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Progress Report

APPENDIX A

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Submitted by
K. R. Everett
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ABSTRACT

Ionic concentration of snow prior to meltoff in 1990 as in previous years ranged widely from point to point within the basin. The order of abundance was SO_4^{2-} , NO_3^- , Cl^- , F^- , Ca^{2+} , PO_4^{3-} , Na^+ , Fe. Sulfate and nitrate concentrations were higher than the five year average and may reflect volcanism to the south. Water content of the snow was 28 percent below the five year mean. Overland flow began on May 12 and was monitored at closely-spaced time intervals for discharge volume and ionic concentrations to better define this relationship in non-channelized flow. Flow in Imnavait Creek and watertracks began on 13 May. The meltoff hydrograph was complex, consisting of multiple surge peaks produced by a periodic sequential upstream release of slush dams in much the same fashion as in 1989. Ionic concentration in both watertrack flow and in Imnavait Creek were closely monitored during meltoff. During the post melt period daily sampling was maintained in watertrack 7 and Imnavait Creek. Rainfall collection and analysis on an eight day schedule was maintained as in previous years. In addition, single event sampling was added through early September to provide background for overland and shallow subsurface flow chemistry. Soil solution composition was monitored on an event basis in conjunction with a similar schedule of precipitation sampling to determine relationships between precipitation and near surface and overland flow. Composition of deeper soil solution was also monitored and sampled for ^{18}O analyses to determine the age structure of water contributed by the active layer to stream and watertracks. A pilot experiment employing salt tracers was conducted across landscape units to determine rates and pathways of soil solution movement in response to individual rain events. This experiment was a precursor to proposed larger grey water addition experiments in 1991. Nutrient addition in rime and fog were also recorded to add detail to the input side of the balance equation.

Two synthesis papers were produced: one detailing the precipitation chemistry (Appendix A) and the second geochemical composition and fluxes within the active layer, watertrack stream flow system for meltoff and post meltoff periods (Appendix B).

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Introduction

The 1990 R4D research program in hydrology and geochemistry emphasized synthesis of data collected during the period 1985 through 1989 (Appendices B and C). Field studies centered on maintaining the essential hydrologic and chemical input - output data set. A detailed evaluation was made of melt-off overland flow and several post melt-off event flows from Plot 4. This was done in cooperation with D. Kane. Soil solution chemistry was monitored (on an event basis) at two depths at 11 sites along vegetation/soil transect 2. A subsurface flow study was begun to determine rate and direction of active layer water flow through and across landscape unit boundaries. This study constituted a pilot study for a larger, more detailed subsurface flow study proposed for 1991 (Everett, attached proposal). Results from these studies will provide a basis for experiments designed to evaluate pollutant (grey water) additions that will be detailed in future proposals. Soil solutions and precipitation were analyzed for ^{18}O in cooperation with L. Cooper to evaluate the contribution of new and old water to stream flow.

Two synthesis chapters were completed. These will be submitted for journal publication and will also constitute the basis for the Elsevier Synthesis Volume to be completed in 1991.

A soil/permafrost coring program was conducted to evaluate paleo erosion and/or deposition and vegetation environments of the R4D (and other similar sites). These studies were funded separately from R4D but the data will be used in the final R4D synthesis and shared with other R4D program scientists (e.g., D. Schell for evaluation of carbon storage and L. Cooper for ^{210}Pb and ^{18}O studies).

Because some of the 1990 field studies have not been initiated, or completed at this time (6 August 1990) they will be described only briefly.

Snow Chemistry

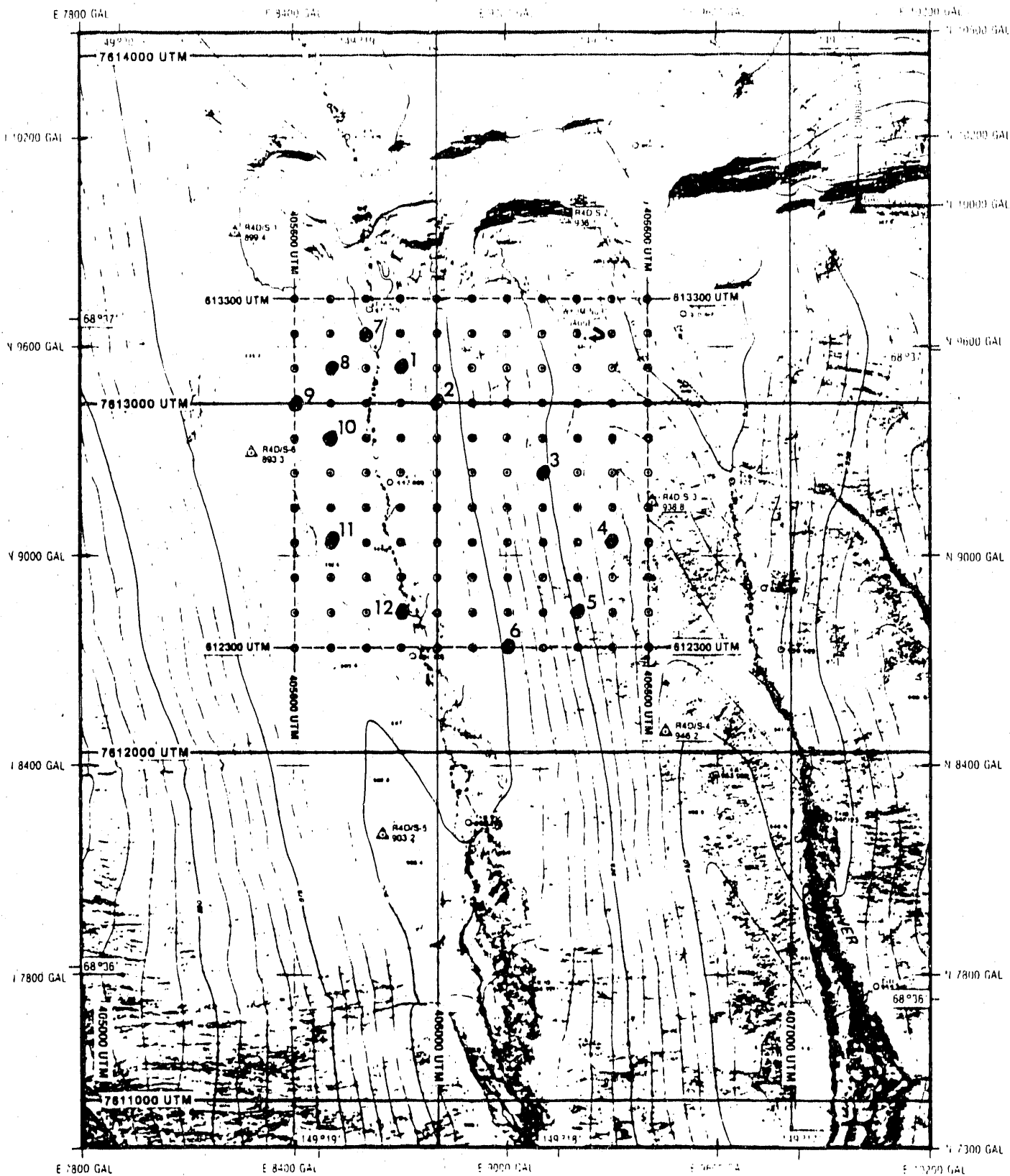
Sampling of the 1989/90 winter snow pack for analysis was begun on 14 May 1990. Twelve sites were sampled (Fig. 1). The data presented in Table 1 display the considerable point to point variability in snow chemistry that has been noted in previous years (see Appendix C of the attached proposal). At the time of sampling some elution had already taken place within the pack due to a brief period of melting in its upper part. Water that moved down refroze at approximately 8 cm. This event occurred in mid April, 1990 (D. Kane pers. Comm.), probably as a consequence of an event superimposed on the much elevated temperature in the circum arctic region that began in January, 1990. The presence of the ice lense appears to have had a significant impact on the hydrology and hydrochemistry of the 1990 meltoff flow.

The higher than normal ($N = 5$) concentration of SO_4 is ascribed to influxes of gas and particulate material discharged from Redoubt Volcano during the winter. Other anthropogenic sources must also be considered (see Appendix B).

Overland Flow

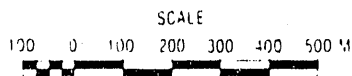
Analysis of the relatively small number of data for meltoff overland flow in 1989 (runoff plot No. 4 of Kane) revealed a relationship existed between water chemistry and the major elements of the discharge event (see Table 1 and Fig. 3, Appendix C). It was decided that sampling intervals during the 1990 event be increased to two hours during the ascending limb (Phase I) and the peak (Phase II). Such sampling and analysis would validate the 1989 results and possibly demonstrate a diel pattern.

Meltoff flow began on 11 May. Analyses are partially complete with mean values for all chemical parameters similar to those of 1989. The



DOE R4D ECOLOGICAL RESEARCH SITE TOOLIK LAKE AREA, NORTHERN ALASKA

GAL grid defined from USGS bench mark



MARKERS:

- UTM GRID POINTS
- ALONG STREAM CHANNELS
- △ PHOTO CONTROL POINTS

■ LOCATION MAP

Figure 1. Location of snow profiles collected for analysis in 1990.

TABLE 1. Analysis of Snow Collected From Twelve Profiles in Innvavik Creek Valley in May 1990 (see Fig. 1)

Pit	Date	pH	EC	Solids	Ca	Mg	Na	K	Fe	Mn	F	Cl	NO ₃	PO ₄	SO ₄
1	5/12/90	5.35	0.519	0.00	-0.056	1)	0.035	0.021	-0.468	1)	0.060	1.000	1.464	0.00	6.966
2	5/12/90	4.88	0.801	9.00	0.618		0.096	0.077	0.653		0.000	0.775	0.686	0.00	1.425
2 ice layer	5/12/90	5.77	0.866	21.54	0.462		0.129	0.022	-0.437		0.803	1.232	2.157	0.00	1.477
3	5/12/90	5.29	2.87	0.71	0.698		0.329	0.042	-0.402		1.487	0.936	0.828	0.00	7.138
4	5/12/90	5.90	0.553	13.33	0.063		0.032	0.019	-0.468		0.000	1.009	1.791	0.00	0.650
5	5/12/90	5.86	0.535	5.83	0.135		0.031	0.003	-0.491		0.000	0.923	0.690	0.00	0.582
6	5/12/90	5.90	0.375	0.00	0.399		0.188	>3PPM	-0.378		0.677	1.069	0.532	0.00	7.231
7.1 layer 1	5/13/90	5.52	0.745	27.50	0.801		0.244	0.049	-0.400		0.000	0.833	0.789	0.00	1.274
7	5/13/90	5.57	3.43	8.00	0.474		0.071	0.023	-0.440		0.000	1.313	3.529	0.00	4.483
7.3 hoar	5/13/90	5.68	1.238	5.38	-0.037		0.055	-0.001	-0.395		0.616	1.689	0.777	2.347	0.417
8	5/13/90	4.72	4.66	0.00	-0.014		0.051	0.004	-0.405		0.915	0.000	0.537	0.000	7.019
9	5/13/90	5.64	0.351	13.11	-0.074		0.070	0.018	-0.373		0.000	0.952	1.745	0.000	0.592
10	5/13/90	5.58	0.772	11.54	0.451		0.180	-0.004	-0.436		0.813	0.967	0.638	0.000	0.642
11	5/13/90	5.62	0.377	15.22	-0.052		0.055	-0.002	-0.437		0.000	1.690	0.000	0.000	0.562
12	5/13/90	5.58	0.49	7.20	-0.095		0.048	-0.009	-0.427		0.644	0.869	0.868	0.000	0.676
Brown ice	5/13/90	5.56		7.00	0.828		0.703	0.121	-0.091		0.000	0.896	0.000	0.000	0.497
Average		5.53	1.239	9.09	0.288	**	0.145	0.026	-0.326	**	0.372	1.010	1.064	0.147	2.602

discharge data are being reduced at this time. Point-in-time measurements of rill flow composition were made during the recessional limb (Phase II) and are in line with those from runoff Plot 4. Event-related overland flow was measured through the post melt-off summer period.

Imnavait Creek Flow

Flow within Imnavait Creek began on 15 May 1990 and followed a pattern similar to that in 1989 (Fig. 2), i.e., it consisted of multiple surge peaks accompanied by large quantities of slush, one of which overtopped the flume and its wing walls removing the water-level recorder and transporting it 50-m downstream. Peak discharge at this time 0815 probably exceeded 40 cfs. Several other near peak flows were recorded in the early morning hours - again a departure from former years when peaks were reached in early evening. In both 1989 and in 1990 very large volumes of snow accumulated in the valley bottom. These masses melted from both bottom and top and acted as temporary dams in successive upstream segments. It is suggested that stream channel geometry (including slope) controlled the impoundment and volume released. The first flow released some 150 m upstream from the flume.

Collection of stream water began some hours prior to measurable discharge. These subnival flowing waters constitute the beginning of the first phase of the discharge event (see Fig. 5, Appendix C) and contain the highest ion concentrations of the flow season. A partial report of the water composition for 1990 is shown in Table 2.

Watertrack Flow

Studies of watertrack discharge and composition began in 1985 with a major emphasis in 1986. Studies on most watertracks have been curtailed or suspended since that time because of thermal degradation beneath the weirs or from chemical contamination uptrack of the weirs. Watertrack 7,

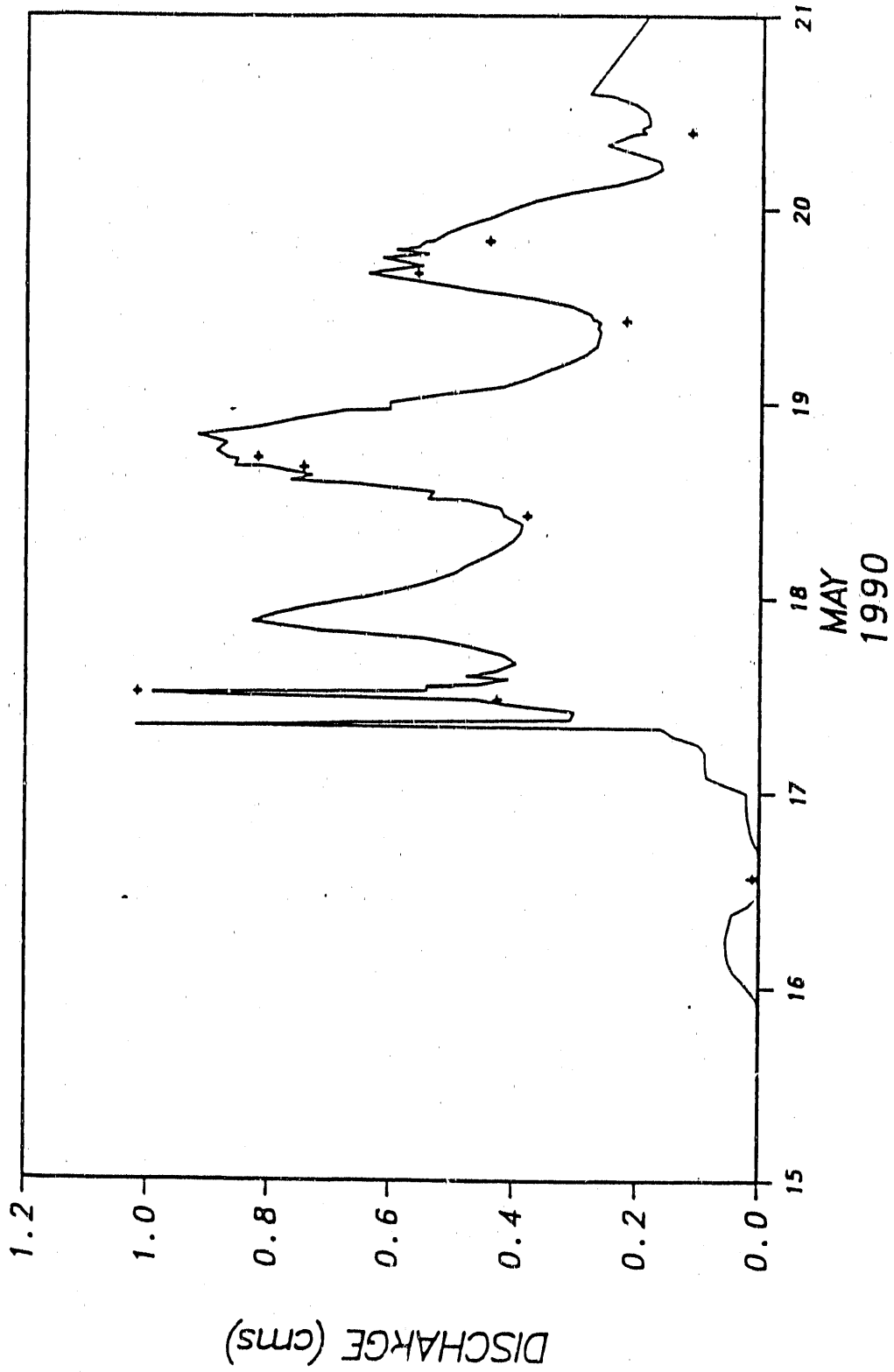


Figure 2. Detail of the 1990 melt-off discharge of Imnavait Creek Plot (from Kane, 1990).

TABLE 2. Partial Chemical Analyses of Melt-off Flows
 Innavaik Creek, May 1990

Time	Date	pH	EC	Solids	F	Cl	NO ₃	PO ₄	SO ₄
13:30	5/13/90	5.46	1.580	7.00	0.00	1.064	1.447	0.00	3.102
15:00	5/13/90	5.03	1.397	41.33	0.00	0.994	0.996	0.00	5.253
09:30	5/14/90	5.47	1.470	6.67	0.00	1.086	1.312	0.00	2.435
14:10	5/14/90	5.43	1.459	5.45	0.00	1.092	1.017	0.00	2.329
15:15	5/14/90	5.29	2.130	9.21	0.00	1.579	0.516	0.00	1.35
14:15	5/15/90	5.47	2.150	10.22	0.00	1.658	0.552	0.00	1.961
10:00	5/16/90	5.30	1.720	9.57	0.00	1.329	0.00	0.00	0.763
14:40	5/16/90	5.41	1.550	11.74	0.00	1.369	0.00	0.00	0.783
15:30	5/17/90	5.30	1.200	2.22	0.00	0.994	0.00	0.00	0.392
17:30	5/17/90	5.26	1.100	0.43	0.00	0.997	0.00	0.00	0.592
11:30	5/17/90	5.19	1.440	0.91	0.00	1.106	0.00	0.00	0.494
13:30	5/17/90	5.27	1.380	7.73	0.00	1.050	0.00	0.00	0.495
20:20	5/17/90	5.26	0.968	0.00	0.00	0.961	0.00	0.00	0.378
18:15	5/18/90	5.41	0.642	0.00	0.00	0.823	0.898	0.00	0.670
16:50	5/18/90	5.42	0.687	0.00	0.00	0.902	0.00	0.00	0.462
22:30	5/18/90	5.43	0.601	0.00	0.00	0.862	0.00	0.00	0.366
16:39	5/19/90	5.53	0.749	0.89	0.00	0.835	0.00	0.00	0.322
22:30	5/19/90	5.57	0.633	0.00	0.00	0.885	0.00	0.00	0.416
09:25	5/20/90	5.47	0.715	1.32	0.00	0.840	0.00	0.00	0.431
08:30	5/21/90	5.50	0.768	8.64	0.00	0.852	0.00	0.00	0.652

All ion values in mg · l⁻¹, EC µS.

however, has been monitored each melt season since 1985. A continuous hydrograph is available for all but 1989. In 1990 it was sampled at close intervals during the snowmelt flow period and daily thereafter except for selected storm events in August (then every two hours). Data from this site has served in analysis of flow and discharge relationships among the various flow components of the southwest-facing slope (Appendix C).

Summer Precipitation

Sampling of wet and dry deposition at Innavait Creek was begun in May of 1986 and the results are summarized in Appendix B. In 1990, wetfall collection was begun on 15 May (dry fall collection was suspended in 1990 due to the lack of a full-time field assistance to insure uncontaminated samples). The wetfall analysis were conducted to EPA standards by Global Geochemistry, Inc., and accompanied with QA/QC (see 1991 proposal) data. Results to date are presented in Table 3.

These data show a substantial departure from weekly and mean values of previous years for pH, NO_3^- , SO_4^{2-} and Ca^{2+} . The decrease in pH is attributed to an increase in mineral acids, H_2SO_4 and HNO_3 . The addition of these acids (and probably organic acids as well) is attributed to the eruption of Redoubt Volcano and possibly in June and July input from large forest fires south of the Brooks Range (see Appendix B). Anthropogenic sources to the north are probably not significant after the first rain. Precipitation, especially rainfall, constitutes the principal input of cations and anions to the valley soils and water.

Event sampling:

In addition to the 8-day composite precipitation sample beginning in mid August, each rainfall event will be sampled to determine ionic input and to support ^{18}O and ^{34}S studies of Cooper et al. Previous spot sampling of single rain events has shown that such an event (in an 8-day composite) can account for 50 percent or more of the composite concentration. The 1990 event samples will be analyzed in Ohio for cations, anions and

TABLE 3. Precipitation Chemistry - Imnavait Creek
(MS 117) 13 May - 3 July 1990

Period	pH	EC ¹⁾	Ca	Mg	Na	K	Cl	NO ₃	SO ₄	NH ₄	F
5/13-5/20	4.21	33.5	0.90	0.14	0.23	0.03	3.60	0.25	2.36	0.08	0.13
5/21-5/27	4.18	29.0	0.71	0.13	0.13	0.01	2.60	0.05	1.59	T	0.20
5/28-6/9	2)	2)	0.44	0.16	0.16	0.08	2)	0.32	1.34	0.05	T
6/10-6/19	4.65	11.7	0.24	0.09	0.09	0.06	0.74	0.19	0.92	0.04	0.02
6/20-6/25	4.02	37.3	0.06	0.28	0.28	0.14	3.44	0.20	0.47	0.07	0.05
6/26-7/3	4.73	9.2	0.26	0.07	0.07	0.06	0.48	0.34	0.53	T	0.03

¹⁾Values in $\mu\text{mho}\cdot\text{cm}^{-1}$

²⁾Bucket contaminated with HCL

organic acids. An attempt will be made to relate concentration to storm trajectories to identify ion sources. ^{18}O and ^{34}S will be analyzed at Oak Ridge National Laboratory. The event composition will be related to soil solution (transect) chemistry.

Fog and rime:

A Whiteface Mountain fog samples was built in 1989 and will be operated in August, 1990, to determine composition of these precipitation forms. Preliminary studies (Cerling and Alexander, 1987, Everett, 1988 and Zukowski, 1990) indicate these forms can supply significant concentrations of NO_3^- , SO_4^{2-} and Ca^+ to the watershed that usually go unrecorded.

Soil Solution (Transect Study)

Soil solution was monitored on an event basis at 20 and 40 cm at 11 stations along toposequence transect 2 in 1988 and 1989. The results of the 1988 survey are published in Walker et al. (1989). Concentration of most ions ranged widely among the sites. In general, however, pH and the concentration of mineral cations decreased downslope at both depths as the organic component increased. Total concentrations (means for all stations) in the upper 20 cm exceeded those at 40 cm by a factor of 2 for most ions; exceptions were K^+ and NO_3^- . Organic acids and DOC were more important at the lower slope sites. These data were used to compute nutrient pool size in solution and were compared to the available (exchangeable) pool (see Appendix C).

The toposequence sites were again sampled on an event basis in August 1990 to further document inter-seasonal variability in ionic concentration vs. slope position and depth within the profile in response to specific storms with known ionic input. Previous experiments have shown that ionic interchange between soil horizons to be very slow (Chapin et al., 1988, and Appendix C). To determine the quantity of precipitation from a given event that reached the lower pool, soil solution was taken

for ^{18}O analysis in cooperation with L. Cooper, Oak Ridge National Laboratory, to determine age composition with depth. The results of these studies of vertical and horizontal transfer of nutrients bears directly on the nutrient movement studies described in the next section and experiments planned for the future (proposal).

Soil Solution (Landscape Unit Study)

A pilot study of soil solution (ion) movement over and within the active layer and across landscape units will begin in August 1990 using salt tracers. A single plot measuring 5 x 10 m will be laid out across the boundary between the toe slope (shrubs, tussock, moss) and riparian flood plain (sedge, moss) landscape units (Walker et al., 1987). Pairs of soil solution samplers will be emplaced to depths of 20 cm and 40 cm (two additional samplers will be placed at 60-65 cm). Soil cores extracted in the process of emplacing the samplers will be used to reconstruct subsurface stratigraphy. Saturated solutions of NaCl and LiNO_3 will be added along the upper boundary such that each solution covers a distance of 1.5 m. The tracers will be added as near the beginning of a rain event as possible. Suction (1 bar) will be applied to all samplers and collections begun 24 hours later. Soil solution will be analyzed for Cl, Na^+ , and NO_3^- . Collection will continue until 2 September. Overland flow samples will be collected along the base line.

Departures in ion concentration greater than 1 SD of the control mean will be plotted in three dimensions and used to calculate movement rate and direction as well as dilution. The results of this study will be combined with those of earlier watertrack studies (Chapin et al., 1988 and Marion and Everett, 1989 and Appendix C) to formulate a larger-scale grey water addition experiment (attached proposal).

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PROGRESS REPORT

APPENDIX B

Precipitation Chemistry at an Arctic Foothills Site, Alaska

K. R. Everett

Byrd Polar Research Center and Department of Agronomy,
The Ohio State University
125 South Oval Mall, Columbus, Ohio 43210

ABSTRACT

The ionic composition of rain, snow, dryfall and rime has been studied at a site in Arctic Alaska approximately 70 km north of the Brooks Range and 210 km south of the Arctic Ocean. The data cover the period September 1985 through September 1988. The ionic burden of the precipitation is small and conditioned principally by air masses originating in the north Pacific and moving northeast across the state. Substantial intra- and inter-year variability is recorded in ionic composition, particularly in rainfall. This is conditioned by episodic events, often of short duration and low volume, e.g. the composition of the atmosphere at the time of the first spring washout rains and later by local storm and extra-regional events such as mountain-generated storms and forest fires in interior Alaska.

Although spatially extremely variable in composition, snow does not record the high concentrations of SO_4^{2-} and NO_3^- usually associated with air masses moving over the Pole or from the southeastern states. In terms of the relative abundance of the various ions in rain and snow, SO_4^{2-} , NO_3^- and Cl^- are the dominant anions and Ca, K and Na are the principal cations. In each of the years SO_4^{2-} and NO_3^- were in excess of H^+ with H_2SO_4 being the principal source of free acidity. Dryfall may be a significant source of K^+ , Ca^{2+} , PO_4^{3-} and NH_4^+ . The mean ionic input to the watershed for the three years of measurement is 36 kg. $\text{ha}^{-1} \cdot \text{a}^{-1}$.

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INTRODUCTION

In arctic Alaska interest in the composition of air began in 1971 at Barrow (71°32'N; 156°16'W) under the aegis of the National Oceanic and Atmospheric Administration (NOAA) (Quakenbush and Bodhaine 1986). This site, considered representative of the arctic atmosphere under prevailing winds, was established to provide background conditions as concerns about global movement of industrial pollutants began to receive attention. Data collection there has been continuous since 1976 as part of the NOAA program for Geophysical Monitoring (GMCC). These programs provide information not only on the flux of aerosols in high latitude air masses but also the chemical composition of the aerosols on a precipitation event basis. In 1983 NOAA sponsored an airborne study (Gas and Aerosol Sampling Program) of the arctic haze phenomenon (Raatz et al. 1985) that provided additional chemical data on the aerosols (Sheridan and Musselman 1985) through the arctic troposphere. Other than these ongoing studies, only sporadic short-term analyses of precipitation, commonly only pH, are available from arctic Alaska.

Beginning in May 1986, systematic collection and analyses of snow, rain and dry precipitation was begun at Imnavait Creek, Alaska, some 208 km south of Prudhoe Bay and 390 km southeast of Barrow at the southern margin of the northern foothills of the Brooks Range (Fig. 1). This study of precipitation chemistry is part of a larger investigation of hydrologic and geochemical fluxes in a small basin (Everett and Ostendorf 1988). The ongoing data set provides a baseline for the area and permits regional and limited inter-regional interpretations.

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Site Description

The Imnavait Creek precipitation sampler is near the crest of the southeast-facing slope of the headwater basin of the creek, at an elevation of 945 m, a.s.l. It is 70 km north of the northern front of the Brooks Range in topography representative of the Foothills Physiographic Section (Wahrhaftig 1965). Mean precipitation for the four years of record is 27 cm, approximately two-thirds falling as rain and the remainder as snow (mid-September to May). It is common for very little precipitation to fall during May and June. Both fog and rime events are common during the early and late summer period, often lasting several days. Regionally, summer winds are from the southwest (Broner et al., 1977). Surface winds at the site are from the southern quadrants during all seasons; the three-year summer mean is 204° (SSW). In May the winds are from the southeast and shift gradually to the south-southwest and southwest as the summer progresses. This same progression is found at the 850 and 500 mb levels but the westerly shift is more pronounced at these levels with the mean August direction from the west-northwest. The primary winter wind direction at the surface is less precisely known but appears to be primarily from the southeast.

Methods

Beginning in 1986 an AeroChem-metric wetfall-dryfall collector was placed about midway of the catchment 80 m off the northeast ridge crest. The sampler is the same as those used in the National Atmospheric Deposition Project (NADP) program (1988). It is equipped

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with a weighing rain gauge and event recorder. Positioning of the sampler and timing of sample collection follows the NADP procedures (Bigelow 1984). The site is operated from mid-May through the first week of September.

Collection of wetfall is made each Tuesday. The sampler bucket is agitated and a small amount of liquid is used to rinse an acid-washed 250 ml bottle and then discarded. The bottle is then filled with a 250 ml sub-sample, capped and stored at approximately 4°C until it is shipped for analysis (usually two to five days). The analyses are performed by Global Geochemistry Corporation in Canoga Park, California, using the same methodology and quality assurance control as used for Environmental Protection Agency (EPA) samples submitted to that laboratory. The dryfall bucket remains on the collector for the entire summer season (approximately 90 days). Once removed it is washed down with 250 ml of deionized water, sealed and allowed to stand for 24 hours at approximately 20°C. A small volume of the sample is used to rinse an acid-washed 250 ml polyethylene bottle and then discarded. The remainder is poured into the bottle which is then sealed and sent for analysis.

Snow samples are collected in early May, prior to the onset of melt-off. Sampling sites are selected at random at several positions on each valley slope and in the valley bottom. At each site three pits are dug to the vegetation surface in a several-meter-square area. One side of each pit is cleaned with a stainless steel knife and a channel sample is taken from the surface to the bottom and placed in a polyethylene bag (the samples from all three pits at each site are placed in one bag). In the field laboratory the samples are allowed

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to melt and a recorded volume of liquid passed through a pre-washed and weighed 0.45 μm filter. The filter is oven-dried and placed in a sealed container to be accurately weighed in the Ohio State University laboratory. Half of the filtrate is placed in a pre-washed 250 ml bottle and frozen. A second 250 ml sample of the filtrate is acidified with ultrapure reagent nitric acid and stored at 4°C. The samples are returned to Columbus, Ohio, for analysis. Analytical procedures follow Standard Methods (16th Edition, 1985). Anions are determined with a Dionex Model 2000i ion chromatograph equipped with a fast-sep column; cations are determined with a Perkin-Elmer 3030B atomic absorption spectrophotometer. Total organic carbon (TOC) is obtained with a Dohrmann Carbon Analyzer. The snow sampling scheme outlined above is considered to provide reasonable mean values for chemical species in the total winter snowfall at the Imnavait Creek site.

In the spring (late May) and fall (late August and early September), rime and fog are common occurrences in the area but at present no systematic sampling has been undertaken. Melted samples of rime are treated in the same manner as snow.

Sources of Error

Factors affecting the quality of the data are most likely to be those encountered during the collection and field preparation of the samples. In the case of the wetfall-dryfall collector, there is always a possibility that foreign materials such as leaves, which are removed with clean tweezers, bird droppings, or other debris may enter the buckets. This is of special concern in the dryfall bucket. When this occurs the bucket is replaced with a clean one and sampling begun

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again (this results in an attenuated sampling season such as 1987). The inclusion of dirt or other unspecified particles in the sample are noted on the data sheets. Megascopic particulate matter is removed from all other samples (snow and rime) within 60 minutes of collection by filtration.

Global Geochemistry Corporation supplies spiked sample data and duplicate data for each analyte in rainfall. Differences in duplicate sets, except for trace readings, are within one percent. In spiked replicates differences between found and expected concentrations are less than five percent. Replication in AA and IC analytes at Ohio State University is within two percent. Replication of machine standards is within one percent. Internal standards are within five percent of EPA standards.

RESULTS AND DISCUSSION

Snow

Sixty and 70 percent of the snow cover accumulates between mid-September and mid-February largely as a result of storms originating in the north Pacific. As the pack builds, its upper surface is redistributed to lower slope positions and into dunes (C. Benson, pers. commun.) by strong winds commonly from the southeast quadrant. By April the pack ranges widely in thickness and density (Liston 1986; Hinzman, pers. commun.). Redistribution erosion and metamorphosis of the pack contribute to substantial chemical heterogeneity (Davies, et al., 1987). Vegetable and soil materials are common, especially in wind slab layers associated with snow dunes. This was particularly significant in 1989 (Table 1) when relatively large amounts of DOC and

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solids were recorded from "dirty" high density wind slab layers. Although the dunes tend to form in the same place from year to year (C. Benson, pers. comm. 1988) the ionic composition of the slab together with its organic components may range significantly from year to year.

There is nothing in the snow chemistry to suggest sources other than terrestrial (Table 1). Nitrate and sulfate are in low concentrations (below detection limits to $5.0 \mu\text{Eq}\cdot\text{l}^{-1}$ and $6.0 \mu\text{Eq}\cdot\text{l}^{-1}$, respectively). Intensive snow sampling was not done in the valley in 1987 and 1988 but single pit data collected by Zukowski et al. (1989) gave a concentration of 4.0 and $5.2 \mu\text{Eq}\cdot\text{l}^{-1}$ for NO_3 and SO_4 respectively. These overall low concentrations especially for SO_4 are somewhat surprising in view of the wintertime over-the-Pole transport recorded in the aerosol measured at Barrow (Rahn and Shaw, 1982; R.S. Artz, pers. comm., 1988) (Table 2). Latitudinal transect measurements of both anions by Zukowski et al. (1989) reveal significantly higher values in the Prudhoe Bay area snow pack. These data suggest that during the winter, southward penetration of sulfate and nitrate-burdened air does not commonly penetrate the southern part of the Foothills with significant amounts of strong acid.

Ion ratios (Table 2) of the various measured cations and anions suggest local terrestrial sources dominate the ionic composition of the snow.

Rainfall

The period of record, although short, indicates considerable year-to-year variability in the apportionment of rainfall to total,

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precipitation; 50 percent in 1985 and 75 percent in 1988. The mean number of rain events, i.e., discrete exposures of the wetfall bucket, for the period of record is 256. A substantial number of these events reflect discontinuous periods of precipitation (many of them too light to be recorded by the rain gauge) within protracted periods of rainy weather. Most of the rainfall is of low intensity (94% at rates $<10 \text{ mm. hr}^{-1}$ and 82% ($<1.0 \text{ mm. hr}^{-1}$) and is evenly distributed over the catchment. It is associated with the dissipating phase of convective storms generated over the Brooks Range or with air masses moving from the north Pacific. The maximum intensity of these rains generally occurs during the first four to five hours of the event. High intensity ($>20 \text{ mm. hr}^{-1}$), short duration rainfall does occur associated with convective storms. The data in Table 3 indicate considerable variability in ion concentration and related parameters among the sampling periods within any one year and between years. It is also apparent that for the most part the rain is an ionically weak solution. Concentrations of most ions are highest in the first rain event of the year (Fig. 2). This is probably due to the washout of residual particles and gases following their build-up during late winter. The very high first event concentrations of most ions recorded in 1988 are attributed to this cause (Rahn and McCaffrey, 1980; Heidam, 1984) It has been noted by others, e.g., Schroder et al. (1987) that a similar phenomena occurs in the early phases of rain events. These authors also noted an inverse relationship between ion concentration and precipitation volume such as is shown in Figure 2. This relationship holds generally even when ionic concentrations over the summer is weighted for precipitation volume.

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In many cases the source of liquid precipitation-borne ions at Imnavait Creek is equivocal. It appears, however, that regional terrestrial sources within the Foothills and northern part of the Brooks Range can supply most of the measured cations, particularly calcium, magnesium and potassium. Ammonium is in low concentrations and is probably of biogenic origin. Sodium is found in generally low concentrations and is probably all of continental origin. Chloride is of marine origin as are bromide and fluoride which are sporadically measurable. These ions may originate from north Pacific air masses which move into the area during the summer period.

Individual storm events which are unrecognized in the 8-day composite samples may in fact dominate the ionic input for a particular sampling period. One such event on 24 August 1987 which produced only 4.8 mm of precipitation (of the 70.6 mm recorded between 16 and 31 August) accounted for 14% of the calcium, 17% of the chloride, 100% of the nitrate, 24% of the sulfate, 100% of the fluoride and 17% of the chloride for the 14-day period. The source of this event cannot be determined with certainty, but it was probably not marine since almost all of the SO_4^{2-} was far in excess of any marine component.

The data in Table 3, particularly those for 1988, which in late July and August are anomalously high with respect to the other periods suggest that single events may have played a role. Two sources of extra regional input to the Imnavait area must be considered. Forest fires south of the Brooks Range may have been an important source of some ions. Records supplied by the Alaska Fire Service (D. Barry, pers. comm. 1988) indicate that during the period (29 July to 13 August) some 20 fires burned in west central Alaska north of 62°N and

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west of 154°W eventually consuming 700,000 acres. After July 12 strong southwest winds accelerated the rate of burning. It is not uncommon under such circumstances that smoke penetrates north of Brooks Range. The chemistry of such smoke is complex, but it is known to contain quantities of NO, NO₂, NH₄⁺ and SO₂⁻, together with a variety of organic compounds (Breysse, 1983).

A second potential source exists at Prudhoe Bay petroleum complex some 210 km to the north. This area may contribute to the late winter build-up of NO₃⁻ and SO₄²⁻. Although mean surface winds during the summer are from the south and southwest, occasional periods of wind from the north and northeast are recorded (Kane, 1989, unpublished data). During the period 14-20 August 1988, the winds were from the NNE when the only measurable precipitation fell. However, the Prudhoe Bay facility appears to be an unlikely source because only a trace amount of NO₃⁻ was recorded. The ion values are substantially higher than can reasonably be expected from a marine source with very large concentrations of K⁺ and Cl⁻, ions generally associated with terrestrial sources. Only a small amount of the free acidity is attributable to mineral acids. The concentration of H⁺ is second only to that of the first (washout) rain event. It seems probable that organic acids generated in forest fires are responsible for the free acidity. Such episodic events may be in the long term very significant in the ionic input to the region as a whole.

In terms of relative abundance of ions in combined rain and snow at Imnavait Creek there is considerable year-to-year variability (Table 4). Nitrate and sulfate are the dominant ions except in 1988 when chloride dominated. Undoubtedly a portion of the chloride is

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marine, but part may also be of forest fire origin. The most significant difference between Imnavait Creek and any of the NADP/NTN sites chosen for comparison is the relative abundance of potassium, an element found in relatively low concentrations in sea water but in high concentration in terrestrial sediments, particularly shale, a rock type common to the Foothills and Brooks Range and a component of the till substrate.

Potassium is also a major component of dryfall where it may be the predominant ion, as in 1986, when it contributed approximately 56% of its yearly total input to the catchment. Local sources of wind-suspended mineral and/or mineral-organic dusts from the Brooks Range river flood plains and sporadic forest fires to the south of the range are important sources for potassium as well as calcium and magnesium.

Acidity

The mean pH of rain and melted snow ranges from slightly acid (5.0) to circum-neutral (5.5). Equivalent ratios of anions to H^+ (Table 4) indicate that for two of the three years, H_2SO_4 was the single most important source of free acidity in rain. In 1988, HNO_3 was slightly more important. In either case the data indicate the concentrations of SO_4^{2-} and NO_3^- were much greater than for H^+ . Sulfate of marine origin constitutes, in most cases, less than 5% of its total concentration. Dayan et al. (1985) in their study of precipitation chemistry in central Alaska also found the concentration of SO_4^{2-} in excess of H^+ in air masses of Arctic origin and suggested either a source of sulfate in salts such as $CaSO_4$, $MgSO_4$, $(NH_4)_2SO_4$ or neutralization of H_2SO_4 by e.g., $CaCO_3$ as reasons for the excess.

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In the summer months most storms affecting the Imnavait Creek area are of north Pacific origin. Dryfall, together with aerosols of forest fire origin, are suggested for both SO_4^{2-} and NO_3^- and the consequent free acidity. The significant amount of organic acids in the Arctic precipitation recorded by R. Harriss (pers. comm., 1989) must also be considered in the apportionment of free acidity in (summer) precipitation at Imnavait Creek. Dayan et al. (1985) attributed 33% of the free acidity at Poker Flat, Alaska to organic acids (RCOO^-).

Rime

The formation of rime takes place principally in late May and in late August when surface and air temperature contrasts are greatest. The contribution of rime and especially fog to the deposition of heavy metals and nitrogen and sulfur compounds have been studied for some time in the Adirondack Mountains (Arons et al., 1988; Falconer and Falconer, 1980) and in California (Waldman et al., 1983). The collection and analysis of rime at Imnavait Creek was begun on an exploratory basis in 1988 to establish its potential ionic input, particularly with respect to sulfate and nitrate. The limited data collected in 1988 indicates this precipitation form cannot be ignored (Table 6) in any evaluation of total precipitation input since the quantity of SO_4^{2-} and NO_3^- for the single event amounted to 0.54 and 0.53 kg. ha^{-1} , respectively, or 8% (each) of the total summer precipitation. Their combined contribution to the acidity was 3 to 10 times that in rainfall with sulfuric acid the largest contributor.

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Dryfall

Dry deposition, just as fog and rime, is recognized as an important source of anions, especially NO_3^- and SO_4^{2-} , as well as heavy metals, and considerable literature exists on sampling techniques and the chemical and physical factors governing its composition and deposition (Sickles et al. 1985; Johannes and Altwicker 1985). Uncertainty surrounding the mechanisms of deposition and resuspension, as well as the potential for contamination in passive collectors, has generally excluded it from discussions of total precipitation influx. Data are included here (Table 7) since no published dryfall information exists for northern Alaska other than air chemistry at the Barrow GMCC site (Quakenbush and Bodhaine 1986). The data presented in Table 7 for Imnavait Creek indicate substantial year-to-year differences in absolute values, relative ionic abundances and flux rates. For example, in 1986 dryfall the deposition rate for SO_4^{2-} was $0.002 \mu\text{g}\cdot\text{cm}^2 \text{d}^{-1}$, and in 1988 it was 4 times greater (in either case it amounted to <3% of the rain influx). On the other hand the calcium flux rate for dryfall was $0.047 \mu\text{g}\cdot\text{cm}^2\cdot\text{d}^{-1}$ or 2 times that of the rainfall.

Seasonality

On the strength of three years data of intra-year patterns, even generalizations about patterns in precipitation chemistry are not possible. Some generalizations are possible, however, with regard to rainfall if episodic events such as forest fires are neglected. The graphic presentation in Figure 2 and regressions shown in Figure 3 suggest that concentrations of calcium, sodium, potassium and chloride tend to peak early and late in the summer. Concentration of SO_4^{2-} and

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NO_3^- peak in spring, mid- to late May through early July, and then decrease to low concentrations. Ammonium concentration is greatest in mid-summer, late June through mid-July, the period of maximum biogenic activity.

Ion Budget

At this point in time calculations of an ionic budget (exclusive of hydrogen) is possible only for rainfall (Fig. 4). The ΔC for the years 1987 and 1988 is less than 5%, which indicates that for all purposes, a balance exists between anions and cations. In 1986, a deficiency of anions (in this case 16%) is attributed to unmeasured and unspecified organic anions. The importance of these anions in the total anion load has already been noted.

The variability from year to year in the volume of the different types of precipitation results in a substantial range in their individual contribution to the total atmospheric input of ions to the watershed (Fig. 5). For the three years of record, the atmospheric input has been 31.7, 29.9 and 46.7 kilograms per hectare per year. This mean is approximately 25% greater than the 8-year mean for the NADP site in Danali.

Conclusions

The short data record indicates the substantial variability in both the quantity and ionic composition of the various types of precipitation falling in the Imnavait Creek watershed, and which constitute the principal ionic input [the role of mineral weathering will be considered, along with the ionic efflux, in a subsequent

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manuscript (Everett, in preparation)]. It appears that the precipitation chemistry is dominated by air masses originating in the southeast and southwest quadrants and reflects a strong continental influence, particularly in summer when local wind-generated dust and extra-regional forest fire inputs (mostly caused by lightning) are important. Nitric, sulfuric and organic acids are the principal contributors to precipitation acidity. The sources of measured anions in summer rainfall are thought to be of biogenic and of forest fire origin. Those associated with snow may represent weak and episodic incursions from anthropogenic sources to the north (Prudhoe Bay) and in air masses moving from the central USSR over the pole. The SO_4^{2-} and NO_3^- in rime may have a northern (non-marine) source. Increased attention to individual, commonly low volume, rain events sub-summed in the eighth day sampling scheme are key to the accurate determination of sources.

A near ionic balance was found in two of the three years of record. Undetermined organic anions are called upon to make up the anion deficiency. On an area basis, the Imnavait Creek watershed receives a total ion input of approximately $36 \text{ kg. ha}^{-1} \cdot \text{a}^{-1}$, chiefly from rain and snow, which from year to year range widely in their individual contribution.

The Imnavait Creek area (and the region generally) does not appear to be significantly affected by anthropogenic sources of ions and provides an excellent base-line against which to measure future changes in precipitation (air quality) induced by both regional and extra-regional sources.

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TABLE 1

Average analysis (mg l^{-1}) with ranges of the Innavaik Creek snow pack

	1986		1989	
	<u>\bar{X}</u>	<u>Range</u>	<u>\bar{X}</u>	<u>Range</u>
pH	5.40	5.1 - 5.50	6.10	6.8 - 5.60
H^+ ($\mu \text{ Eq l}^{-1}$)	4.00	7.6 - 3.00	0.79	0.16 - 2.50
Ec (Sm)	.65	0.45- 1.55	0.30	0.48 - 0.21
Na^+	0.15	0.0 - 0.46	0.05	0.02 - 0.10
K^+	0.15	0.0 - 0.39	0.01	0.03 - 0.00
Ca^{2+}	0.33	0.20- 0.50	0.21	0.10 - 0.41
Mg^{2+}	0.06	0.00- 0.10	0.02	0.008- 0.027
Cl^-	0.56	0.34- 0.83	0.00	0.00
F^-	0.21	0.0 - 0.24	0.00	0.00
PO_4^{2-}	T*	0.0 - T	T	0.00 - T
NO_3^-	T	0.0 - T	0.32	0.10 - 0.49
SO_4^{2-}	T	0.0 - T	0.30	0.07 - 0.62
DOC	-	-	0.94	0.27 - 1.50
Solids	3.60	<0.50- 7.30	18.50	2.40 -45.90

*generally below limit of the slow column

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TABLE 3

Weekly Precipitation Chemistry, Innavait Creek Catchment 1986 - 1988
 Concentrations in Mg·l⁻¹

Year	Variable	Unit	June					July					August			N
			05/18-06/04	06/05-06/11	06/12-06/18	06/19-06/24	06/25-07/02	07/03-07/09	07/10-07/16	07/17-07/23	07/24-07/30	07/31-08/06	08/07-08/13	08/14-08/20	08/21-08/31	
1986	H ⁺	μEq·l ⁻¹			0.52	3.47	4.76	4.90	7.59	4.10	2.63	8.12	4.44	0.71	1.54	3.02
1987			5.30	4.82	14.13	4.03	2.04	5.31	4.68	3.80	4.17	5.31	4.27	4.37	4.03	5.25
1988			524.81	---	4.79	4.10	7.08	7.08	9.33	9.55	7.41	9.33	4.68	41.69	1.35	9.77
1986	Zn	μM	---	---	1.74	0.42	0.71	---	0.50	0.18	0.12	0.24	0.17	0.75	0.34	0.52
1987			0.50	0.77	0.74	0.43	0.42	0.35	0.10	0.04	0.14	0.16	0.11	0.10	3.64	0.58
1988			72.55	---	0.37	0.14	0.43	0.32	0.48	0.39	2.30	0.41	0.31	1.05	0.40	0.60
1986	Ca ²⁺	mg·l ⁻¹	---	---	1.70	0.27	0.18	---	0.16	0.05	0.01	0.002	0.023	0.17	0.11	0.27
1987			0.22	0.13	0.14	0.07	0.06	0.05	0.04	0.01	N	N	0.02	0.02	0.00	0.07
1988			1.49	---	0.13	N	0.15	0.07	0.13	0.08	0.11	0.02	0.34	0.91	0.34	0.36
1986	Mg ²⁺	mg·l ⁻¹	---	---	0.12	0.03	0.02	---	0.01	0.01	0.003	0.002	b	0.03	0.02	0.03
1987			0.02	0.01	0.02	0.01	0.02	0.02	N	N	N	0.02	0.004	0.002	N	0.01
1988			0.10	---	0.01	0.01	0.01	0.01	0.02	0.06	0.10	0.11	0.13	0.10	0.06	0.06
1986	K ⁺	mg·l ⁻¹	---	---	0.49	0.10	0.18	---	0.53	0.11	0.06	0.002	0.02	1.02	0.41	0.31
1987			0.04	0.37	0.16	0.08	0.22	0.05	N	N	N	0.23	N	0.014	N	0.11
1988			0.85	---	0.03	0.004	0.04	0.01	0.01	0.01	0.11	0.003	0.55	1.01	0.02	0.22
1986	Na ⁺	mg·l ⁻¹	---	---	0.70	0.14	0.35	---	0.07	0.07	0.16	0.013	N	0.60	0.22	0.16
1987			0.05	0.08	0.19	0.07	0.04	0.08	0.01	0.00	0.01	0.01	N	0.02	0.01	0.05
1988			1.05	---	0.06	0.02	0.03	0.01	0.01	0.03	0.21	0.29	0.02	2.18	0.04	0.33
1986	F ⁻	mg·l ⁻¹	---	---	0.43	0.02	0.06	---	---	---	0.01	0.025	0.002	N	0.01	0.08
1987			0.03	N	0.01	N	0.01	0.02	0.01	N	N	0.01	0.01	N	N	0.01
1988			0.00	---	N	0.01	0.03	0.12	0.02	0.02	1.25	N	N	N	N	0.21
1986	Br ⁻	mg·l ⁻¹	---	---	N	N	N	---	0.01	N	0.00	N	0.002	N	N	(0.01)
1987			N	N	N	N	N	N	0.05	0.06	N	N	N	N	N	(0.06)
1988			N	---	N	N	N	N	N	N	N	N	N	1.38	N	(1.38)
1986	Cl ⁻	mg·l ⁻¹	---	---	0.44	0.21	0.63	---	0.14	0.11	0.10	0.03	N	1.04	0.43	0.37
1987			0.10	0.18	0.32	0.21	0.09	0.17	0.03	0.01	0.03	0.05	0.02	0.05	0.04	0.10
1988			2.07	---	0.07	0.02	0.10	0.04	0.32	0.07	0.41	1.25	0.06	2.85	0.16	0.62
1986	NO ₃ ⁻	mg·l ⁻¹	---	---	0.36	0.03	0.04	---	0.10	0.22	0.03	0.05	N	0.12	N	0.12
1987			0.13	0.04	N	0.11	0.40	0.02	0.01	N	N	0.02	N	0.004	N	0.06
1988			0.25	---	N	N	0.01	0.01	0.01	0.02	0.96	N	N	N	N	0.11
1986	NO ₂ ⁻	mg·l ⁻¹	---	---	4.14	0.48	0.27	---	0.50	0.13	0.07	0.16	0.11	0.18	0.12	0.62
1987			0.37	0.56	0.15	0.50	0.07	0.08	N	N	N	N	0.05	0.01	N	0.22
1988			14.92	---	N	N	0.24	0.18	0.12	0.24	0.34	2.02	0.09	N	N	1.51
1986	SO ₄ ²⁻	mg·l ⁻¹	---	---	1.36	0.38	0.93	---	0.36	0.17	0.13	0.21	0.18	0.35	0.24	0.43
1987			0.41	0.50	0.31	0.23	0.35	0.11	0.07	0.05	0.17	0.04	0.09	0.12	0.14	0.22
1988			0.83	---	0.10	N	0.21	0.09	0.11	0.21	0.18	1.63	0.04	0.70	0.11	0.35
1986	PO ₄ ³⁻	mg·l ⁻¹	---	---	N	N	0.05	---	0.05	0.05	0.03	0.05	0.03	N	N	0.04
1987			N	N	N	0.07	0.27	N	N	N	N	N	N	N	N	0.03
1988			N	---	N	0.40	0.03	N	0.03	N	0.29	N	0.07	N	N	0.07
1986	Gran Acidity	Eq·l ⁻¹	---	---	NV	NV	12.00	11.60	9.30	NV	14.40	10.90	NV	NV	9.00	11.53
1987			13.40	22.60	NV	13.00	NV	13.30	9.50	9.20	11.50	11.60	13.50	12.70	11.10	12.91
1988			NV	---	18.80	10.50	16.50	13.40	19.90	15.60	20.20	17.20	14.80	57.10	NV	20.40
1986	A/C		---	---	0.73	0.76	1.01	---	0.31	0.73	0.62	0.90	0.98	0.57	0.74	0.79
1987			0.44	0.81	0.43	0.74	0.54	0.63	0.43	0.50	0.67	0.25	0.67	0.57	0.64	0.62
1988			0.44	---	0.26	0.21	0.74	0.64	0.81	0.69	1.10	0.68	0.29	0.15	0.30	0.53
1986	Rain-fall	mm	---	---	0.50	16.40	2.20	---	21.90	17.50	29.50	55.50	13.90	6.80	11.40	175.6 ¹⁾
1987			4.10	1.93	NV	5.53	20.31	11.53	19.84	23.77	16.39	11.81	22.52	22.20	36.41	196.7
1988			NV	16.55	1.92	26.78	7.23	19.78	19.78	6.99	4.10	23.83	14.94	13.99	8.67	160.6
1986	Wind Direc.	degrees	---	---	135	250	225	---	225	200	225	225	180	200	200	207
1987			166	202	NV	169	125	325	135	152	207	222	171	259	264	202
1988																

--- b No liquid precipitation
 N Negative value indicates trace concentration below instrument range
 NV No value reported
 = Excluded from mean
 1) Total rainfall
 () Insufficient data to calculate a valid mean

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TABLE 4

Relative abundance of various ions in liquid and snow precipitation at
Imnavait Creek, Barrow and selected NADP/NTN sites.

Imnavait Creek (1986)	SO ₄ > NO ₃ > K > Cl > Na > Ca > NH ₄ >> PO ₄ >> F > Mg
Imnavait Creek (1987)	SO ₄ >> Cl > NH ₄ > K > NO ₃ > Ca > PO ₄ > Na >> Mg > F
Imnavait Creek (1988)	Cl > NO ₃ ; SO ₄ Na > Ca; K >> PO ₄ ; Mg; F >> NH ₄
Barrow [†]	Cl >>> SO ₄ >>> NO ₃
Denali ^{††}	SO ₄ >> NO ₃ > Cl > Na > Ca ₂ K > Mg; NH ₄
New Jersey ^{††}	SO ₄ >> NO ₃ >>> Cl > NH ₄ > Na > Ca > Mg > K
South Dakota ^{††}	NO ₃ > SO ₄ > NH ₄ > Ca > Cl > Na >> K; Mg
Florida ^{††}	SO ₄ >> NO ₃ > Cl > Na > Ca > NH ₄ > Mg > K
California ^{††}	NO ₃ >> SO ₄ > Cl; NH ₄ Na > Ca > Mg > K
New Hampshire ^{††}	SO ₄ > NO ₃ >>> Na > Cl; NH ₄ > Ca >> Mg; K
Mt. Moosilauke, N.H. [†]	SO ₄ >> NO ₃ >>> NH ₄ > Cl > Na > K >> Mg
Kansas ^{††}	SO ₄ > NO ₃ >>> NH ₄ ; Ca > Cl > Na >>> K; Mg
Oklahoma ^{††}	SO ₄ > NO ₃ >>> Ca > NH ₄ > Cl > Na > K >> Mg

[†]NOAA-GMCC station data

^{††}NADP.NTN site

=equal concentration

>1x

>>2x

>>>3x

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TABLE 5

Equivalent ratios showing relative maximum contributions of acids
to the acidity of precipitation at Imnavait Creek.

	<u>1986</u>	<u>1987</u>	<u>1988</u>
$\text{SO}_4^{2-}/\text{H}^+$	2.37	0.81	1.09
NO_3^-/H^+	1.61	0.47	1.37
$(\text{SO}_4^{2-} + \text{NO}_3^-)/\text{H}^+$	3.98	1.28	2.46

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TABLE 6

Partial elemental and ionic composition of rime,
Imnavait Creek, Alaska, 1988.

pH	H^+ ($\mu\text{Eq l}^{-1}$)	Ec (Sm^{-1})	Ca^{2+}	K^+	Mg^{2+}	Na^+	Cl^-	F^-	NO_3^- *	SO_4^{2-} *
			mg l ⁻¹							
5.9	1.3	3.55	0.21	0.01	0.03	0.06	T**	0.0	0.58	0.57

*M. Zukowski (pers. commun.) obtained values for NO_3^- of 0.61 mg l^{-1} and SO_4^{2-} 0.41 mg l^{-1} for a spring rime event in the same area in 1986.

**T = trace

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TABLE 7

Dryfall elemental concentration in the wash liquor
in mg l^{-1} in 1986 and 1988[†]

Ion	Sample Period	
	1986 6/3 - 9/1	1988 5/12 - 9/18
Ca^{2+}	2.76	0.54
Mg^{2+}	0.54	0.11
K^+	4.15	0.55
Na^+	0.16	0.06
NH_4^+	0.03	0.78
NO_3^-	0.07	0.43
SO_4^{2-}	0.13	0.52
PO_4^{3-}	0.03	0.56
F^-	0.01	0.02
Cl^-	0.10	0.19
H^+ ($\mu\text{Eq}\cdot\text{l}^{-1}$)	0.02	0.71
pH	7.62	6.15
Cond. (Sm)	1.61	0.98

[†] 1987 data incomplete due to contamination in bucket.

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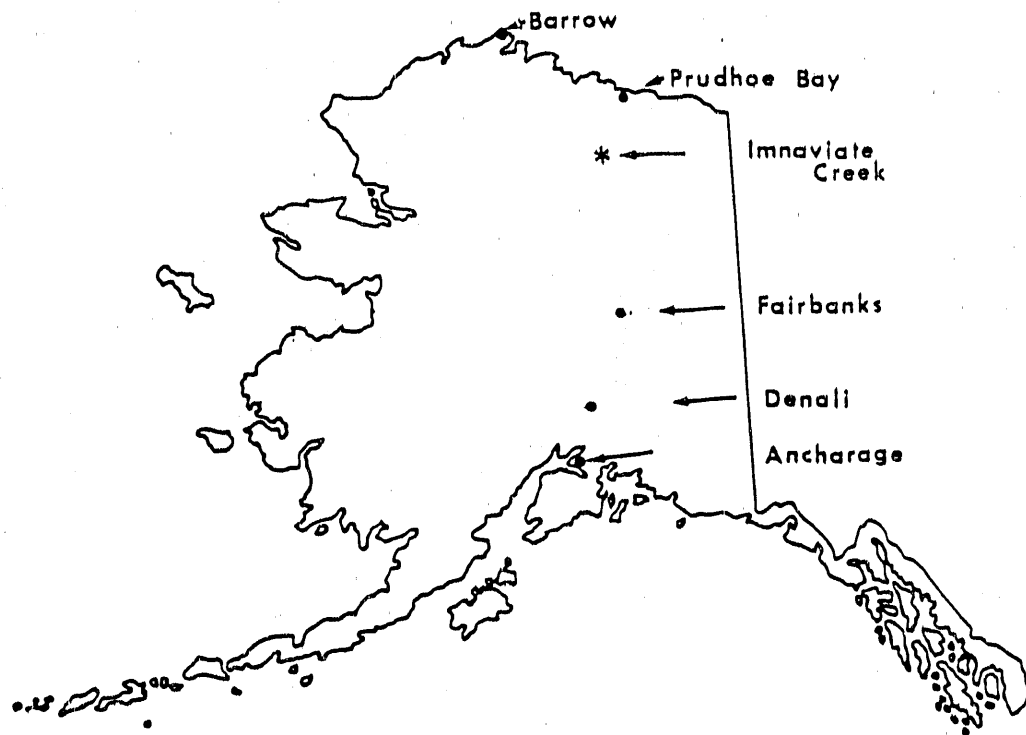
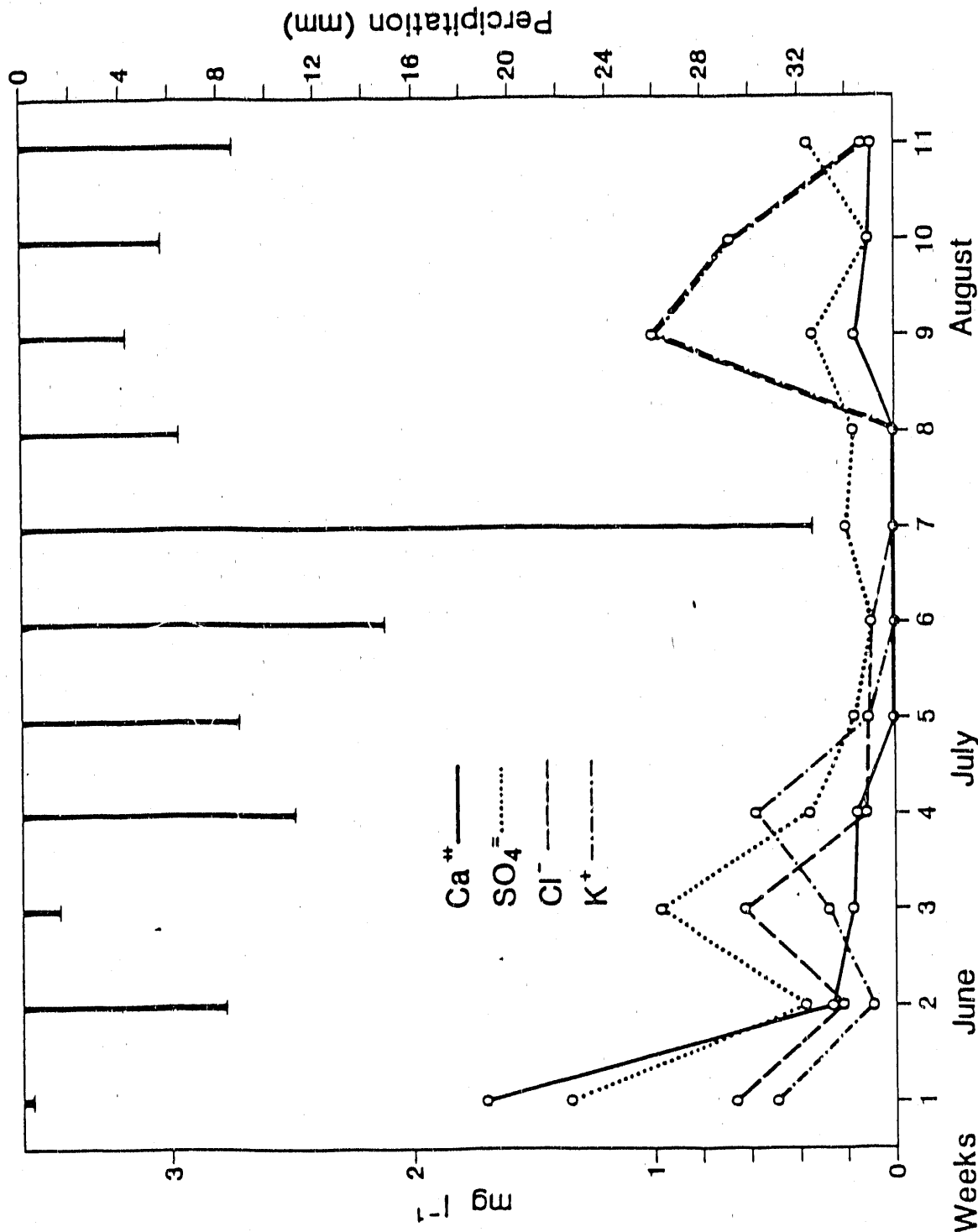


Figure 1. Imnavait Creek research site relative to Barrow (an active GMCC site), Prudhoe Bay, Fairbanks and Anchorage (major urban centers in Alaska) and Denali National Park,* (site of NAOP/NTN station).

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Figure 2. Concentration of selected ions in rain water vs. total precipitation in 8-day sampling intervals at Imnavait Creek, Alaska.

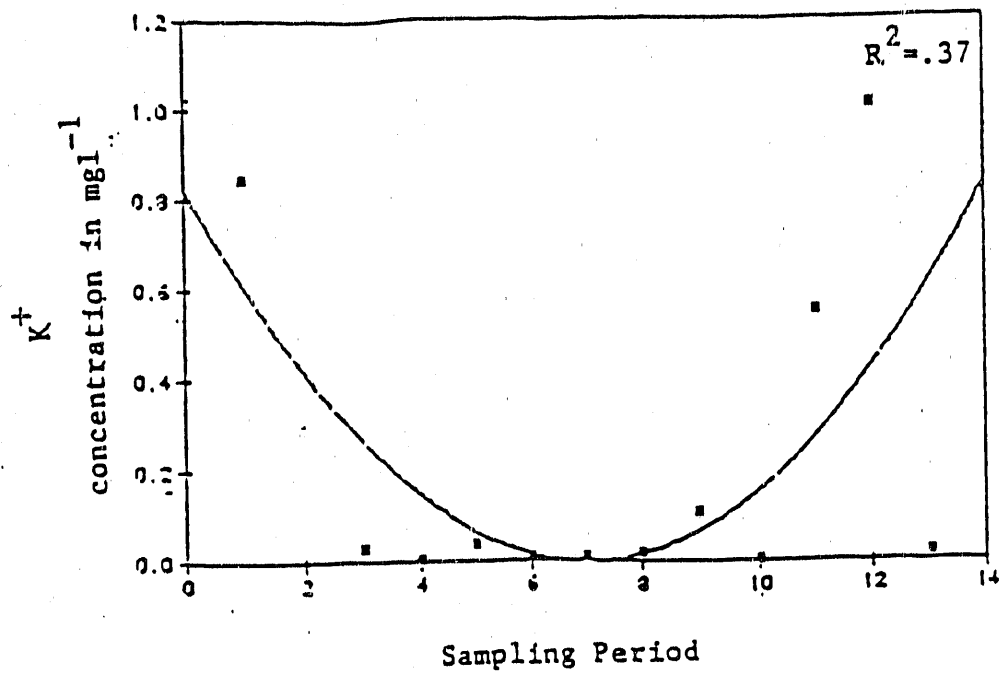
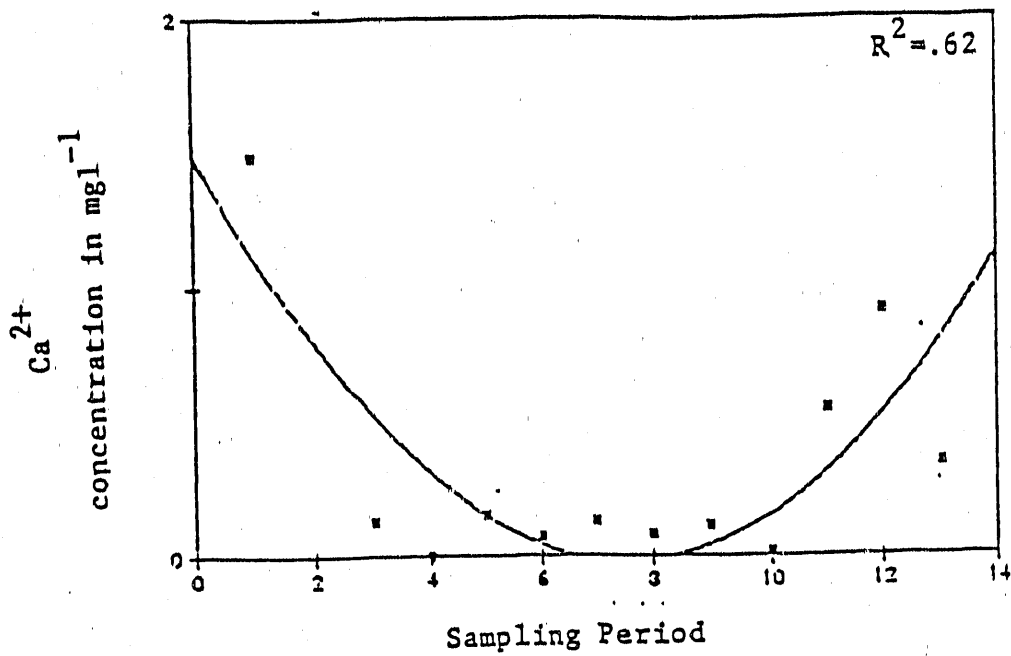


Figure 3. Second order polynomial regressions suggesting concentration peaks for calcium and potassium occur in Spring and Fall.

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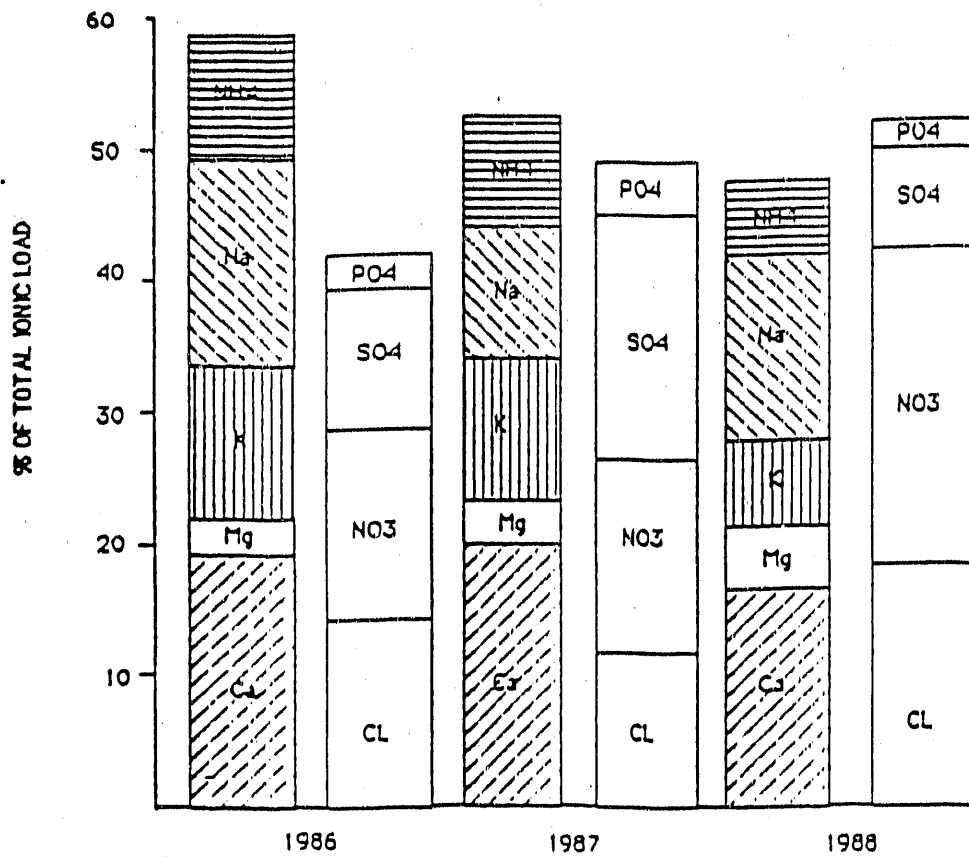


Figure 4. Distribution of the mean ionic load (exclusive of hydrogen) in rainfall for 3 years of record at Imnavait Creek.

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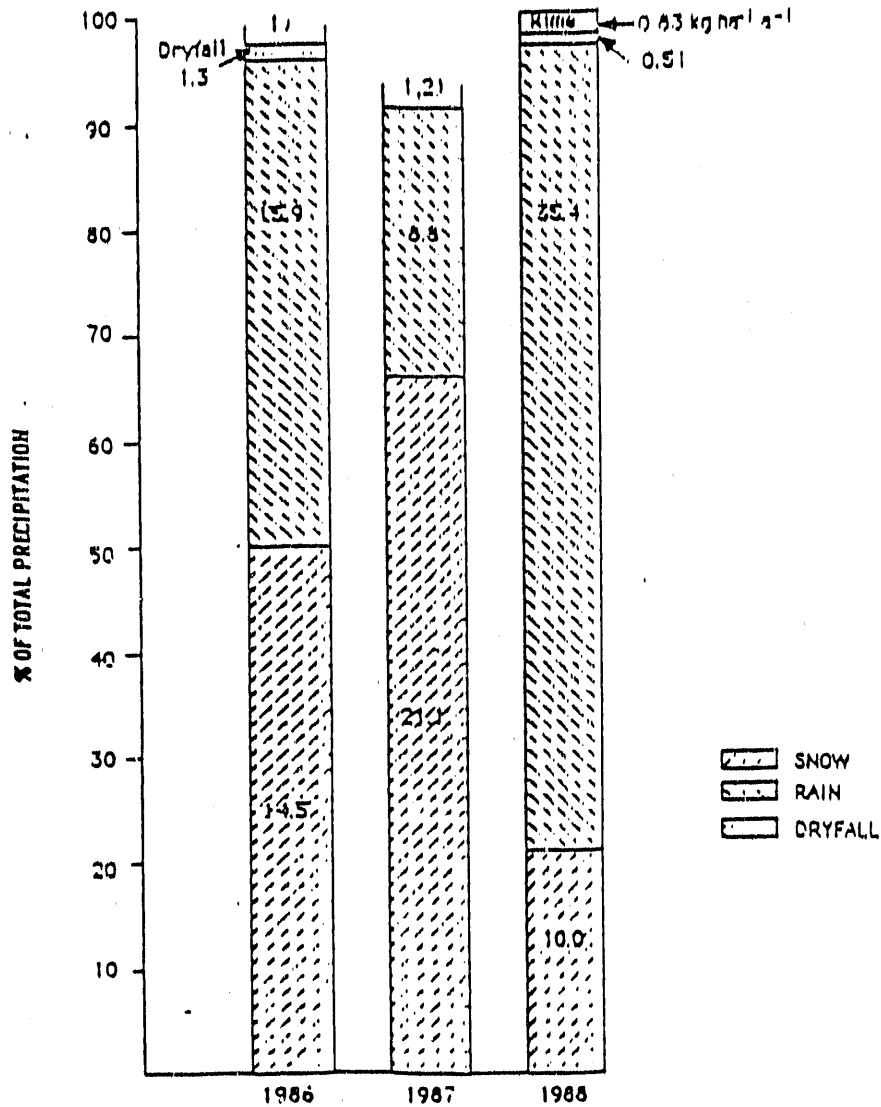


Figure 5. Apportionment of total ionic load by precipitation type for the years 1986-1988 in the Innavait Creek catchment. Numerical annotations indicate total ionic load in $\text{Kg ha}^{-1} \text{a}^{-1}$. (1) No rime samples; (2) no data due to contamination.

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PROGRESS REPORT

APPENDIX C

Surface Water Chemistry of a Small Arctic Drainage Basin

by

K.R. Everett, D.L. Kane and L.D. Hinzman

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INTRODUCTION

The data and interpretations that follow represent a synthesis of hydrologic and geochemical investigations that span five years. They were undertaken as part of the first phase of a larger study funded by the Department of Energy on the response of an arctic ecosystem to various types and intensities of disturbance. Because water (including snow) is the principal vector by which nutrients are moved into, within, and out of the various landscape components of the ecosystem, documentation of its temporal and spatial distribution, composition, volume and rate of movement was a necessary precursor to the second, or disturbance phase of the program. These data also supply necessary inputs to the hierarchical array of models being developed (J. Reynolds, pers. comm.) to portray functional relationships and to predict responses to disturbance at a variety of scales.

The major components of this study are shown in a schematic representation of the southwest-facing slope of Innavait Creek valley (Fig. 1).

SITE DESCRIPTION

The headwater basin of Innavait Creek is typical of many foothills drainage basins north of the Brooks Range in its geochemistry. The catchment comprises 210 ha (Fig. 1). The creek heads in a nearly level strangmoor with many poorly defined and anastomosing waterways. The strangmoor narrows down valley, and the creek comes to occupy a single, relatively straight channel in a narrow flood plain. For much of its length (2.9 km), the channel is commonly less than 0.5 m wide and deep, confined by peaty materials and roots (the mean fall is 0.16 m/m). At irregular intervals are nearly circular to oblate pools 1 to 5-m long (dimension), and up to 2 m deep (the beaded drainage pattern typical of small streams in the Arctic, where ice-rich

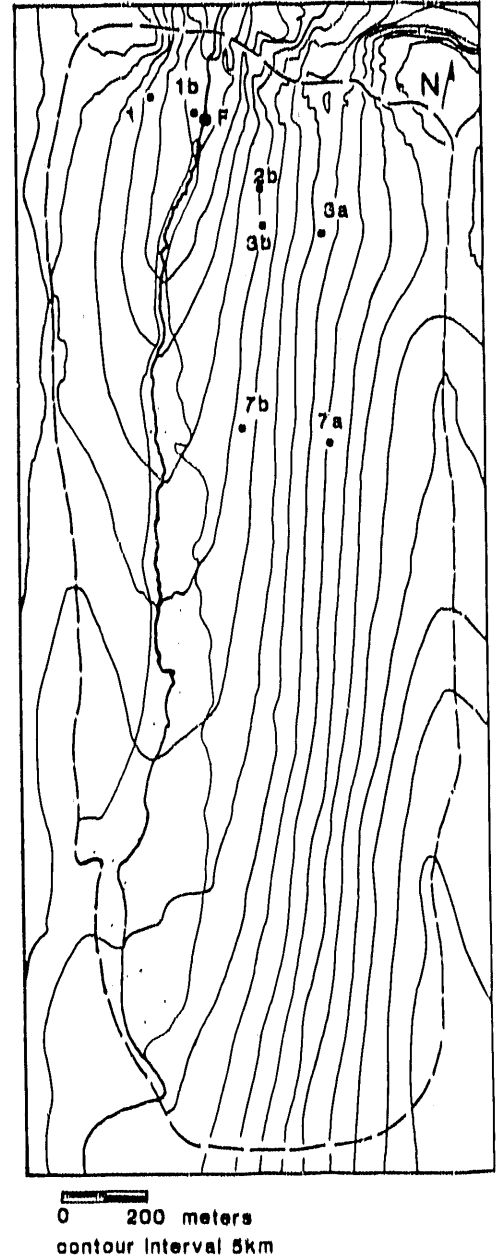
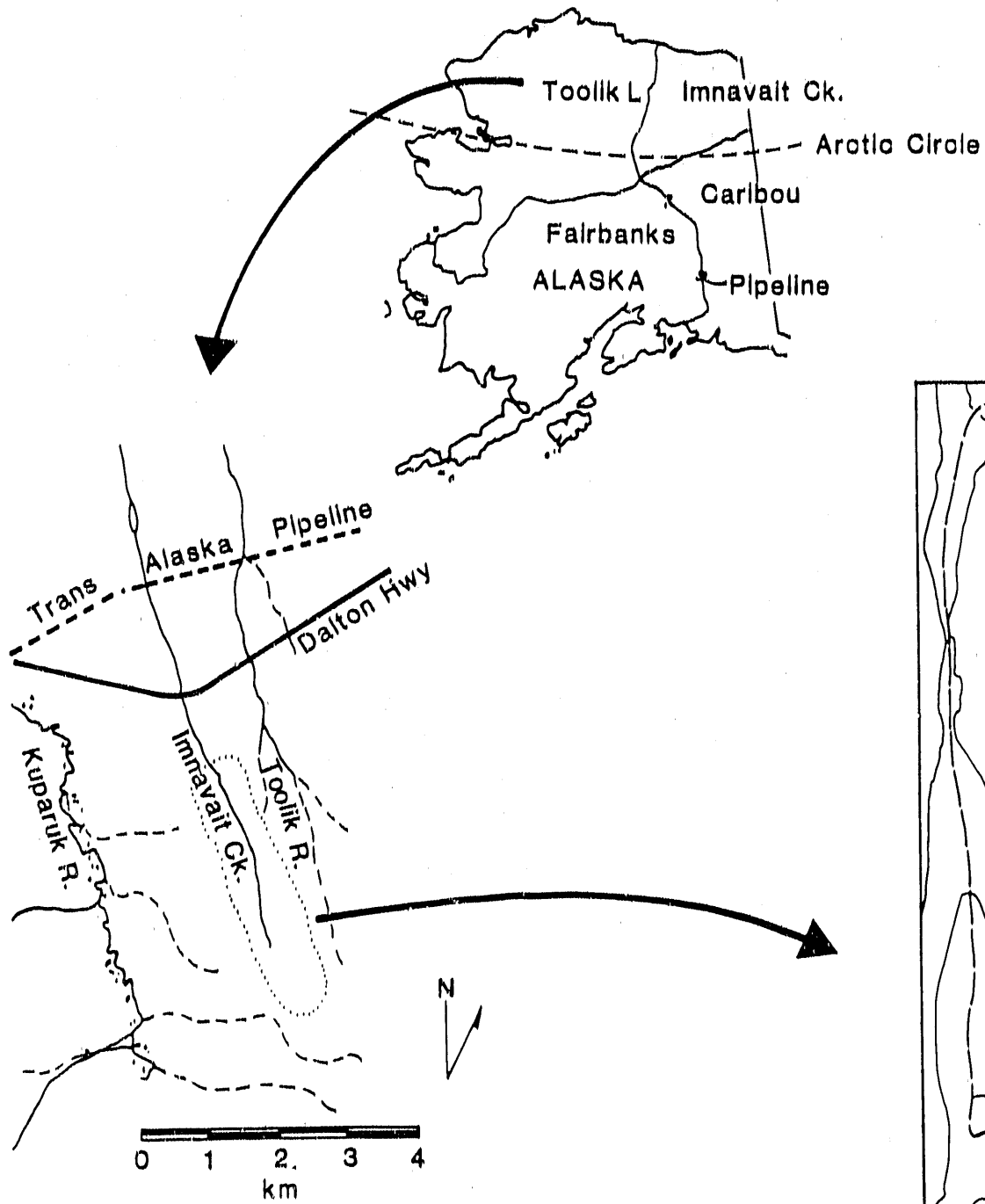


Figure 1. Geographic reference for the Imnavait Creek study area.

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permafrost occurs) (Hopkins et al., 1955; Oswood et al., 1989). As fall increases, boulders are exposed in the channel segments between beads. At the exit point of its headwater basin, the creek has cut through a ridge of sandstone, beyond which, it occupies a narrow valley floor for some 11 km before joining the headwaters of the Kuparuk River.

The slopes flanking the creek have a rather uniform gradient; are underlain by frozen acid till, and support a tussock, dwarf-schrub tundra in which Sphagnum moss is a major component.

The longer and higher southwest-facing slope is characterized by numerous, mostly ephemeral drainage ways, termed watertracks. These features commonly display poorly defined "head waters" on the upper slope (Fig. 2). Throughout much of their course downslope, the shallow valleys are marked by a concentration of dwarf shrubs. The course of the watertrack again becomes poorly defined as it crosses the toe slope and joins the flood plain of Imnavait Creek. The areas of individual watertrack drainage basins range from 0.5 ha to 4 ha.

METHODS

Beginning in 1986 an AeroChem-Metric wetfall-dryfall collector was placed about midway of the catchment, 80-m off the northeast ridge crest (Fig. 2). The sampler is the same as those used in the National Atmospheric Deposition Project (NADP) program (1988). It is equipped with a weighing rain gauge and event recorder. Positioning of the sampler and timing of sample collection follows the NADP procedures (Bigelow 1984). The site is operated from mid-May through the first week of September.

Collection of wetfall is made each Tuesday. The sampler bucket is agitated and a small amount of liquid is used to rinse an acid-washed 250 ml

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U.S. GEOLOGICAL SURVEY

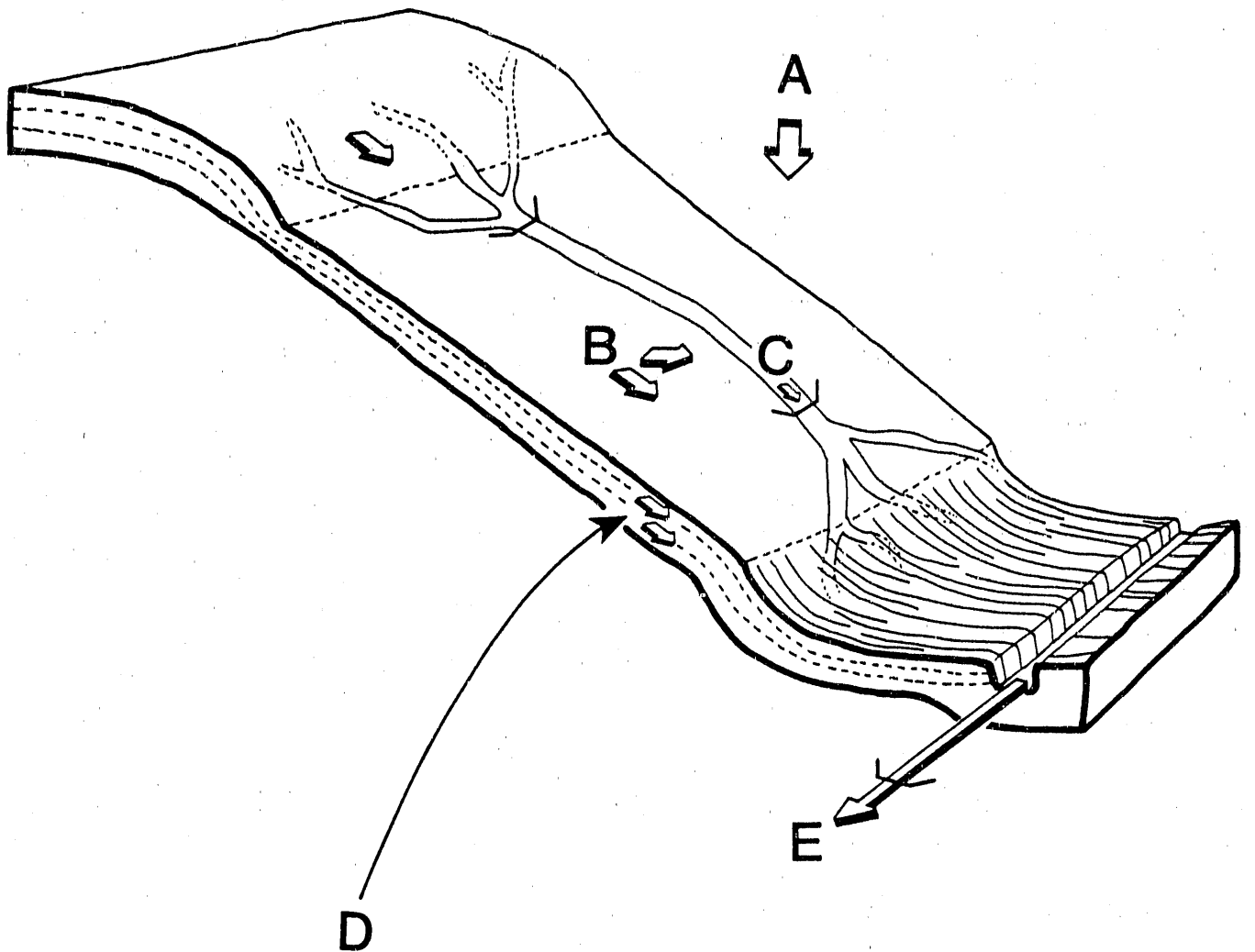


Figure 2. Cartoon showing major components of hydrology-geochemistry research effort of Imnavait Creek.

- A = Atmospheric input
- B = Overland flow
- C = Watertrack flow
- D = Soil solution (active layer)
- E = Imnavait Creek flow

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bottle and then discarded. The bottle is then filled with a 250 ml subsample, capped and stored at approximately 4°C until it is shipped for analysis (usually two to five days). The analyses are performed by Global Geochemistry Corporation in Canoga Park, California, using the same methodology and quality assurance control as used for Environmental Protection Agency (EPA) samples submitted to that laboratory. The dryfall bucket remains on the collector for the entire summer season (approximately 90 days). Once removed, it is washed down with 250 ml of deionized water, sealed and allowed to stand for 24 hours at approximately 20°C. A small volume of the sample is used to rinse an acid-washed 250 ml polyethylene bottle and then discarded. The remainder is poured into the bottle which is then sealed and sent for analysis.

Snow samples are collected in early May, prior to the onset of melt-off. Sampling sites are selected at random at several positions on each valley slope and in the valley bottom. At each site three pits are dug to the vegetation surface in a several-meter-square area. One side of each pit is cleaned with a stainless steel knife and a channel sample is taken from the surface to the bottom and placed in a polyethylene bag (the samples from all three pits at each site are placed in one bag). In the field laboratory the samples are allowed to melt and a recorded volume of liquid passed through a pre-washed and weighed 0.45 µm filter. The filter is oven-dried and placed in a sealed container to be accurately weighed in the Ohio State University laboratory. Half of the filtrate is placed in a pre-washed 250 ml bottle and frozen. A second 250 ml sample of the filtrate is acidified with ultrapure reagent nitric acid and stored at 4°C. The samples are returned to Columbus, Ohio, for analysis. Analytical procedures follow Standard Methods (16th Edition, 1985). Anions are determined with a Dionex Model 2000i ion chromatograph equipped with a fast-sep column; cations are determined with a

Perkin-Elmer 3030B atomic absorption spectrophotometer. Total organic carbon (TOC) is obtained with a Dohrmann Carbon Analyzer. The snow sampling scheme outlined above is considered to provide reasonable mean values for chemical species in the total winter snowfall at the Imnavait Creek site.

In the spring (late May) and fall (late August and early September), rime and fog are common occurrences in the area but at present no systematic sampling has been undertaken. Melted samples of rime are treated in the same manner as snow.

OVERLAND FLOW

The melt event is generally bracketed by the onset of snowpack ablation (early May) to the disappearance of non-drift snow cover (late May to early June [Fig. 3]; see Benson et al., 1990; Liston, 1988 and Kane et al., 1990 for details).

Overland flow on the hillslopes begins once the snowpack has become isothermal and the detention storage has been filled. Unfilled pore spaces in the upper few centimeters of the soil beneath the snow pack are produced during the winter as upward heat flow from the soil, which results in moisture movement out of the near surface materials results in recrystallization of the lower part (10-15 cm) of the snowpack (Woo, 1982; Santeford, 1978 and Hinzman et al., 1989). Kane et al. (1989) estimates that in the Imnavait Creek basin the unfilled pore space prior to melt requires 1.5 cm of water to re-wet. Once this takes place subnival overland flow can begin. This flow, directed either toward Imnavait Creek or to a watertrack tributary drainage, takes place in spatially discontinuous rills, usually between tussocks. Discharges estimated for the larger, more continuous rills, range to 0.09 l. sec^{-1} ($\approx 1.4 \text{ gal. hr}^{-1}$).

TABLE 1
 Runoff Chemistry, Plot 4, 1989
 mg·l⁻¹

ION	SNOW	PHASE I	PHASE II	PHASE III
pH	6.10	5.69	5.71	6.12
Ec	0.30	1.22*	1.72	0.84*
Ca	0.21	0.68*	0.50*	0.30*
Mg	0.02	0.37*	0.25*	0.14*
Na	0.05	0.27*	0.17*	0.08*
K	0.01	1.25*	1.00*	0.61*
Fe	0.02	0.11*	0.11	0.17
Mn	T	0.13*	0.09*	0.07
Cl	T	0.46*	0.12*	0.06*
NO ₃	0.32	0.28	0.08*	0.06
PO ₄	T	0.00	0.00	0.05*
SO ₄	0.30	0.25	0.08*	0.02*
DOC	0.94	22.82*	19.79	13.40*
Solids	18.50	9.25	37.26	14.58

*considered significant at 1 σ

T = trace

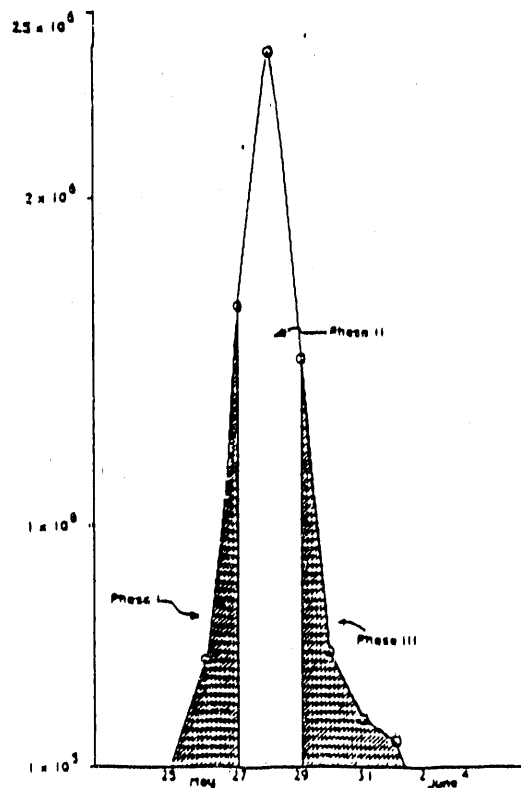


Figure 3. Snowmelt hydrograph for plot K-4, 1989 (L. Hinzman, unpublished data)

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Brimblecombe et al., 1985; Trantor et al., 1987; Johannessen and Henricksen, 1978, have shown the water reaching and filling the void pore space to be significantly different from its source snow, due to processes of chemical fractionation. Zukowski (1990) studied this phenomenon at Imnavait Creek and found enrichment factors for anions (Cl^- , NO_3^- and SO_4^{2-}) three to nine times that of the bulk snow, with most of it taking place during the first 40 percent of the ablation period.

Discharge of overland flow at Imnavait Creek has been measured since 1985 and is described in Hinzman and Kane (1990). Chemical analyses of these waters that eventually contribute to the first flow in Imnavait Creek, were conducted in 1986, and in greater detail in 1989 and 1990. These data are summarized in Table 1 and Figure 3. In this table the data are broken down relative to the discharge hydrograph for runoff plot No. 4 (89 m²) (Fig. 4) and are shown in relation to the discharge phase recognized for Imnavait Creek. The early overland flow shows a significant increase in concentration over that of the bulk snow for all parameters except pH, NO_3^- and SO_4^{2-} . The first snowmelt runoff can be expected to be enriched in most ions due to fractionation (Zukowski, 1990; Kopple, R.V., 1987; Barry and Price, 1987; Seip, 1978). Additional, and by far the greatest, enrichment takes place as the snow meltwater interacts with the surface and the materials composing the detention storage zone. The only ions to show apparent decreases (based on 16 samples) are Cl^- and NO_3^- , however, the low number of samples yields a low significance. In the case of NO_3^- , the decrease is probably due to biological uptake during transit.

These values are shown in Table 1 as the first phase of overland flow, ranging from three to 125 times the bulk snow for metal cations. The spectacular increase in the biologically important ion, Potassium, probably

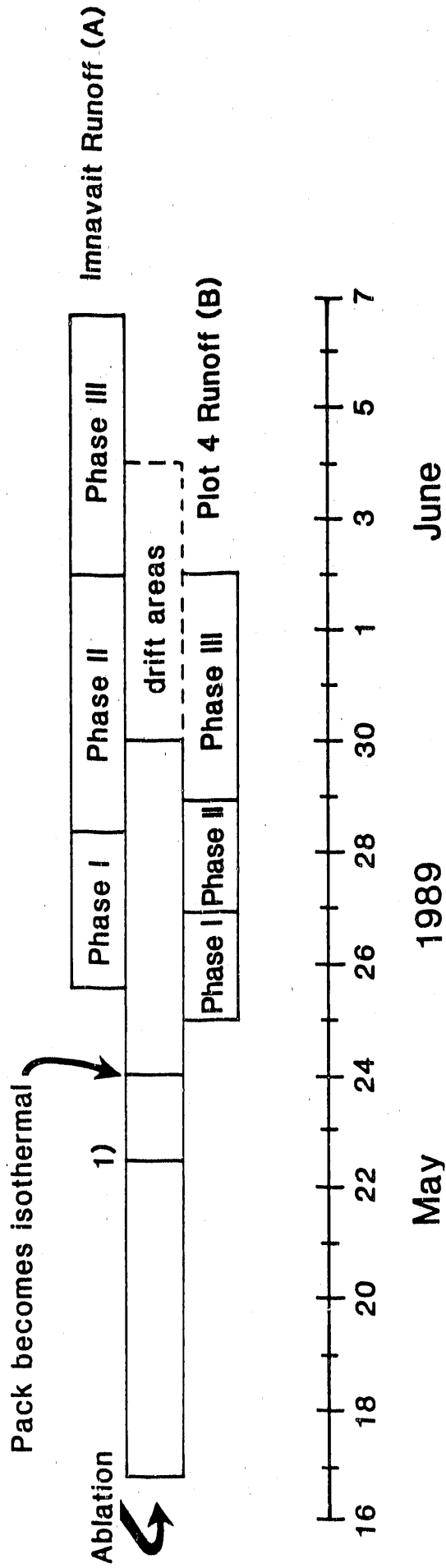


Figure 4. Temporal distribution of significant elements of snow melt hydrology, Imnavait Creek, Alaska, 1989 (see attached hydrographic and chemical data. 1) Point when detention storage should have been filled.

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represents desorption from organic exchange sites, as well as releases from lysed cells and leached from leaves, where it is in soluble ionic form (Gauch, 1972 cited in Chapin, 1975). Also of interest is the enrichment of Mg^{2+} relative to Ca^{2+} . Relative concentrations of these two ions in the later phases of overland flow and in channelized surface flow favor calcium by 2:1. It is suggested that at the temperature-pH conditions during this early phase of melt, together with elevated CO_2 common in the lower part of the snow profile in early spring, produces conditions that favor adsorption of Ca^{2+} to minute calcite crystals present in the upper surface of the organic/live moss fraction of the soil and possibly to the organics themselves. The relatively more soluble Mg^+ would move out.

Also noteworthy is the decrease (although nonsignificant) in both NO_3^- and SO_4^{2-} in the first overland flow. Cadde et al. (1987) noted a similar decrease in both ions in snowmelt water that had interacted with the surface. Again, adsorption or organic exchange sites may be important. Biological uptake is not ruled out since microbial and root respiration are known to at least $-0.3^\circ C$ (Chapin, 1974a; Flanagan and Bunnell, 1980). The nearly constant pH (reduction from bulk snow in Phase I is not significant at one S.D.) is consistent with the concentration of these acid anions.

During the following phases of overland flow [Peak (II) and recession (III)], ionic concentrations fall sharply, a situation also noted by Caddie et al. (1987) in their studies in northern Michigan. The substantial increase in organic carbon also merits consideration in the broader picture of carbon transport and carbon balance in Alaskan upland tundra ecosystems. Schell (1990) contends that such ecosystems, and specifically, Imnavait Creek, are carbon-losing and have been so far, for at least the last 2400 years.

Watertrack flow

From year to year the initiation of flow within watertracks is coincident or nearly so, with that of the overland flow. Regardless of the catchment area, first peak flow takes place within 18 hours of the overland flow peak (Fig. 5). This is in line with concentration times of 10 m in 24 hours recorded for overland flow by Kane et al. (1990) using tracers. The very limited data set relating chemical concentration during the three discharge phases (Table 2) indicates an early enrichment in ionic concentrations, primarily in the first peak flow, with concentrations similar to those of Phase I and II of overland flow. Phase III, the recessional link of the hydrograph, terminates in a second, and the major flow peak for watertracks of all catchment sizes. This flow has a relatively lower ionic concentration than the first part of the discharge and represents in-track snowmelt and the water from the later phases (II and III) of overland flow. This second and major peak of discharge is essentially, consistent with that of Imnavait Creek.

The amplitude of the second peak reflects not only the relative size of the catchment but the amount of snow within the watertrack itself. By noon on May 30, 1989, the catchment of watertrack 2B was essentially snow-free with little snow remaining in the tracks, while at 7B, the catchment was 85 percent (estimated) snow-free but the track retained considerable snow.

Two weirs were placed in several watertracks in the basin. One weir was placed high on the slope at the microtopographic break that separates the dry and snowbed vegetation of the crest and slope shoulder from the moist tussock-dominated tundra of the mid and lower slope (Walker et al., 1987 [also see Fig. 2]). The lower weir was placed at the last constriction in the channel before it becomes multi channeled as it passes from the toe slope into the riparian zone of Imnavait Creek. Intensive sampling was done in 1986 to

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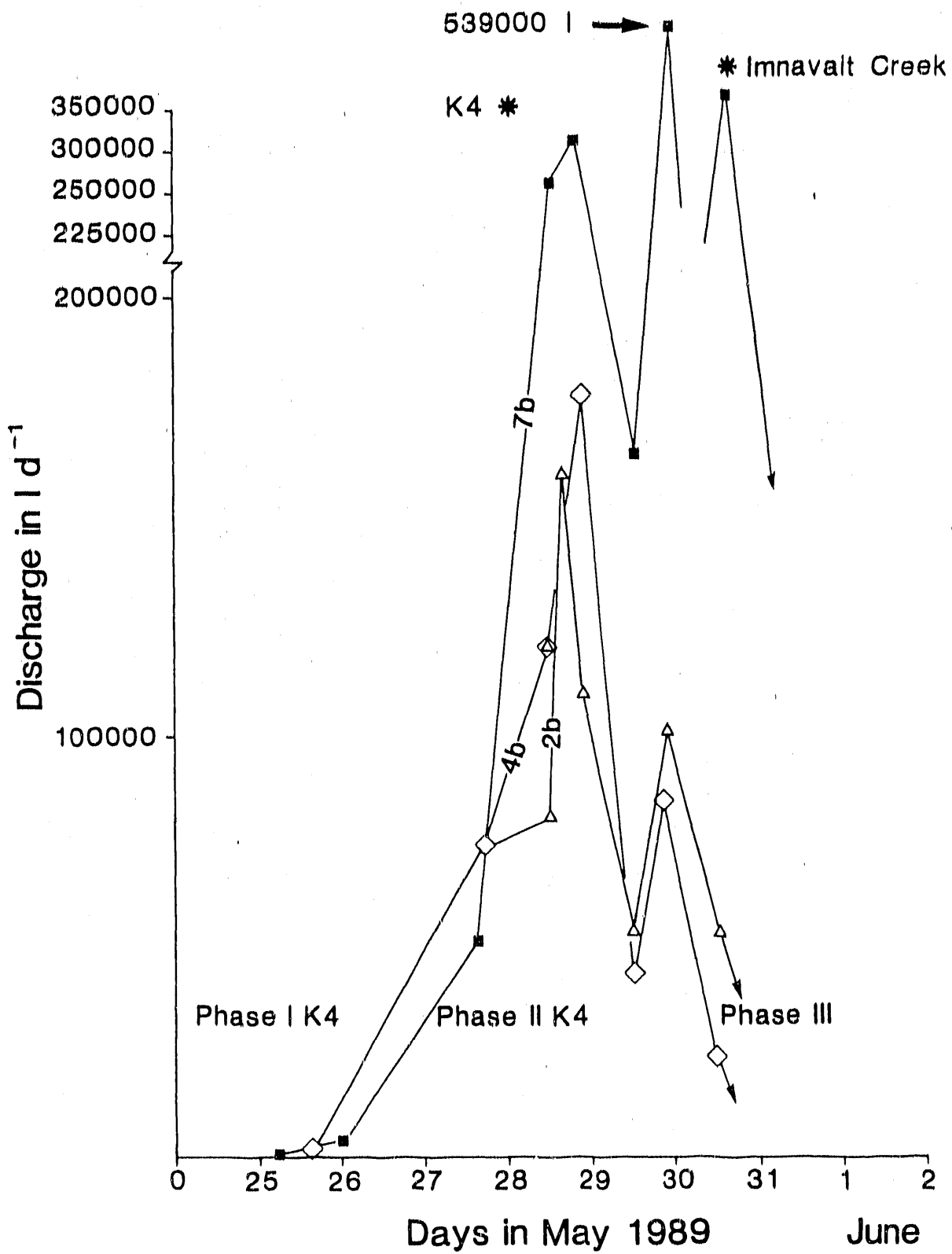


Figure 5. Snowmelt hydrographs for watertrack 7B (0.33 ha), 4B (0.20 ha) and 2B (0.10 ha). Phase numerals refer to temporal components of discharge from overland flow plot K4. Astrix marks time of peak flow from K4 and Imnavait Creek (Phase II) in 1989.

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Table 2. Chemical Concentrations in the Early Snowmelt Period Flow in Watertrack 7B

	pH	Ec	Ca	Mg	Fe	Mn	Na	K	F	Cl	NO ₃	SO ₄	PO ₄	DOC
Phase I ¹⁾	5.9	2.4	1.1	0.50	0.09	0.19	0.34	0.85	0.0	T	0.0	0.25	0.0	25.7
Phase II	5.4	2.0	0.42	0.24	0.03	0.11	0.15	1.09	0.0	T	0.0	0.06	0.0	18.1
Phase III	5.9	0.80	1.6	0.06	0.03	0.08	0.05	0.54	0.0	T	0.0	0.16	0.0	12.9

13

¹⁾ refer to Fig. 4

T = trace

Ion concentrations are in Mg·l⁻¹, Ec in Sm²

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determine the extent to which composition and catchment size influenced the ionic composition of the runoff. The data presented in Table 3 is for watertrack 7 on the southwest-facing slope and for a watertrack of comparable size on the opposing, much shorter and more mineral-dominated slope. Contacts between the two slopes are apparent in both sampling intervals and reflect the greater areal extent of mineral soil on the northeast-facing slope in the abundance of all cations. Contrasts between the catchments of either watertrack are not significant in the melt-off period when the highly variable composition of the snow dominates. Difference in catchment composition is most clearly shown by the decrease in most melt-off flow concentration of cations, including H^+ between the upper and lower weirs.

The presence of relatively high concentrations of SO_4^{2-} in both sampling periods in the upper catchment of watertrack 1 is not understood. The high value recorded in the post melt-off flow represents measurable quantities only after 1 August, probably in response to decreased biological demand and oxidation.

Imnavait Creek flow

In the earliest phase of snowmelt runoff in Imnavait Creek, small volumes of water (< 0.02 cfs), move between the base of the valley snow pack and ice of frozen stream water. This flow contributes to the bottom-up saturation of the valley snow pack and represents the initial phase of overland and watertrack flow from the surrounding slopes. The stream ice consists of bubbly clear ice; that in the flume approach shows a laminated structure and represents the residual stream flow. Overlapping this is a spatially discontinuous, laminated accumulation of reddish-brown ice that commonly lacks bubbles and is chemically distinct from the white ice (Table 4). This

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TABLE 3

Mean concentrations in $\text{mg}\cdot\text{l}^{-1}$

Ion	MELTOFF 6/1/86 - 6/11/86				POST MELTOFF 6/12/86 - 9/7/86			
	7A	7B	1A	1B	7A	7B	1A	1B
pH	5.10	5.22	5.75	5.70	5.52	5.35	5.95	6.00
Ca	0.78	0.84	1.20	1.42	1.26	0.84	1.56	1.44
Mg	0.28	0.36	0.28	0.61	0.34	0.41	0.65	0.60
Na	0.12	0.27	0.51	0.64	0.13	T	0.61	0.60
K	1.20	0.88	1.02	1.03	0.20	0.00	0.16	0.25
Cl	0.21	0.25	0.18	0.16	0.03	0.04	0.06	0.07
NO ₃	0.00	0.30	0.00	0.00	0.00	0.00	0.00	0.00
SO ₄	0.00	0.00	0.98	0.11	0.00	0.36	1.54	0.33
Solids	8.41	6.05	6.10	6.22	4.38	3.53	4.59	3.88

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Table 4. Mean ionic concentration in mg.l^{-1} in brown and clear ice in Imnavait Creek prior to melt.

	pH	DOC	Ca	Mg	Na	K	F	NO ₃	Cl	SO ₄
Clear	6.70	3.11	-	-	-	-	0.0	0.0	T	0.31
Brown	6.23	5.60	1.91	0.14	0.22	0.12	T	0.10	T	0.77

T = trace

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material is believed to be soil solution "squeezed" out discontinuously along the base of the toe slope as upward and downward freezing of the active layer progressed in early winter. Its color reflects both dissolved and suspended organic cations. Individual samples and analyses are too few to establish significant differences but sufficient to suggest a two-fold increase in all measured variables in the brown ice. The overall ionic contribution of this material to the very early discharge is unknown, but is probably small in relation to that of the overland flow.

The measurable subnival flow continues to increase over the next 8 to 36 hours as the flood plain snow pack becomes completely saturated and discolored. It is during this period that the highest ionic concentration of the snowmelt and subsequent runoff period occur (see preceding section). Eventually the slush mass gives way, sometimes catastrophically, to open channel flow and a precipitous increase in discharge. A similar increase in discharge takes place in watertrack flow but remains essentially subnival because the snow pack is on a slope and does not saturate as rapidly from the bottom up and clear out the channel.

During this phase of runoff pH may reach a seasonal minimum (Table 5). Concentrations of all other variables drop significantly - in part due to dilution, and in part because the ionic load of the meltwater has been reduced (the melting snow having lost most of its ions during the early melt phase [Johannessen et al., 1980]) and most of the early desorbed ions and other dissolved materials flushed from the thin near-surface soil layer.

The final, or recessional phase of melt-off, constitutes between 45 and 90 percent of the event. Ionic concentrations during this phase continue to decrease with mean concentration values for the "atmospheric" ions SO_4^{2-} , NO_3^- , PO_4^{3-} and Na^+ reaching seasonal lows with respect to the post-melt phase.

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TABLE 5. Mean ion concentration for three periods of snow melt flow for Imnavait Creek 1989

(Values in mg.l^{-1})

	Snowpack Ablation 349 hours	Phase I (18%) 41 hours	Phase II (37%) 93 hours	Phase III (45%) 254 hours	Post Melt
pH	6.10	6.07	5.90	6.28	6.29
H ⁺	0.79	0.85	1.25	0.52	0.51
Ec	0.30	0.15	0.14	0.08	0.12
Na	0.05	0.51	0.28	0.17	0.20
K	0.01	1.10	0.72	0.31	0.011
Ca	0.21	0.85	0.65	0.41	0.79
Mg	0.02	0.39	0.28	0.17	0.28
Fe	-	0.07	0.06	0.08	0.08
Mn	-	0.05	0.08	0.03	0.01
Cl	0.00	0.004	0.07	0.02	T
PO ₄	T	0.00	0.00	0.00	T
SO ₄	0.30	0.96	0.30	0.03	0.18
DOC	0.94	15.44	14.58	10.59	13.15
Solids	18.50	11.64	2.67	18.50	5.14
\bar{Q} (cfs)	NA	4.70	23.30	2.46	0.85

T = trace

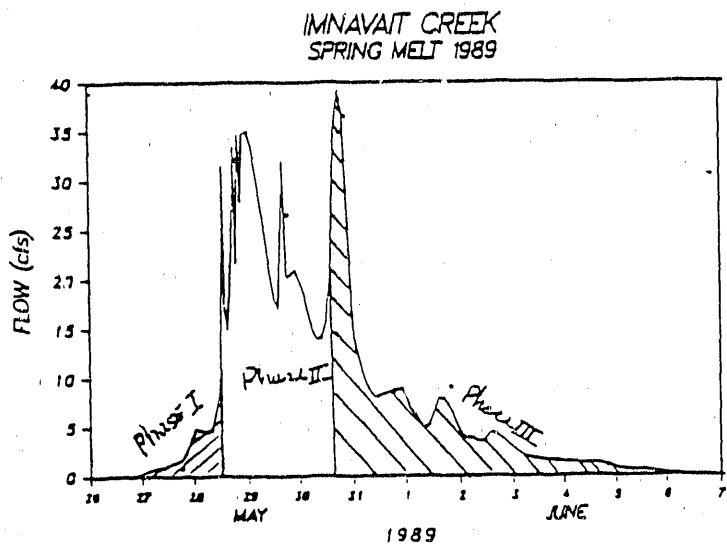


Figure 6. Snowmelt discharge hydrograph for Imnavait Creek. Patterns refer to mean ion concentration values shown in Table 7. Data plot from Kane (1989).

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The general pattern of ion concentrations during the snowmelt runoff (and their relationship to concentrations in the post-melt phase) is consistent from year to year, although mean concentrations and ranges for individual ions are strongly controlled by conditions antecedent to melt off.

The ionic concentration drops progressively during the melt-off discharge with the lowest mean values recorded in recessional flow (Phase III, Table 5 and Fig. 6). During the period of measurement (1985-1990), the melt-off discharge has accounted for between 50 and 80 percent of the total annual loss of ions and organic carbon from the basin (Table 6).

POST MELT-OFF PERIOD

Precipitation - frequency, characteristics and composition

During the period of record summer precipitation, including snow, contributes 40 to 60 percent of the yearly discharge of Imnavait Creek (Kane, 1989). It ranges widely in quantity and composition between years and between sampling intervals. Because of the sampling procedure used for rainfall, individual events as well as eight-day composite samples, can be analyzed.

Rain events are few in late May and early June, only two trace events have been recorded during the snowmelt period. Periods of rain, both convective and frontal, begin and increase in frequency from the third week in June, with August having the most rain. The mean number of rain events recorded for the summers of 1985-1988 was 256. A substantial number of these reflect discontinuous periods of precipitation (many of them too light to be recorded by the rain gauge) within protracted periods of rainy weather. Most rainfall is of low intensity (94% at rates $< 10 \text{ mm hr}^{-1}$ and 82% $< 1.0 \text{ mm hr}^{-1}$) and evenly distributed over the catchment and is associated with the dissipating

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TABLE 6. 1989 Snowmelt Budget, Imnavait Creek. Concentrations in Kg.

	Snow Pack	Snowmelt	Difference	Snowmelt Discharge as a % of Seasonal Total Discharge of the ion or radical
Na	16.28	84.70	(-) 68.42	72
Ca	68.36	190.06	(-) 121.70	60
K	3.26	205.55	(-) 202.29	99
Mg	6.51	82.34	(-) 75.83	64
Fe	6.50	20.16	(-) 13.66	20
Mn	T	21.13	(-) T	93
Cl	T	17.31	(-) 17.31	100
PO ₄	T	T	0.00	0
NO ₃	104.16	14.22	(+) 89.94	37
SO ₄	97.65	89.18	(+) 8.47	38
DOC	305.97	4302.87	(-) 3996.90	66

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phase of convective storms generated over the Brooks Range, or with air masses moving from the north Pacific. Maximum intensities generally occur in the first four or five hours of the event.

High intensity ($> 20 \text{ mm hr}^{-1}$), short-duration rainfall is associated with convected storms. Average concentrations for selected chemical parameters from 1986-1988 are shown in Table 7. A detailed treatment of precipitation chemistry is given in Everett (1990-Appendix B).

TABLE 7
Mean concentration in mg.l^{-1} , of selected ions in samples
for the years 1986-1989 Imnavait Creek

Year	$\text{H}^{+(1)}$	Ca^{2+}	Mg^{2+}	K^+	Na^+	Cl^-	NH_4^+	NO_3^-	SO_4^{2-}	PO_4^{3-}
1986	3.02	0.27	0.03	0.31	0.26	0.37	0.12	0.62	0.43	0.04
1987	5.25	0.07	0.01	0.11	0.05	0.10	0.06	0.22	0.22	0.03
1988	9.77	0.36	0.06	0.22	0.33	0.62	0.11	1.51	0.35	0.07
1989	4.58	0.17	0.02	0.01	0.02	0.32	0.03	0.02	0.11	0.09

¹⁾ $\mu \text{ eq.l}^{-1}$

(given in Everett, 1990-Appendix B)

Overland flow

The dry period following snowmelt runoff, coupled with an increase in active layer thickness at a rate of 0.41 cm d^{-1} , results in a substantial increase in potential detention storage, so that by mid-June, between 9 and 11 cm of the soil would be thawed. This depth includes most of the living

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vegetation-mat and the underlying fibrous organic soil horizon, with both high porosity and permeability (unsaturated hydraulic conductivities between 194 and $0.104 \text{ cm sec}^{-1}$ and porosities between 0.90 and 0.86 [Hinzman et al., 1989]).

The lower boundary of this horizon corresponds to a large decrease in hydraulic conductivity (10 to 10^2 times) and serves to channel subsurface flow. Individual rainfalls capable of filling the potential detention storage (minimum 15 mm) and producing overland flow are rare. The only such event recorded during the study produced 37 mm. in 1 hour. It is probable that during sustained rains and during rain events that occur when antecedent moisture is high, may produce short, spatially and temporally discontinuous episodes of overland flow.

Protracted rainfall events that produce or follow high antecedent soil moisture are common and produce active layer and watertrack flow. As the rain water passes into the surface horizon it is partially neutralized (Table 8). Its ionic contribution to the resulting flow ranges widely, conditioned by the history of the air mass. For the event analyzed in Table 5, rainfall contribution of potassium was sufficient to account for its concentration in surface flow. The elevated concentration in soil solution represents release through leaching and cell lysis. Chloride is the only other ion contributed by rainfall in significant amounts and it is probably the primary source for the ions in all flow compartments.

Both calcium and magnesium are deposited with most rain events (and are major components of dry fall [Everett, 1990, Appendix B]) but the primary source for these ions. Both are released to surface flow through leaching of vegetation and weathering of airborne carbonates, primarily in loess. The significant increase in both ions in soil solution represents a combination of

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Table 8. Comparison of mean surface and subsurface flow chemistry for the period
2 August through 24 August 1989. Ionic data in Mg. l⁻¹

	pH	Ca	Mg	Na	K	Fe	Mn	NO ₃	Cl	SO ₄	DOC	Solids
Rainfall	4.9	0.10	0.01	0.03	0.02	-	-	0.00	0.21	0.09*	-	-
Overland flow ¹⁾	6.1	0.63	0.46	0.22	0.03	0.22	0.01	0.58	0.39	0.75	15.4	5.86
Soil Solution ²⁾	-	1.60*	0.41	0.69	0.16	0.22	0.13	0.55	0.14*	0.39	-	37.69
Soil Solution ³⁾	-	2.25*	0.73*	0.77	0.17	0.82*	0.28	1.00	0.41	0.39	-	37.69
Watertrack Flow ⁴⁾	6.1	0.43	0.37	0.19	0.01	0.11	T	0.16	0.46	0.54	13.00	4.39
Imnavait Creek ⁵⁾	6.1	0.82	0.30	0.06	0.02	0.13	T	0.23	0.51	0.51	12.90	5.0

¹⁾ Includes shallow subsurface flow lining vegetation mat and fibrous organic soil horizon at runoff plot 4 (N = 3).

²⁾ 20 cm depth; N = 21,

³⁾ 40+ cm depth; N = 21,

⁴⁾ N = 16

⁵⁾ N = 13

* significant at 16.

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desorption and weathering of primary carbonates, probably from loess in the shallow soil solution and from till in the deeper solution.

Because of the very low permeability, rich lower soil horizon mass flow is restricted to spatially discontinuous fractures and/or boundaries. Flow at the permafrost boundary may occur (Everett, 1980-unpublished data). Thus, these soil layers do not contribute rapidly to composition of the surface waters. Chemical interchange between the deeper horizons and the surface is primarily by diffusion.

The solubilities of both iron and manganese are strongly dependent upon the redox state and pH. Flow at the surface and near-surface in the watershed has dissolved oxygen levels of 10-12 percent (M. Oswood, pers. communication, 1986) and it is likely that both species are largely in insoluble forms. These concentrations do not differ significantly in surface flow (Table 8). The relatively high concentration in the deeper soil solution attests to the widespread anoxic conditions at depth in the hydric soils of the area (Everett, 1980; Walker et al., 1987).

The cations just discussed together with silica (Marion, 1989) are measurable in nearly every sample. This is not the case for the biologically important ionic SO_4^{2-} and NO_3^- . Both ions are added to the basin in rainfall in which their concentration may range widely depending upon the strength of the anthropogenic contribution, industry to the north and forest fires south of the Brooks Range (Everett, 1989). Except for sporadic appearances in water-track flow and in Imnavait Creek, sulfate and nitrate are found only during a short post melt-off period before biological demand exceeds the rate of supply of inorganic nitrogen, and again in late August coincident with the onset of plant senescence. Both ions appear to be present in soil solution nearly all of the time. In the upper 20 cm it is probable that SO_4^{2-} results from

oxidation of cell proteins and NO_3^- from mineralization of the hydrolyzable fraction of organic materials. If interchange takes place between the upper and lower 20 cm of the soil it is slow and the concentration of SO_4^{2-} and NO_3^- are proportional to amounts on the solid phase (Dymbe and Christophersen, 1980).

In both overland and watertrack flow DOC and suspended solids (mostly organics) shows a relatively narrow range in concentration from one rainfall event to the next. Concentrations of DOC are similar to those of Imnavait Creek and constitute a significant component of total carbon transport from the catchment.

Imnavait Creek

The plots of mean (daily) concentration vs. principal hydrologic events (low flow < 0.50 cfs and high flow) over the course of the summer of 1989 (and each of the other years) (Fig. 6) reinforce the conclusion that concentrations of most ions are greatest during melt-off. During this period seasonal biochemical trends within the drainage basin dictate the availability of ions for transport, e.g., NO_3^- , SO_4^{2-} , Fe, or Cl^- (the ionic composition of rainfall during high flow periods [> 0.5 cfs] is not related to compositional trends in stream chemistry). Detailed sampling of distinct storm events has shown a decrease in pH and an increase in DOC and electrical conductivity in the early phase of the ascending limb of the hydrograph (Everett et al., 1989 [this is missed when events are analyzed by daily sampling]). A concomittant increase in concentration of anions or cations was not recorded.

The clearest flow related and seasonal trends are observed in the dissolved (DOC) organic and particulate organic (POC) components. Since most of the water reaching Imnavait Creek has passed on or through organic-rich

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soils, they can be expected to contain significant quantities of dissolved organic carbon and organic acids. Oswood et al. (1989) measured the DOC/POC ration at 29.9 and Peterson et al. (1986) have shown similar values for tundra streams. Their relationship to the discharge hydrograph is shown in Figure 7. The seasonal loss of carbon (Kg ha^{-1}) constitutes ___% of the total amount of stored carbon (Oechel et al., 19__) and lends support to Schell's hypothesis that at present (and probably for the last 2500 years) the upland tundra has been loosing more carbon than it gains. Oswood et al. (1989) recognizes a decreasing loss of both carbon and nitrogen in the stream with time over the melt season.

When a comparison of stream chemistry is made among years a rather different picture emerges (Table 9) in which there is a substantial yearly consistency in concentrations, especially for the metal cations (Ca^+ , Mg^+ , Na^+ , K^+ , Fe, Mn), pH and conductivity, DOC and solids. There is also a consistency in the year-to-year ratios of the cations, e.g., $\text{Ca}^+ : \text{Mg}^+$. These relationships represent a consistency in supply and release of the ions (dry fall chemical weathering of minerals in the near-surface soil horizon, leaching organic materials). With regard to the anions there is considerable variability between years conditioned by large year-to-year ranges in atmospheric input as well as biochemical uptake storage and release in the soil/plant system.

SUMMARY

The data presented in Figure 8 attempts to summarize discussion of post meltoff flow chemistry in terms of significant compartments and to estimate rates of solute transport in an upland tundra watershed. The concentrations for calcium (always in excess of biological demand) are for a single date

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IMNAVAIT CREEK DISCHARGE

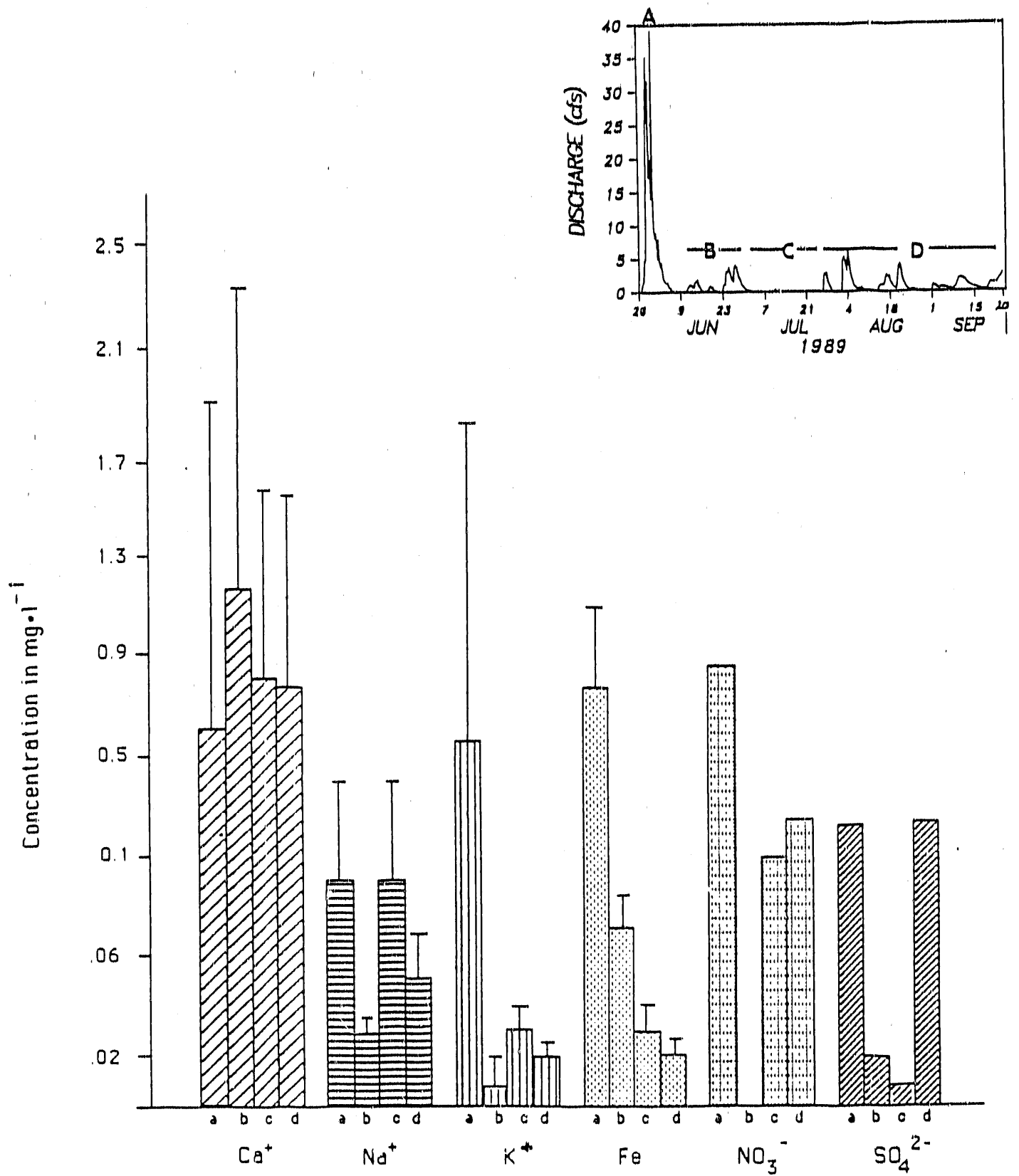


Figure 7. Mean concentration in $\text{mg}\cdot\text{l}^{-1}$ of selected ions for major discharge periods in 1989. A-D refer to hydrograph inset.

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TABLE 9

Mean concentrations of selected ions and other chemical variables
in Innavait Creek discharge for the years 1985 through 1989.

Year	pH	H ⁺	Ec	Ca ⁺	Mg ⁺	Na ⁺	K ⁺	Fe ²⁺	Mn ²⁺	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	DOC	Solids
1985	5.85	1.41	0.10	1.09	0.33	0.20	0.13	NA	NA	0.59	0.00	0.00	NA	NA
1986	5.87	1.35	0.15	1.32	0.43	0.10	0.07	NA	NA	0.13	0.08	0.40	10.46	4.10
1987	5.77	1.70	0.13	1.18	0.38	0.18	0.08	0.44	0.04	0.17	0.00	0.04	9.77	4.65
1988	5.92	1.20	0.24	0.99	0.28	0.18	0.14	0.55	0.05	0.51	0.04	0.15	12.18	6.79
1989	6.27	0.54	0.10	0.72	0.26	0.17	0.16	0.09	0.01	T	0.13	0.21	11.99	6.92

*Hydrogen is expressed in $\mu\text{Eq. l}^{-1}$, all other ions are expressed in mg. l^{-1} ; DOC and Solids are in mg. l^{-1} ;
T = trace amount; NA = not analyzed.

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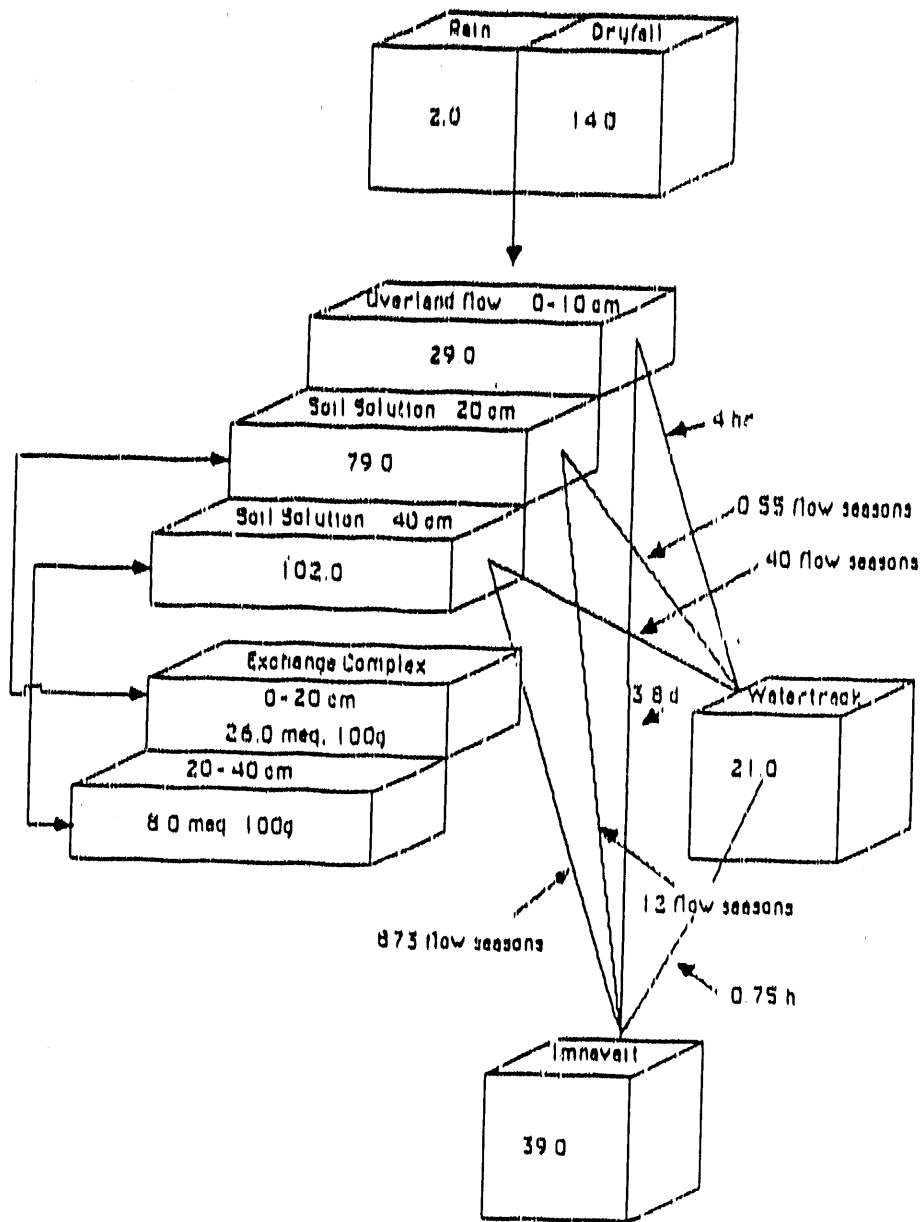


Figure 8. Calcium concentration in the various flow compartments of the Imnavait Creek watershed on August 1, 1989. (Overland flow, soil solution, watertrack flow and Imnavait Creek flow). Rainfall concentration is from the 7-day period preceding August 1. Dryfall concentration computed from season total. Exchange complex concentrations taken from soil profil analysis in 1988. All concentrations other than exchange samples are in mg l^{-1} . Arrows represent flow pathways. Minimum concentration times between soil solution/overland flow and watertracks are based upon a straight-line distance of 25 m (interfluve to track center) [Everett, personal observation; Chapin et al., 1989 and Kane et al., 1989, Marion and Everett, 1989]. Concentration times between soil solution/overland flow and Imnavait Creek are based on a straight-line distance of 550 m (Chapin et al., 1989). Concentration time between watertracks and Imnavait Creek used the equation $T_c = (2 L_n / 35)^{0.47}$ (Bruce and Clark, 1966).

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following a precipitation event (16 mm precipitation in the preceeding 24 hours). It seems likely that during periods of low antecedent moisture that Imnavait Creek is supplied with ions from the lower slope-toe slope and strangmoor areas and from similar parts of the watertrack basins or shallow subsurface flow. Thus periods of low main channel flow should correspond to higher ionic concentrations (water supplied by soil solution with higher ionic concentration). At present this cannot be substantiated because of system "noise" and overriding seasonal trends. Detection of higher concentrations of some ions following prolonged dry periods in the environment requires closely-spaced sampling during the first 5-10% of the rising levels of the hydrograph (Fig. 7).

The mean concentrations of the various ions and chemically-related variables transported during the post-meltoff flow period are presented in Table 10 with the snowmelt discharge values and a season balance for the basin is shown.

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TABLE 10

Summary tabulation of ionic input and output in the Innavaik Creek basin for melt-off and post-melt-off periods. All values in (Kg).

ION	A	B	C	D	SEASON BALANCE ⁽³⁾	
	SNOWPACK ⁽¹⁾	MELTOFF Q	SUMMER PRECIPITATION	POST-MELTOFF		
Na ⁺	16.28	84.70	10.79	32.76	(-)	90.39
Ca ²⁺	68.36	191.05	91.75	129.40	(-)	159.35
K ⁺	3.26	205.56	5.40	1.80	(-)	198.69
Mg ²⁺	6.51	82.34	10.79	45.86	(-)	110.90
Fe ²⁺	6.50	20.16	6.50 ⁽²⁾	13.10	(-)	10.46
Mn ²⁺	T	21.13	T	1.64	(-)	Est.
Cl ⁻	T	38.44	172.70	T	(+)	172.70
PO ₄ ³⁻	T	T	48.57	T	(+)	48.57
NO ₃ ⁻	104.16	14.22	10.79	22.93	(+)	77.80
SO ₄ ²⁻	97.65	89.18	59.37	29.48	(+)	38.29
DOC	305.97	4002.86	-- ²	2153.97	(-)	5847.00
Solids	6022.00 ⁽⁴⁾	2016.08	-- ²	814.93	(+)	3191.00

(1) Pre-melt snow cover (N=18)

(2) Not analyzed in 1989.

(3) A + C - B + D

(4) Represents redistribution of materials already in the basin.

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