ANIMIDA Task 7
Partitioning of Potential Anthropogenic Chemicals between Dissolved and Particulate Phases in Arctic Rivers and the Coastal Beaufort Sea

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Table of Contents

Table of Contents (continued)

List of Tables

List of Figures

List of Figures (continued)

List of Figures (continued)

EXECUTIVE SUMMARY

The Arctic Nearshore Impact Monitoring in the Development Area (ANIMIDA) Program was developed to monitor potential environmental changes related to oil and gas development in the Beaufort Sea with a special focus on the Northstar development. The ANIMIDA Program included a variety of biological and chemical studies. This report presents results from study of the partitioning of potential anthropogenic chemicals between dissolved and particulate phases in arctic rivers and the coastal water of the Beaufort Sea.

In the dissolved form, trace metals and organic substances are generally more biologically available and have a greater chance to induce toxic effects in organisms. In general, concentrations of dissolved trace metals in coastal seawater are controlled by river runoff, adsorption on suspended sediment and biological uptake. During 2001 and 2002, concentrations of dissolved metals were determined for the Sagavanirktok, Kuparuk and Colville rivers and for coastal water of the Beaufort Sea. The underlying theme in this effort was to understand the natural sources, transport pathways and concentrations of dissolved metals in the coastal Beaufort Sea. The natural processes that help regulate concentrations of dissolved substances must be understood before attempting to identify anthropogenic perturbations.

Field activities for ANIMIDA Task 7 included sampling of rivers and offshore water during open-water periods of July-August 2000, 2001 and 2002 plus through-ice and river break-up efforts during May-June 2001 and 2002. Rivers are a major source of dissolved metals to the study area. The Sagavanirktok River was sampled daily during June 2001 and 2002 and the other two rivers were sampled every two to five days as logistics permitted. Samples of water and suspended sediment from the Sagavanirktok River also were collected at mile 401 on the Dalton Highway, and at the site of a gauging station maintained by the U.S. Geological Survey (U.S.G.S.), about 100 miles south of Deadhorse.

Concentrations of the following dissolved and particulate metals: arsenic (As), barium (Ba), calcium (Ca), copper (Cu), iron (Fe), potassium (K), magnesium (Mg), manganese (Mn), sodium (Na), nickel (Ni), lead (Pb) and zinc (Zn), particulate aluminum (Al) and dissolved and particulate organic carbon (DOC and POC) were determined for the three rivers during June to August 2001 and 2002. Concentrations of dissolved trace metals were low, but different among the three rivers. For example, in the Sagavanirktok River, the following average concentrations of dissolved metals were determined: Pb at 15 ng/L, Cu at 0.6 µg/L and Ba at 32 µg/L whereas in the Colville River these three metals were found at concentrations of 60 ng/L, 2 µg/L and 50 µg/L, respectively.

The most striking trend in the dissolved data was found for DOC with maximum levels of DOC in the Sagavanirktok River >8 mg/L during peak flow relative to 2 mg/L at lower flow (Figure ES-1). Concentrations of Fe, Mn, K and Cu followed trends for DOC quite
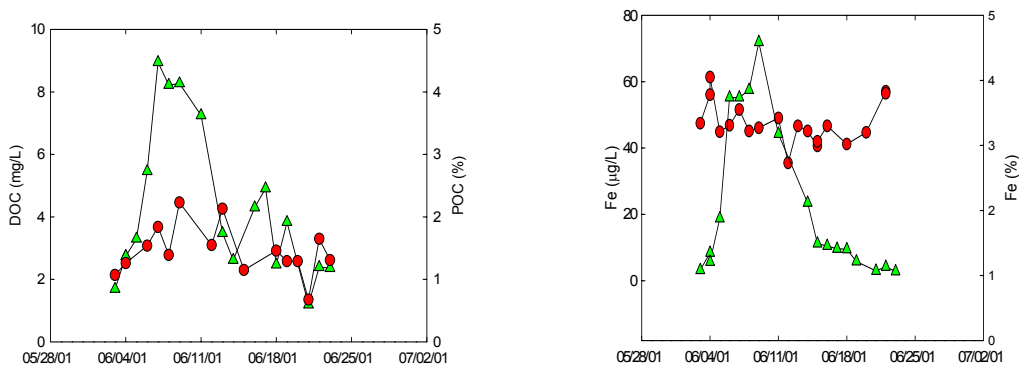
Figure ES-1. Concentrations of dissolved (triangles) and particulate (circles) organic carbon (DOC and POC) and dissolved (triangles) and particulate (circles) iron (Fe) in the Sagavanirktok River during June 2001.

well (e.g., Fe in Figure ES-1). These trends are consistent with a pulse of exuded, DOC-rich water from thawing soils in the drainage basin that occurred shortly after the initial melt event during the period of peak flow. Trends for dissolved Fe, Mn and K, also derived from thawing soils, matched the trend observed for DOC. Concentrations of dissolved Cu followed DOC relatively well; however, the magnitude of change was somewhat less than observed for the other elements. For dissolved Ba, Ni and Pb, concentrations shifted only slightly in response to the increase in levels of DOC. Concentrations of particulate metals (on the basis of µg metal/g suspended sediment) were rather uniform during June 2001 and fit metal/Al ratios defined for bottom sediment in the coastal Beaufort Sea. In most cases, very little (<10%) of the metal burden of the rivers was in the dissolved phase during the June period of high flow.

The forms of the metals and controls on concentrations of dissolved metals in rivers are important to understanding subsequent behavior in the saline water of the coastal Beaufort Sea. Concentrations of dissolved and particulate Ba varied directly among the rivers (Figure ES-2) and thus a simple distribution coefficient (K_d) was used to explain observed concentrations, where

$$K_d = \frac{\text{(concentration of particulate metal in µg metal/g particles)}}{\text{(concentration of dissolved metal in µg metal/g water)}} .$$

When this approach was used for Ba, the fit was quite good with the K_d for Ba averaging $2.4 \pm 0.5 \times 10^4$ for all the rivers (Figure ES-2). This trend supports the concept that concentrations of Ba in suspended sediment regulate concentrations of dissolved Ba. The same approach also was applied to Pb and Cu; however, the fit was less consistent, suggesting that other factors, such as complexation with organic matter influences concentrations of dissolved Pb and Cu.
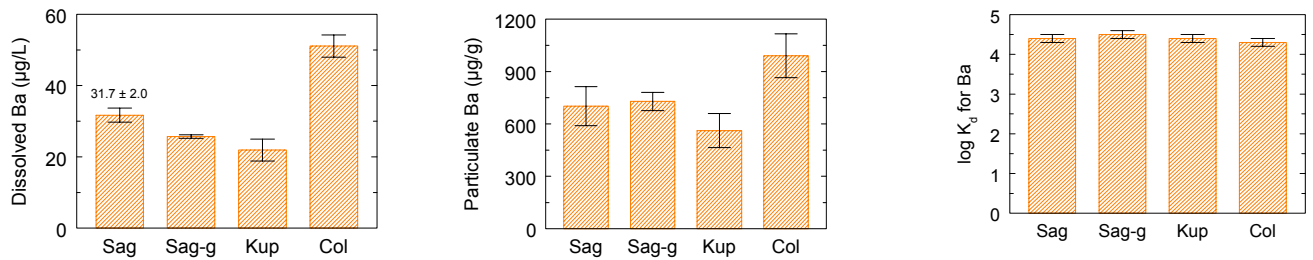
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) in the Sagavanirktok (Sag),
Kuparuk (Kup) and Colville (Col) rivers during summer 2001 and log of the
distribution coefficient (K_d) for Ba. Sag-g identifies upstream location at site of
U.S.G.S. gauge.

Concentrations of dissolved trace metals in the saline water of the coastal Beaufort Sea
were generally lower than found in the rivers with the following observations: Pb at 4-7
ng/L, Cu at 0.5 µg/L and Ba at 13 µg/L. Concentrations of total Hg in the coastal
Beaufort Sea also were low at about 0.5-0.8 ng/L. Schematic representations for the
distributions of dissolved As and Ba are shown in Figure ES-3. Concentrations of As
increased from the rivers to the sea and concentrations of Ba decreased.
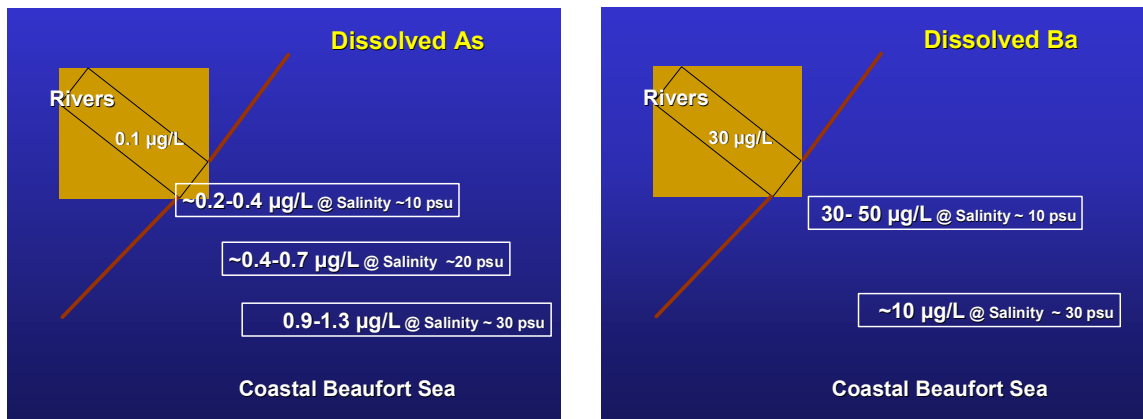
Figure ES-3. Generalized distributions of dissolved arsenic (As) and barium (Ba) in source rivers
and coastal water of the Beaufort Sea.

The Total PAH (TPAH) concentrations in whole seawater samples (dissolved +
particulate fractions) were low and ranged from 22 to 68 ng/L. The TPAH of the
particulate fraction of the seawater samples ranged from 13.2 to 18.5 ng/L. The PAH
distribution for the particles shows a petrogenic or petroleum hydrocarbon composition,
characterized by a predominance of the 2- and 3-ringed alkyated PAH compounds, with a

lower abundance of 4-, 5- and 6-ringed PAH. The PAH in the seawater samples were primarily associated with suspended sediment. The composition of the PAH in the suspended sediment was similar to that observed for riverine and benthic sediment in the ANIMIDA study area. Analysis of the dissolved fraction showed no detectable PAH in the dissolved phase in support of the statement that the PAH are bound to suspended sediment and do not partition to any great extent into the dissolved phase.

The main conclusions from ANIMIDA Task 7 are as follows: (1) concentrations of dissolved trace metals and PAH in the study area are very low and characteristic of pristine water, (2) concentrations of some metals can be modeled with a simple distribution coefficient, and (3) active physical, chemical and biological processes are at work to create a dynamic, yet predictable, distribution of dissolved trace metals in the study area. Such information will be useful for long-term monitoring (years, decades and centuries) and will provide an evolving capability for predicting impacts from any spills or other releases of chemicals within the drainage basin or the coastal sea.

1.0 INTRODUCTION

The Arctic Nearshore Impact Monitoring in the Development Area (ANIMIDA) Program was developed to monitor potential environmental changes related to oil and gas development in the Beaufort Sea with a special focus on the Northstar development. This report presents results from study of partitioning of potential anthropogenic chemicals between dissolved and particulate phases. The study was designed to determine concentrations of dissolved chemicals in the coastal Beaufort Sea and identify the degree of partitioning with suspended sediment. Samples of water and suspended sediment were collected from three area rivers and a segment of the coastal Beaufort Sea that encompassed Northstar Island and the Liberty Prospect (Figure 1-1).

Concentrations of dissolved and particulate substances in the water column are sensitive indicators of low levels of environmental contamination in a coastal setting. Because of the transient nature of some dissolved constituents, along with difficulties in collection and analysis of samples, potential anthropogenic chemicals are usually monitored by analyzing sediment and biota. However, at this point in the evolution of environmental research in the coastal Beaufort Sea, study of dissolved and particulate phases for potential anthropogenic chemicals seemed warranted. In the dissolved form, trace metals and organic substances are generally more biologically available and have a greater chance to induce toxic effects in organisms. Most spills in coastal areas, whether an oil, aqueous or solid discharge, will first impact the water column. A dependable capability for predicting the behavior of potential anthropogenic chemicals under various discharge or sediment resuspension scenarios is needed. Furthermore, no reliable, consistent data set for dissolved trace substances is presently available for the coastal Beaufort Sea.

The case for studying dissolved and particulate phases of potential anthropogenic chemicals in the Beaufort Sea is enhanced by the relatively uniform composition of suspended sediment in area water. If partitioning between dissolved and particulate phases can be predicted, then the response of the system to addition of any anthropogenic chemical also may be predicted. Do dissolved trace substances stay in solution or are they adsorbed on suspended particles? In addition to addressing these issues, a solid database for dissolved constituents has been produced to provide a potentially valuable marker for long-term changes in the system that does not presently exist.

The overall objectives for ANIMIDA Task 7 were as follows:

1. To determine concentrations of selected metals and organic substances in dissolved and particulate forms in water of the source rivers and the coastal Beaufort Sea.

2. To determine partitioning coefficients (particulate/dissolved) for selected metals and organic substances.

3. To determine the partitioning between dissolved and particulate phases for polynuclear aromatic hydrocarbons (PAH) in North Slope crude oil from a laboratory spiking experiment using Beaufort Sea water.
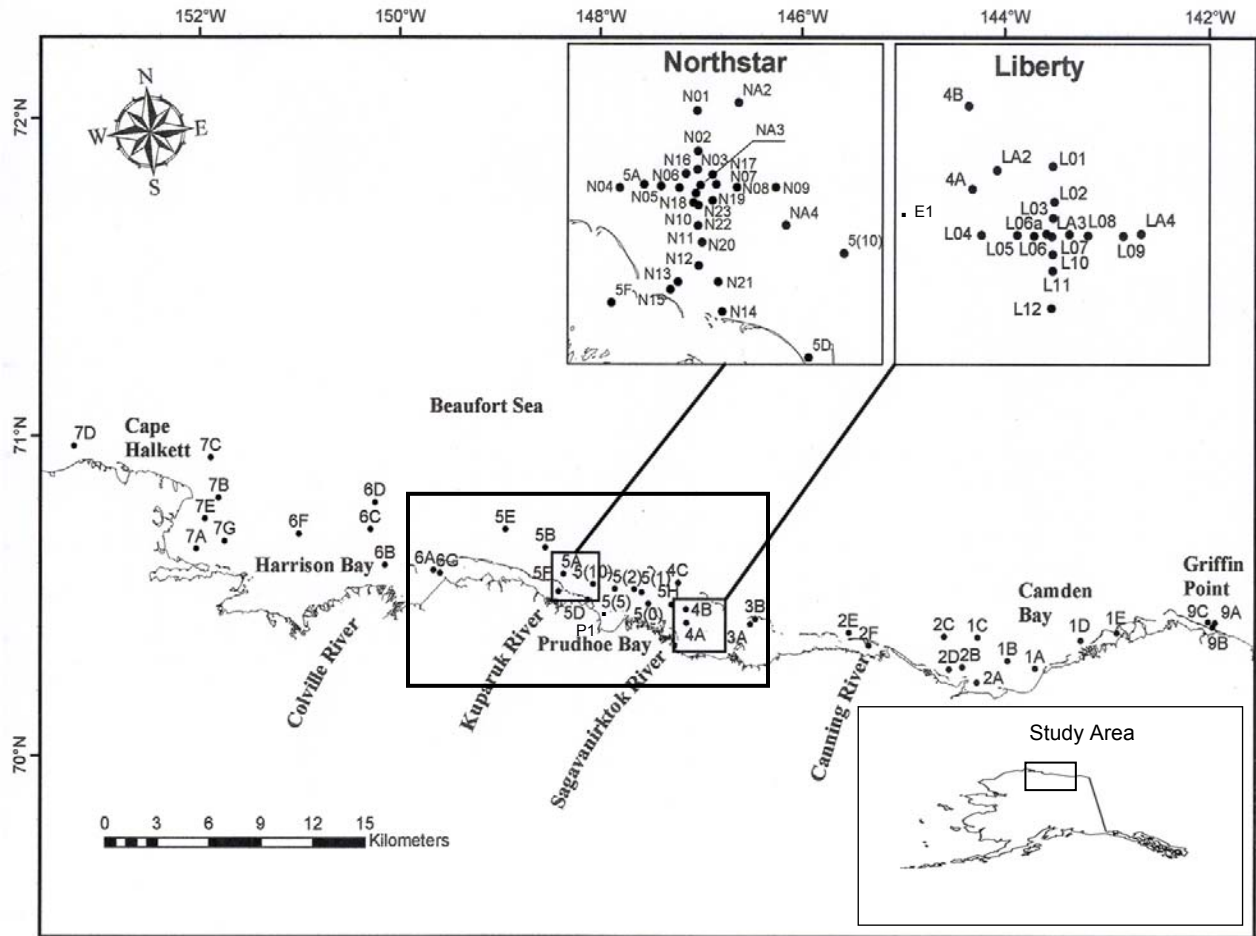
Figure 1-1. Map showing the western portion of the coastal Beaufort Sea with inset maps of Alaska, the oil production site at Northstar Island and a possible future drilling site at Liberty Prospect. The ANIMIDA study focused mainly on the area shown in the shaded box.

The underlying theme in this effort is to understand the natural sources, transport pathways and concentrations of dissolved substances in the coastal Beaufort Sea. The natural processes and variations in concentrations of dissolved substances must be understood before attempting to identify anthropogenic perturbations.

Field activities for ANIMIDA Task 7 included sampling offshore water and rivers during open-water periods of July-August 2000, 2001 and 2002 plus through-ice and river break-up efforts during May-June 2001 and 2002. The strong ties between ANIMIDA Tasks 5 and 7 lead to some overlap in reporting. The Results and Discussion section for ANIMIDA Task 7 will not restate the details of work reported in Trefry et al. (2004). Instead, the focus here will be on concentrations and mechanisms that control dissolved substances in the source rivers and offshore water of the coastal Beaufort Sea.

6

2.0 METHODS

2.1 Sample Collection

2.1.1 Source Samples

Water samples were collected from the Sagavanirktok, Colville and Kuparuk rivers in 1-L, acid-washed, low-density, polyethylene (LDPE) bottles. Some samples were obtained by wading into the river, waiting until any disturbed sediment was washed down stream, and then opening an acid-washed 1- or 2-L, LDPE bottle below the surface of the water. When the bottle was full, it was sealed beneath the surface, retrieved, placed in a plastic bag, labeled and stored in a cooler for return to the on-site laboratory facilities to be filtered. During May-June 2001 and 2002, samples from the Sagavanirktok and Kuparuk rivers were collected by a special water sampler that held acid-washed LDPE bottles and could be lowered from bridges across the river.

2.1.2 Offshore Water and Suspended Sediment Measurements during Open-Water Period

Seawater samples were collected from the bow of a small rubber boat while rowing upstream or upwind. An acid-washed 1- or 2-L LDPE bottle was opened at about 10 cm below the surface of the water. When the bottle was full, it was sealed beneath the surface, retrieved, and placed in a plastic bag for storage. In the on-site laboratory, the water samples were vacuum filtered through polycarbonate filters (Poretics[®], 47-mm diameter, 0.4-µm pore size). Prior to the field effort, the filters were acid washed in 5N HNO_3, rinsed three times with distilled, deionized water (DDW), dried and then weighed to the nearest µg using a Sartorius[®] Model M3P electronic balance under cleanroom conditions. Vacuum filtration at an on site laboratory was carried out in a Class-100 laminar-flow hood using acid-washed glassware. The filtered water was acidified with 1 mL of ULTREX[®] HNO_3 per liter of water and stored in a separate, acid-washed LDPE bottle. Particle-bearing filters were sealed in acid-washed petri dishes, labeled, double-bagged in plastic bags and then stored until dried and re-weighed in the Marine & Environmental Chemistry Laboratories at Florida Institute of Technology (FIT).

2.2 Laboratory Analyses: Inorganic Parameters and Organic Carbon

2.2.1 Particulate and Dissolved Organic Carbon

Samples for particulate organic carbon (POC) and dissolved organic carbon (DOC) were prepared by filtration of seawater and river water through pre-combusted Gelman[®] Type A/E glass fiber filters mounted on acid-washed filtration glassware within a Class-100 laminar-flow hood. The POC filters were sealed in acid-washed petri dishes, labeled, double bagged in plastic and then stored frozen until dried at FIT. The dissolved samples saved for DOC were placed in acid-washed glass vials with Teflon[®]-lined caps, labeled, and frozen until analysis at FIT.

At FIT, the POC filters were treated with H_3PO_4 to remove inorganic carbon phases, rinsed with DDW, dried and their particulate mass determined. The filters were then placed in ceramic boats and combusted at 900°C in a Shimadzu® TOC-5050A carbon system with SSM-5000A solid sampling module following the manufacturer's instructions. The POC content of the samples was determined using a four-point calibration curve with pure sucrose as the standard. The calibration curve was checked every 10 samples by analyzing the certified reference material (CRM) MESS-2, a marine sediment issued by the National Research Council of Canada (NRC).

The DOC concentrations of the seawater and river water samples were calculated by difference, total carbon (TC) minus inorganic carbon (IC) as determined by combustion in the Shimadzu® TOC-5050A system. Four-point calibration curves were prepared using potassium hydrogen phthalate (TC) and sodium bicarbonate (IC). The calibration curve was checked every 10 samples by repeat analysis of a mid-range standard.

2.2.2 Dissolved Metals, Major Ions, Chlorinity and Alkalinity

The seawater concentrations of dissolved As, Cd, Cr, Cu, Pb and Zn were determined on extracts obtained using a reductive precipitation procedure derived from Nakashima et al. (1988). In this procedure, ultra-high purity Pd, Fe and $NaBH_4$ are used to precipitate the metals that are then collected by filtration and redissolved in ultra-high purity HNO_3 and HCl. This procedure was carried out using 400-mL aliquots of seawater and a seawater CRM (CASS-3 issued by the NRC) with a final extract volumes of ~4 mL, resulting in a ~100-fold concentration of the seawater metals prior to analysis. The extracts were transferred to acid-washed 7.5-mL LDPE bottles, sealed, labeled and then stored in a plastic bag until analysis. Concentrations of dissolved Ba were determined directly on diluted aliquots of the seawater samples. River water samples were analyzed directly for Ba, Ca, Cu, Fe, K, Mg, Mn, Na and Ni as described below. Concentrations of Pb and Zn in river water were determined by reductive precipitation of 400-mL aliquots of the samples and the river water CRM SLRS-3 (issued by the NRC). Labware used in the extraction procedure and subsequent analysis was acid-washed with hot HNO_3 and rinsed three times with reagent water prior to use.

Total dissolved Hg levels in seawater and river water were determined on separate portions that had been treated with bromine monochloride solution (Szakacs et al., 1980) to oxidize organic ligands and preserve the samples until analysis.

The metal concentrations of the river water, river water extracts, CRMs and blanks were determined by flame atomic absorption spectrometry (FAAS), graphite furnace atomic absorption spectrometry (GFAAS), inductively coupled plasma-mass spectrometry (ICP-MS) or cold-vapor atomic fluorescence spectrometry (CVAFS) (Table 2-1). Concentrations of Ca, K, Mg and Na in river water were measured directly by FAAS - using a Perkin-Elmer® Model 4000 AAS. Concentrations of dissolved As in the extracts were determined by GFAAS with a Perkin-Elmer® Model 5100PC AAS equipped with an HGA-600 graphite furnace and AS-60 autosampler. Dissolved Pb and Zn concentrations of the river water extracts were quantified by ICP-MS using a Perkin-

Elmer[®] ELAN 5000 instrument. Dissolved Cu, Fe and Mn concentrations were measured directly for river water using a Perkin-Elmer[®] Model 4000 AAS equipped with an HGA-400 graphite furnace and AS-40 autosampler. Dissolved Ba and Ni concentrations were determined directly on the river water samples by ICP-MS using a Perkin-Elmer[®] ELAN 5000 instrument. Mercury in water samples was preconcentrated by gold amalgamation followed by analysis with CVAFS using a Brooks-Rand[®] Model III Mercury System.

The metal concentrations of the seawater, seawater extracts, CRMs and blanks were determined by GFAAS, ICP-MS or CVAFS (Table 2-1). Concentrations of dissolved Cr and Cu in the extracts were determined by GFAAS using a Perkin-Elmer[®] Model 4000 AAS with an HGA-400 graphite furnace and AS-40 autosampler. The As concentrations of the seawater extracts were determining using a Perkin-Elmer[®] Model 5100PC AAS with an HGA-600 graphite furnace and AS-60 autosampler. Dissolved Cd, Pb and Zn concentrations of the seawater extracts were quantified by ICP-MS using a Perkin-Elmer[®] ELAN 5000 instrument. Dissolved Ba concentrations were measured directly on the seawater samples by ICP-MS using a Perkin-Elmer[®] ELAN 5000 instrument and multiple-spike Method of Standard Additions. Total dissolved Hg concentrations were determined by CVAFS using a Brooks-Rand[®] Model III Mercury System following preconcentration by gold amalgamation.

River water chlorinity (Cl^-), sulfate (SO_4^{2-}) and fluoride (F^-) concentrations were determined by ion chromatography using a Dionex[®] DX-600 ion chromatograph (IC). Standard curves were prepared utilizing a Dionex[®] Five Anion Standard certified solution. The IC column was a Dionex[®] IonPac AS9-HC and the eluent was 9mM $NaHCO_3$. Alkalinity was determined by titration using the method of Strickland and Parsons (1972).

2.2.3 Trace and Major Metals in Suspended Sediment

Filters bearing suspended sediment and milligram quantities of standard reference material (SRM) #2704, a river sediment SRM issued by the National Institute of Standards and Technology (NIST), were digested in stoppered, 15-mL Teflon[®] test tubes using Ultrex II[®] HNO_3, HF and HCl. The sealed tubes were placed in an 80°C water bath where refluxing of the acids completely dissolved the particles on the filters. After digestion, the resultant solutions were transferred to acid-washed, 15-mL polyethylene bottles, diluted to ~6 mL with DDW rinses of the Teflon[®] tubes and stored in a plastic bag until analyzed.

Metal concentrations for the digested particulate samples, SRMs and blanks were determined by FAAS, GFAAS or ICP-MS in a manner compatible with EPA Series 7000, 6010A and 7470 (USEPA, 1993), respectively. Concentrations of particulate Al, Fe and Zn were determined by FAAS using a Perkin-Elmer[®] Model 4000 AAS. Concentrations of Cr and Cu were determined by GFAAS using a Perkin-Elmer[®] Model 4000 AAS equipped with an HGA-400 graphite furnace and AS-40 autosampler.

Concentrations of As were quantified by GFAAS using a Perkin-Elmer® model 5100 instrument equipped with an HGA-600 graphite furnace and an AS-60 autosampler. Values for Ba, Cd and Pb were determined by ICP-MS using a Perkin-Elmer® ELAN 5000 instrument. In all cases, the instrument manufacturers' specifications were followed and adherence to QA/QC requirements was maintained.

Table 2-1. Summary of instrumental methods and method detection limits (MDL) for metal analysis of suspended sediment (dry weight basis) and water.

Metal	Suspended Sediment		Water	
	Method	MDLs (µg metal/g, dry weight)	Method	MDLs (µg metal/L)
Al – aluminum	FAAS	1500	-	-
As – arsenic	GFAAS	1.8	GFAAS	0.00811
Ba – barium	ICP-MS	9	ICP-MS	0.1
Ca – calcium	FAAS	230	FAAS	0.01 mg/L
Cd – cadmium	ICP-MS	0.03	ICP-MS	0.0001
Cr – chromium	FAAS	0.33	GFAAS	0.005
Cu – copper	FAAS	0.4	GFAAS	0.003
Fe – iron	FAAS	250	GFAAS	0.01
K – potassium	FAAS	250	FAAS	0.02 mg/L
Hg – mercury	-	-	CVAFS	0.03 ng/L
Mg – magnesium	FAAS	40	FAAS	0.01 mg/L
Mn – manganese	FAAS	170	GFAAS	0.1
Na – sodium	FAAS	0.7	FAAS	0.008 mg/L
Ni – nickel	ICP-MS	0.2	ICP-MS	0.02
Pb – lead	ICP-MS	82	ICP-MS	0.002
Zn – zinc	FAAS	2	ICP-MS	0.01
POC/DOC	Shimadzu® Carbon System	0.01%	Shimadzu® Carbon System	0.1 mg/L

Notes: CVAFS = Cold Vapor Atomic Fluorescence Spectrometry
FAAS = Flame Atomic Absorption Spectrometry
GFAAS = Graphite Furnace Atomic Absorption Spectrometry
ICP-MS = Inductively Coupled Plasma-Mass Spectrometry
MDL = Method Detection Limit

2.3 Quality Assurance and Quality Control for Inorganic Parameters and Organic Carbon

2.3.1 Sample Tracking Procedure

All sediment samples were collected by, transported by and stored by personnel from FIT. Upon return-to or arrival at the laboratory, each sample was carefully inspected to insure that it was intact and that the identification number was clearly readable. All samples for organic carbon were kept frozen (-20°C) until processed for analysis.

2.3.2 Quality Control Measurements for Analysis

For this project, QC measures included balance calibration, instrument calibration (FAAS, GFAAS, CVAAS, ICP-MS, TOC analyzer, and *in-situ* instrument sensors), matrix spike analysis for each metal, duplicate sample analysis, analysis of CRMs and SRMs, procedural blank analysis and standard checks. With each batch of up to 20 samples, two procedural blanks, two CRMs or SRMs, two duplicate samples and two matrix-spiked samples were analyzed. Data quality objectives (DQOs) for these quality control measurements are provided in Table 2-2.

2.3.3 Instrument Calibration

Electronic balances used for weighing samples and reagents were calibrated prior to each use with certified NIST-traceable standard weights. All pipets (electronic or manual) were calibrated prior to use. Each of the spectrometers used for metal analysis was initially standardized using a three- to five-point calibration with a linear correlation coefficient of $r \geq 0.999$ required before experimental samples could be analyzed. Analysis of complete three- to five-point calibrations and/or single standard checks alternated every 5-10 samples until all the analyses were complete. The relative standard deviation (RSD) between complete calibration and standard checks was required to be <15% or recalibration and reanalysis of the affected samples were performed.

2.3.4 Matrix Spike Analysis

Matrix spikes were prepared for a minimum of 5% of the total number of samples analyzed and included each metal to be determined. Results from matrix spike analysis using the method of standard additions provide information on the extent of any signal suppression or enhancement due to the sample matrix. If necessary (i.e., spike results outside 80-120% limit), spiking frequency was increased to 20% and a correction was applied to the metal concentrations of the experimental samples.

2.3.5 Duplicate Sample Analysis

Duplicate samples from homogenized field samples (as distinct from field replicates) were prepared in the laboratory for a minimum of 5% of the total samples. These laboratory duplicates were included as part of each set of sample digestions and analyses and provide a measure of analytical precision.

2.3.6 Procedural Blank Analysis

Two procedural blanks were prepared with each set of 20 samples to monitor potential contamination resulting from laboratory reagents, glassware and processing procedures. These blanks were processed using the same analytical scheme, reagents and handling techniques as used for the experimental samples.

2.3.7 CRM and SRM analysis

A common method used to evaluate the accuracy of environmental data is to analyze reference materials, samples for which consensus or "accepted" analyte concentrations exist. The following CRMs and SRMs were used to check accuracy for dissolved metals: nearshore seawater CASS-3 (NRC), river water SLRS-3 and SLRS-4 (NRC) and natural water #1640 (NIST). Milligram quantities of the following CRMs and SRMs were used to assess accuracy for suspended sediment: marine sediment CRM MESS-2 (NRC) and Buffalo River sediment SRM#2704 (NIST). Metal concentrations obtained for the reference materials were required to be within 20% of accepted values for >85% of other certified analyses. Results for dissolved metals are listed in Table 2-3; results for suspended sediment are presented in Trefry et al. 2004. Data for QA/QC measurements for each cruise are given with the complete data sets in Appendices A, B and C.

Table 2-2. Data quality objectives and criteria.

Element or Sample Type Criteria	Minimum Frequency	Data Quality Objective/Acceptance
Initial Calibration	Prior to every batch of samples Standard Curve	3-5 point curve depending on the element and a blank Correlation coefficient r ≥ 0.999 for all analytes
Continuing Calibration	Must end every analytical sequence; for flame, repeat all standards every 5 samples; for graphite furnace and ICP-MS, recheck standard after every 8-10 samples	%RSD <15% for all analytes
Certified and Standard Reference Materials	Two per batch of 20 samples	Values must be within 20% of accepted values for >85% of the certified analytes and within 25% for Hg
Method Blank	Two per batch of 20 samples	No more than 2 analytes to exceed 5x MDL
Matrix Spike and Spike Method Blank	Two per batch of 20 samples	80-120%
Lab Duplicate	Two per batch of 20 samples	RSD <25% for 65% of analytes

Table 2-3. Results for reference materials for dissolved metals.

Standard (SRM) or Certified (CRM) Reference Material	Certified Concentrations[a] (µg/L)	This Study[b] (µg/L)
CRM CASS-3 (NRC)		
As (n = 8)	1.09 ± 0.07	1.06 ± 0.04
Ba (n = 2)	-	8.9 ± 0.4
Cd (n = 7)	0.030 ± 0.005	0.027 ± 0.001
Cr (n = 6)	0.092 ± 0.006	0.092 ± 0.001
Cu (n = 6)	0.517 ± 0.062	0.538 ± 0.016
Pb (n = 7)	0.012 ± 0.004	0.012 ± 0.002
Zn (n = 7)	1.24 ± 0.25	1.11 ± 0.08
CRM SLRS-3 (NRC)		
Ba (n = 6)	13.4 ± 0.2	13.6 ± 0.2
Ca (n = 5)	6.0 ± 0.4 mg/L	6.1 ± 0.2 mg/L
Fe (n = 5)	100 ± 2	101 ± 2
K (n = 5)	0.7 ± 0.1 mg/L	0.7 ± 0.1 mg/L
Mg (n = 5)	1.6 ± 0.6 mg/L	1.6 ± 0.1 mg/L
Mn (n = 5)	3.9 ± 0.3	3.8 ± 0.2
Na (n = 5)	2.3 ± 0.2 mg/L	2.3 ± 0.1
Pb (n = 5)	0.086 ± 0.007	0.084 ± 0.004
Zn (n = 5)	1.04 ± 0.09	1.05 ± 0.04
CRM SLRS-4 (NRC)		
Cu (n = 2)	1.81 ± 0.08	1.82 ± 0.04
Pb (n = 3)	0.086 ± 0.007	0.086 ± 0.002
Zn (n = 3)	0.93 ± 0.10	0.89 ± 0.03
SRM #1640 (NIST)		
Ba (n = 6)	148.0 ± 2.2	147.5 ± 2.0
Cu (n = 5)	85.2 ± 1.2[c]	84.9 ± 1.8
Ni (n = 5)	27.4 ± 0.8[c]	27.7 ± 0.7

[a] ± 95 confidence limits.
[b] ± 1 standard deviation.
[c] Reference Value (provided by NIST, not certified).

2.4 Organic Analyses

During the 2001 summer field season, eight large volume (4 L) samples of Beaufort Sea water were collected for PAH analyses. Three samples were collected at sites near Northstar Island, three were collected at Beaufort Sea Monitoring Program (BSMP) stations, and two were collected at stations near Liberty Prospect. Eight replicate samples were collected at station 3A (Figure 1-1). One of the station 3A replicates was analyzed with the other Beaufort Sea seawater samples. The remaining seven replicates were used in a spiking study to assess partitioning of potential organic contaminants between the dissolved and particulate phases.

Analysis for organic contaminants was conducted by ADL/ICF's environmental chemistry laboratory[1]. The analyses were conducted in accordance with the laboratory's standard operating procedures (SOPs) and generally followed the same procedures used in previous BSMP studies (Boehm et al., 1990). The aqueous samples were analyzed for PAH by gas chromatography with detection by mass spectrometry (GC/MS). Targeted compounds are listed in Table 2-4. This section describes the analytical methods that were used to perform the organic chemical analyses.

2.4.1 Aqueous Sample Preparation

The 4-L aqueous samples were filtered through pre-combusted glass fiber filters to isolate the dissolved and particulate phases. The filtered water and filtrate samples were refrigerated until sample preparation and were extracted within 7 days of preparation to meet holding time requirements. The filter samples were prepared using a procedure based on United States Environmental Protection Agency (USEPA) Method 3550A, Ultrasonic Extraction (USEPA, 1993). The method modifications included orbital shaking of the sample in extraction solvent for 1 hour following the final sonication to enhance recovery of target contaminants. The filtered water samples were prepared using a procedure based on USEPA Method 3510C, Separatory Funnel Liquid-Liquid Extraction. A volume of approximately 4 L was extracted for each sample. Surrogate compounds were spiked into the samples after the first addition of solvent and before the first extraction. All samples were spiked with "low-level" surrogates (as defined by the laboratory SOP) because target compound concentrations in the samples were expected to be at trace levels. A procedural blank, blank spike, and blank spike duplicate were prepared and analyzed with each sample extraction batch. Clean filters were used for the procedural blank and blank spikes associated with the filter samples.

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[1] During the course of this program, the prime contractor Arthur D. Little (ADL) filed for bankruptcy protection and was subsequently sold off by division. The environmental consulting and laboratory division of ADL was purchased by ICF Consulting in May 2002. To avoid confusion and remain consistent, the laboratory will be referred to throughout this report as the ADL/ICF laboratory. The ADL/ICF laboratory performed organic analysis on dissolved and particulate samples for the ANIMIDA program under Task Order 7. The ADL standard operating procedures (SOPs) were adopted, as is, with no technical changes by ICF. In March 2003, ICF closed the environmental laboratory located in Cambridge, MA. Fortunately, all necessary samples analyses for this program were completed prior to the close of the laboratory. Copies of all SOPs and the hard-copies and electronic instrument files for the organic chemistry data are archived at the ICF Consulting office in Lexington, MA.

Table 2-4. Target list of polynuclear aromatic hydrocarbons and alkyl polynuclear aromatic hydrocarbons.

Compound	Reporting Code	Internal Standard/ Surrogate Reference	Compound	Reporting Code	Internal Standard/ Surrogate Reference
Naphthalene	C0N	A/1	Benzo[a]anthracene	BAA	B/3
C1-Naphthalenes	C1N	A/2			
C_2-Naphthalenes	C2N	A/2	Chrysene	C0C	B/3
C_3-Naphthalenes	C3N	A/2	C_1-Chrysenes	C1C	B/3
C_4-Naphthalenes	C4N	A/2	C_2-Chrysenes	C2C	B/3
			C_3-Chrysenes	C3C	B/3
Acenaphthylene	ACEY	A/2	C_4-Chrysenes	C4C	B/3
Acenaphthene	ACE	A/2			
Biphenyl	BIP	A/2			
			Benzo[b]fluoranthene	BBF	B/4
Fluorene	C0F	A/2	Benzo[k]fluoranthene	BKF	B/4
C_1-Fluorenes	C1F	A/2	Benzo[e]pyrene	BEP	B/4
C_2-Fluorenes	C2F	A/2	Benzo[a]pyrene	BAP	B/4
C_3-Fluorenes	C3F	A/2	Perylene	PER	B/4
			Indeno[1,2,3-c,d]pyrene	IND	B/4
Anthracene	C0A	A/3	Dibenzo[a,h]anthracene	DAH	B/4
Phenanthrene	C0P	A/3	Benzo[g,h,i]perylene	BGP	B/4
C_1-Phenanthrenes/Anthracenes	C1P/A	A/3			
C_2-Phenanthrenes/Anthracenes	C2P/A	A/3			
C_3-Phenanthrenes/Anthracenes	C3P/A	A/3			
C_4-Phenanthrenes/Anthracenes	C4P/A	A/3			
Dibenzothiophene	C0D	A/3			
C_1-Dibenzothiophenes	C1D	A/3	Surrogate Compounds		
C_2-Dibenzothiophenes	C2D	A/3	Naphthalene-d_8	D8N	A/1
C_3-Dibenzothiophenes	C3D	A/3	Acenaphthene-d_{10}	D10ACE	A/2
			Phenanthrene-d_{10}	D10PH	A/3
Fluoranthene	FLANT	A/3	Benzo(a)pyrene-d_{12}	D12BAP	B/4
Pyrene	PYR	A/3			
C_1-Fluoranthenes/Pyrenes	C1F/P	A/3	Internal Standard		
C_2-Fluoranthenes/Pyrenes	C2F/P	A/3	Fluorene-d_{10}	D10F	A
C_3-Fluoranthenes/Pyrenes	C3F/P	A/3	Chrysene-d_{12}	D12C	B

Internal Standard/Surrogate Reference indicates internal standard used for quantitation and surrogate compound used to correct analytical results.
2-ring PAHs include: napthalenes, acenaphthylene, acenaphthene, biphenyl, and fluorenes.
3-ring PAHs include: anthracenes, phenanthrenes, and dibenzothiophenes.
4-ring PAHs include: fluoranthenes, pyrenes, benzo(a)anthracene, chrysenes, benzo(b)fluoranthene, and benzo(k)fluoranthene.
5-ring PAHs include: benzo(e)pyrene, benzo(a)pyrene, perylene, indeno(1,2,3-cd)pyrene, and dibenz(a,h)anthracene Benzo(g,h,i)perylene is a 6-ring PAH.

After solvent extraction, samples were concentrated using a Kuderna-Danish concentrator on a hot water bath. The extracts were reduced to a measured final volume under a stream of nitrogen. The final sample extracts were spiked with PAH internal standards, as appropriate for each extract. In general, the extracts were concentrated to approximately 250 μL before adding the internal standards to lower detection limits.

2.4.2 Analysis for Polynuclear Aromatic Hydrocarbons by Gas Chromatography/Mass Spectrometry

Analysis for PAHs was performed using a method based on USEPA Method 8270 (USEPA, 1993). The method modifications include analysis for an expanded list of PAH (Table 2-4) and operation in the selected ion monitoring mode to lower detection limits.

The sample extract was injected onto a 30-m long by 0.25-mm ID fused-silica capillary column with DB-5 bonded phase. This column provided baseline resolution of target PAHs. The injection port is designed for splitless injection and includes a silanized wide-bore glass liner containing a plug of silanized glass wool to reduce high-molecular-weight mass discrimination.

Qualitative identification of target compounds was made by comparison to a standard mixture of target PAHs. Identification of alkyl PAHs was made by comparison to reference oil samples analyzed with each batch of samples. The concentrations of the individual PAHs were calculated relative to one of the two internal standards that were spiked into the sample just prior to instrumental analysis. The target PAH concentrations were quantified using average response factors (RFs) generated from the five-point calibration curve. To quantify the alkyl PAH, homologue groups were assigned the RF of their respective parent PAH compound. Compound concentrations were corrected based on surrogate recoveries. A variety of diagnostic ratios and parameters are used for data interpretation (Table 2-5).

2.4.3 Oil Spike Study Procedure

Approximately 640 mg of wet (360 mg dry) homogenized Beaufort Sea sediment from sample 00-N23-01-PHC were added to each of the seven replicate 4-L water samples collected at station 3A. Sample 00-N23-01-PHC was selected for spiking because it was mostly fine-grained sediment (98.6% silt + clay) and had a representative Total PAH concentration of 540 μg/Kg. Assuming all of the fine-grained sediment became suspended in addition to the original total suspended solids (TSS) concentration for sample 3A, the final TSS for the spiked samples was 95 mg/L. Each sample also was spiked with ~200 mg of North Slope crude oil. The North Slope Crude oil was a Valdez Terminal composite crude oil collected in March 1989. A sediment blank was generated by adding ~640 mg of wet homogenized Beaufort Sea sediment to 4 L of distilled/deionized water. Clean magnetic stir bars were added to each sample jar. The samples were stirred for 24 hours at ~100 rpm in a walk-in refrigerator, held at 4°C $\pm$ 2°C. Approximately 3 L of the sample were removed from the sample jars by placing a clean Teflon® tube into the sample. The end of the Teflon® tube was covered with a

small piece of clean aluminum foil to prevent the uptake of any potential oil sheen while passing through the surface of the water. The samples were siphoned from near the bottom of the sample jar while the stir bar was spinning. The samples were then filtered through pre-combusted glass fiber filters to isolate the dissolved and particulate phases. The filtered water and filter samples were refrigerated until sample preparation and were extracted within 7 days of preparation to meet holding time requirements. To avoid loss of the lower molecular weight PAHs, the filter samples were not dried and weighed after filtering to determine the suspended sediment mass collected on the filter.

Table 2-5. Diagnostic ratios and parameters for polynuclear aromatic hydrocarbons.

Parameter	Relevance in Environmental Samples
N/P	The naphthalenes (N) to phenanthrenes/anthracenes (P) ratio is diagnostic for inputs of fresh petroleum, and as a weathering indicator. Naphthalenes are characteristic of fresh crude oil; the ratio decreases with increased weathering. (N= Naphthalene series [C0N + C1N + C2N + C3N + C4N]; P= Phenanthrene/Anthracene Series [C0P/A + C1P/A + C2P/A + C3P/A + C4P/A]).
Perylene	A biogenic PAH formed during the early diagenesis in marine and lacustrine sediment; may be associated with terrestrial plant source precursors.
Total PAH	The sum of all PAH target analytes; includes 2- through 6-ring parent PAH and C1 - C4 alkyl-substituted PAH.
2-Ring PAH	The sum of PAH compounds with 2 rings (napthalenes, acenaphthylene, acenaphthene, biphenyl, and fluorenes).
3-Ring PAH	The sum of PAH compounds with 3 rings (anthracenes, phenanthrenes, and dibenzothiophenes).
4-Ring PAH	The sum of PAH compounds with 4 rings (fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, and benzo[k]fluoranthene).
5^+-Ring PAH	The sum of PAH compounds with 5 or 6 rings (benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3,-c,d]pyrene).
Pyrogenic PAH	The sum of combustion PAH compounds (4-, 5-, and 6-ring PAH: fluoranthene, pyrene, chrysene, benzo[a]anthracene, benzo[b]fluoranthene, benzo[k]fluoranthene, benzo[a]pyrene, dibenz[a,h]anthracene, benzo[g,h,i]perylene, and indeno[1,2,3,-c,d]pyrene.
Petrogenic PAH	The sum of petrogenic PAH compounds (2-, 3-, and 4-ring PAH: naphthalenes [C0 - C4], acenaphthene, acenaphthylene, fluorene [C0 - C3], phenanthrenes [C0 - C4], dibenzothiophenes [C0 - C3], chrysenes [C1 - C4], and fluoranthenes/pyrenes [C1 - C3]).
Pyrogenic/Petrogenic	The ratio of pyrogenic PAH compounds to petrogenic PAH compounds is useful for determining the relative contribution of pyrogenic and petrogenic hydrocarbons and in differentiating hydrocarbon sources.

3.0 RESULTS AND DISCUSSION

The Results and Discussion for this report begin with the input of dissolved and particulate substances by rivers and then transition to the transport and distribution of dissolved and particulate substances in the coastal Beaufort Sea. Most of the data are for trace metals and organic carbon. The final two sections present some data for PAH and results of a spiking experiment. As a preview, the following seven sections make up the Results and Discussion.

 3.1 Source Rivers 2001: Transport of Dissolved and Particulate Metals and Organic Carbon.

 3.2 Source Rivers 2002: Transport of Dissolved and Particulate Metals and Organic Carbon.

 3.3 Transport of Dissolved and Particulate Metals and Organic Carbon by Rivers to the Coastal Beaufort Sea.

 3.4 Partitioning of Metals between Dissolved and Particulate Phases in Rivers.

 3.5 Dissolved and Particulate Metals in the Coastal Beaufort Sea.

 3.6 Dissolved and Particulate Organic Substances in Seawater.

 3.7 Spike Study for Polycyclic Aromatic Hydrocarbons

3.1 Source Rivers 2001

3.1.1 Transport of Water and Suspended Sediment

Concentrations of dissolved and particulate metals (As, Ba, Ca, Cu, Fe, K, Mg, Mn, Na, Ni, Pb and Zn), particulate Al and dissolved and particulate organic carbon (DOC and POC) were determined for the Sagavanirktok, Kuparuk and Colville rivers (Figure 3-1 and Table 3-1) during May to August 2001. Conductivity and concentrations of dissolved major elements (Ca, Mg, Na, K, bicarbonate and sulfate) were determined in river water to evaluate differences in composition and the degree of chemical weathering among rivers.

Most rivers that drain into the Arctic Ocean carry 40 to 80% of their annual volume of water during peak flow in May, June and July (Arnborg et al., 1967; Gordeev et al, 1996). Studies in the Alaskan Arctic have shown that concentrations of TSS in the Colville River follow the same trend as water flow with >70% of the annual discharge of TSS occurring during May and June (Arnborg et al., 1967). Large seasonal discharges of water and suspended sediment at high latitudes emphasize the importance of annual spring floods to the arctic hydrologic cycle.

The three rivers studied during the ANIMIDA program, the Sagavanirktok, Kuparuk and Colville rivers (Figure 3-1), lie within the Arctic climatic zone where annual temperatures average -12°C and mean precipitation is ~12 cm/yr (Telang et al., 1991). The drainage basins of these Arctic rivers include the following three physiographic provinces: the Arctic Mountain Province, the Arctic Foothills Province, and the Arctic Coastal Plain Province (Payne et al., 1951). Based on the classification scheme proposed
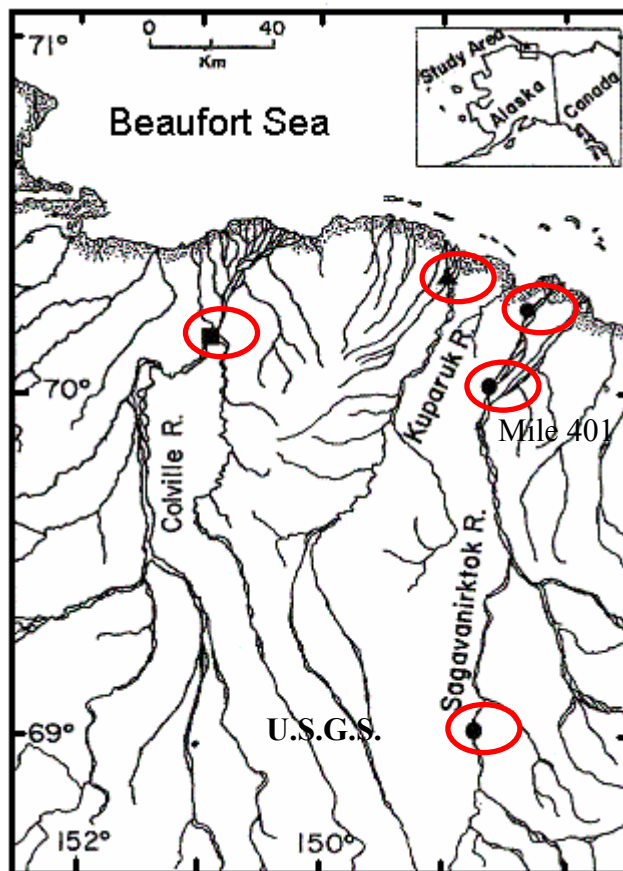
Figure 3-1. Map showing locations of sampling sites in the Colville, Kuparuk and Sagavanirktok rivers with inset map showing study area.

Table 3-1. Locations of river sampling sites.

Site	Latitude (N)	Longitude (W)
Sagavanirktok River (near Prudhoe Bay)	70° 15.033′	148° 18.484′
Sagavanirktok River (~30 km upstream at mile 401 on the Dalton Highway)	70° 01.684′	148° 37.781′
Sagavanirktok River (U.S.G.S. gauge at mile 327 on the Dalton Highway)	69° 00.527′	148° 49.214′
Kuparuk River	70° 19.812′	149° 00.527′
Colville River	70° 09.519′	150° 56.791′

by Craig and McCart (1975), the Sagavanirktok and Colville rivers can be classified as mountain streams that drain snowfields and glaciers in the Brooks Range. In contrast, the yellow-colored water of the Kuparuk River is more representative of a tundra stream (Lock et al., 1989). All three rivers flow into the coastal Beaufort Sea.

Rivers are a major source of water and sediment to the ANIMIDA study area during spring runoff and on an annual basis. The river-borne water and sediment carry a full, natural complement of dissolved and particulate elements that are physically and chemically weathered from the mountains and tundra bordering the coastal Beaufort Sea. To understand possible anthropogenic perturbations to the ANIMIDA study area, one must first understand the composition, flow characteristics and amounts of incoming sediment and water. In this regard, the Sagavanirktok, Kuparuk and Colville rivers (Figure 3-1 and Table 3-1) were sampled during spring runoff (May-June) in 2001 and 2002 and during the summers (July-August) of 2000, 2001, and 2002. During breakup, the Sagavanirktok River was sampled daily and the other two rivers were sampled every two to five days as logistics permitted.

Water discharge data were taken from United States Geological Survey (U.S.G.S.) gauges on the Sagavanirktok (#15908000) and Kuparuk (#15896000) rivers (U.S.G.S., 2001). The gauge on the Sagavanirktok River is located ~160 km upstream from the bridge near Prudhoe Bay where the daily samples were collected and the gauge incorporates only ~20% of the drainage basin. The U.S.G.S. gauge for the Kuparuk River is located <5 km upstream from our sampling location and receives water discharge from >90% of the drainage basin. Flow data for the Colville River were collected only during the period of peak flow by Baker et al. (2001); the U.S.G.S. does not maintain a gauge on the Colville River.

Water began to flow in the Sagavanirktok River on June 3, 2001 (Figures 3-2 and 3-3). Samples were collected daily from June 3 to June 23 and later on July 30 and August 8 from the bridge near the Prudhoe Bay Operations Center (PBOC). Samples also were collected at mile 401 on the Dalton Highway on June 5, 11, 12, 16, 19 and 21 and at the site of a gauging station (mile 327 on the Dalton Highway) maintained by the U.S.G.S. on June 14 and 21, about 150 km south of Deadhorse.

Concentrations of TSS in the Sagavanirktok River at PBOC increased from ~40 mg/L on June 3, 2001, to 600 mg/L within 10 days on June 12 and then decreased to ~30 mg/L by June 18 (Figure 3-2). A secondary pulse occurred about June 23 when concentrations of TSS rose to ~90 mg/L following a rain storm (Figure 3-2). Data for water flow at the U.S.G.S. gauge, located ~150 km upstream, followed a similar trend. A 1- to 2-day offset between the peaks in TSS and water flow is due to the 150 km difference in location between the gauge and primary sampling site (Figure 3-1). Results for TSS in the Sagavanirktok River at mile 401 on the Dalton Highway and the U.S.G.S. gauge site (mile 327 on the Dalton Highway) were similar to results from the PBOC bridge, considering a lag time of several hours (mile 401) to 2 days (mile 327).
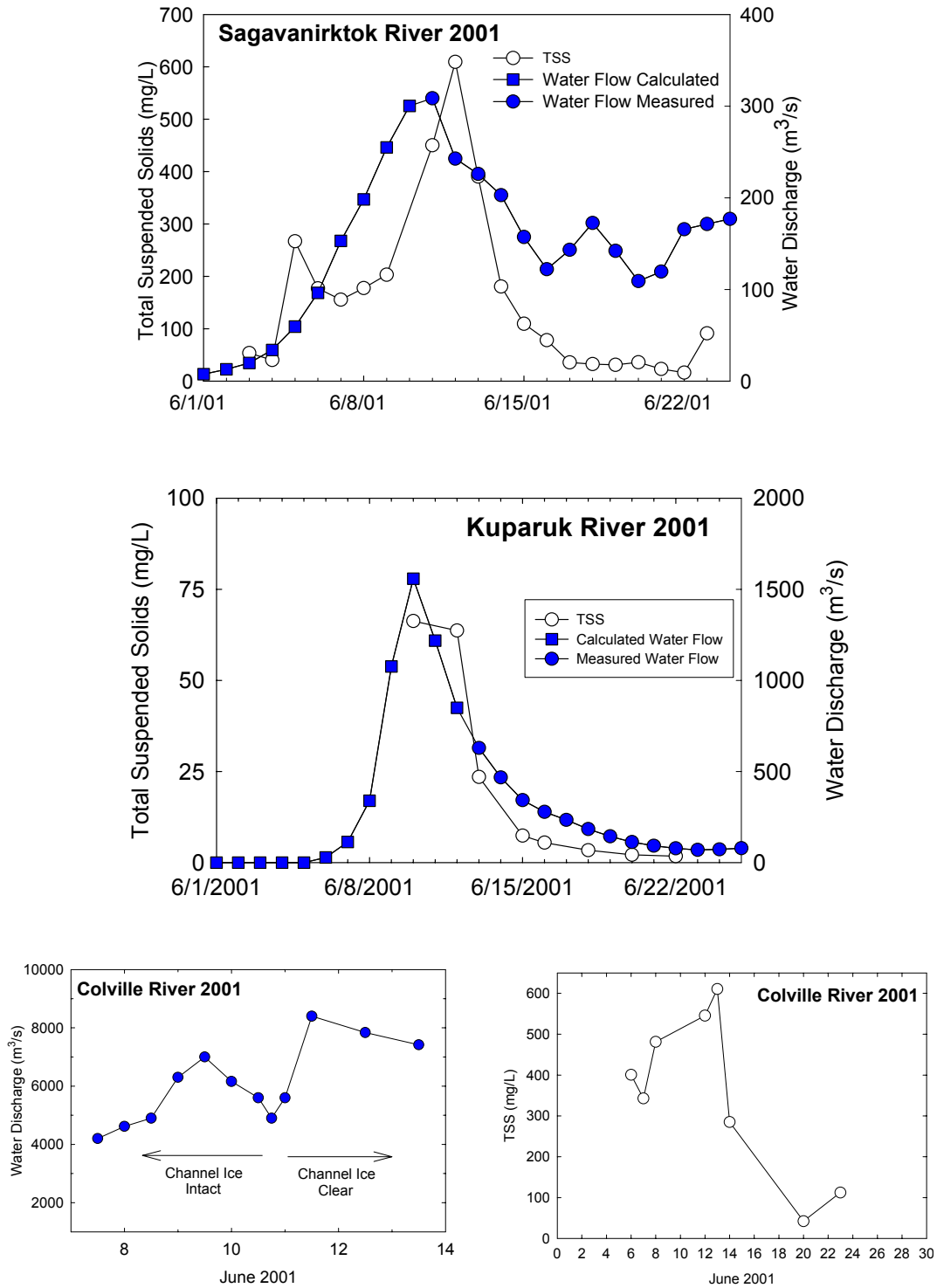
Figure 3-2. Water flow and concentrations of total suspended solids (TSS) for the Sagavanirktok, Kuparuk and Colville rivers during June 2001. Water data for the Sagavanirktok and Kuparuk rivers are from the U.S. Geological Survey. Flow data for the Colville River during peak flow are from Baker et al. (2001); the U.S.G.S. does not maintain a water flow gauge on the Colville River.

Sagavanirktok River on May 25 and June 11, 2001 at bridge near Prudhoe Bay Operations Center.

Kuparuk River causeway/bridge (eastern segment of river) shown under water during peak flow on June 11, 2001 and then high and dry and rebuilt on June 20, 2001.

Colville River at Monument 1 during peak flow on June 9, 2001 and later at lower flow on June 20, 2001.

Figure 3-3. Sagavanirktok, Kuparuk and Colville rivers during June 2001.

The flow gauge in the Sagavanirktok River was not installed by the U.S.G.S. until the river was free of ice on June 10, 2001, ~7 days after water flow began. Thus, during 2001 and most other years, the ascending limb of the hydrograph is calculated, not measured for the Sagavanirktok River. Furthermore, because the gauge is upstream in the western drainage basin of the Sagavanirktok River, the gauge covers only ~20% of the watershed and may not characterize flow patterns for the entire basin. During 2001, the total volume of water measured at the U.S.G.S. gauge in the Sagavanirktok River was ~1.3 km^3, yielding a total extrapolated (from 20% to 100%) flow of ~6.5 km^3 y^{-1} (U.S.G.S., 2001). About 30% of the total annual water flow of Sagavanirktok River was discharged during June (Figure 3-2).

The spring flood during June carried ~60% of the total annual water discharge in the Kuparuk River (Figures 3-2 and 3-3). In the Kuparuk River, concentrations of TSS reached peak values of 60 mg/L on June 10, 2001 and decreased to <5 mg/L after June 16 (Figure 3-2). Peak flow recorded for the Kuparuk River was about 600 m^3/sec on June 12, 2001, decreasing to <50 m^3/sec after June 28, 2001. Values for TSS were ~0.6 mg/L during August 2001 for the Kuparuk River.

Concentrations of TSS in the Colville River followed similar trends to those observed for the Sagavanirktok River with maximum levels of about 600 mg/L on June 13, 2001 (Figures 3-2 and 3-3). Values for TSS were about 6 mg/L during August 2001 for the Colville River. During the spring snow melt, flow in the Colville River (6,000 to 9,000 m^3/sec) was an order-of-magnitude greater than in the Sagavanirktok or Kuparuk rivers.

3.1.2 Trends in Concentrations of Dissolved Major Ions

In the Sagavanirktok, Kuparuk and Colville rivers conductivity and concentrations of dissolved Ca and Mg and carbonate alkalinity (CA) decreased as discharge increased (Table 3-2, Figure 3-4). For example, concentrations of dissolved Ca decreased by 27% from 1450 μeq/L on June 3rd to 1060 μeq/L during maximum peak discharge on June 8th in the Sagavanirktok River (Figure 3-4b). Carbonate alkalinity correlated well with concentrations of dissolved Ca + Mg (r = 0.98) for all three rivers and decreased by a grand average of ~21% during peak discharge (Figure 3-5). The strong correlation between Ca + Mg and CA with a slope close to 1 is typical of drainage basins containing primarily carbonate rocks. Concentrations of fluoride and sulfate also decreased during peak discharge in the Sagavanirktok River, but were below detection limits (F$^-$ <3 μeq/L and SO$_4^{2-}$ <4 μeq/L) in the Kuparuk River. Concentrations of sulfate were above detection limits in the Colville River, but were ~3 to 6 fold less than in the Sagavanirktok River during off-peak and peak discharge, respectively (Table 3-2). Elevated concentrations of sulfate and fluoride in the Sagavanirktok River were likely due to the lithology of the drainage basin as discussed below. Both the Sagavanirktok and Colville rivers extend into the Brooks Range whereas the Kuparuk River receives runoff only from the foothills and coastal plain, suggesting that potential sources of sulfate are located in the mountains. Concentrations of fluoride were slightly above detection limits (2-3 fold) in the Sagavanirktok River because phosphate rocks (possibly apatite) containing F are present in Lisburne Limestone, a geologic formation only exposed in the

23

Table 3-2. Conductivity (Cond.) and concentrations of total dissolved solids (TDS), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), hydrogen ion (H^+), carbonate alkalinity (CA), sulfate, chloride (Cl), fluoride (F), silicon (Si) and dissolved organic carbon (DOC) in the Sagavanirktok, Kuparuk and Colville rivers during peak and off-peak discharge in June 2001.

River		Cond. (μS)	TDS (μeq/L)	Ca (μeq/L)	Mg (μeq/L)	Na (μeq/L)	K (μeq/L)	H^+ (neq/L)	CA (μeq/L)	Sulfate (μeq/L)	Cl (μeq/L)	F (μeq/L)	Si (μM)	DOC (μM)
Peak Discharge														
Sagavanirktok (n = 10)	Mean	184	3410	1180	340	45	21	18	1430	355	44	8	34	421
	Std. Dev.	± 24	± 410	± 120	± 80	± 10	± 8	± 4.4	± 140	± 121	± 24	± 1	± 4	± 206
	Range	147-218	2950-4150	1060-1330	270-470	32-65	6-30	12-25	1270-1700	225-569	19-83	7-10	28-40	167-742
Kuparuk (n = 3)	Mean	67	1030	380	90	36	30	47	462	ND	63	ND	19	1170
	Std. Dev.	± 13	± 140	± 50	± 10	± 5	± 3	± 19	± 69		± 11		± 0.3	± 136
	Range	56-81	870-1140	330-440	80-90	30-39	27-32	33-69	383-504		50-71		18-19	1050-1320
Colville (n = 1)	Mean	55	1260	286	148	78	29	32	668	62	15	ND	27	835
	Std. Dev.												± -	± 160
	Range													667-1100
Off-Peak Discharge														
Sagavanirktok (n = 10)	Mean	246	4590	1480	540	53	10	9.7	1810	670	25	11	44	244
	Std. Dev.	± 11	± 260	± 102	± 40	± 6	± 3	± 2.9	± 91	± 55	± 5	± 1	± 3	± 99
	Range	233-264	4250-4980	1350-1630	500-590	46-68	8-15	7-15	1660-1930	595-753	19-35	11-12	38-49	117-408
Kuparuk (n = 3)	Mean	112	2010	744	140	46	16	19	1010	ND	64	ND	32	728
	Std. Dev.	± 3	± 70	± 19	± 10	± 3	± 1	± 1.0	± 48		± 9		± 4	± 39
	Range	108-115	1930-2060	722-760	130-150	44-49	15-17	17-19	960-1040		53-69		29-37	692-788
Colville (n = 3)	Mean	111	1960	549	270	110	34	27	783	212	27	ND	43	454
	Std. Dev.	± 19	± 300	± 57	± 20	± 23	± 8	± 8.2	± 150	± 46	± 10		± 4	± 160
	Range	90-125	1610-2140	4490-593	250-290	83-126	24-39	20-36	615-880	159-243	16-35		39-46	342-608
World Average*		-	1250	670	260	223	33	-	850	172	162	-	173	-

*Meybeck, 1979

ND = not detected.

24
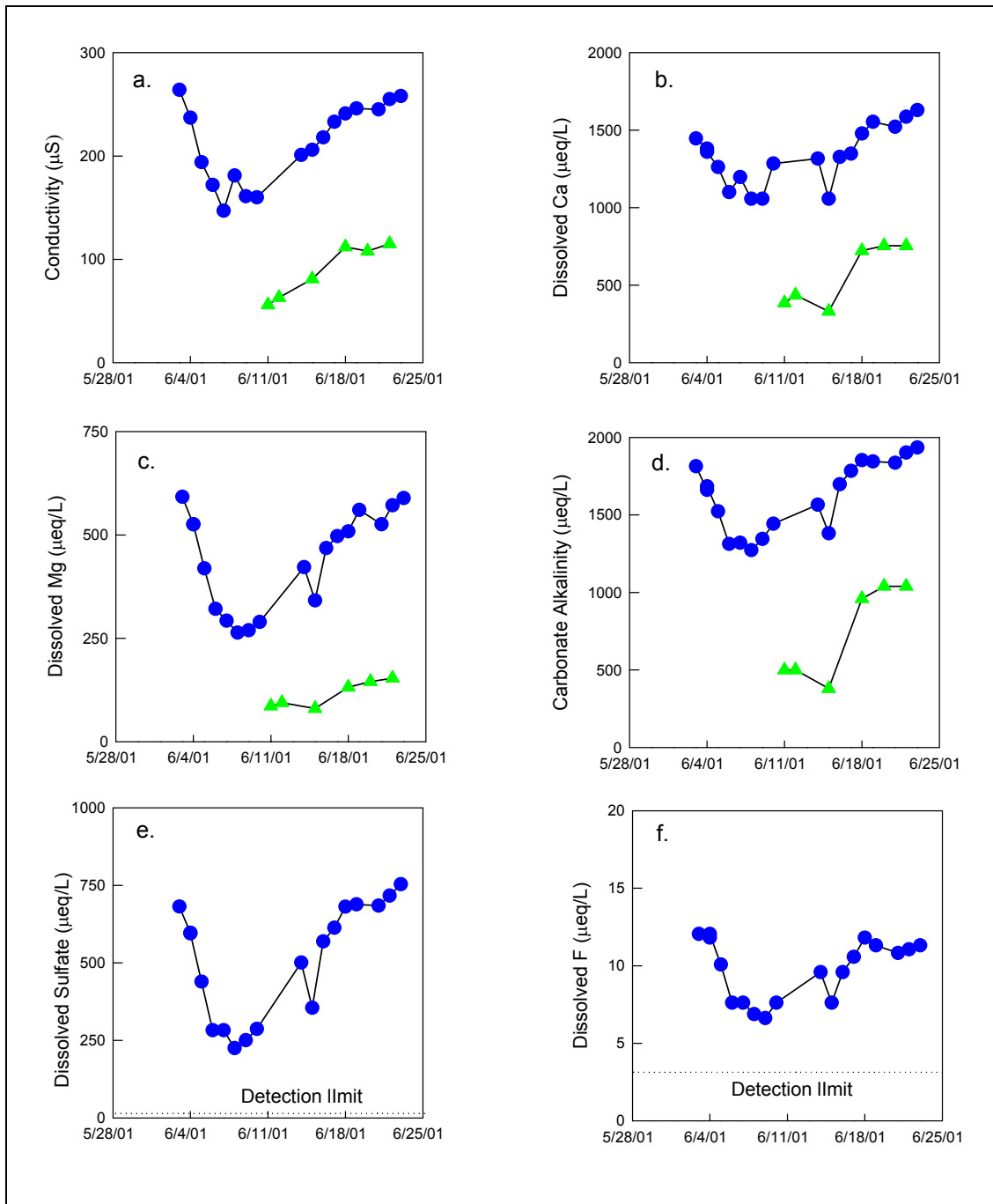
Figure 3-4. (a) Conductivity and concentrations of dissolved (b) calcium (Ca), (c) magnesium (Mg), (d) carbonate alkalinity, (e) sulfate and (f) fluoride (F) in the Sagavanirktok River (●) and Kuparuk River (▲) during June 2001. Concentrations of sulfate and F were below detection limits in the Kuparuk River.
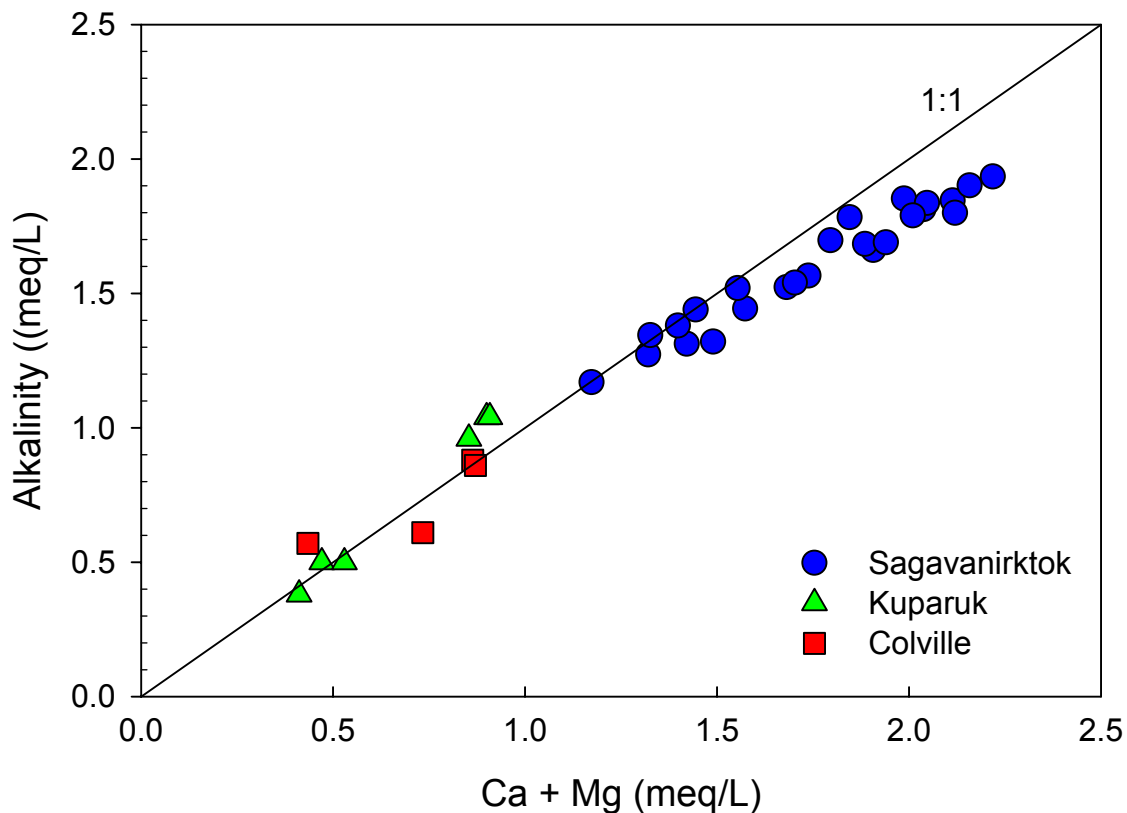
Figure 3-5. Concentrations of dissolved calcium plus magnesium (Ca + Mg) versus carbonate alkalinity in the Sagavanirktok, Kuparuk and Colville rivers. Line shows 1:1 relationship.

drainage basin of the Sagavanirktok River (Payne et al., 1951).

Concentrations of dissolved Si also decreased during peak discharge in the Sagavanirktok, Kuparuk and Colville rivers by 23%, 40% and 37%, respectively (Table 3-2). Low levels of dissolved Si in these rivers (18-46 μM) contrast sharply with the trend found in the Yukon River where concentrations of dissolved Si increase from ~120 μM to >180 μM during peak discharge (Edmond et al., 1996). This apparent discrepancy will be discussed below.

In contrast to decreasing concentrations of Ca, Mg, CA, sulfate and F during peak discharge, concentrations of K, DOC and H^+ (expressed as H^+ activity in neq/L) increased during peak discharge (Figure 3-6). In the arctic, during peak discharge of snowmelt, runoff is confined to the upper-most organic soil horizon (O-horizon) and surface litter. As soils thaw, ions leached from organic matter or concentrated in soil interstitial water and pools of water on the tundra (ponds, lakes, boggy areas) are transported with snowmelt into rivers. This phenomenon results in increased concentrations of K and DOC and lower pH in river water during the spring floods.

Concentrations of dissolved K increased from 6 μeq/L on June 3 to ~30 μeq/L on June 8, 2001, and averaged 52% higher during peak than off-peak discharge in the Sagavanirktok River (Figure 3-6a, Table 3-2). Similar trends were found in the Kuparuk River. During off peak discharge, concentrations of dissolved K in both the Sagavanirktok and Kuparuk rivers were ~2 to 3 fold lower than the world average (Table 3-2). In contrast, concentrations of dissolved K were similar to the world average in the Colville River during both peak and off- peak discharge.
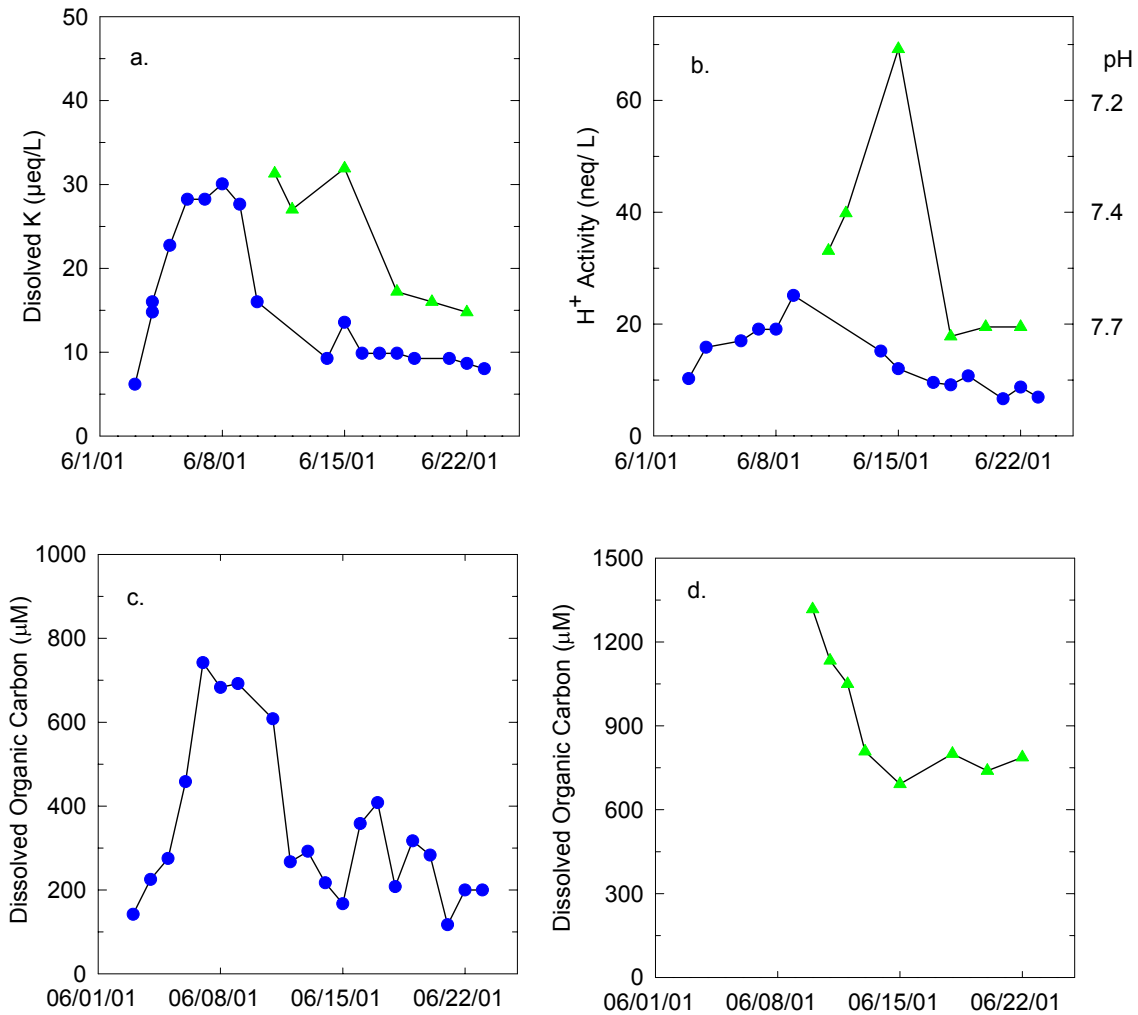
Figure 3-6.   Concentrations of dissolved (a) potassium (K) and (b) hydrogen ion (H^{+}) and pH in the Sagavanirktok (●) and Kuparuk (▲) rivers, and dissolved organic carbon in the (c) Sagavanirktok River and (d) Kuparuk River during June 2001.

27

Higher concentrations of dissolved K in the Colville River are consistent with known geology of the Colville Formation (Upper Cretaceous) where biotite, a K-rich mineral, was found to be 40-70% of the heavy mineral assemblage (Payne et al., 1951).

3.1.3 Interrelationships among Major Ions

Factor analysis with varimax rotation (Reeder et al., 1972) was used to assess the relationships among dissolved Ca, Mg, Na, K, Cl, sulfate, F, CA, Si, H^+, and DOC in the Sagavanirktok River for 2001. Significant positive loadings are shown in bold and negative loadings are italicized (Table 3-3). The results show that 3 factors explained ~90% of the variance among samples.

Table 3-3. Varimax factor matrix of dissolved ions and dissolved organic carbon (DOC) for the Sagavanirktok River. Values listed in table are significant at p = 0.05.

Element	Factor (% of Variance Explained)		
	#1 (53%)	#2 (24%)	#3 (12%)
Ca	**0.89**		
Mg	**0.84**		
K	*-0.64*	**0.66**	
Na			**0.99**
F	**0.84**		
Cl	*-0.69*		**0.53**
Sulfate	**0.84**		
CA	**0.85**		
H^+	*-0.50*	**0.55**	
DOC		**0.87**	
Si	**0.85**		

Extraction Method: Principal Component Analysis.
Rotation Method: Varimax with Kaiser Normalization.

Factor 1 explains ~53% of the variance among analytes and is characterized by high positive scores for Ca, Mg, F, sulfate, CA, Si and moderately high negative scores for K, Cl, and H^+ (Table 3-3). High positive scores for Ca, Mg, F, sulfate, and CA are consistent with chemical weathering of limestone, dolomite and S-bearing rock. Negative loadings for K, Cl, and H^+ show that these chemical species are derived from different source minerals and are transported at high levels at peak flow as previously discussed. The elements with positive loadings for Factor 1 are transported at slightly lower concentrations during peak discharge.

Factor 2 accounts for ~24% of the total variance with significant loadings for K, H^+ and DOC. This factor supports an earlier discussion that increases in concentrations and sources of these three components are linked to the release of K, DOC and H^+ from vegetation, soils, ponds and surface water via the infiltration of snowmelt and subsequent discharge into the rivers.

Factor 3 has a strong positive loading for Na (0.99), a moderate positive loading for chloride (0.53) and explains ~12% of the variance among samples. The low concentrations of chloride are likely derived from inputs of cyclic salts, but additional sources of Na from feldspars are likely present. Therefore, the relationship between Na and Cl in Factor 3 is most likely derived between a cyclic salt source for both ions and an additional source for Na.

3.1.4 Reconstruction of Chemical Weathering to Produce Major Ion Concentrations of Rivers

Rember (2002) characterized the river-borne particles and reconstructed the composition and amounts of the minerals that were chemically weathered to yield the concentrations of the dissolved major ions found in the Sagavanirktok, Kuparuk and Colville rivers. The complete section from Rember (2002) is provided in Appendix D, including the details of the calculations. The dominant rock type that is chemically weathered in each of the three rivers is carbonate (limestone and dolostone) that accounts for >80% of the dissolved solids.

During peak discharge in the Sagavanirktok River, a total of ~96 mg/L of rock was chemically weathered during peak discharge in the Sagavanirktok River, with ~34% from evaporites, 58% from carbonates and 8% from silicates (Figure 3-7).

During off-peak discharge in the Sagavanirktok River, the amount of rock weathered increased to 136 mg/L (Figure 3-7, Sagavanirktok Off-Peak pie). This was consistent with the processes that occur during the spring floods in northern Alaska. During peak discharge, runoff is confined to the O-horizon and snowmelt is proceeding at a rapid rate. Therefore, the lack of an active layer, combined with a relatively short residence time (contact time) of the snowmelt in the drainage basin, does not allow minerals to undergo extensive chemical weathering. However, during off-peak discharge, the volume of snow melting decreases and therefore the residence time of snowmelt in the mountains and coastal plain probably increases allowing for increased chemical weathering of the rocks in the drainage basin.

In the Kuparuk River drainage basin, ~28 and 46 mg/L of carbonate and silicate rock were weathered during peak and off-peak discharge respectively (Figure 3-8). These values are significantly lower (2-3 fold) than the amount of rock weathered in the Sagavanirktok River. This suggests that the chemical weathering of rocks from the Brooks Range (and additional sources of SO_4^{2-}) have a large impact on the chemical composition of river water. In contrast to the Sagavanirktok and Colville rivers, no Na-silicate minerals were needed for the reconstruction of minerals weathered in the Kuparuk River, suggesting that the source of Na-silicates also may be primarily found in the Brooks Range. However, due to the lack of evaporites and relatively low concentrations of carbonates, silicate rock weathering accounted for ~20 and 9% of the total rock weathered in the drainage basin of the Kuparuk River during peak and off-peak discharge, respectively.

The weathering of carbonates plus evaporites in the Colville River accounted for 76 and 81% of the rocks weathered during peak and off-peak discharge respectively (Figure 3-9). However, the amount of rock weathered was more similar to the Kuparuk than the Sagavanirktok River (Figure

3-9). As discussed above, evaporite and carbonate minerals are most abundant in the drainage basin of the Sagavanirktok River and are more rapidly weathered than silicate minerals.
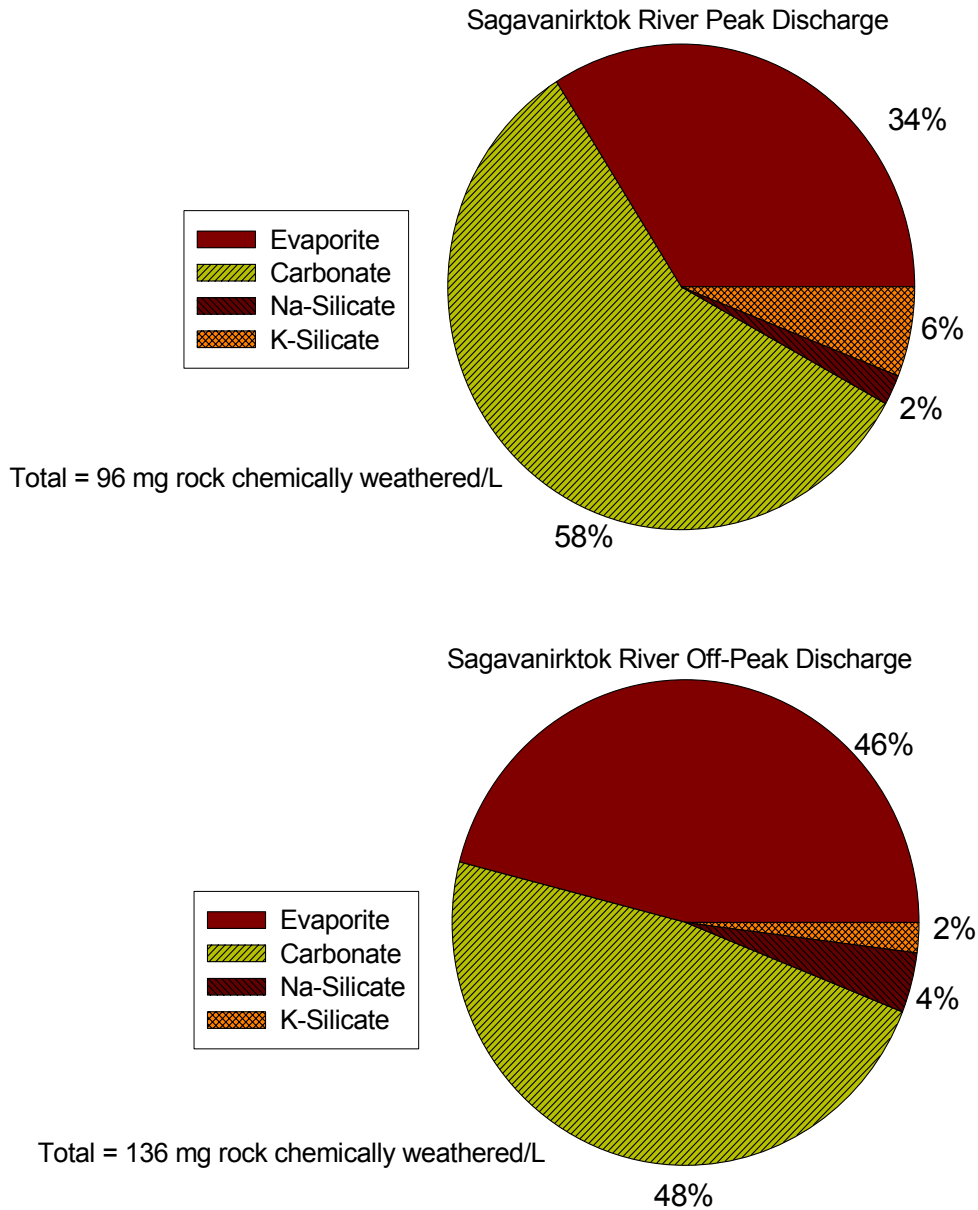
Figure 3-7. Fraction of different rock types that were chemically weathered to produce the observed concentrations of dissolved major elements in the Sagavanirktok River during peak and off-peak flow in 2001.

Kuparuk River Peak Discharge

80%

Carbonate
K-Silicate

20%

Total Rock Weathered = 28 mg/L

Kuparuk River Off-Peak Discharge

91%

Carbonate
K-Silicate

9%

Total Rock Weathered = 46 mg/L
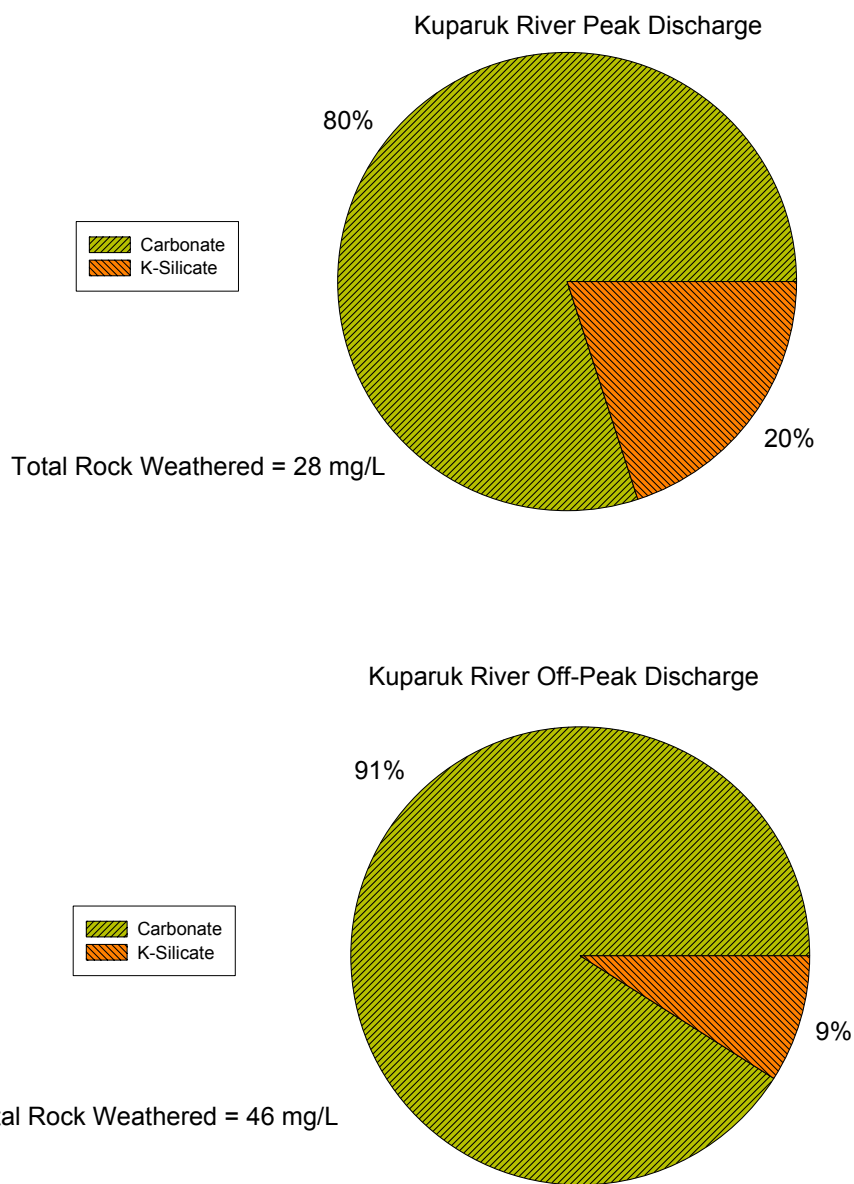
Figure 3-8. Fraction of different rock types that were chemically weathered to produce the observed concentrations of dissolved major elements in the Kuparuk River during peak and off-peak flow in 2001.

Colville River Peak Discharge

58%

Legend:
- Evaporite
- Carbonate
- Na-Silicate (?)
- K-Silicate

18%

25%

Total Rock Weathered = 36 mg/L

Colville River Off-Peak Discharge

28%

53%

Legend:
- Evaporite
- Carbonate
- Na-Silicate
- K-Silicate

13%

6%

Total Rock Weathered = 60 mg/L
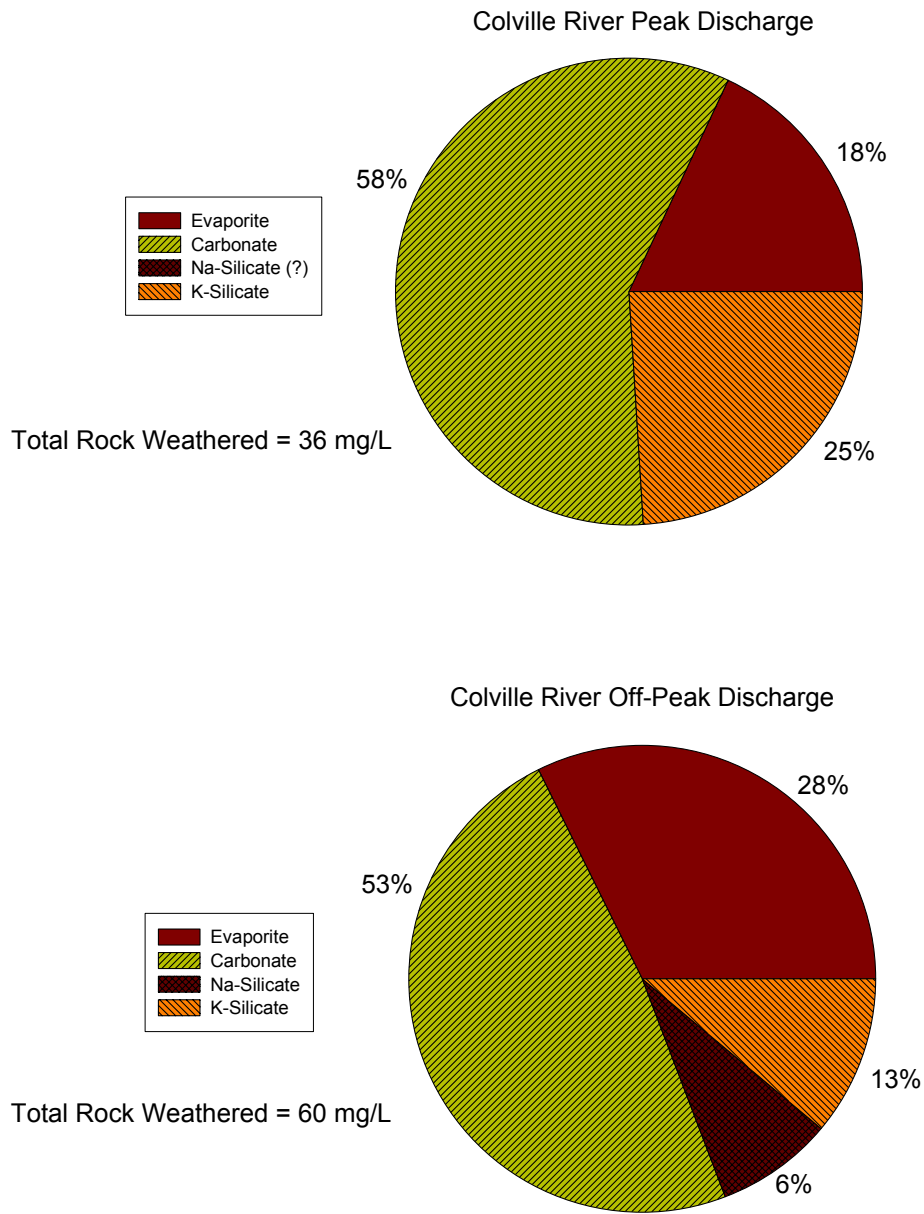
Figure 3-9. Fraction of different rock types that were chemically weathered to produce the observed concentrations of dissolved major elements in the Colville River during peak and off-peak flow in 2001.

3.1.5 Dissolved Organic Carbon and Trace Metals

During the first 5 days of discharge (June 3 to 7, 2001), concentrations of DOC in the Sagavanirktok River increased sharply from 2.0 to 8.9 mg/L, levels that are up to 6 times greater than during off-peak discharge (Figure 3-10, Table 3-4). Similar trends for concentrations of DOC also were observed in the Kuparuk and Colville rivers, where peak concentrations were 15.8 and 13.2 mg/L, respectively (Table 3-4). Higher concentrations of soluble organic matter from soils, surface ponds and bottom sediment in the Kuparuk and Colville rivers, relative to the Sagavanirktok River, reflect differences in the nature of the drainage basins as described later in this report.

During peak discharge in June 2001, average concentrations of DOC in the Sagavanirktok, Kuparuk and Colville rivers averaged 2 to 5 times higher than concentrations measured during off-peak discharge in June (Table 3-4). Increased concentrations of DOC during peak flow were amplified with respect to total transport by increases in water discharge. The spring thaw is clearly a key period for transport of DOC to the Arctic Ocean from the Alaskan Arctic.

Concentrations of DOC also have been observed to increase during peak water discharge in many rivers of the world (Cauwet and Meybeck, 1987; Depetris and Paolini, 1991; Cauwet and Sidorov, 1996; Boyer et al., 1997). This phenomenon is caused when snowmelt or rising water levels percolate through litterfall and DOC-rich interstitial water in the upper soil horizon where concentrations of DOC can be >96 mg/L, (Boyer et al., 1997; Michaelson et al., 1998). Depetris and Paolini (1991) found that concentrations of DOC increased during a flooding event in the Parana River such that the discharge-weighted mean increased from ~6.0 mg/L up to 10.2 mg/L and more than doubled the transport rate of DOC. A positive correlation between DOC and
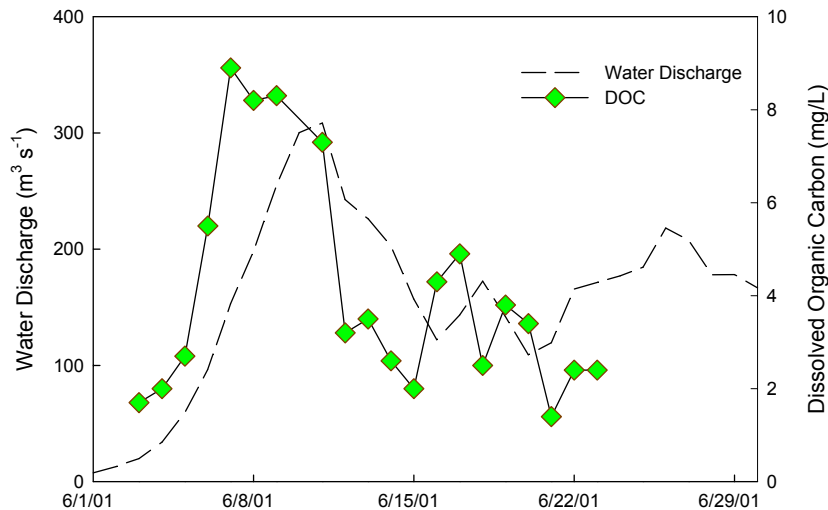
Figure 3-10. Concentrations of dissolved organic carbon and water discharge for the Sagavanirktok River during June 2001 and 2002. Water flow data from U.S.G.S. (2001).

Table 3-4. Concentrations of total suspended solids (TSS), dissolved metals and dissolved organic carbon (DOC) in the Sagavanirktok, Kuparuk and Colville rivers during peak and off-peak discharge in June 2001.

River		Ba (μg/L)	Cu (μg/L)	Fe (μg/L)	Pb (ng/L)	Zn (μg/L)	DOC (mg/L)	TSS (mg/L)
Peak Discharge								
Sagavanirktok (n = 11)	Mean	31.8	0.79	38.1	27.8	0.22	5.0	267
	Std. Dev.	± 2	± 0.5	± 24.0	± 12.6	± 0.11	± 2.5	± 171
	Range	27.5-35.1	0.57-0.96	11.2-72.0	15.5-46.6	0.13-0.44	2.0-8.9	78-609
Kuparuk (n = 5)	Mean	19.5	0.80	212	53.0	0.38	14.0	63
	Std. Dev.	± 1.5	± 0.08	± 27	± 0.8	± 0.3	± 1.6	± 6
	Range	18.0-21.0	0.72-0.86	181-232	52.4-53.9	0.36-0.41	12.6-15.8	55-66
Colville (n = 3)	Mean	50.7	2.5	80.9	60.1	0.14	10.0	468
	Std. Dev.	± 3.6	± 0.2	± 29.9	± 9.3	± 0.02	± 1.9	± 272
	Range	46.7-53.8	2.2-2.7	59.9-102	53.5-66.5	0.11-0.17	8.0-13.2	333-610
Off-Peak Discharge								
Sagavanirktok (n = 9)	Mean	31.6	0.40	6.8	13.5	0.12	2.9	31
	Std. Dev.	± 0.3	± 0.1	± 2.9	± 5.8	± 0.04	± 1.2	± 12
	Range	30.9-31.7	0.29-56	2.8-9.5	7.0-19.1	0.08-0.16	1.4-4.9	14-40
Kuparuk (n = 5)	Mean	23.5	0.77	64.2	40.6	0.29	8.7	4.0
	Std. Dev.	± 2.2	± 0.04	± 21.3	± 13.3	± 0.01	± 0.5	± 2.4
	Range	18.5-26.6	0.71-0.81	36.7-116	21.8-59.7	0.27-0.31	8.3-9.5	1.7-7.4
Colville (n = 3)	Mean Std. Dev. Range	51.6 ± 3.3 49.3-53.4	1.6 ± 0.1 1.5-1.7	50.3 ± 43.0 19.9-80.4	40.6 ± 8.9 27.6-50.6	0.26 ± 0.1 0.19-0.33	5.4 ± 1.9 4.1-7.3	89 ± 41 42-113

water flow also was reported for the Lena River where concentrations of DOC were at least 30 to 40% higher during the spring floods than during September (Cauwet and Sidorov, 1996).

Concentrations of dissolved Fe, Cu, Pb and Zn followed trends shown for DOC (Figure 3-11). In the Sagavanirktok River, concentrations of dissolved Fe increased sharply from 3 to 72 µg/L in ~7 days. Then, as flow decreased, concentrations of dissolved Fe returned to ~3 mg/L within 8 days of maximum levels. Concentrations of dissolved Cu, Pb and Zn in the Sagavanirktok River also increased to maximum levels during peak flow (Figure 3-11). These values at peak discharge are approximately 3, 5.5 and 6 times greater, respectively, than during off-peak discharge and occurred at a time when water flow was ~250% greater at the Sagavanirktok River gauge, indicating that net transport of dissolved metals, like DOC, was greatly enhanced during peak discharge.
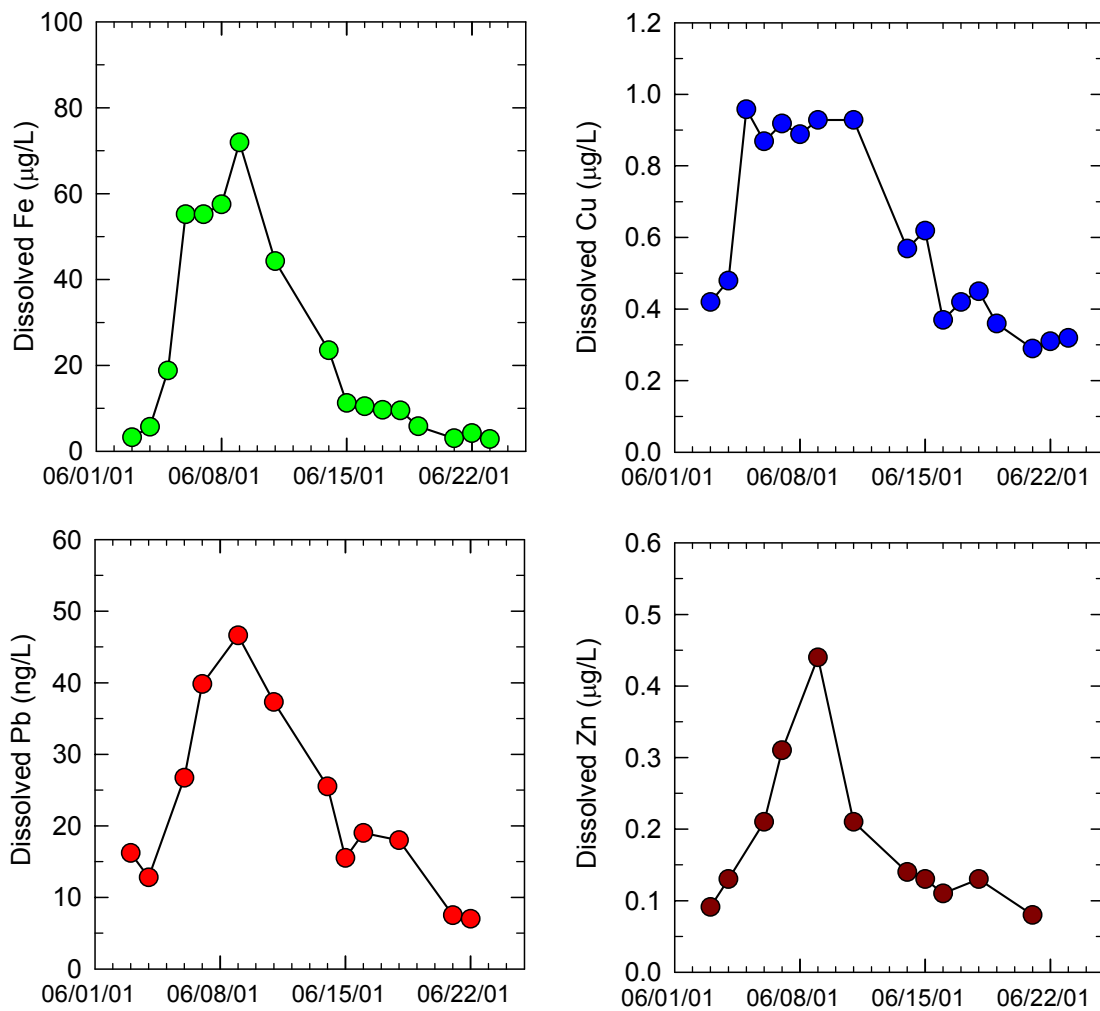
Figure 3-11.   Concentrations of dissolved iron (Fe), copper (Cu), lead (Pb) and zinc (Zn) in the Sagavanirktok River during June 2001.

Strong correlations (r ≥ 0.82) were found for DOC versus Cu, Fe, Pb and Zn (Table 3-5). The trends, correlations and timing for peak levels of trace metals and DOC support the idea that metals and DOC are strongly influenced by the discharge of soil interstitial water and shallow surface water that is diluted by melt water and flushed from surrounding soils into the Sagavanirktok River. During the short summers, the arctic coastal plain is covered with pools of standing water and lakes where DOC accumulates and trace metals are leached from soils. The permafrost, along with a topography that averages <2 m on the coastal plain, inhibit lateral water flow during the summer months, thereby extending the residence time of the surface water in the system. Then, increased surface runoff in the spring, after the long frozen winter (8 to 9 months), provides a direct pathway for the release of accumulated DOC and dissolved metals into the rivers from the thawing ponds and soils.

Table 3-5. Pearson's correlations between dissolved trace metals and dissolved organic carbon (DOC) in the Sagavanirktok River during June 2001. All correlations are significant at $p = 0.01$.

	Cu	Fe	Pb	Zn
Cu	1			
Fe	0.86	1		
Pb	0.89	0.93	1	
Zn	0.79	0.90	0.90	1
DOC	0.82	0.90	0.91	0.87

Average concentrations of dissolved Fe, Pb, Zn and organic carbon in the Kuparuk River during peak and off-peak discharge were ~2 to 5 times higher than in the Sagavanirktok River (Table 3-4). Concentrations of dissolved Cu in the Kuparuk River were not significantly different (t-test, $\alpha=0.5$) during peak versus off-peak flow. Data collected from the Colville River showed similar trends to those for the Sagavanirktok and Kuparuk rivers. During peak discharge, average concentrations of DOC, Cu, Fe and Pb in the Colville River were 1.5 to 2 times higher than during off-peak flow (Table 3-4). In general, concentrations of dissolved metals and DOC in the Colville River were higher than those found in the Sagavanirktok River, but less than in the Kuparuk River (Table 3-4).

The higher concentrations of DOC and dissolved metals in both the Kuparuk and Colville rivers, relative to the Sagavanirktok River, are most likely related to differences in lithology and soil pH (organic acids). Previous studies have shown that the Sagavanirktok River drains primarily limestone deposits and has concentrations of dissolved Ca that are ~2 times higher than in the Kuparuk and Colville rivers (Telang et al., 1991). Walker and Webber (1979) show that westward of the carbonate-rich Sagavanirktok River, soil pH decreases from >7 to <6 as the tundra shifts from wet alkaline to wet acidic because soils become rich in organic acids. Other studies have shown that soil pH can decrease to 4.2 in tussock tundra and heath ecosystems (Valentine and Binkley, 1992). In addition, Parkinson (1977) found an inverse relationship between calcium carbonate equivalents and organic matter concentration in the region. These data suggest that soils within the Kuparuk and Colville drainage basins may undergo more intense chemical weathering due to higher concentrations of organic acids and lower pH.

Concentrations of dissolved Cu, Fe, Pb, Zn and DOC from this study in the Alaskan Arctic during July and August 2001, when water flow was greatly reduced (<50 m³/sec), are consistent with concentrations found in other arctic rivers during the months of August and September (Table 3-6). For example, concentrations of dissolved Pb during August in the Sagavanirktok, Kuparuk and Colville rivers are within the range of concentrations found in the Lena, the Ob and the Yenisey rivers during September and are 2 to 6 times lower than the world average (Table 3-6). Concentrations of dissolved Pb in the Sagavanirktok and Kuparuk rivers are lower than concentrations found in a mountain watershed in Sierra Nevada, California where Pb concentrations were ~8.7 ng/L (43 pM) and considered to be natural levels for river water (Erel et al., 1991). Lower concentrations of dissolved metals in arctic rivers during the summer and fall suggest that anthropogenic contamination is minimal and that spring discharge in the Alaskan Arctic provides an important transport mechanism for DOC and organically-bound, dissolved metals.

Table 3-6. Ranges and average concentrations of dissolved metals and dissolved organic carbon (DOC) during August and September (off peak) in rivers of the Alaskan and Russian Arctic.

River	Reference	Ba (µg/L)	Cu (µg/L)	Fe (µg/L)	Pb (ng/L)	Zn (µg/L)	DOC (mg/L)
Sagavanirktok	(this study)	39	0.29	2.1	7.0	0.03	1.1
Kuparuk	(this study)	33	0.95	10.3	4.4	0.03	6.3
Colville	(this study)	74	0.70	3.8	11.6	0.03	3.8
Lena	1, 2, 3	18	0.76-0.95	24-47	-	0.08	5.9-7.9
Lena	4	-	0.62	22.9	17	0.04	-
Ob-Irtysh	3, 5	14	1.8-2.4	24-37	11-17	-	7.4-9.9
Yenisey	3, 5	17	1.4-1.9	14-18	5-6	-	4.0
World Average	6, 7	-	1.5	40	31	0.6	5.8

(1) Guieu et al., 1996; (2) Guay and Falkner, 1998 (3) Cauwet and Sidorov, 1996; (4) Martin et al., 1993; (5) Dai and Martin, 1995; (6) Martin and Windom, 1991; (7) Meybeck, 1982

In contrast with Cu, Fe, Pb and Zn, concentrations of dissolved Ba in the Sagavanirktok River varied by only ± 7% (coefficient of variation, CV = [standard deviation/mean) x 100] during peak discharge (Table 3-4, Figure 3-12). Concentrations of dissolved Ba were even less variable (CV < 1%) during off-peak discharge (Table 3-4, Figure 3-12). Dissolved Ba concentrations decreased by up to 25% when water flow increased by 250% at the Sagavanirktok gauge. These data indicate that concentrations of dissolved Ba were not enhanced by the flushing of metals from soils and were only slightly affected by dilution during peak flow.
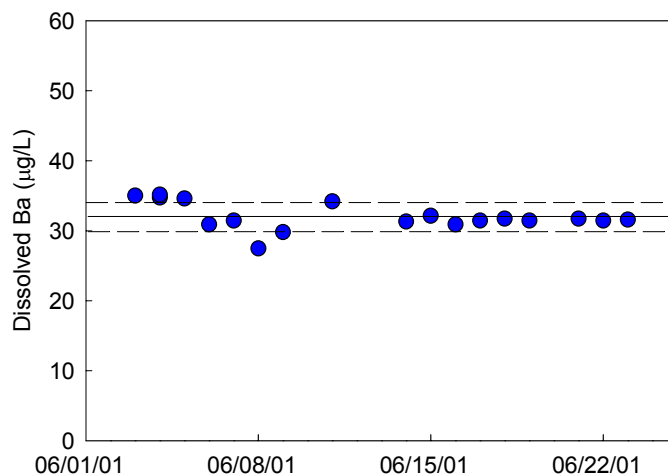
Figure 3-12. Concentrations of dissolved barium (Ba) in the Sagavanirktok River during June 2001. The solid line is the mean value and dashed lines represent ±2 standard deviations from the mean.

Concentrations of dissolved Ba in the Sagavanirktok, Kuparuk, and Colville rivers are within the range of 19 to 79 µg/L reported by Guay and Falkner (1998) for arctic rivers of North America. These data support the conclusion by Guay and Falkner (1998) that concentrations of dissolved Ba in Arctic rivers of North America are higher than those determined for any of the Eurasian Arctic rivers (Table 3-6). Guay and Falkner (1998) suggested that differences in concentrations between arctic rivers in North America and Eurasia are due to the chemical composition and weathering characteristics within their respective drainage basins. As discussed below, data from this study suggest that partitioning of Ba between the dissolved and particulate phases may control concentrations of dissolved Ba in rivers of the Alaskan Arctic.

3.1.6 Particulate Trace Metals and Organic Carbon

Concentrations of particulate Cu, Pb, Zn (µg/g dry weight), Fe and OC (% dry weight) in the Sagavanirktok River were more uniform than observed for the dissolved species (Figure 3-13). In general, concentrations of Cu (CV = 8.5%), Pb (CV = 11%), and Zn (CV =5.7%) were less variable than concentrations of Fe (CV =16%) and POC (CV =31%) (Table 3-7). In sharp contrast with dissolved Cu, Fe, Pb and Zn, particulate concentrations of these four metals were poorly correlated with organic carbon (r < 0.15), and relatively well correlated with particulate Al (Table 3-8). The poor correlations for POC versus Cu, Fe, Pb and Zn suggest that POC does not play a significant role in controlling concentrations of particulate trace metals in the Sagavanirktok River, but that the aluminosilicate (clay) content is more important.

38
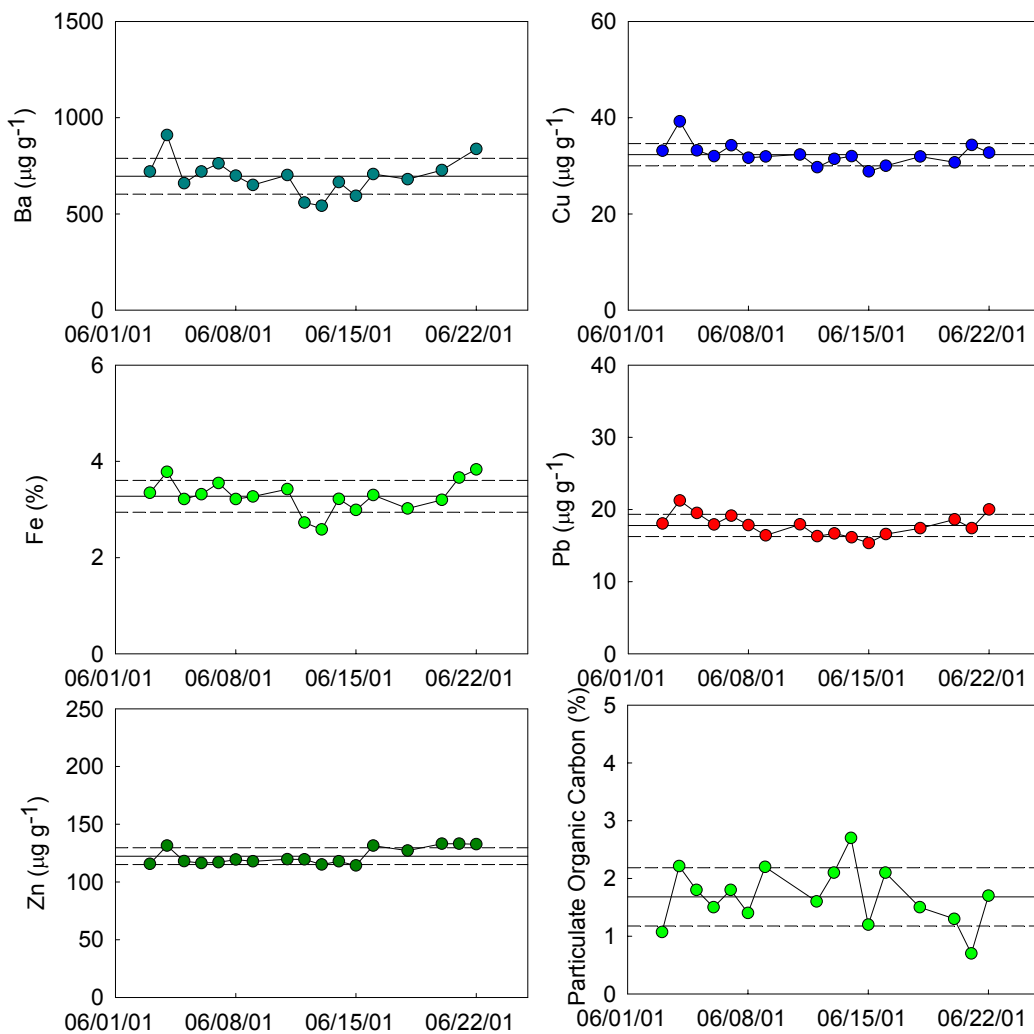
Figure 3-13. Concentrations of particulate barium (Ba), copper (Cu), iron (Fe), lead (Pb), zinc (Zn) and particulate organic carbon (POC) in the Sagavanirktok River during June 2001. The solid line shows mean concentrations in each plot and dashed lines represent ±2 standard deviations from the mean.

Table 3-7. Concentrations of particulate trace metals and particulate organic carbon (POC) in the Sagavanirktok, Kuparuk and Colville Rivers during June 2001. Peak and off-peak concentrations are presented for the Kuparuk River due to distinct differences in the concentrations of some trace metals during those periods.

River		Al (%)	Ba (µg/g)	Cu (µg/g)	Fe (%)	Pb (µg/g)	Zn (µg/g)	POC (%)
Sagavanirktok	Mean Std. Dev. Range	5.6 ± 0.9 4.0-7.7	702 ± 113 542-1008	32.8 ± 2.8 29.7-39.2	3.3 ± 0.4 2.6-4.0	18.0 ± 2.0 16.0-23.4	123 ± 7 115-135	1.60 ± 0.49 0.7-2.7
Kuparuk Peak Discharge	Mean Std. Dev. Range	5.2 ± 0.5 4.6-5.8	615 ± 88 497-743	32.3 ± 5.8 25.7-37.2	3.6 ± 0.2 3.3-3.8	15.7 ± 0.7 14.7-16.6	124 ± 13 110-145	4.6 ± 1.1 3.3-5.9
Kuparuk Off-Peak Discharge	Mean Std. Dev. Range	3.5 ± 0.5 2.7-4.0	469 ± 70 397-559	29.9 ± 1.3 28.6-31.2	3.7 ± 0.3 3.1-4.2	14.4 ± 8.3 4.0-22.5	92.1 ± 21 69-116	4.9 ± 2.0 2.8-7.6
Colville	Mean Std. Dev. Range	8.3 ± 0.3 8.0-8.9	989 ± 125 890-1190	40.8 ± 2.3 36.9-42.6	5.0 ± 0.3 4.7-5.3	24.0 ± 6.8 19.8-36.0	130 ± 11 116-147	2.24 ± 0.56 1.7-3.3

Table 3-8. Correlations for particulate trace metals and particulate organic carbon (POC) in the Sagavanirktok River during June 2001.

	Al	Ba	Cu	Fe	Pb	Zn
Al	1					
Ba	0.91**	1				
Cu	0.78**	0.80**	1			
Fe	0.97**	0.89**	0.78**	1		
Pb	0.79**	0.88**	0.87**	0.76**	1	
Zn	0.76**	0.66**	0.53*	0.64**	0.62	1
POC	-0.14	0.11	0.14	-0.07	0.01	-0.13

** Correlation is significant at the 0.01 level.
* Correlation is significant at the 0.05 level.

The trends in concentrations of particulate Ba in the Sagavanirktok River follow closely with those observed for Fe, suggesting that concentrations of particulate Ba also are controlled by the aluminosilicate content of the suspended solids (Figure 3-14). The correlation coefficient for particulate Al and Ba (r = 0.91) for the Sagavanirktok River indicates that variations in particulate Ba concentrations result from shifts in Al concentrations during peak and off-peak discharge (Figure 3-14). To further illustrate this relationship, concentrations of particulate Ba from the Kuparuk and Colville rivers were pooled with data for the Sagavanirktok River. The data in Figure 3-14a include values from all three rivers with a range of ~2 to >600 mg/L for TSS, and concentrations of POC ranging from <1 to >7%. Therefore, variations in concentrations of particulate Ba in the Sagavanirktok, Kuparuk and Colville rivers result mainly from dilution of fine-grained aluminosilicates by larger-grained sands and other non-aluminosilicate minerals.
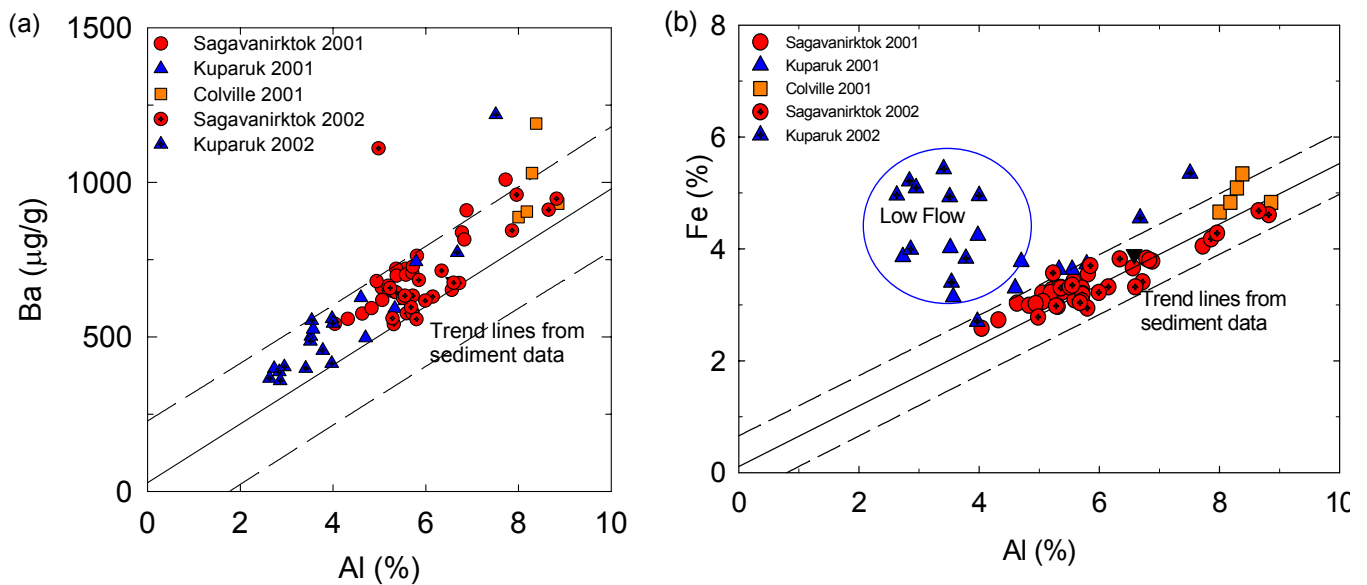
Figure 3-14. Concentrations of particulate aluminum (Al) versus (a) barium (Ba) and (b) iron (Fe) for the Sagavanirktok, Kuparuk, and Colville rivers during June 2001 and 2002. Solid lines are from a linear regression for sediment data from the ANIMIDA study area and dashed lines show 99% prediction interval for sediment data. Data points for off-peak discharge in the Kuparuk River were not included in the linear regression for the Al vs. Fe plot.

During peak discharge, as the banks of the Kuparuk River eroded and the river transported higher concentrations of TSS (> 50 mg/L), concentrations of particulate Fe, Pb and Zn correlated well (r = 0.98, 0.76, 0.93, respectively) with levels of particulate Al and the metal/Al ratios agreed within 15% with the results found for the Sagavanirktok River (Figure 3-14). However, when TSS concentrations decreased to an average of 4 mg/L in the Kuparuk River during low flow, the average Fe/Al ratio increased by ~35% relative to the Sagavanirktok River (Figure 3-14). These data suggest that elevated concentrations of particulate Fe (6400 nM or 3.7% dry weight) relative to Al (14600 nM or 3.5% dry weight) during low flow (Figure 3-14) may be influenced by high concentrations of dissolved Fe (>60 µg/L) in the Kuparuk River that potentially enhance the formation of Fe hydrous oxides and increase concentrations of particulate Fe. Similarly, concentrations of particulate Pb and Zn increased with Fe and were elevated

above levels that would be predicted from the Al concentration and possibly result from scavenging by hydrous Fe-oxides.

Concentrations of particulate Cu, Fe and Pb in the Colville River averaged 25 to 40% higher than concentrations found in the Sagavanirktok and Kuparuk rivers (Table 3-7). However, particles from the Colville River also had 50% higher concentrations of Al indicating that sources of suspended sediment in the western Brooks Range are richer in fine-grained aluminosilicates or less diluted by non-aluminosilicate minerals (Table 3-7).

3.1.7 Major Elements in Suspended Solids

Concentrations of particulate Al, Fe, Ca, Mg, K and Na were determined for the Sagavanirktok, Kuparuk and Colville rivers (Table 3-9). Concentrations of particulate Ca in the Sagavanirktok, Kuparuk and Colville rivers did not correlate well with Al (r < 0.2) (Figure 3-15). In the Kuparuk and Colville rivers, average concentrations of particulate Ca were ~6 to 10 fold lower than concentrations found in the Sagavanirktok River. The poor correlation for Ca with Al (r<0.2) suggests that the fraction of particulate Ca derived from aluminosilicate minerals was small. In addition, these data agree with dissolved Ca and CA data from this study and suggest that rocks in the drainage basin of the Sagavanirktok River are more carbonate-rich than those in the drainage basins of the Kuparuk and Colville rivers.

Table 3-9. Concentrations of particulate metals (as % dry weight) in the Sagavanirktok, Kuparuk and Colville Rivers during June 2001.

River		Al (%)	Ca (%)	Fe (%)	K (%)	Mg (%)	Na (%)
Sagavanirktok (n = 22)	Mean	5.6	6.7	3.3	1.7	0.85	0.30
	Std. Dev.	± 0.9	± 0.99	± 0.4	± 0.25	± 0.11	± 0.03
	Range	4.0-7.7	4.9-8.9	2.6-4.0	1.4-2.3	0.7-1.2	0.24-0.37
Kuparuk (n = 8)	Mean	4.4	1.0	3.7	1.1	0.46	0.39
	Std. Dev.	± 1.04	± 0.2	± 0.4	± 0.2	± 0.20	± 0.07
	Range	2.7-5.8	0.8-1.5	3.1-4.2	0.6-1.3	0.12-0.69	0.32-0.50
Colville (n = 6)	Mean	8.3	0.70	5.0	2.0	1.1	0.51
	Std. Dev.	± 0.3	± 0.30	± 0.3	± 0.07	± 0.20	± 0.08
	Range	8.0-8.9	0.60-1.2	4.7-5.3	1.9-2.1	0.8-1.2	0.39-0.59
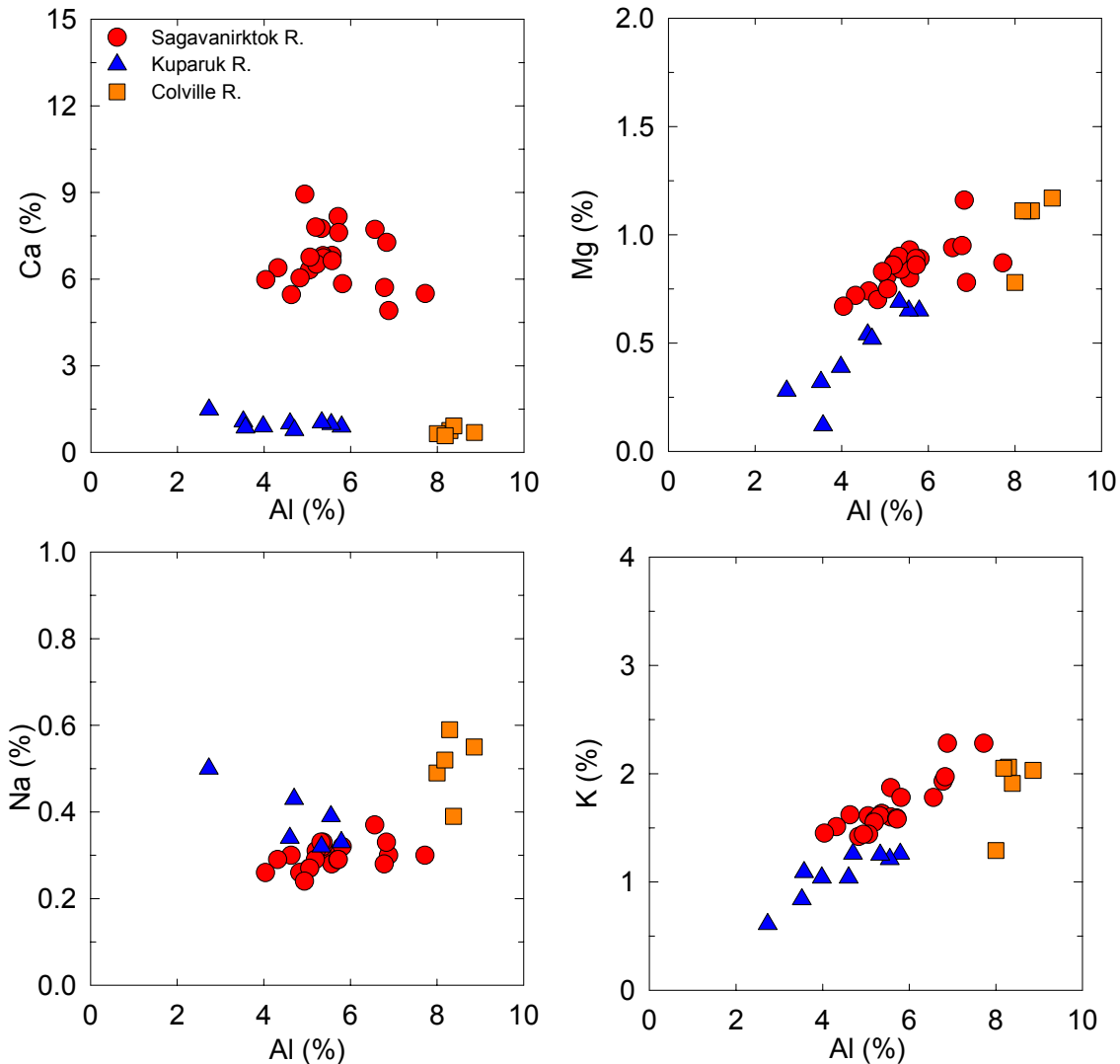
Figure 3-15. Concentrations of particulate aluminum (Al) versus (a) calcium (Ca), (b) magnesium (Mg), (c) sodium (Na) and (d) potassium (K) for the Sagavanirktok, Kuparuk and Colville rivers during June 2001.

Correlations for Mg versus Al in the Sagavanirktok River (r = 0.89) and combined Kuparuk and Colville rivers (r = 0.95) were high (Figure 3-15). However, the ratio of Mg to Al in the Sagavanirktok River (0.15 ± 0.02) was statistically greater (t-test, α = 0.05) than the ratio for the Kuparuk (0.10 ± 0.03) and Colville (0.13 ± 0.02) rivers. These data indicate that the suspended solids in the Sagavanirktok River were slightly enriched with Mg relative to the Kuparuk and Colville rivers. In addition to the good correlation for Mg versus Al, concentrations of Mg also correlated well with Fe in the Sagavanirktok River and Colville rivers (r = 0.80) (Figure 3-15). Therefore, Mg- and Fe-bearing aluminosilicate minerals (e.g., chlorite, biotite) present in the drainage basin of the Sagavanirktok, Kuparuk and Colville rivers are more likely to be potential sources of particulate Mg as discussed below (Payne et al., 1951; Darby et al., 1989).

The good correlation for dissolved Ca versus Mg in the Sagavanirktok, Kuparuk and Colville rivers supports carbonate weathering as the dominant source of dissolved Ca and Mg. However,

43

the poor correlation of Ca versus Mg in the suspended solids from each river suggests that carbonates are not highly abundant in the particulate fraction. The correlations found for Mg versus Fe and Al suggest that the aluminosilicate fraction is not highly weathered and does not greatly contribute to concentrations of dissolved Mg in the Sagavanirktok, Kuparuk and Colville rivers.

Concentrations of particulate K averaged 1.7%, 1.1% and 2.0% in the Sagavanirktok, Kuparuk and Colville rivers (Table 3-9). In addition, concentrations of particulate K correlated well with the concentration of Al in the suspended solids (Figure 3-15). Similar to the results found for Mg, particles in the Sagavanirktok River were slightly enriched in K (K:Al = 0.31 ± 0.03) relative to the Kuparuk (0.24 ± 0.03) and Colville rivers (0.24 ± 0.03).

Average concentrations of particulate Na were determined to be ~25 and 40% higher, in the Kuparuk and Colville rivers, respectively, than in the Sagavanirktok River (Table 3-9). However, no distinct trends or relationships were found for Na versus Al (Figure 3-15).

The concentrations of Al, Fe, K, Mg and Na in suspended sediment from the Sagavanirktok and Kuparuk rivers were less than average values for continental crust (Wedepohl, 1995). However, concentrations of particulate Ca in the Sagavanirktok River averaged 1.7 fold greater than average values for continental crust and agreed with previous observations that carbonates dominate the lithology of the Sagavanirktok River drainage basin. Concentrations of particulate Al, Fe and K were similar to average values for continental crust in the Colville River. Higher concentrations of K-silicates are consistent with observations that the Colville River drains a relatively larger proportion of exposed K-rich silicate minerals (biotite) from the Cretaceous (Payne et al, 1951). In all cases, concentrations of particulate Mg and Na were less than average values for continental crust.

3.2 Source Rivers 2002

3.2.1 Overview and Transport of Water and Suspended Sediment

Spring breakup in the Sagavanirktok River for 2002 was very different from what was observed in 2001. First, the start of river flow was almost two weeks earlier (May 20, 2002 versus June 2, 2001). Second, after flow had been ongoing for about one week, the air temperatures cooled well below freezing and the river refroze (Figures 3-16 and 3-17). The same trend was observed offshore as river water initially flowed out over and under the ice and then the surface layer of river water froze over the 2-m thick layer of winter ice. The river re-thawed within four days, but water flow was less than during the earlier discharge period (Figure 3-17).

The TSS and turbidity data for 2002 showed the same initial steep increase in levels of suspended particles to ~350 mg/L (Figure 3-17), similar to, but lower than the observed peak TSS of ~600 mg/L in 2001 (Figure 3-2, page 21). However, subsequent cold temperatures and freezing of the river truncated the flooding process and led to TSS levels <10 mg/L on May 31, 2002, the final day of sampling before the ice prevented sampling for two days. Then, as the river re-melted, the increase in flow led to another peak in discharge of suspended sediment at >200 mg/L (Figure 3-17). Data for turbidity are shown on Figure 3-17 to point out that turbidity

Sagavanirktok River at bridge near Prudhoe Bay Operations Center flowing on May 22, 2002,
and re-frozen on May 29, 2002.

Kuparuk River during and after three-day flood period in May 2002.

Colville River during June 2002.

Figure 3-16. Sagavanirktok, Kuparuk and Colville rivers during May-June 2002.

(a)

(b)
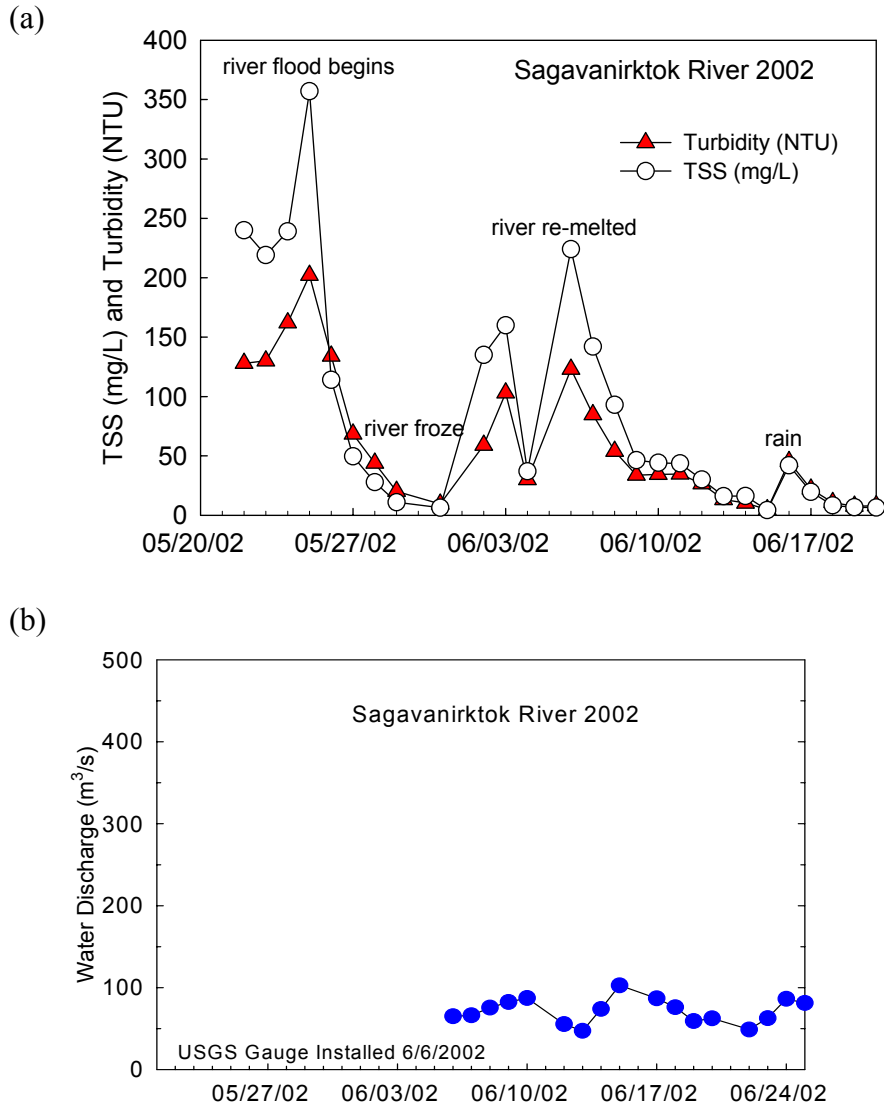
Figure 3-17. (a) Concentrations of total suspended solids (TSS) and turbidity for the Sagavanirktok River during May-June 2002 and (b) Water discharge (from U.S. Geological Survey) in Sagavanirktok River for June 2002.

data are available for all water samples (Appendix A) and that the two indicators of suspended sediment levels track one another very well. Unfortunately, the U.S.G.S. was not able to install their gauge for water flow until June 6, 2002 (Figure 3-17), and therefore no data are available for the events described above.

Conductivity in the Sagavanirktok River followed a more compressed trend in 2002 with a shorter time of 4 days at <200 µS (Figure 3-18) relative to the 8-day period of water flow with conductivity <200 µS observed in 2001 (Figure 3-4, page 25). Concentrations of TSS decreased to ~3 mg/L in late June and were ~1 mg/L in August, similar to levels observed in 2001.
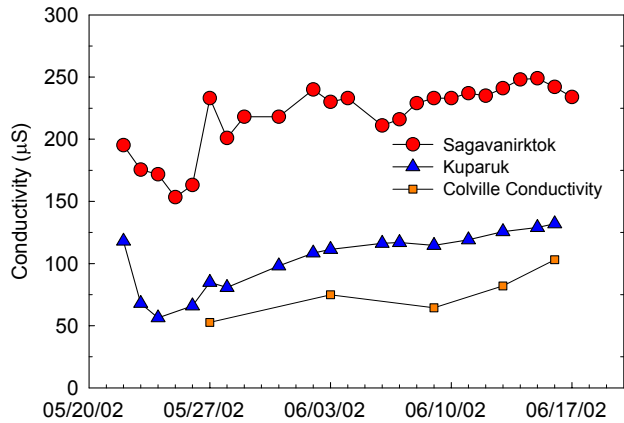
Figure 3-18. Conductivity in the Sagavanirktok, Kuparuk and Colville rivers during May-June 2002.

During 2002, we were fortunate to directly observe and sample the Kuparuk River during its brief (1 to 2 day) flood (Figures 3-16 and 3-19). The strong pulse of water that characterizes flooding in the Kuparuk River occurred on May 23, 2002. The flood receded by May 25 (Figure 3-16). The complete flood cycle in the Kuparuk River occurred before the onset of colder temperatures and refreezing of the rivers.
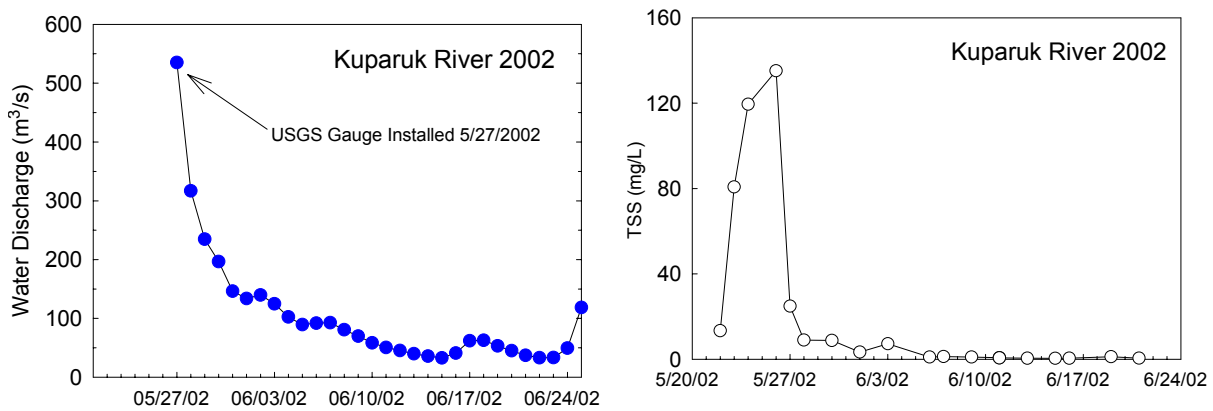
Figure 3-19. Water flow and concentrations of total suspended solids (TSS) and turbidity for the Kuparuk River during May-June 2002 (flow data from U.S. Geological Survey).

Maximum levels of TSS in the Kuparuk River during 2002 (Figure 3-19) were double maximum levels of ~60 mg/L during 2001. The higher levels of TSS observed during 2002 are most likely due to sampling at peak flow. Turbidity and concentrations of TSS in the Kuparuk River during both years may have peaked at higher levels than we observed (Figure 3-19). Unfortunately, due to washing out of the road and the intense flow conditions, we were able to sample only the eastern-most braid of the river during peak flow in both 2001 and 2002. Conductivity in the Kuparuk River during 2002 (Figure 3-18) followed a similar trend at similar values to those observed in 2001 (Figure 3-4, page 25) with a minimum of ~50 µS at peak flow, increasing to ~120 µS after the spring flood receded.

Access to the Colville River by helicopter was limited during 2002 due to the early onset of the spring floods and an increased focus on the under-ice effort near Prudhoe Bay. Data from Baker et al. (2002) show a short, strong pulse of water at >6000 m^3/sec for 4-5 days (Figure 3-20). Duplicate samples for TSS on May 27, 2002, showed levels >600 mg/L. Levels of TSS decreased to 112 mg/L on June 3 and to <50 mg/L on and after June 12. Conductivity for the Colville River during the 2002 flood (Figure 3-18) event was similar to that observed in 2001 (Table 3-12). During both years, the Colville River had the lowest conductivity of the three rivers, most likely due to the high water flow of the river and greater dilution of dissolved solids.
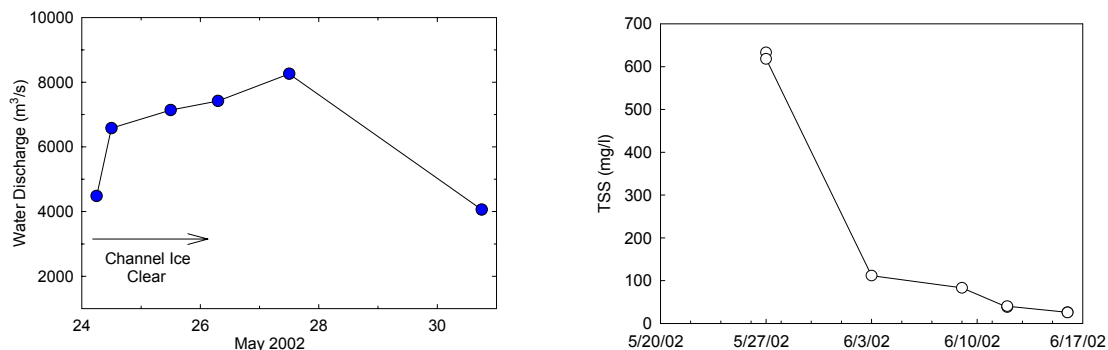
Figure 3-20. Water flow and concentrations of total suspended solids (TSS) in the Colville River during May-June 2002. Flow data from Baker et al. (2002).

3.2.2 Trends in Concentrations of Dissolved Major Ions

Concentrations of major dissolved ions Ca, Mg, Na, K, Cl, sulfate, F and alkalinity (HCO_3^- + CO_3^{2-}) also were determined for river water samples collected during May-June 2002 (Table 3-10). Concentrations of dissolved Ca, Mg and sulfate (Figure 3-21) followed similar patterns in the Sagavanirktok River during May-June 2002 and June 2001. Concentrations of each ion decreased during peak flow. The more complex flow pattern for the Sagavanirktok River during 2002 did not alter concentrations during peak flow. Concentrations of dissolved Ca, Mg and sulfate (Figure 3-21) in the Kuparuk River for 2002 were similar to those observed in 2001; and the trend in concentrations also showed decreased levels during peak flow.

In contrast to decreasing concentrations of Ca, Mg, CA, sulfate and F during peak discharge (Table 3-10 and Figure 3-21), concentrations of K increased during peak discharge in both the Sagavanirktok and Kuparuk rivers (Figure 3-22). The trend is similar to that described for the spring floods of 2001. Peak concentrations of DOC were observed during the spring floods of 2002 in the Kuparuk River, but not in the Sagavanirktok River (Figure 3-23). This distinction was most likely due to the thawing and refreezing processes and how they retarded to release of DOC from the soil active layer. The Kuparuk River went through a complete discharge process prior to the period of refreezing that occurred; however, the spring flood in the Sagavanirktok River did reach completion prior to the period of refreezing. Because of the strong similarities in concentrations of major ion between 2002 and 2001, the same statistical and chemical weathering calculations were not repeated.

Table 3-10. Conductivity (Cond.) and concentrations of total dissolved solids (TDS), calcium (Ca), magnesium (Mg), sodium (Na), potassium (K), carbonate alkalinity (CA), sulfate, chl;oride (Cl), fluoride (F), silicon (Si) and dissolved organic carbon in the Sagavanirktok and Kuparuk rivers during peak discharge in June 2002.

River		Cond. (µS)	TDS (µeq/L)	Ca (µeq/L)	Mg (µeq/L)	Na (µeq/L)	K (µeq/L)	CA (µeq/L)	Sulfate (µeq/L)	Cl (µeq/L)	F (µeq/L)	Si (µM)	DOC (µM)
Peak Discharge													
Sagavanirktok (n = 26)	Mean Std. Dev. Range	222 ± 27 153-249	4250 ± 640 3020-4980	1640 ± 204 1210-1850	450 ± 96 260-530	44 ± 8 25-51	8.5 ± 4 5-17	1590 ± 215 1190-1880	498 ± 142 259-663	22.1 ± 13.7 9-52	7 ± 4 2-16	36 ± 4 29-47	451 ± 111 330-701
Kuparuk (n = 19)	Mean Std. Dev. Range	102 ± 23 56-132	2030 ± 480 1470-2550	836 ± 212 410-1010	135 ± 25 100-163	50 ± 16 38-70	14.4 ± 6.2 7-29	907 ± 245 380-1180	16.2 ± 11 9-33	71.5 ± 23.2 40-131	2 ± 1 1-4	25 ± 7.7 16-39	761 ± 218 505-1140
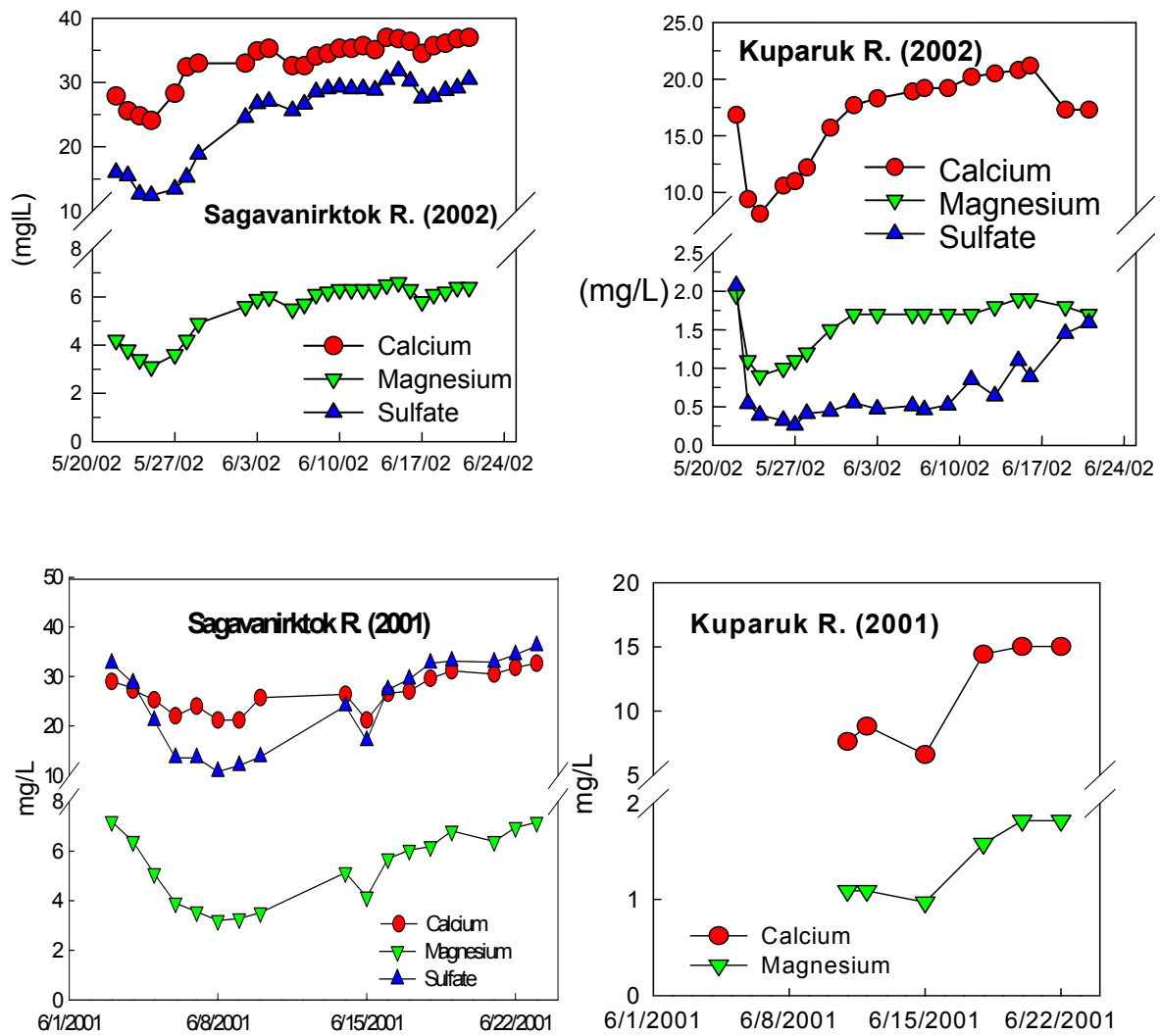
Figure 3-21. Concentrations of dissolved calcium, magnesium and sulfate in the Sagavanirktok and Kuparuk rivers during June 2002 and 2001. Concentrations of sulfate in the Kuparuk River were below detection limits in 2001.

Figure 3-22. Concentrations of dissolved potassium (K) in the Sagavanirktok and Kuparuk rivers during June 2002.
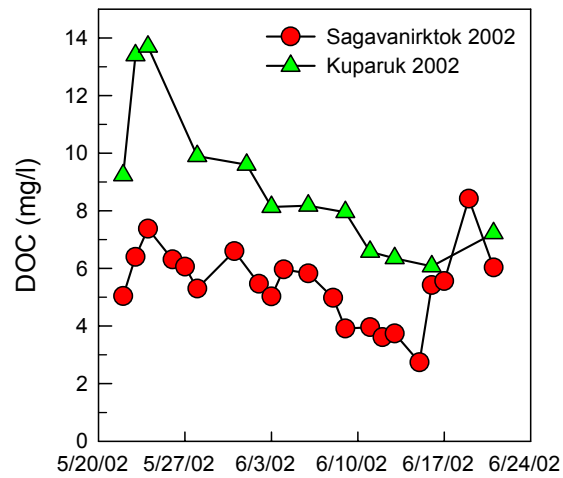
Figure 3-23. Concentrations of dissolved organic carbon (DOC) in the Sagavanirktok and Kuparuk rivers during June 2002.

3.2.3 Dissolved Trace Metals and Dissolved Organic Carbon

Concentrations of Cd, Cu, Fe, Mn, Pb and Zn in the Sagavanirktok River were higher during the peak flow for 2002 relative to off-peak levels in June 2002 (Table 3-11 and Figures 3-24 and 3-25). However, the mean and maximum concentrations of dissolved Ba, Cu, Fe, Pb and Zn in the Sagavanirktok River during May-June 2002 were lower than observed during 2001 (Table 3-11). As described in the previous section, this trend is most likely related to the unusual flow pattern and lower levels of DOC during the spring 2002 flood in the Sagavanirktok River.

In the Kuparuk River, the peak in concentrations of K and DOC during peak flow (Figures 3-22 and 3-23) coincided with peak levels of Cu, Fe and Mn (Figure 3-24). However, with the exception of Ba, the same trend of lower levels of metals during 2002 versus 2001 also was observed for the Kuparuk River, most likely because of the lower levels of DOC in the 2002 rather than a difference in the flow pattern.

Overall, concentrations of Fe and K from the Sagavanirktok and Kuparuk Rivers for both 2001 and 2002 were directly related to concentrations of DOC (Figure 3-26). Release of soil nutrients and metals during the early stages of the spring thaw and flood event, combined with complexation of metals by DOC, help explain these observations.

Table 3-11. Concentrations of dissolved metals and dissolved organic carbon (DOC) and total suspended solids (TSS) in the Sagavanirktok, Kuparuk and Colville rivers during peak discharge in 2002 and 2001.

River		Ba (µg/L)	Cu (µg/L)	Fe (µg/L)	Pb (ng/L)	Zn (µg/L)	DOC (mg/L)	TSS (mg/L)
Sagavanirktok 2002 (n = 23)	Mean	29.9	0.34	31	17	0.22	5.4	96
	Std. Dev.	± 2.1	± 0.16	± 29	± 10	± 0.17	± 1.3	± 104
	Range	25.8-33.5	0.06-0.59	4.0-101	6-40	0.03-0.63	2.7-8.4	3.5-369
Kuparuk 2002 (n = 13)	Mean	26.4	0.28	81	30	0.29	9.1	22
	Std. Dev.	± 3.9	± 0.12	± 51	± 13	± 0.15	± 2.6	± 41
	Range	18-31.8	0.15-0.56	17-171	16-66	0.11-0.64	6.1-13.7	0.49-135
Sagavanirktok 2001 (n = 11)	Mean	31.8	0.79	38.1	27.8	0.22	5.0	267
	Std. Dev.	± 2	± 0.5	± 24.0	± 12.6	± 0.11	± 2.5	± 171
	Range	27.5-35.1	0.57-0.96	11.2-72.0	15.5-46.6	0.13-0.44	2.0-8.9	78-609
Kuparuk 2001 (n = 5)	Mean	19.5	0.80	212	53.0	0.38	14.0	63
	Std. Dev.	± 1.5	± 0.08	± 27	± 0.8	± 0.3	± 1.6	± 6
	Range	18.0-21.0	0.72-0.86	181-232	52.4-53.9	0.36-0.41	12.6-15.8	55-66
Colville 2001 (n = 3)	Mean	50.7	2.5	80.9	60.1	0.14	10.0	468
	Std. Dev.	± 3.6	± 0.2	± 29.9	± 9.3	± 0.02	± 1.9	± 272
	Range	46.7-53.8	2.2-2.7	59.9-102	53.5-66.5	0.11-0.17	8.0-13.2	333-610
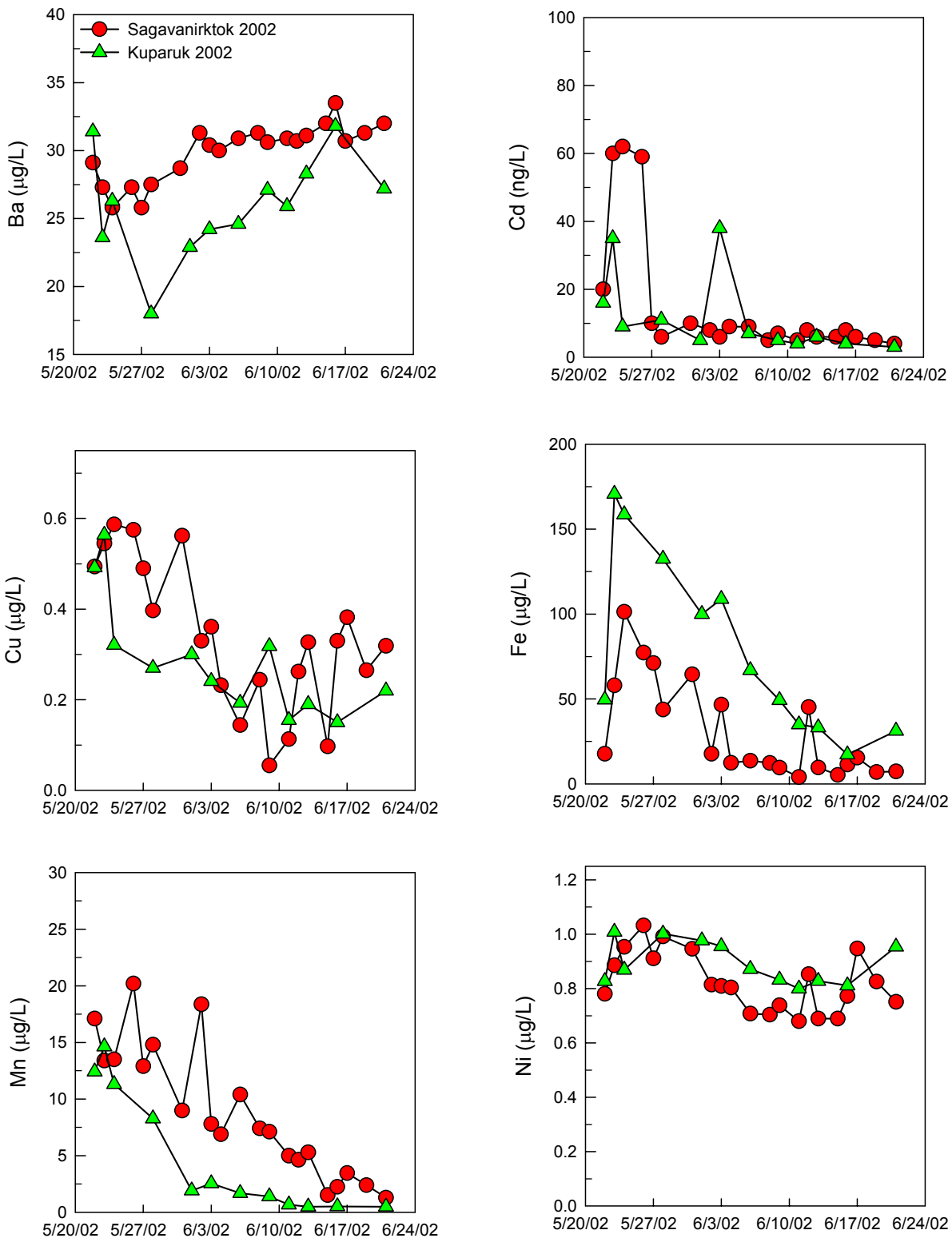
Figure 3-24. Concentrations of dissolved barium (Ba), cadmium (Cd), copper (Cu), iron (Fe), manganese (Mn) and nickel (Ni) in the Sagavanirktok and Kuparuk rivers during June 2002.

54

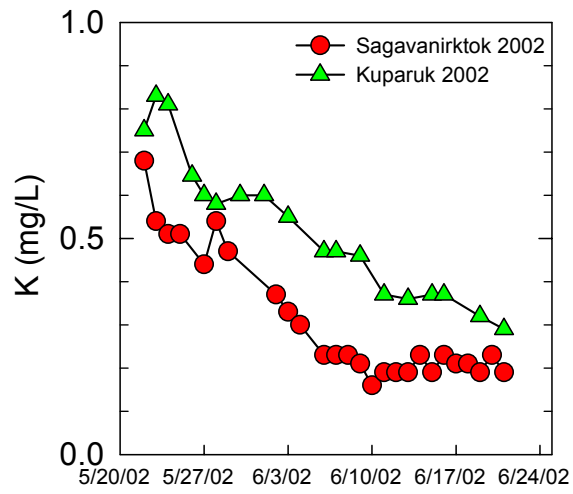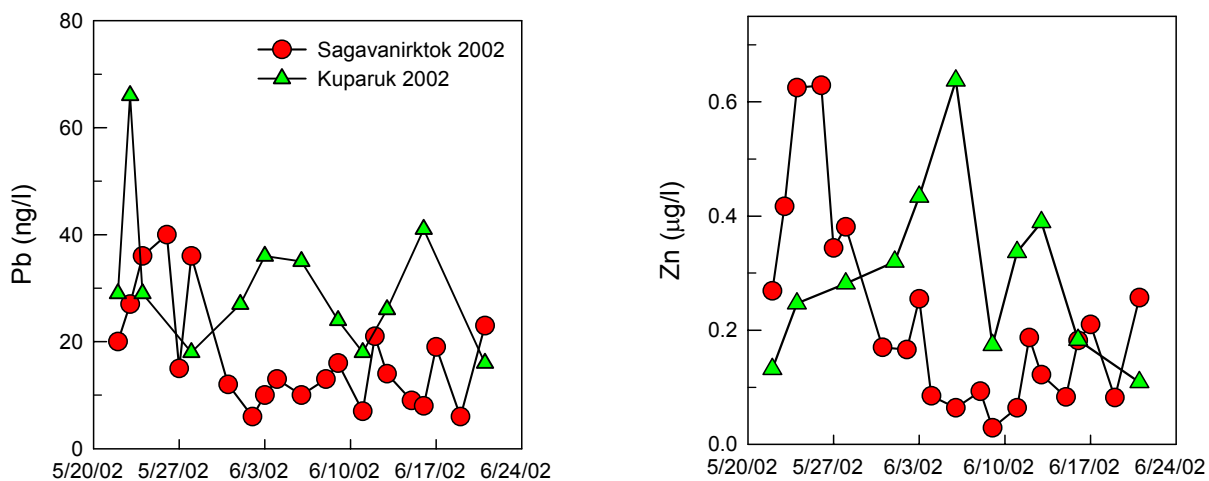Figure 3-25. Concentrations of dissolved lead (Pb) and zinc (Zn) in the Sagavanirktok and Kuparuk rivers during June 2002.
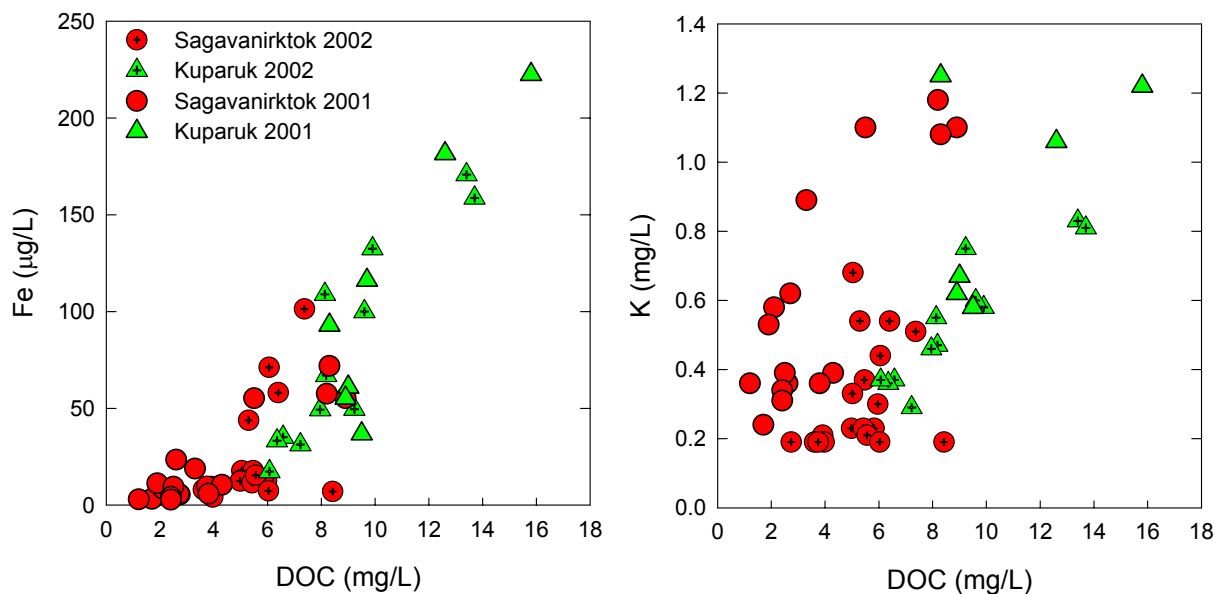
Figure 3-26. Concentrations of dissolved organic carbon (DOC) versus dissolved iron and potassium for the Sagavanirktok and Kuparuk rivers for June 2001 and 2002.

3.2.4 Particulate Trace Metals and Organic Carbon

Mean concentrations of particulate Al, Ba, Cu, Fe, Pb and Zn (μg/g dry weight) for samples collected during May-June 2002 were similar (within ±10-20%) to values determined for the 2001 samples (Table 3-12). In contrast with 2001, concentrations of particulate trace metals and Al varied during June with increased concentrations observed when the river slowed down and refroze. The slow down led to settling of larger particles and an increase in the fractional amounts of fine-grained aluminosilicates. Concentrations of particulate Ba (Figure 3-27) provide an example of the observed trend. However, the Ba/Al and other metal/Al ratios did not change significantly during June. Once again, concentrations of particulate Ba, Cu, Fe and Zn were poorly correlated with organic carbon and relatively well correlated with particulate Al (Table 3-13). The poor or negative correlations for POC versus Cu, Fe and Zn suggest that POC does not play a significant role in controlling concentrations of particulate trace metals in the Sagavanirktok River but that the aluminosilicate (clay) content is more important.

Table 3-12. Concentrations of aluminum, barium, copper, iron, lead, zinc and particulate organic carbon (POC) in the Sagavanirktok and Kuparuk rivers during May-June 2002.

River		Al (%)	Ba (μg/g)	Cu (μg/g)	Fe (%)	Pb (μg/g)	Zn (μg/g)	POC (%)
Sagavanirktok 2002	Mean	6.2	698	33.3	3.5	11.9	142	1.6
	Std. Dev.	± 1.1	± 160	± 5.7	± 0.6	± 4.1	± 31	± 0.3
	Range	5.0-8.8	541-1110	25.6-45.4	2.8-4.7	4.3-23.2	116-214	1.2-2.4
Kuparuk 2002 Peak Discharge	Mean	4.0	537	28.4	4.5	18.9	152	5.3
	Std. Dev.	± 1.5	± 237	± 6.0	± 0.8	± 3.8	± 62	± 3.1
	Range	2.6-7.5	358-1219	17.6-38.5	2.7-5.4	10.3-24.6	81-263	1.7-10.9
Sagavanirktok 2001	Mean	5.6	702	32.8	3.3	18.0	123	1.6
	Std. Dev.	± 0.9	± 113	± 2.8	± 0.4	± 2.0	± 7	± 0.49
	Range	4.0-7.7	542-1008	29.7-39.2	2.6-4.0	16.0-23.4	115-135	0.7-2.7
Kuparuk 2001 Peak Discharge	Mean	5.2	615	32.3	3.6	15.7	124	4.6
	Std. Dev.	± 0.5	± 88	± 5.8	± 0.2	± 0.7	± 13	± 1.1
	Range	4.6-5.8	497-743	25.7-37.2	3.3-3.8	14.7-16.6	110-145	3.3-5.9
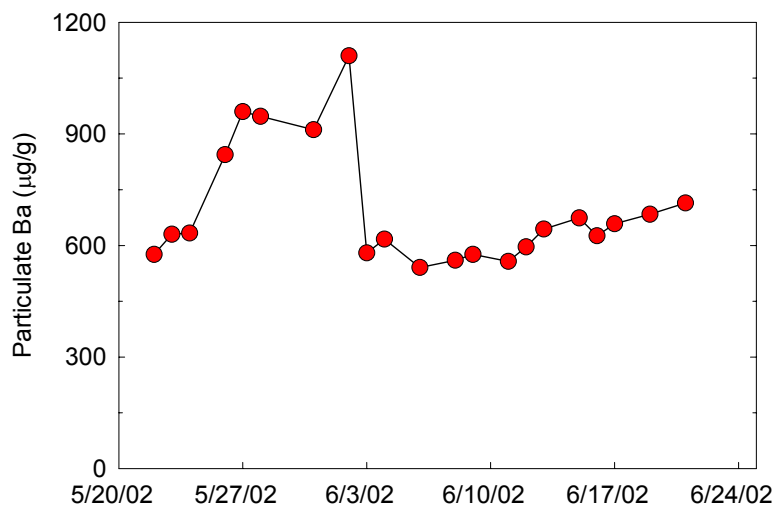
Figure 3-27. Concentrations of barium (Ba) for suspended sediment from the Sagavanirktok River for May-June 2002.

Table 3-13. Correlations for particulate trace metals and particulate organic carbon (POC) in the Sagavanirktok River during June 2002.

	Al	Ba	Cu	Fe	Pb	Zn
Al	1					
Ba	0.58**	1				
Cu	0.91**	0.50*	1			
Fe	0.92**	0.59**	0.88**	1		
Zn	0.90**	0.56*	0.96**	0.91**	0.16	1
POC	-0.39	-0.10	-0.14	-0.52	-0.64**	-0.18

** Correlation is significant at the 0.01 level.
* Correlation is significant at the 0.05 level.

3.3 Transport of Dissolved and Particulate Trace Metals and Organic Carbon by Rivers to the Coastal Beaufort Sea

Values for transport of metals and organic carbon by rivers to the coastal Beaufort Sea are difficult to calculate due to limitations in flow and chemical data as well as possible contributions from summer rainstorms. Nevertheless, by comparing transport during peak discharge in June with transport during the remainder of the year, a sense of the relative importance of spring floods to annual budgets was obtained. Calculations for material transport are presented here for the Kuparuk and Sagavanirktok rivers during 2001 because data for water flow are available (U.S.G.S., 2001).

Water discharge in the Kuparuk River for 2001 was divided into three periods: (1) 0.3×10^{12} L (25% of total) during three days of flood discharge in June, (2) 0.4×10^{12} L (33% of total) during the 21 off-peak days in June and (3) 0.5×10^{12} L (42% of total) during the remaining 90 days of the water year (U.S.G.S., 1971-2001). By combining water flow data with average concentrations of DOC for each time period, 42% of the annual load of DOC ([(0.25)(14.0 mg/L)]/[(0.25)(14.0 μM) + (0.33)(8.7 mg/L) + (0.42)(375 4.5 mg/L)] x100%) from the Kuparuk River was delivered to the Beaufort Sea in 3 days. Using the same approach shown above for DOC, the following fractions of the annual loads of dissolved metals were carried by the Kuparuk River in three days of peak flow: Ba (16%), Cu (36%), Fe (67%), Pb (47%) and Zn (46%).

Using the U.S.G.S. data for the Sagavanirktok River and assuming that it represents discharge flow for 20% of the system, then the annual flow can be scaled up and grouped as follows: (1) 1.0×10^{12} L (17% of total) of peak flow during 12 days in June, (2) 1.2×10^{12} L (18% of total) of off-peak flow during 16 days in June and (3) 4.2×10^{12} L (65% of total) during the remaining 90 days of the water year (U.S.G.S., 1971-2001). Using DOC data, 33% of the annual load of DOC [(0.17)(5.8 mg/L)]/[(0.17)(5.8 mg/L) + (0.18)(2.4 mg/L) + (0.65 x 2.4 mg/L)] x 100%) was transported to the coastal Beaufort Sea in 12 days. Using the same approach, the fractions of the annual transport of dissolved metals carried by the Sagavanirktok River in 12 days were as follows: Ba (15%), Cu (38%), Fe (74%), Pb (50%) and Zn (40%).

Calculations for annual transport of elements with suspended sediment are based on two time periods (1) peak flow and (2) off-peak flow in June plus the remainder of the summer, because sediment transport was predominantly during peak flow and because differences in concentrations of elements in the particulate form (on a dry weight basis) varied only slightly among time periods. During the three days of peak water flow in the Kuparuk River in June 2001, TSS averaged 63 mg/L to yield a sediment discharge of ~19,000 t. During the off-peak period in June and the remainder of the summer, TSS values averaged 4 and ~0.5 mg/L, respectively, resulting in an additional total of 1,900 t of sediment discharged. Thus, >90% of the annual transport of particulate Pb occurred during peak flow in the Kuparuk River during three days ([(0.90)(15.7 μg/g)] /[(0.10)(14.4 μg/g) + (0.90)(15.7 μg/g)] x 100%). Using the same approach, >89% of the other particulate metals and POC were transported to the coastal Beaufort Sea by the Kuparuk River in 3 days.

For the Sagavanirktok River, TSS averaged 267 mg/L during peak discharge in June to yield 267,000 t of sediment during the 12-day peak period. Concentrations of TSS averaged 31 and 1.3 mg/L during the off-peak period in June and the remainder of the summer, respectively, transporting an additional 36,000 t of sediment to the coastal Beaufort Sea. Particulate metal concentrations in the Sagavanirktok River did not vary greatly during peak and off-peak periods (Table 3-12) and therefore, >88% of particulate Pb, the other metals and POC were transported during the 12 days of peak discharge ([0.88)(18.3 µg/g)]/[(0.12)(18.3 µg/g) + (0.88)(18.3 µg/g] x 100%).

Results from this study also provide a direct comparison of the relative abundances of dissolved and particulate forms of metals and organic carbon in the arctic rivers of Alaska. During the brief periods of peak flow, the dissolved fraction accounted for 57% ([5.8 mg/L]/[(5.8 mg/L) + (16 mg/g/0.267 g/L) x 100%]) and 83% of DOC transport in the Sagavanirktok and Kuparuk rivers, respectively (Table 3-14). When combined with the off-peak data, the results indicate that DOC was dominant form of OC discharged to the coastal Beaufort Sea from these Alaskan arctic rivers. Dissolved Ba accounted for >14% of total Ba transport during peak flow and at least 59% of Ba transport during off-peak flow in June (Table 3-14). In the Sagavanirktok River, <3% of the total Fe, Pb and Zn were in the dissolved phase during both peak and off-peak periods, whereas dissolved Cu was ≥9% of the total Cu, possibly due to complexation by DOC (Cabaniss and Shuman, 1998).

Table 3-14. Percentage of trace metals and organic carbon in the dissolved phase during peak and off-peak discharge in the Sagavanirktok and Kuparuk rivers.

		Ba	Cu	Fe	Pb	Zn	OC
Sagavanirktok River							
Dissolved (%)	Peak	14	9	0.5	0.6	0.7	57
Dissolved (%)	Off-peak	59	29	0.6	2	3	83
Kuparuk River							
Dissolved (%)	Peak	33	28	9	5	4.6	83
Dissolved (%)	Off-peak	93	87	30	41	44	98

3.4 Partitioning of Metals between Dissolved and Particulate Phases in Rivers

The chemical forms of metals in rivers are an important starting point for understanding their subsequent behavior in the saline water of the coastal Beaufort Sea. Concentrations of dissolved and particulate Ba varied by a factor of 2 to 3 among rivers (Figure 3-28). However, concentrations of dissolved Ba varied in proportion to concentrations of particulate Ba (Figure 3-28). Therefore, distribution coefficients (K_d) were used to model the behavior of dissolved and particulate Ba during the spring discharge and summer samples. Distribution coefficients provide a measure of partitioning between dissolved and particulate phases and were calculated in this study using

$$K_d = \frac{\text{(concentration of particulate metal in } \mu g \text{ metal/g particles)}}{\text{(concentration of dissolved metal in } \mu g \text{ metal/g water)}}$$

where the conceptual perspective is shown below by considering that dissolved Ba^{2+} can adsorb and desorb from suspended particles in a predictable manner.

Despite significant differences in concentrations of dissolved and particulate Ba among rivers, the K_d values calculated for Ba were statistically equal (t-test, $\alpha = 0.05$), with the following average for samples collected during June, July and August; $2.3 \pm 0.3 \times 10^4$ (average log $K_d = 4.36$) in the Sagavanirktok River, $2.6 \pm 0.5 \times 10^4$ in the Kuparuk River and $2.1 \pm 0.4 \times 10^4$ in the Colville River (Figure 3-28). These results suggest that partitioning of Ba between dissolved and particulate phases is an equilibrium controlled process between free Ba^{2+} and suspended particles. Considering the large variations in water discharge, TSS, and concentrations of organic carbon, the apparent uniformity of the distribution coefficients for Ba indicates that discharge, TSS and organic carbon have little impact on the partitioning of Ba between dissolved and particulate phases.

The broader implication of these results for the biogeochemistry of Ba in rivers is potentially important. Do concentrations of particulate and dissolved Ba in other rivers follow similar behavior? Unfortunately, investigators have seldom determined both particulate and dissolved Ba concentrations for the same sample in rivers and the only data identified to date are for concentrations of particulate and dissolved Ba from another northern Alaskan River, the Kuskokwim River (Wang, 1999). The average K_d based on 5 samples was $2.6 \pm 0.6 \times 10^4$. These preliminary results suggest that differences between the North American and Eurasian concentrations for dissolved Ba, such as those found by Guay and Falkner (1998) are linked to geology by being dependent upon the Ba concentrations of river particles.
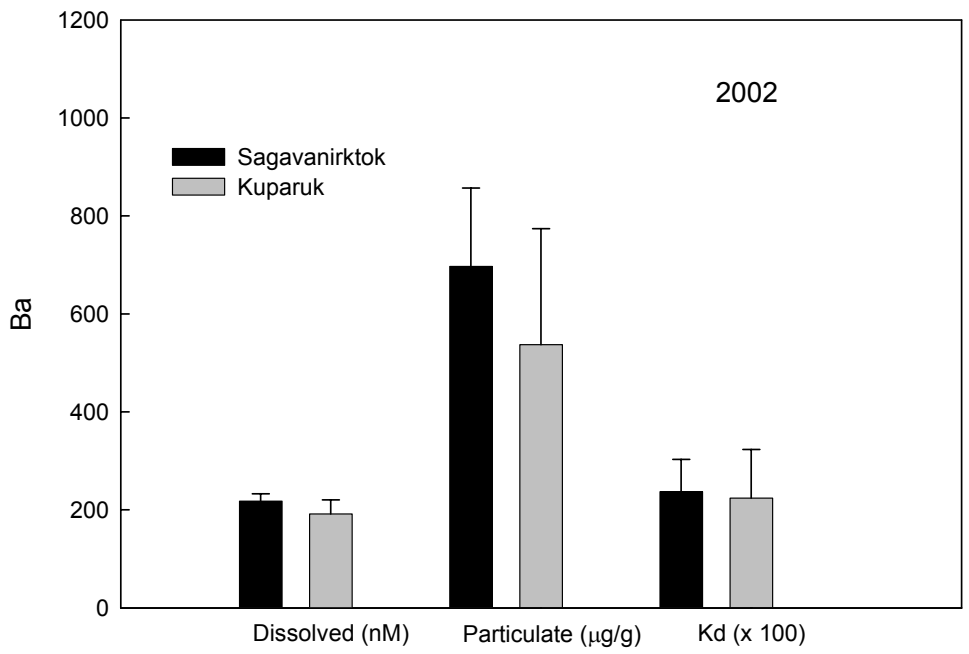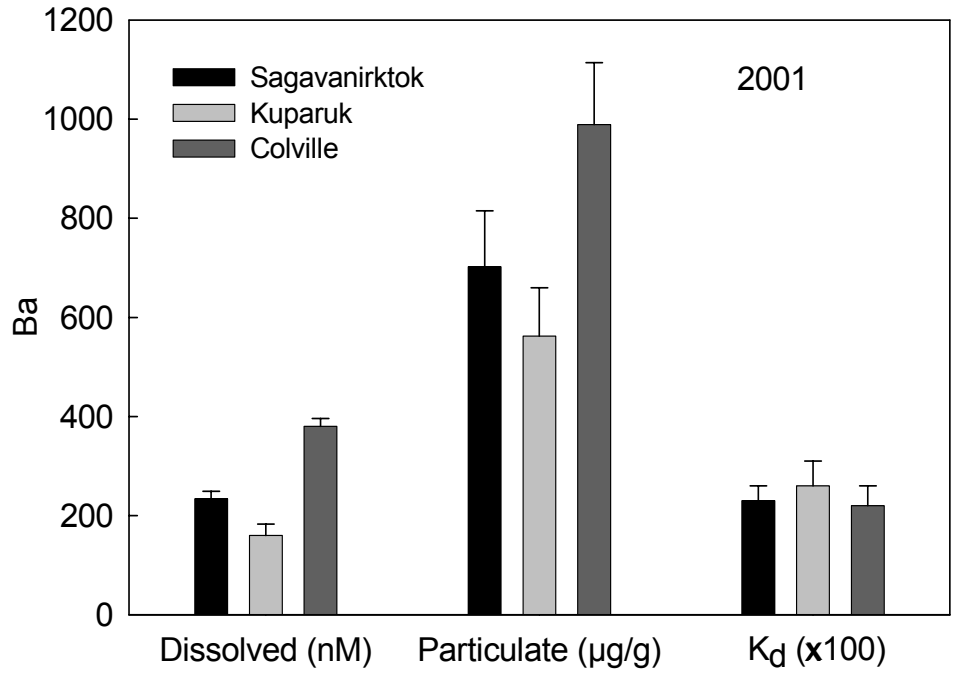
Figure 3-28. Average concentrations of dissolved and particulate barium (Ba) and distribution coefficients (K_d) for Ba in the Sagavanirktok, Kuparuk and Colville rivers.

The combined effect of significantly increased concentrations of dissolved Cu, Pb (Figure 3-29) and Zn during peak discharge with relatively constant concentrations of particulate metals suggest that a K_d is less likely to explain dissolved concentrations of these metals. During peak discharge, K_d values (x 10^4) for Cu (4.4), Pb (116) and Zn (67) were 40 to 50% lower than during off-peak discharge in the Sagavanirktok River. In contrast, concentrations of DOC were ~40% greater during peak discharge. Strong correlations between dissolved metals and DOC suggest that elevated concentrations of organic ligands during peak discharge alter partitioning of Cu, Pb and Zn between dissolved and particulate phases. Thus, K_d values, are potentially more useful in low DOC riverine environments. Results from previous studies in rivers have shown that distribution coefficients for Cu, Pb and Zn often have order-of-magnitude differences where a large fraction of the variance can be explained by concentrations of DOC (Shafer et al., 1999).
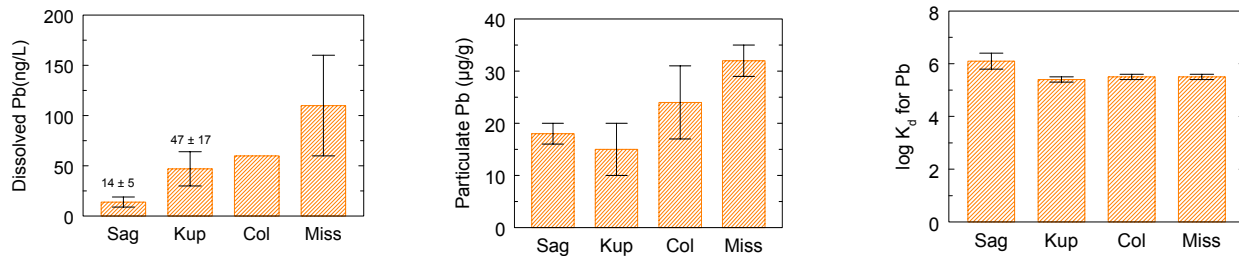
Figure 3-29. Concentrations of dissolved and particulate lead (Pb) in the Sagavanirktok, Kuparuk and Colville Rivers during summer 2001 and log K_d for Pb. Results for the Mississippi River (Miss) are presented for comparison (Trefry et al., 1986). Scaling for K_d is as log K_d, so log K_d = 6 is the same as K_d = 100 x 10^4.

3.5 Dissolved and Particulate Metals in the Coastal Beaufort Sea

Concentrations of dissolved As, Ba, Cd, Cr, Cu, Hg, Pb and Zn (Tables 3-15, 3-16 and 3-17) were determined for samples of saline water from the coastal Beaufort Sea. Concentrations of these elements were markedly lower than pertinent freshwater or salt water criteria established by the U.S. EPA (Table 3-18). Concentrations of total Hg in the coastal Beaufort Sea also were low at about 0.5-0.8 ng/L, relative to levels of ~2 ng/L in the source rivers; all of which were well below established water quality criteria. With respect to dissolved trace metals, area rivers and coastal seawater are pristine. We also determined concentrations of selected metals in samples of snow collected during 2002 at inland and offshore locations (Table 3-18). The concentrations of metals in snow were generally about 10 times lower than average values in the rivers and lower than values for river water during pre-peak flow.

A schematic look at concentrations of dissolved As (Figure 3-30) shows a progressive increase in concentrations from low levels in rivers to about 10 times higher levels in coastal seawater. This trend is typical for As and results from a combination of limited sources in crustal rocks and a relatively long residence time in seawater (~40,000 years, Broecker and Pang, 1984).

Table 3-15. Means and standard deviations (SD) for salinity, total suspended solids (TSS), and concentrations of dissolved metals and dissolved organic carbon (DOC) for water collected from the coastal Beaufort Sea during August 2000.

2000 Station Grouping		Salinity (psu)	TSS (mg/L)	As (µg/L)	Ba (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (ng/L)	Pb (ng/L)	Zn (µg/L)	DOC (mg/L)
North Star Area (n=2)	Mean ± SD	22 ±4	7.3 ±4.0	0.55 ±0.02	29 ±0.1	0.018 ±0.001	0.055 ±0.005	0.57 ±0.02	0.4 ±0.10	5 ±1	0.13 ±0.02	1.2 ±0.1
Liberty Area (n=2)	Mean ± SD	22 ±0.2	10.3 ±1.6	0.54 ±0.13	20 ±1	0.025 ±0.004	0.081 ±0.06	0.53 ±0.03	0.9 ±0.1	5 ±2	0.24 ±0.00	1.0 ±0.1
Beaufort Sea Monitoring Program (n=2)	Mean ± SD	21 ±2	9.9 ±7.3	0.37 ±0.01	32 ±1	0.017 ±0.001	0.059 ±0.002	0.53 ±0.01	0.4 ±0.1	5 ±1	0.22 ±0.06	1.1 ±0.0
Cumulative. (n=6)	Mean ± SD	22 ±3	8.2 ±4.8	0.49 ±0.11	27 ±6	0.020 ±0.004	0.065 ±0.013	0.54 ±0.03	0.5 ±0.3	5 ±1	0.20 ±0.06	1.1 ±0.1

Table 3-16. Means and standard deviations (SD) for salinity, total suspended solids (TSS), and concentrations of dissolved metals and dissolved organic carbon (DOC) for water collected from the coastal Beaufort Sea during August 2001.

2001 Station Grouping		Salinity (psu)	TSS (mg/L)	As (µg/L)	Ba (µg/L)	Cd (µg/L)	Cr (µg/L)	Cu (µg/L)	Hg (**ng/L**)	Pb (**ng/L**)	Zn (µg/L)	DOC (mg/L)
North Star Area (n=5)	Mean ± SD	18 ±5	3.9 ±1.8	0.43 ±0.16	34 ±10	0.019 ±0.003	0.10 ±0.03	0.66 ±0.10	1.3 ±0.3	6 ±3	0.15 ±0.03	2.1 ±0.4
Liberty Area (n=2)	Mean ± SD	14 ±2	6.7 ±1.2	0.34 ±0.04	28 ±0.4	0.023 ±0.004	0.10 ±0.02	0.57 ±0.12	- -	22 ±7	0.21 ±0.003	2.0 ±0.7
Beaufort Sea Monitoring Program (n=4)	Mean ± SD	16 ±4	5.5 ±2.3	0.33 ±0.12	32 ±7	0.023 ±0.007	0.08 ±0.01	0.64 ±0.04	- -	8 ±3	0.15 ±0.03	1.7 ±0.2
Cumulative. (n=11)	Mean ± SD	17 ±4	5.0 ±2.2	0.38 ±0.13	32 ±8	0.021 ±0.005	0.09 ±0.02	0.64 ±0.08	- -	10 ±7	0.16 ±0.04	1.9 ±0.4

Table 3-17. Means and standard deviations (SD) for salinity, total suspended solids (TSS), and concentrations of dissolved metals and dissolved organic carbon (DOC) for water collected from the coastal Beaufort Sea during August 2002.

2002 Station Grouping		Salinity (psu)	TSS (mg/L)	As (µg/L)	Ba (µg/L)	Cd (µg/L)	Cu (µg/L)	Hg (**ng/L**)	Pb (**ng/L**)	Zn (µg/L)	DOC (mg/L)
North Star Area (n=11)	Mean ± SD	22 ±4	2.5 ±1.5	0.49 ±0.17	15 ±3	0.026 ±0.004	0.44 ±0.16	2.0 (n=1)	7 ±2	0.12 ±0.10	2.2 ±0.7
Beaufort Sea Monitoring Program (n=21)	Mean ± SD	20 ±4	1.9 ±1.2	0.52 ±0.13	14 ±2	0.028 ±0.005	0.48 ±0.07	0.6 ±0.3 (n=4)	7 ±3	0.11 ±0.05	1.9 ±1.0
Cumulative (n=32)	Mean ± SD	20 ±5	2.1 ±1.3	0.51 ±0.14	14 ±2	0.027 ±0.005	0.47 ±0.11	0.9 ±0.7 (N=5)	7 ±3	0.11 ±0.07	2.1 ±0.8

Table 3-18. Concentrations of selected dissolved metals (0.4 µm filtered) in snow, Sagavanirktok River water and Beaufort Sea water compared with U.S. EPA criteria for freshwater and saltwater.

Concentrations of Dissolved Metals
(ng/L or parts per trillion)

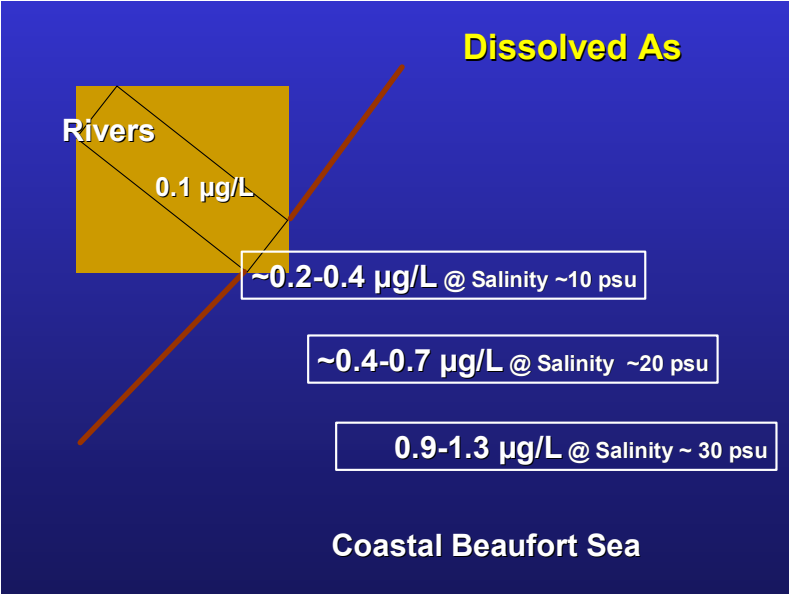|	As	Ba	Cu	Pb
Terrestrial Snow	9	750	58	7
Marine Snow	33	570	70	-
Sagavanirktok River	130	32,000	590	21
Coastal Beaufort Sea	1200	12,000	650	7
Federal Fresh Water Quality Criteria	150,000	1×10^6	9000	2500
Federal Salt Water Quality Criteria	36,000	1×10^6	3100	8100

Figure 3-30. Generalized distribution of dissolved arsenic (As) in source rivers and coastal water of the Beaufort Sea.

The schematic look at the concentrations and cycling of As in Figure 3-30 is presented as concentrations of As in snow, river water, and summer seawater versus salinity in Figure 3-31. If a simple mixing curve is developed between the river water and highest salinity offshore water, concentrations of As during summer at mid-salinities were lower than predicted by the spring mixing curve. The apparent removal of As may be due to biological uptake or scavenging by iron oxides or clays.

Figure 3-31. Concentrations of dissolved arsenic (As) versus salinity (practical salinity units) where values for snow and river water plot close to the zero points of the graph relative to summer seawater (circles). Line shows straight line mixing curve for river water and saline water from the Beaufort Sea.

In contrast with As, concentrations of Ba were about 3 times higher in the open, saline water of the Beaufort Sea relative to the source rivers (Figure 3-32). Furthermore, Figure 3-32 shows the characteristic desorption of Ba from particles during freshwater-seawater mixing. Concentrations of Ba were about 50 times lower in snow than river water (Figure 3-33). As river water mixes with seawater at low salinity (<10 psu) Ba desorbs from river-borne particles due to increasing concentrations of competing cations. Then, concentrations of Ba generally follow simple mixing with increasing salinities.

Figure 3-32. Generalized distribution of dissolved barium (Ba) in source rivers and coastal water of the Beaufort Sea.
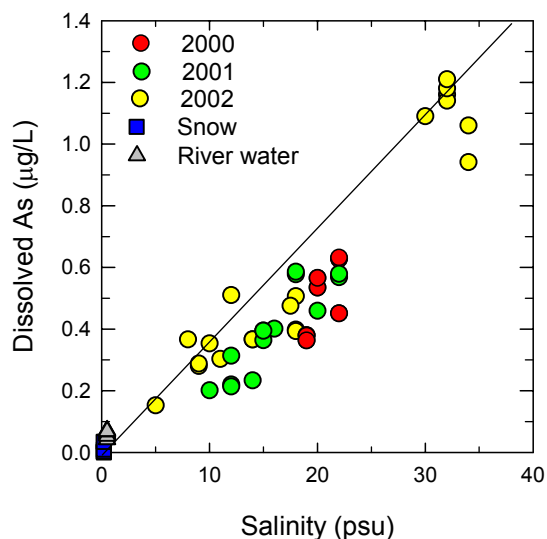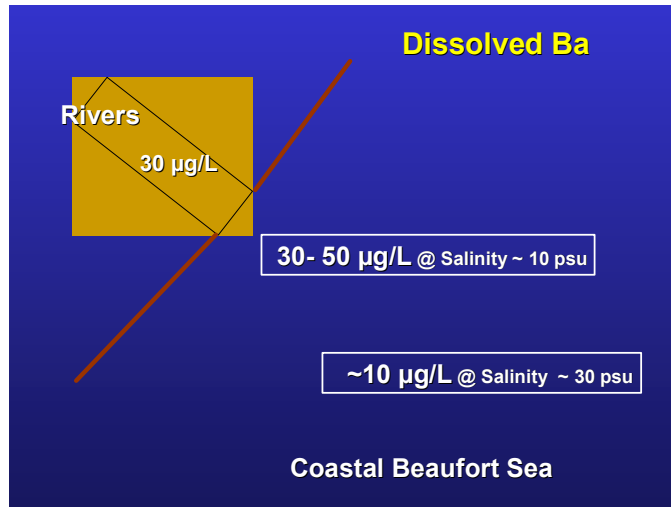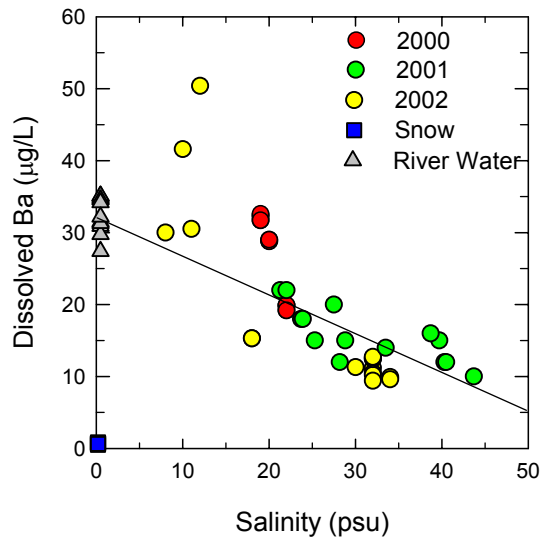

Figure 3-33. Concentrations of dissolved barium (Ba) versus salinity (practical salinity units) where values for snow and river water plot close to zero salinity relative to values for summer seawater (circles). Line shows straight line mixing curve for river water and saline water from the Beaufort Sea.

3.6 Dissolved and Particulate Organic Substances in Seawater

The Total PAH (TPAH) concentrations in the whole seawater samples (dissolved + particulate fractions) were low and ranged from 22 to 68 ng/L (parts per trillion in Table 3-19). The TPAH of the particulate fraction of the seawater samples ranged from 21.1 to 54.8 ng/L and the concentration in the dissolved fractions ranged from 13.2 to 18.5 ng/L (Table 3-19). The PAH distributions of the particulate seawater samples were very similar suggesting a similar source of hydrocarbons in all samples. Examples of representative BSMP and Northstar station PAH distribution histograms are presented in Figure 3-34. The PAH distribution of the particulates shows a petrogenic or petroleum hydrocarbon composition, characterized by a predominance of the 2- and 3-ringed alkyated PAH compounds, with a lower abundance of 4-, 5-, and 6-ringed PAH. One exception is phenanthrene, the most abundant individual PAH detected in the samples, and to a lesser degree naphthalene and C1-phenanthrenes. However, these three analytes also were detected in the procedural blank at comparable concentrations, indicating that the observed abundances of these analytes are laboratory artifacts. In general, the PAH distribution of the particulate fractions is similar to the pattern observed in the river sediment and surface benthic sediment from the region (Brown et al., 2003). The dissolved phase of the water samples had only trace level concentrations and both the PAH levels and distributions were similar to the associated laboratory procedural blank. Based on these results, and accounting for the procedural blank PAH concentrations, PAH concentrations in the dissolved phase of the samples were below detection limits.

A t-test procedure was used to determine if any key PAH parameters (Table 3-19) were significantly different between the water samples collected at Northstar stations ($n = 4$) and at BSMP/Liberty stations ($n = 4$). The BSMP station 5A is located within 3 Km of the Northstar Island and thus was included as a Northstar region station for the statistical analyses. Concentration variables were log-transformed prior to analysis to normalize the distributions. No significant differences were found between the Northstar stations and the BSMP/Liberty stations. Partition coefficients were not calculated for the individual PAH compounds in the Beaufort Sea seawater samples due to the majority of trace and non-detect values reported for the dissolved fraction.

Overall, the results of the Beaufort Sea seawater organic analyses show low levels of PAH with a composition generally similar to the riverine and benthic sediment of the region. The PAH in the seawater samples are primarily associated with the suspended sediment in the particulate fraction. The analyses of the dissolved fraction show no appreciable PAH in the dissolved phase (after comparison to laboratory blank levels), indicating that the PAH are tightly bound to the suspended particulate matrix and do not readily partition into the dissolved phase.

Table 3-19. Summary data for polycyclic aromatic hydrocarbons (PAH) in Beaufort Sea water samples

Station	Sample Type	Units	Total PAH	2-Ring PAH	3-Ring PAH	4-Ring PAH	5$^+$-Ring PAH
Filter Samples							
3A	Particulate	ng/L	22.0	8.38	8.48	3.32	1.85
4A	Particulate	ng/L	40.8	20.0	11.0	6.59	3.13
5A	Particulate	ng/L	32.7	12.9	10.5	7.91	1.42
L08	Particulate	ng/L	48.4	21.8	12.0	10.5	4.09
L12	Particulate	ng/L	54.8	16.4	20.5	15.4	2.59
N01	Particulate	ng/L	21.1	7.54	7.68	4.64	1.21
N10	Particulate	ng/L	40.7	15.4	13.6	8.50	3.25
N13	Particulate	ng/L	38.8	16.2	11.7	8.13	2.80
Blank	Particulate	ng/L	9.86	6.13	2.93	0.80	0.00
Filtered Water Samples							
3A	Dissolved	ng/L	16.9	14.6	1.30	0.93	0.07
4A	Dissolved	ng/L	13.2	10.6	1.30	1.25	0.09
5A	Dissolved	ng/L	14.7	13.2	0.96	0.60	0.00
L08	Dissolved	ng/L	14.4	11.8	1.40	1.13	0.06
L12	Dissolved	ng/L	17.7	14.6	1.80	1.28	0.08
N01	Dissolved	ng/L	18.5	16.4	1.22	0.87	0.00
N10	Dissolved	ng/L	15.9	14.0	1.13	0.73	0.00
N13	Dissolved	ng/L	16.1	13.9	1.45	0.74	0.00
Blank	Dissolved	ng/L	12.7	10.2	1.72	0.75	0.00
Whole Water Samples							
3A	Whole Water	ng/L	37.6	22.5	9.26	4.05	1.80
4A	Whole Water	ng/L	50.8	29.1	11.5	7.33	2.98
5A	Whole Water	ng/L	45.4	25.3	10.8	8.02	1.33
L08	Whole Water	ng/L	59.0	31.9	12.5	10.8	3.83
L12	Whole Water	ng/L	68.5	29.7	20.8	15.5	2.47
N01	Whole Water	ng/L	40.1	24.1	9.09	5.62	1.24
N10	Whole Water	ng/L	54.0	28.5	13.8	8.67	3.03
N13	Whole Water	ng/L	52.6	29.1	12.4	8.37	2.63
Blank	Whole Water	ng/L	22.6	16.4	4.65	1.55	0.00

Figure 3-34. Distribution histogram for polycyclic aromatic hydrocarbons (PAH) in Beaufort Sea
seawater samples 3A-01 and N01-01 – particulate fraction.

Figure 3-35. Distribution histogram for polycyclic aromatic hydrocarbons PAH) in Beaufort Sea
seawater samples 3A-01 and procedural blank – dissolved fraction.
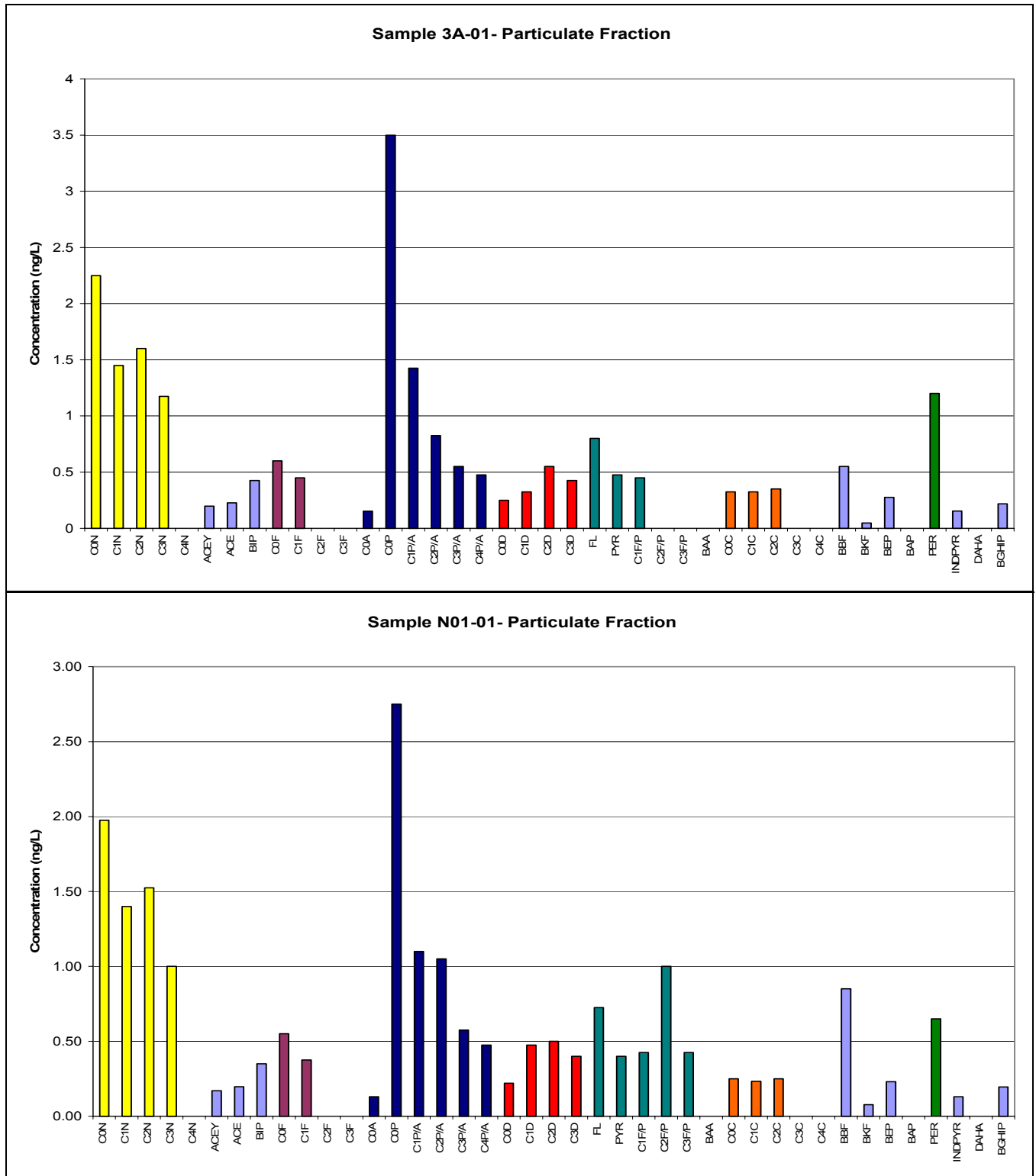
3.7 Spike Study for Polycyclic Aromatic Hydrocarbons

The primary purpose of the Spike Study was to determine equilibrium kinetics for release and uptake of selected organic substances during sediment resuspension events. The PAH concentration data from the dissolved and particulate phases will be evaluated to determine the degree of uptake or release of crude oil PAH components from particles. These data will serve as a baseline for future oil spill modeling, and will provide information on the dissolved phase PAH, potential particulate sorption of PAH, and subsequent re-deposition as would be the case in an open water oil spill in "storm conditions" in the nearshore Beaufort Sea.

The TPAH concentration of the whole water samples in spike study was quite variable and ranged from 39,700 to 145,000 ng/L. The TPAH concentration in the dissolved fraction (equivalent to a water accommodated fraction – WAF) of spike study samples ranged from 23,500 to 71,300 ng/L and the TPAH concentration in the particulate spike study samples ranged from 970 to 80,200 ng/L (Table 3-20). The high degree of variability seen in the particulate sample concentrations was likely due to particulate oil or micro-emulsion oil droplets becoming entrained in the water phase of some samples during the mixing phase of the study. Despite the variability in the particulate sample concentrations, the PAH distributions were very similar for the seven replicate samples, and as expected, are similar to the North Slope Crude oil used to dose the samples with a predominance of 2- and 3- ringed alkyl PAH and lower levels of alkylated 4-ring PAH (Figures 3-36 and 3-37). The PAH distributions of the dissolved sample replicates were also similar to each other. However, the PAH distributions in these samples (Figure 3-36) is more representative of a WAF, and shows a preferential enrichment of the more water soluble 2-ringed PAH (i.e., naphthalene > C1-naphthalenes > C2-napththalenes > C3-naphthalenes > C4- naphthalenes) and substantially lower levels of the less soluble 3-ring PAH (flourenes, phenanthrenes, and dibenzothiophenes) and trace level or non-detects for the 4-, 5-, and 6-ring PAH.

Partition coefficients were not calculated for the individual PAH compounds in the spiked Beaufort Sea seawater samples due to the high degree of variability observed in the particulate sample concentrations. However, the total PAH concentrations of the whole water samples are generally within the range of WAF samples prepared from crude oil and diesel (Hokstad, et al., 1999; Neff, et al., 2000). It should be noted that the whole water samples from the spike study include a substantial amount of suspended sediment (~95 mg/L) which is not normally included in the preparation of WAFs. The dissolved fraction of the spike study samples are probably more representative of a typical WAF preparation and the TPAH concentrations of the dissolved fraction are substantially lower than those reported by Neff et al., 2000 for crude oil, condensate and diesel. The lower PAH concentrations observed in the spike study are likely due to the lower solubility of the PAH at 4°C versus room temperature (20°C), which is typical for WAF preparation in other studies.

Table 3-20. Data summary for polycyclic aromatic hydrocarbons (PAH) in Beaufort Sea spike water study.

Station	Spiked With	Sample Type	Units	Total PAH	2-Ring PAH	3-Ring PAH	4-Ring PAH	5+-Ring PAH
Filter Samples								
3A-01	None	Particulate	ng/L	22.0	8.38	8.48	3.32	1.85
3A-02	Oil and Sediment	Particulate	ng/L	4450	1990	2050	383	16.2
3A-03	Oil and Sediment	Particulate	ng/L	5080	2160	2400	502	26.0
3A-04	Oil and Sediment	Particulate	ng/L	76600	38400	31600	6460	145
3A-05	Oil and Sediment	Particulate	ng/L	972	324	512	125	10.9
3A-06	Oil and Sediment	Particulate	ng/L	36600	17200	15900	3410	73.4
3A-07	Oil and Sediment	Particulate	ng/L	6450	3140	2740	554	21.6
3A-08	Oil and Sediment	Particulate	ng/L	80200	38000	35000	7020	159
Blank	Sediment only	Particulate	ng/L	79.1	27.3	25.3	17.0	9.58
Filtered Water Samples								
3A-01	None	Dissolved	ng/L	16.9	14.7	1.30	0.93	0.07
3A-02	Oil and Sediment	Dissolved	ng/L	35200	32900	2270	79.4	1.24
3A-03	Oil and Sediment	Dissolved	ng/L	40400	37100	3160	114	0.87
3A-04	Oil and Sediment	Dissolved	ng/L	48800	44100	4510	154	2.13
3A-05	Oil and Sediment	Dissolved	ng/L	34700	32100	2460	86.0	1.52
3A-06	Oil and Sediment	Dissolved	ng/L	71300	65000	6140	190	0.98
3A-07	Oil and Sediment	Dissolved	ng/L	23500	21900	1550	54.2	0.71
3A-08	Oil and Sediment	Dissolved	ng/L	65200	58300	6670	200	1.22
Blank	Sediment only	Dissolved	ng/L	44.2	26.9	14.6	2.29	0.38
Whole Water Samples								
3A-01	None	Whole water	ng/L	37.6	22.5	9.26	4.05	1.80
3A-02	Oil and Sediment	Whole water	ng/L	39700	34900	4320	462	17.4
3A-03	Oil and Sediment	Whole water	ng/L	45500	39200	5560	617	26.8
3A-04	Oil and Sediment	Whole water	ng/L	125000	82500	36100	6610	147
3A-05	Oil and Sediment	Whole water	ng/L	35600	32400	2970	211	12.4
3A-06	Oil and Sediment	Whole water	ng/L	109000	82200	22000	3600	74.4
3A-07	Oil and Sediment	Whole water	ng/L	30000	25100	4290	608	22.3
3A-08	Oil and Sediment	Whole water	ng/L	145000	96400	41700	7210	160
Blank	Sediment only	Whole water	ng/L	123	54.2	39.8	19.3	9.96
Spiking Sediment and Oil								
N23[1]		Sediment	ng/0.36g	195	60.8	59.7	42.9	31.6
North Slope Crude[2]		Oil	ng/200 mg	2780000	1720000	894000	162000	3460

Note[1] – 360 mg (dry weight) of N23 sediment was used for spiking samples.   Note[2] – 200 mg of North Slope Crude was used for spiking samples.

Figure 36. Distribution histogram for polycyclic aromatic hydrocarbons (PAH) in spiked sample
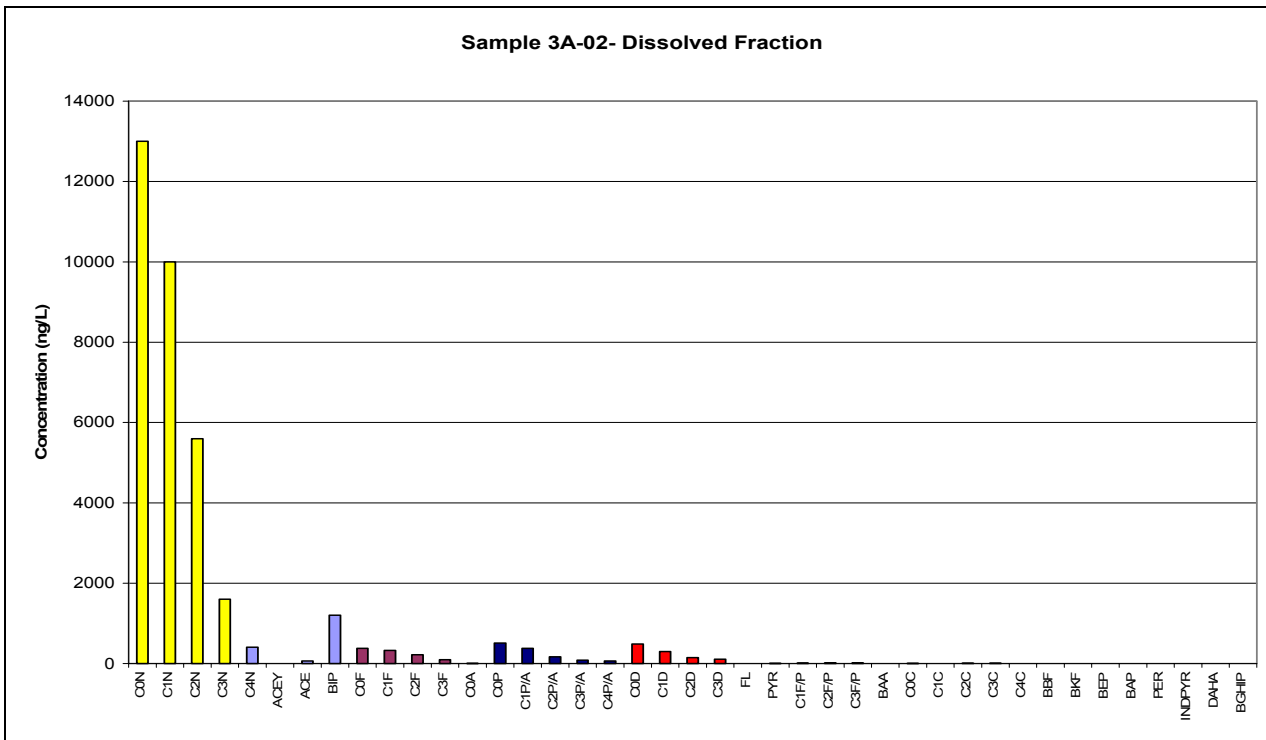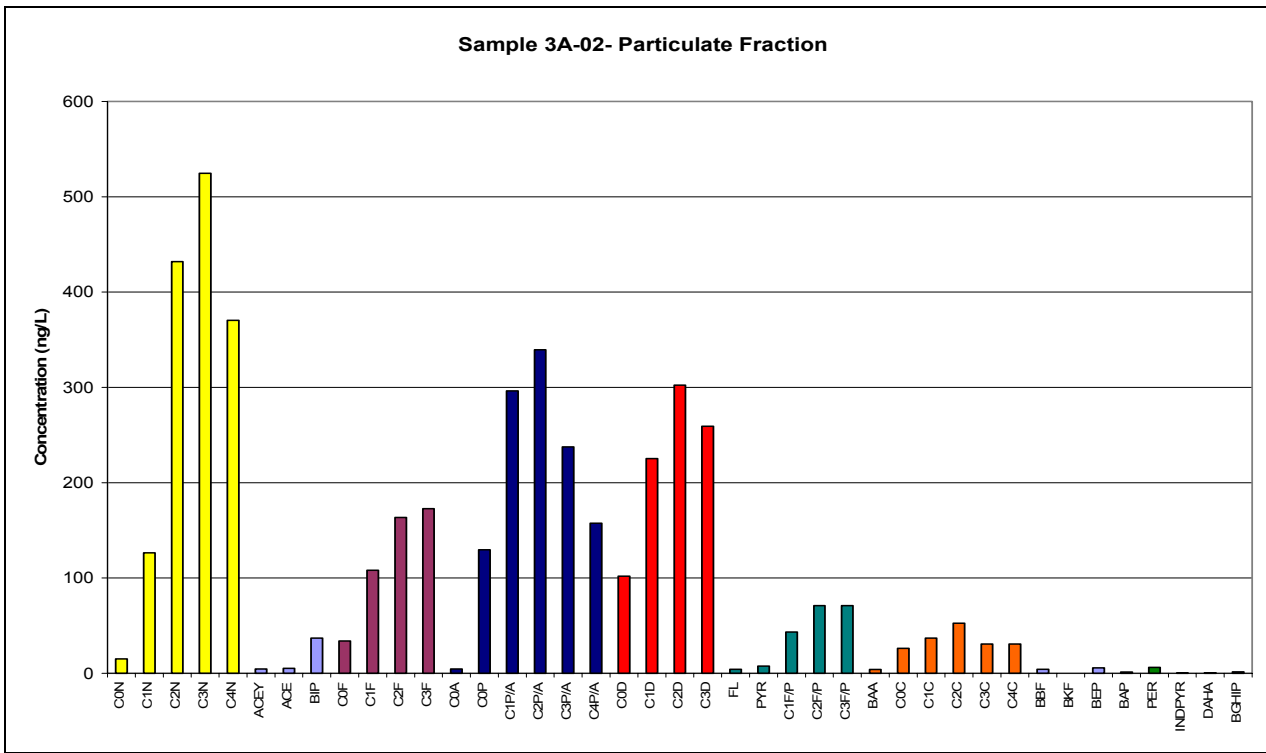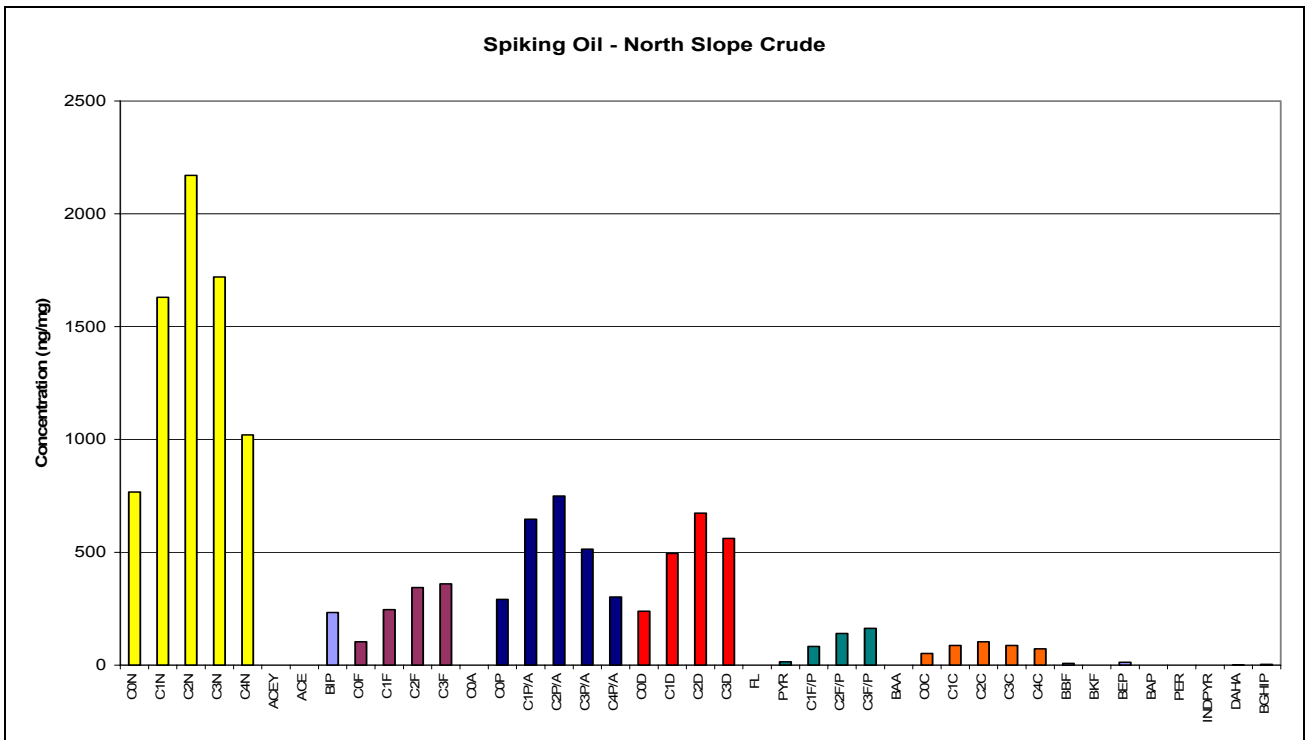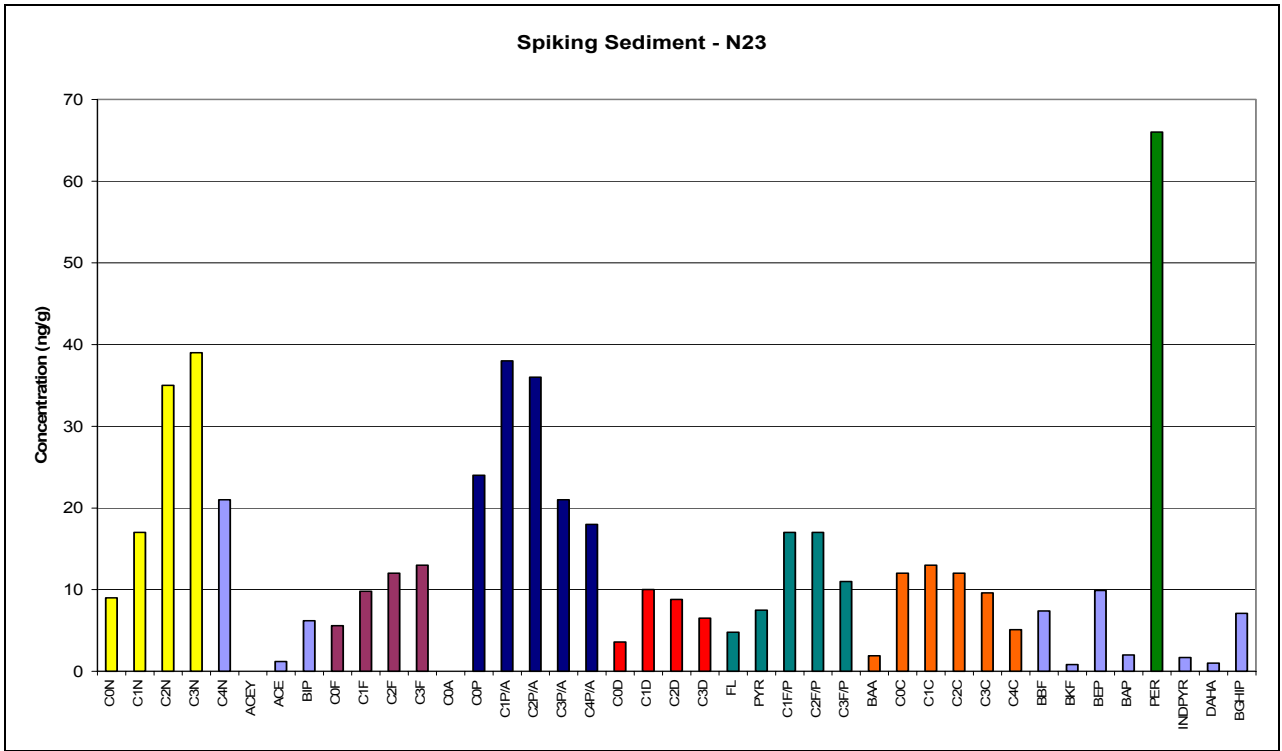3A-02 – particulate and dissolved fractions.

Figure 37. Distribution histogram for polycyclic aromatic hydrocarbons (PAH) in spiking
sediment and oil.

4.0 Summary and Conclusions

Water flow during the three- and 12 day spring flooding events in the Kuparuk and Sagavanirktok rivers during June 2001 accounted for ~17% and ~25%, respectively, of the annual discharge of water (U.S.G.S., 1971-2001). High-resolution sampling of the Sagavanirktok River during peak flow revealed that concentrations of dissolved Cu, Fe, Pb, Zn and organic carbon increased by 2 to 25 fold at maximum discharge. Strong positive correlations for concentrations of dissolved metals versus DOC suggest that soil interstitial water and surface water that were flushed from the drainage basins were primary sources of metals and DOC. During off-peak discharge in August, when water flow and levels of TSS decreased, concentrations of dissolved metals in the Sagavanirktok and Kuparuk rivers were among the lowest values reported for world rivers.

Trends in concentrations of dissolved trace metals and organic carbon in the Kuparuk and Colville rivers were similar to those observed in the Sagavanirktok River. However, concentrations of dissolved metals and DOC were, on average, higher than those observed in the Sagavanirktok River during June 2001. These higher concentrations in the Kuparuk and Colville rivers appeared to be related to differences in lithology and vegetation in the drainage basins. Soils westward of the carbonate rich Sagavanirktok River are more acidic. These lower pH soils are likely to support enhanced chemical weathering and increased concentrations of dissolved metals and DOC.

In contrast with Cu, Fe, Pb and Zn, concentrations of dissolved Ba remained relatively constant in each river throughout the sampling period with the Sagavanirktok River at 234 ± 14 nM, the Kuparuk River at 171 ± 16 nM and the Colville River at 376 ± 24nM. These data suggest that concentrations of dissolved Ba were not significantly influenced by increases in water discharge or concentrations of TSS and DOC. Concentrations of dissolved Ba vary in proportion to concentrations of particulate Ba in the Sagavanirktok, Kuparuk and Colville rivers. Considering the large range of TSS, water discharge and DOC found during this study, we speculate that the fraction of exchangeable fraction of Ba associated with the particles may control concentrations of dissolved Ba.

Concentrations of particulate Cu, Fe, Pb, Zn and OC did not follow the trends observed for the dissolved fraction and were relatively constant on a dry weight basis throughout the spring floods. In addition, concentrations of particulate metals correlated well with particulate Al but were poorly correlated with POC showing that clays rather than organic matter control particulate metal concentrations.

Increases in water discharge during the spring flood events coincided with increased concentrations of TSS, dissolved metals, and OC and account for a large fraction of the annual transport. In the Kuparuk and Sagavanirktok rivers, >16% of the water flow and >80% of the annual sediment discharge occurred during three and 12-day periods, respectively. This large pulse of water carried more than one-third of the annual dissolved load of Cu, Fe, Pb, Zn and OC and >80% of the particulate metals to a coastal Beaufort Sea that was covered with a 2-m thick layer of ice.

Results from analyses of Beaufort Sea seawater show low levels of PAH with a composition generally similar to the riverine and benthic sediment of the region. The PAH in the seawater samples were primarily associated with the suspended sediment in the particulate fraction. The analyses of the dissolved fraction show no appreciable PAH in the dissolved phase, indicating that the PAH were tightly bound to the suspended particulate matrix and did not readily partition into the dissolved phase. For the spike study, the results indicate that while the PAH in the whole water samples from the study were comparable to typical WAF PAH levels, the dissolved PAH were substantially lower due to the low water temperature used to approximate Beaufort Sea conditions during the spike study.

The main conclusions from ANIMIDA Task 7 are the following: (1) concentrations of dissolved trace metals and PAH in the study area are very low and characteristic of pristine water, (2) concentrations of some metals can be modeled with a simple distribution coefficient, and (3) active physical, chemical and biological processes are at work to create a dynamic, yet predictable, distribution of dissolved trace metals. Such information will be useful for long-term monitoring of the area (years, decades and centuries) and will provide us with an evolving capability for predicting impacts from any spills or other releases of chemicals within the drainage basin or coastal sea.

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6.0 Appendices

The appendices listed below are tabulated on the CD attached to hard copies of this report or as separate files on this CD.

Appendix A: Data for Dissolved and Particulate Metals and Organic Carbon from Rivers for 2001 and 2002

Appendix B: Chemical Data for Under Ice Samples for 2001 and 2002
     Appendix B1: CTD Under Ice for 2001
     Appendix B2: CTD Under Ice for 2002

Appendix C: Data for Dissolved and Particulate Metals in the Coastal Beaufort Sea for 2000, 2001 and 2002
     Appendix C1: Aanderaa Data for Summer 1999-2002

Appendix D: Rember, R.D. (2002) Composition of Dissolved and Suspended Matter Transported by the Sagavanirktok, Kuparuk and Colville Rivers in the Alaskan Arctic. Ph.D. Dissertation, Florida Institute of Technology, 106 pp.

Acknowledgements

The Department of the Interior Mission

As the Nation's principal conservation agency, the Department of the Interior has responsibility for most of our nationally owned public lands and natural resources. This includes fostering sound use of our land and water resources; protecting our fish, wildlife, and biological diversity; preserving the environmental and cultural values of our national parks and historical places; and providing for the enjoyment of life through outdoor recreation. The Department assesses our energy and mineral resources and works to ensure that their development is in the best interests of all our people by encouraging stewardship and citizen participation in their care. The Department also has a major responsibility for American Indian reservation communities and for people who live in island territories under U.S. administration.

The Minerals Management Service Mission

As a bureau of the Department of the Interior, the Minerals Management Service's (MMS) primary responsibilities are to manage the mineral resources located on the Nation's Outer Continental Shelf (OCS), collect revenue from the Federal OCS and onshore Federal and Indian lands, and distribute those revenues.

Moreover, in working to meet its responsibilities, the **Offshore Minerals Management Program** administers the OCS competitive leasing program and oversees the safe and environmentally sound exploration and production of our Nation's offshore natural gas, oil and other mineral resources. The MMS **Royalty Management Program** meets its responsibilities by ensuring the efficient, timely and accurate collection and disbursement of revenue from mineral leasing and production due to Indian tribes and allottees, States and the U.S. Treasury.

The MMS strives to fulfill its responsibilities through the general guiding principles of: (1) being responsive to the public's concerns and interests by maintaining a dialogue with all potentially affected parties and (2) carrying out its programs with an emphasis on working to enhance the quality of life for all Americans by lending MMS assistance and expertise to economic development and environmental protection.