics showed more variability. For all sites taken together, there was no significant correlation between distance from the pipeline terminal and snowpack concentrations of alkylated aromatics ($R^2 = 0.04$, $p = 0.34$, $n = 7$), however the sites on Thompson Pass did show decreasing concentrations of alkylated aromatics with distance from the pipeline terminal (figure 2) and with increasing elevation.

AA$_{Total}$ loading was estimated from measured concentrations and snow water equivalence at each of the sites. The largest AA$_{Total}$ loading was 68.2 g ha^{-1} at TK, while the smallest loading occurred at VG at 21.3 g ha^{-1} (table 5). Similar to concentrations of alkylated aromatics there was no significant correlation between alkylated aromatic loading and distance from the pipeline terminal.

Investigations of alkylated aromatic accumulation in snow are extremely limited. Some attention has been given to the surface adsorption processes that mediate scavenging these types of compounds by snow and ice crystals (e.g. Roth *et al* 2004). Recent laboratory studies (Fries *et al* 2006) suggest a lack of BTEX adsorption to non-growing ice crystals which they attribute to reversible adsorption processes. Comparisons of these laboratory studies to the field studies reported here are limited by differences in the substrate under different experimental conditions. For example, the absorption behavior of semi-volatile organic compounds depends on the ambient temperature as well as the thickness of the thin film (Chen *et al* 2006). On ice, such a thin film is known to exist, the quasi-liquid-layer (QLL). The thickness of the QLL is a function of the solute load and temperature of snow crystals (Cho *et al* 2002). The laboratory studies of Fries *et al* (2006) were conducted at $-20\,^{\circ}$C, which is 16 $^{\circ}$C lower than the average temperature at which field samples were collected. Differences in crystal composition must also be considered. Ice crystals from deionized water do not account for the presence of dissolved solutes in the QLL. Since both of these lead to higher QLL thickness on natural ice surfaces relative to pure water ice at $-20\,^{\circ}$C, it is plausible that adsorption of BTEX is enhanced on snow of the seasonal cover at the sites that were sampled around Valdez.

Precipitation has been viewed as the primary vehicle for the removal of organic compounds from the atmosphere. Recent evidence suggests, however, that reactions with hydroxyl radical may be an equally efficient removal mechanism (Stephanou 2004). Johnson *et al* (2004) proposed the formation of secondary organic aerosols by the photooxidation of toluene. These secondary organics would contribute to the total organic carbon levels, but would not be detected as BTEX. Oxidation of alkylated aromatics during atmospheric transport away from a source could produce a lower proportion of BTEX in the snowpack's total organic carbon pool as distance from the source increased. Of the total organic carbon levels measured in the Valdez snowpacks (table 3), the alkylated aromatic fraction ranged between 0.04 and 0.17, and decreased with increasing distance from the pipeline terminal (figure 3). The largest fraction (0.17) occurred on the pipeline terminal side of Port Valdez at site VT, while the smallest fraction occurred at TU, the farthest
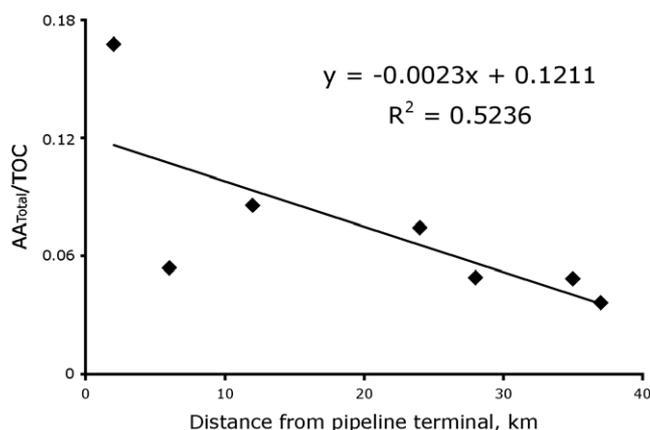
Figure 3. The total alkylated aromatic (AA_{Total}) fraction of total organic carbon (TOC) in the Valdez snowpack decreases with increasing distance from the pipeline terminal.

site from the terminal (figure 3). This finding is consistent with the idea that the Port of Valdez could be a point source for alkylated aromatics, and that some attenuation occurs as alkylated aromatics are transported away from the source region.

4. Conclusions

Snowpack solute concentrations at seven sites around the city of Valdez and three sites around the city of Juneau on the Gulf of Alaska were relatively low. While source apportionment is not completely clear, a strong linear correlation between Na^+ and Cl^- concentrations at both sites, as well as the excellent agreement for the SO_4^{2-}:Na^+ ratio found in Juneau samples with that of bulk seawater, support a marine air mass source for major solutes in the snowpack. The primary difference in snow chemistry between the two areas was substantially higher sulfate levels in Valdez samples compared to those of Juneau. Lead was found only at very low levels at two Valdez sites. Valdez snow samples consistently showed the presence of alkylated aromatics which were absent from those at the Juneau sites. Since the bulk of the snowfall received at both locations originates from large frontal storms in the Gulf of Alaska, a local source for alkylated aromatics in the Valdez snowpacks is suggested. The current population of Juneau is approximately seven times that of Valdez with a proportionately larger number of aircraft, marine vessels, and automobiles potentially contributing to the alkylated aromatic load. The absence of these solutes in the snowpack around Juneau indicates small combustion engines do not contribute significantly to the elevated levels found in Valdez. Within the Valdez region, concentrations of alkylated aromatics in the snowpack were lowest at the site located furthest from the trans-Alaska pipeline terminal loading facility and the alkylated aromatic fraction of total organic carbon decreased with increasing distance from the pipeline terminal. Taken together, these results suggest that the operations of the trans-Alaska pipeline terminal contributes to alkylated aromatic loading in seasonal snowpacks in the Valdez region.

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