The Distribution and Elemental Composition of Suspended Particulate Matter in Norton Sound and the Northeastern Bering Sea Shelf: Implications for Mn and Zn Recycling in Coastal Waters

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ABSTRACT

The distribution and elemental composition of suspended particulate matter in Norton Sound and the northeastern Bering Sea shelf were studied in July 1979. Samples were analyzed for total suspended matter and particulate C, N, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, and Zn. The results show that the bulk of suspended material in Norton Sound consists of sedimentary material discharged from the Yukon River and resuspended bottom sediments. The Yukon River material enters the sound from the southwest, is transported north and northeast around the perimeter of the sound, and exits from the northwest.

The concentrations of the major and trace elements in the particulate matter and their elemental ratios with aluminum indicate that: K, Ca, Ti, Cr, Fe, Ni, and Cu are primarily associated with aluminosilicate material derived from the Yukon River and resuspended sediments, and C and N are primarily associated with terrestrial organic material in estuarine samples and marine organic material in offshore samples. Significant enrichments of Mn and Zn, observed in the offshore samples, are attributed to Mn recycling in the sediments followed by precipitation of Mn onto particulate phases in the water column, with the Mn oxyhydroxides scavenging Zn.

INTRODUCTION

Particles suspended in seawater play a major role in regulating the chemical forms, distributions, and deposition of many of its constituents. This is particularly true in coastal waters where dissolved and particulate matter in runoff from rivers interacts with seawater. Particles in coastal waters are the result of continuing physical, chemical, biological, and geological processes and are the precursors of marine sediments. These processes may include the supply of inorganic and organic substances from river runoff, aeolian fallout and coastal erosion, resuspension of previously deposited sediments, biological production of organic materials, and chemical adsorption-desorption and flocculation processes. Variations in the composition of particles in suspension can be sensitive indicators of such processes. In this chapter we present the results of a survey of the distribution and elemental composition of suspended material in Norton Sound and the northeastern Bering Sea shelf. The results are related to known patterns of water circulation and previously published information on the chemical composition of suspended material from the Yukon River. We present arguments to support the position that Mn and possibly Zn undergo dissolved-to-particulate phase changes as a result of interactions between suspended matter and dissolved species within Norton Sound.

HISTORICAL BACKGROUND

Previous work on suspended matter in Norton Sound has been limited to studies of LANDSAT photographs and distributions of suspended matter. Sharma et al. (1974) used density-sliced LANDSAT photographs and sea-truth measurements to study distributions of suspended matter in Norton Sound during the late summer of 1973. Concentrations of suspended matter were highest near the mouth of the Yukon River (range: 2-8 mg/l) and in Norton Bay (range: 3-4 mg/l), in the northeast corner of the sound. The authors postulated that the general pattern of cyclonic circulation in the sound caused suspended material to be transported to the north and northeast along the coast. The authors also noted that unusually high concentrations of particulate matter (>9.0 mg/l) were observed throughout the water column in the region approximately 30 km south-southwest of Nome. They suggested that this plume could have been a detached portion of the Yukon River plume which was isolated by tidal pulsation.

Cacchione and Drake (1979) combined surveys of suspended matter during September and October 1976 and July 1977 with deployments of a tripod (GEOPROBE) containing instruments designed to measure bottom currents, pressure, temperature, and light transmission and scattering to study dispersal patterns of suspended matter in Norton Sound. They described the transport of suspended materials as dominated by distinctly different quiescent and storm regimes. The quiescent regime was characterized by relatively low levels of sediment transport caused by tides and mean flow to the north and northeast, augmented by surface waves during spring tides. The authors stated that in this period, much of the fine-grained suspended matter present over the prodelta was resuspended at shallow depths during spring tide and transported northward with the mean current. The storm regime, which occurs during the months of September through November, was characterized by strong southerly and southwesterly winds which generate waves with heights of 1-3 m and periods of 8-11 sec. The storm events cause near-bottom shear velocities in excess of that required for resuspension of bottom sediments and, as a result, more than 50 percent of the sediment transport occurs during this regime.

Although there is no background information on the chemistry of suspended matter in Norton Sound, extensive studies of trace-metal partitioning in various phases of Yukon River materials were conducted by Gibbs (1973, 1977). He concluded that transition metals associated with oxyhydroxide coatings and crystalline phases comprised the major fraction (72-91 percent) of riverine transition metal transport to the sea. Particulate organic phases contained the next largest fraction (3-16 percent of the total). Metals in solution and metals sorbed to particulate materials made up the remainder (5-15 percent of the total).

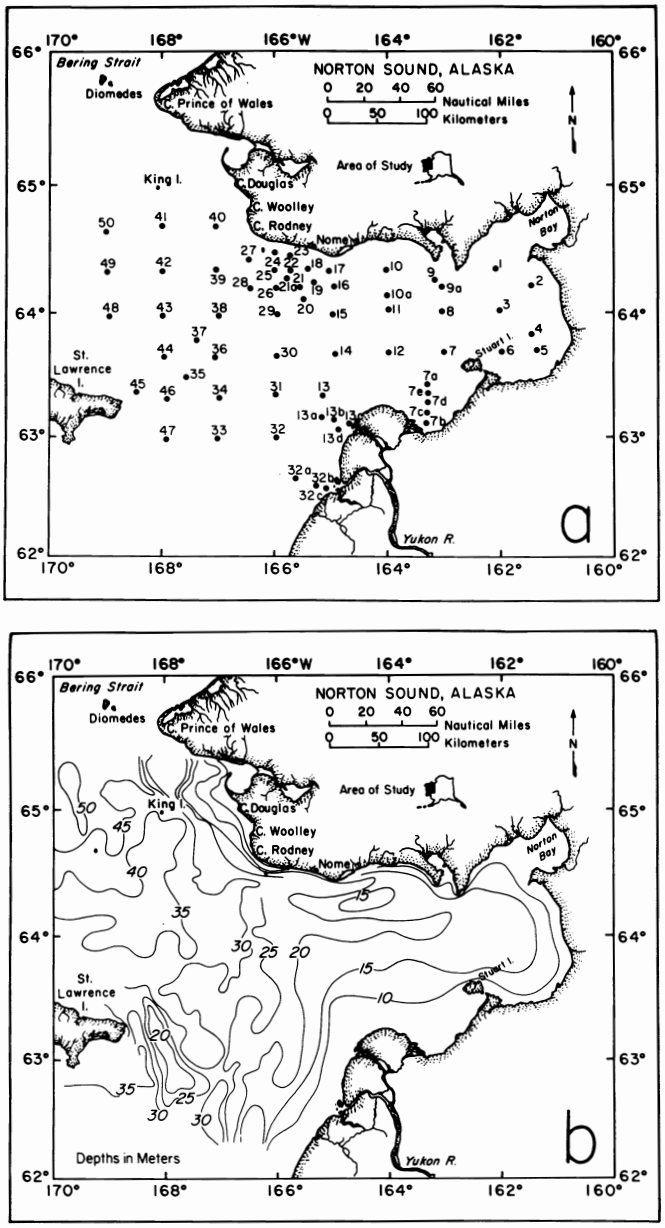

Figure 20-1. Physiographic setting of Norton Sound showing: (a) locations of suspended matter stations, 7-18 July 1979 (b) bathymetry in meters.

THE STUDY REGION

Norton Sound is a shallow embayment of the Bering Sea in the central region of the west coast of Alaska (Fig. 20-1). It extends east-west about 220 km and north-south about 150 km. The Yukon River, which flows into the southwest quadrant of the embayment, is the major source of fresh water and suspended matter to the sound as well as to the entire eastern Bering Sea shelf. Its annual load of suspended matter, 88 × 10^6 tons, ranks 18th among the major rivers of the world (Inman and Nordstrom 1971). The annual discharge curve for the Yukon River (Fig. 20-2) is unimodal with peak flow occurring during June and low flow conditions persisting throughout the winter months. Additional lesser freshwater influx into the sound occurs along the coastline east of the Yukon River Delta and along the northern coast.

Water circulation in the vicinity of Norton Sound has been described by several authors (Coachman et al. 1975, Muench and Ahlnäs 1976, Muench et al. Chapter 6, this volume). The shelf water west of Norton Sound, the Alaskan coastal water, has a net northward flow of about 1.5 × 10^6 m^3/sec. About one-third of this flow passes between St. Lawrence Island and the mouth of Norton Sound. This flow induces the cyclonic water circulation inside Norton Sound. The intensity of the cyclonic flow appears to be affected by local winds and by freshwater runoff. The eastern half of the sound is characterized by two vertically well-mixed layers. The upper layer contains runoff water from the coastal rivers; the lower layer contains cold, dense residual water formed during the previous winter. Both water masses follow the general pattern of cyclonic flow in the region, although much more sluggishly than surface and bottom waters further to the west.

The distribution of sediments in Norton Sound has been summarized (McManus et al. 1974, Sharma 1974, Nelson and Creager 1977, and McManus et al. 1977). In the central and southern regions, the sediments consist of very fine grained sands and silts which are modern. In the northern region, silty sands predominate everywhere except for a narrow strip along the coast between Cape Nome and Cape Douglas. Here, coarse sands and gravels predominate because bottom currents have caused almost complete erosion of the fine-grained sediments. Approximately one-half to two-thirds of the sediment load of the Yukon River is deposited as a band of sediments extending from the Yukon River Delta northward and eastward around the perimeter of the sound. The remaining sediment load of the Yukon River is transported to the north through Bering Strait and deposited in the Chukchi Sea.

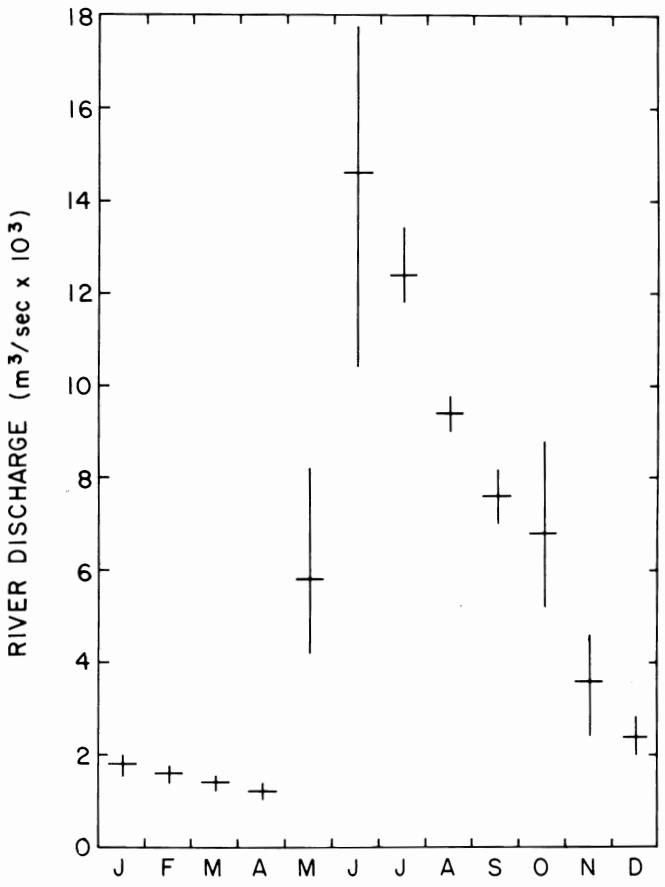

Figure 20-2. Monthly means and ranges for Yukon River discharge. Data compiled from U.S.G.S. streamflow obtained at Pilot Station (located approximately 200 km upstream from the river mouth) for period of record: 1975-78.

EXPERIMENTAL PROCEDURES

Sampling methods

In order to obtain information about the distribution and composition of suspended matter in Norton Sound, samples were collected as part of an interdisciplinary survey of the region (7-18 July 1979). Fig. 20-1 shows the locations of the stations occupied during the survey. Water samples were collected in General Oceanics Model 1070 10-l PVC Top Drop Niskin bottles from the surface and 5 m above the bottom, and from intermediate depths along two vertical sections spanning the length of the

sound (Transect I: Stations 3, 4, 8, 11, 15, 20, 29, 38, 43, and 48; Transect II: Stations 1, 9, 10, 17, 18, 22, 25, 27, 39, 42, and 49). To avoid loss of rapidly settling particles (Gardner 1977, Calvert and McCartney 1979), aliquots from each Niskin bottle were rapidly withdrawn (within 10 to 15 minutes of collection) and vacuum-filtered through preweighed 0.4-μm pore-size Nuclepore polycarbonate filters (47 mm in diameter for suspended matter concentration determination and 25 mm in diameter for elemental analyses other than C and N) and precombusted 0.45-μm pore-size Selas silver filters (25 mm in diameter for C and N analyses). All samples were rinsed with three 10-ml aliquots of deionized membrane-filtered water (adjusted to pH 8.0), placed in individual polycarbonate petri dishes with lids slightly ajar for a 24-hour desiccation period over sodium hydroxide, and then sealed and stored for subsequent laboratory analysis.

Temperature and salinity data were obtained with a Plessey Model 9040 CTD system equipped with a Model 8400 data logger. This system sampled several times per second for simultaneous values of conductivity, temperature, and depth. The data were averaged to provide 1-m temperature and salinity values, from which sigma-t was computed. The sigma-t values are accurate to ±0.02 sigma-t units.

Analytical methods

Total concentrations of suspended matter were determined gravimetrically. The weighing precision (2σ = ±0.011 mg) and volume reading error (±10 ml) yield a combined coefficient of variation in suspended matter concentration of approximately 1 percent. This variability is probably overshadowed, however, by that associated with the sampling precision as reported by Feely et al. (1979) for other Alaskan coastal waters, where the relative standard deviation ranged from 5 to 25 percent.

The major (Mg, Al, Si, K, Ca, Ti, and Fe) and trace (Cr, Mn, Ni, Cu, and Zn) elements in the suspended matter were determined by x-ray secondary-emission (fluorescence) spectrometry using a Kevex Model 0810A-5100 x-ray energy spectrometer and the thin-film technique (Baker and Piper 1976). A silver x-ray tube (operated at 50 kV, 40 mA) was used to excite a sequence of secondary targets (Fe target for Mg through Cr; Se target for the remaining elements) which efficiently fluoresced the range of elements in each sample. Standards were prepared from suspensions of finely ground U.S.G.S. Standard Rocks (W-1, BCR-1, AGV-1, and GSP-1; 90 percent by volume were less than 15 μm in diameter as determined by scanning electron microscopy) collected on Nuclepore filters identical to those used for sample acquisition. At a filter loading of 325 $\mu g/cm^2$ the determination limits (three times the minimum detection limits) were less than 0.25 percent and 13 ppm for the major and trace elements, respectively. The relative standard deviations resulting from 10 replicate analyses of a sample with a similar weight distribution were less than 3 percent for major elements and less than 8 percent for trace elements.

The amorphous Mn and Zn in the poorly structured oxyhydroxide phase of selected suspended matter samples were determined by the method of Bolger et al. (1978). Desiccated samples were leached with 5 ml of 25 percent (v/v) Ultrex acetic acid at room temperature for two hours. The resulting supernate was filtered through an acid-cleaned polypropylene-glass apparatus containing a 0.4-μm Nuclepore filter. The residue was rinsed with quartz-distilled water, then filtered; the supernate was combined with the original supernate, acidified with 0.5 ml of concentrated Ultrex HCl, and stored in an acid-cleaned polyethylene bottle. The Mn and Zn in this solution (weak-acid-soluble) were analyzed by flameless atomic absorption procedures using standard addition methods. The remaining solid suspended matter (weak-acid-insoluble) was dissolved in an Ultrex HCl-HNO_3-HF matrix following Eggimann and Betzer (1976) and analyzed for Mn and Zn in a similar manner.

Analysis of total particulate carbon and nitrogen in the suspended matter was performed with a Hewlett Packard Model 185B CHN analyzer. In this procedure, particulate carbon and nitrogen compounds were combusted to CO_2 and N_2 (micro Pregl-Dumas method), chromatographed on Poropak Q, and detected sequentially with a thermal conductivity detector following a modification of the procedure outlined by Sharp (1974).[1] NBS acetanilide was used for standardization. Analyses of replicate surface samples yield relative standard deviations ranging from 2 percent to 10 percent for carbon and 7 percent to 14 percent for nitrogen.

[1] Because the silver filters used for sample acquisition could not be accurately weighed, carbon and nitrogen data were determined on a mass-per-volume basis. Weight percent data for carbon and nitrogen were obtained by comparison with suspended matter loadings obtained with the 47-mm Nuclepore filters.

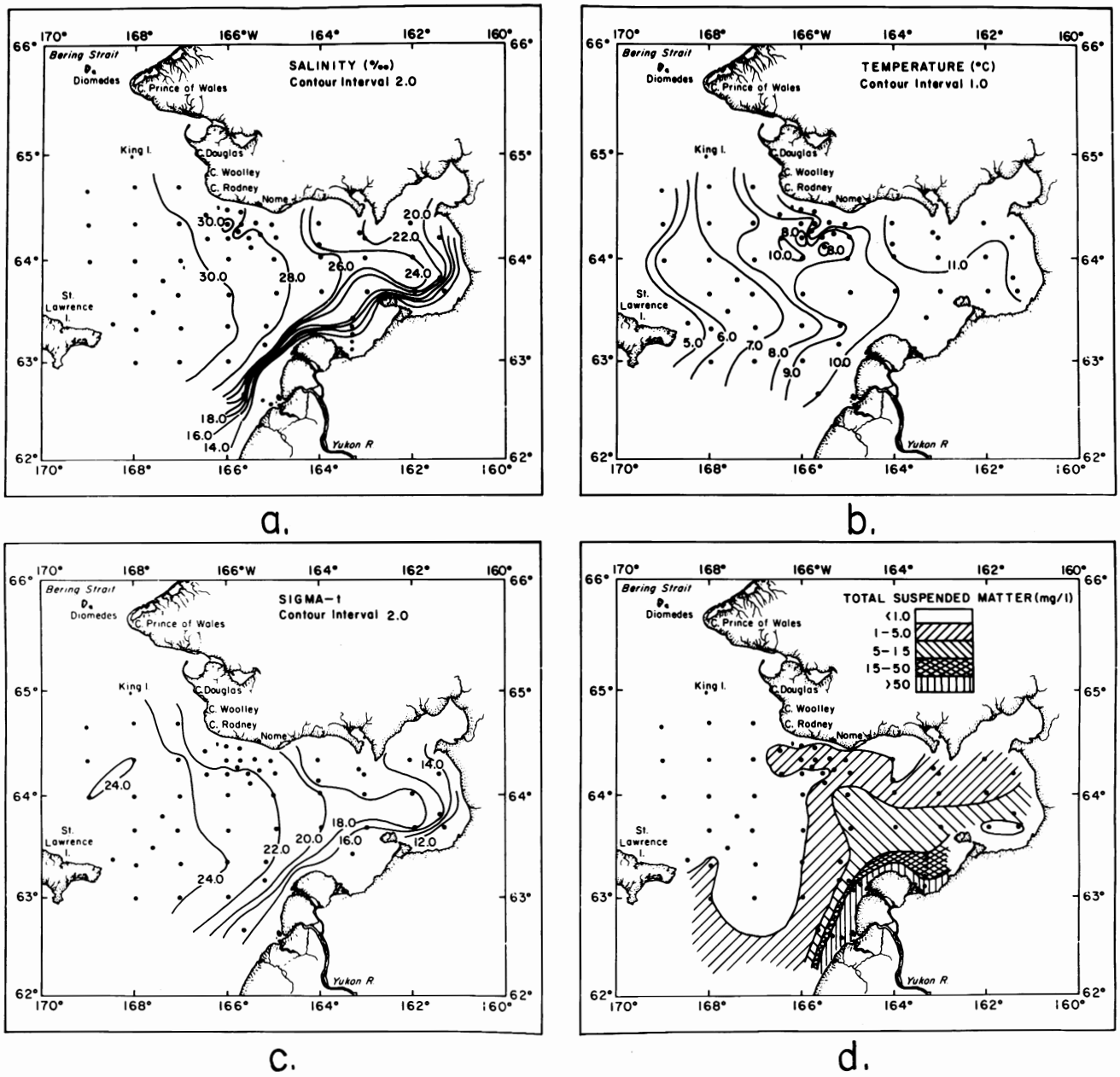

Figure 20-3. Distribution of: (a) salinity (b) temperature (c) sigma-t (d) total suspended matter at the surface in Norton Sound, 7-18 July 1979.

RESULTS AND INTERPRETATIONS

Distribution and transport of suspended matter

Figs. 20-3 and 20-4 show the distributions of salinity, temperature, sigma-t, and total suspended matter at the surface and 5 m above the bottom for the July 1979 cruise in Norton Sound. As shown in Fig. 20-3, surface distributions of particulate matter were dominated by the discharge of sedimentary material from the Yukon River. Surface concentrations of suspended matter were highest near the mouth of the Yukon River, where values ranging between 100 and 154 mg/l were observed. The Yukon River plume (as indicated by the 5.0-mg/l isopleth) extended to the north and northeast across the length of the sound. Another portion of the plume with lesser concentrations of suspended matter (1.0-2.7 mg/l) extended north and northwest to a point about 20 km southwest of Cape Rodney. Both portions

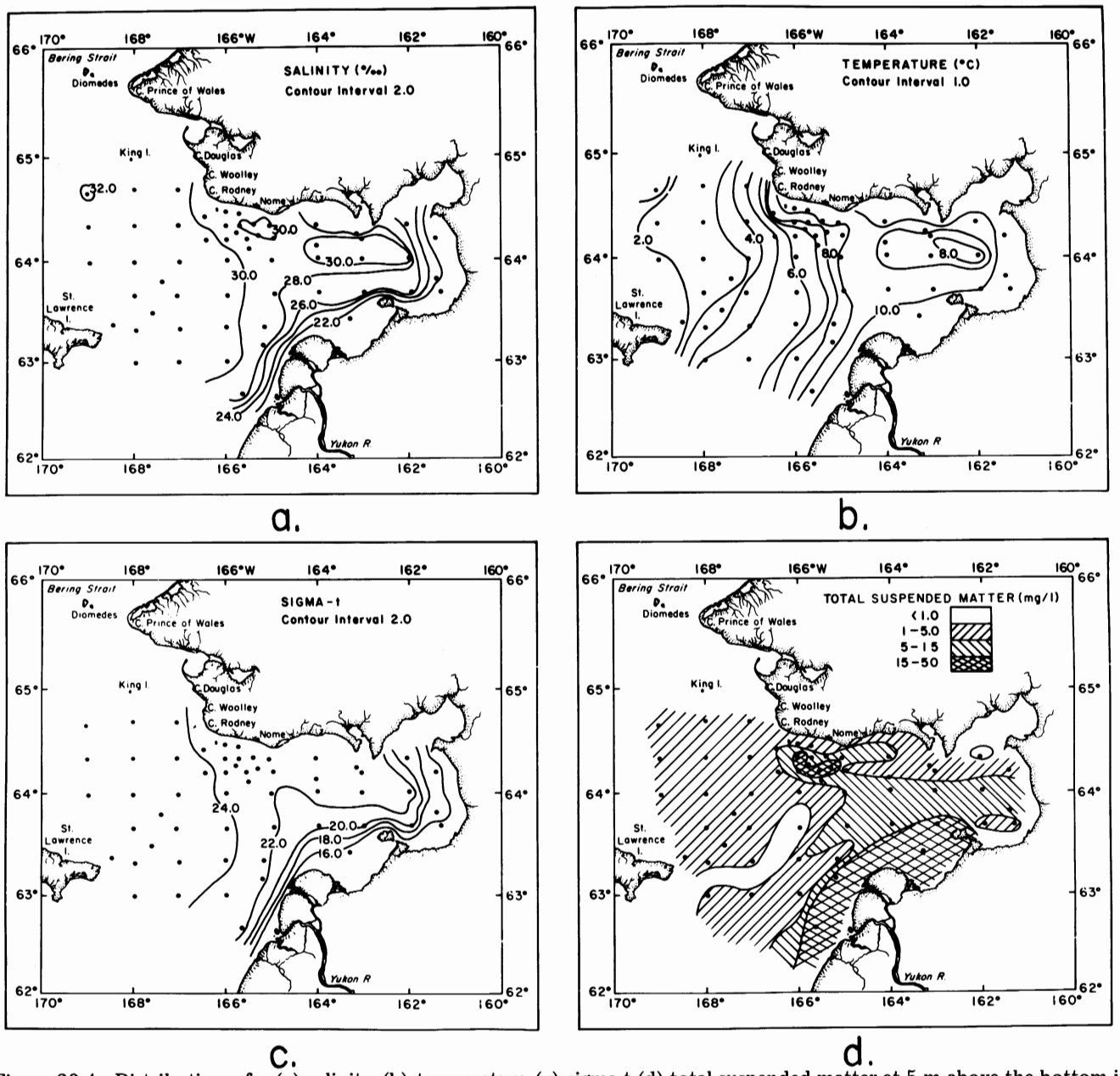

Figure 20-4. Distribution of: (a) salinity (b) temperature (c) sigma-t (d) total suspended matter at 5 m above the bottom in Norton Sound, 7-18 July 1979.

appear to have originated from the Yukon River, and their trajectories tend to follow the general pattern of cyclonic circulation in the sound (i.e., Yukon River material enters the sound from the southwest, is transported north and northeast around the inside perimeter of the sound, and exits from the northwest). These data are supported by the salinity and temperature measurements, which indicated movements of low-salinity (12-24°/oo), relatively warm (10-11 C) water to the northeast along the coast. These results are consistent with the general conclusions of Sharma et al. (1974) from suspended matter data obtained in August 1973. They are also consistent with dispersal patterns of the Yukon River plume inferred from LANDSAT satellite photographs (Nelson et al. 1975). For example, Fig. 20-5 shows a LANDSAT photograph of the Yukon River plume taken on 20 July 1979. The plume, which appears in lighter grey tones than the less turbid water, can be traced as far north as approximately 70 km from the Yukon River Delta and as far east as 50 km from Stuart Island. These features are also consistent with the data of Cacchione and Drake (1979) from surveys made during quiescent periods in September 1976 and July 1977. Thus, it appears that the transport processes described above predominate throughout

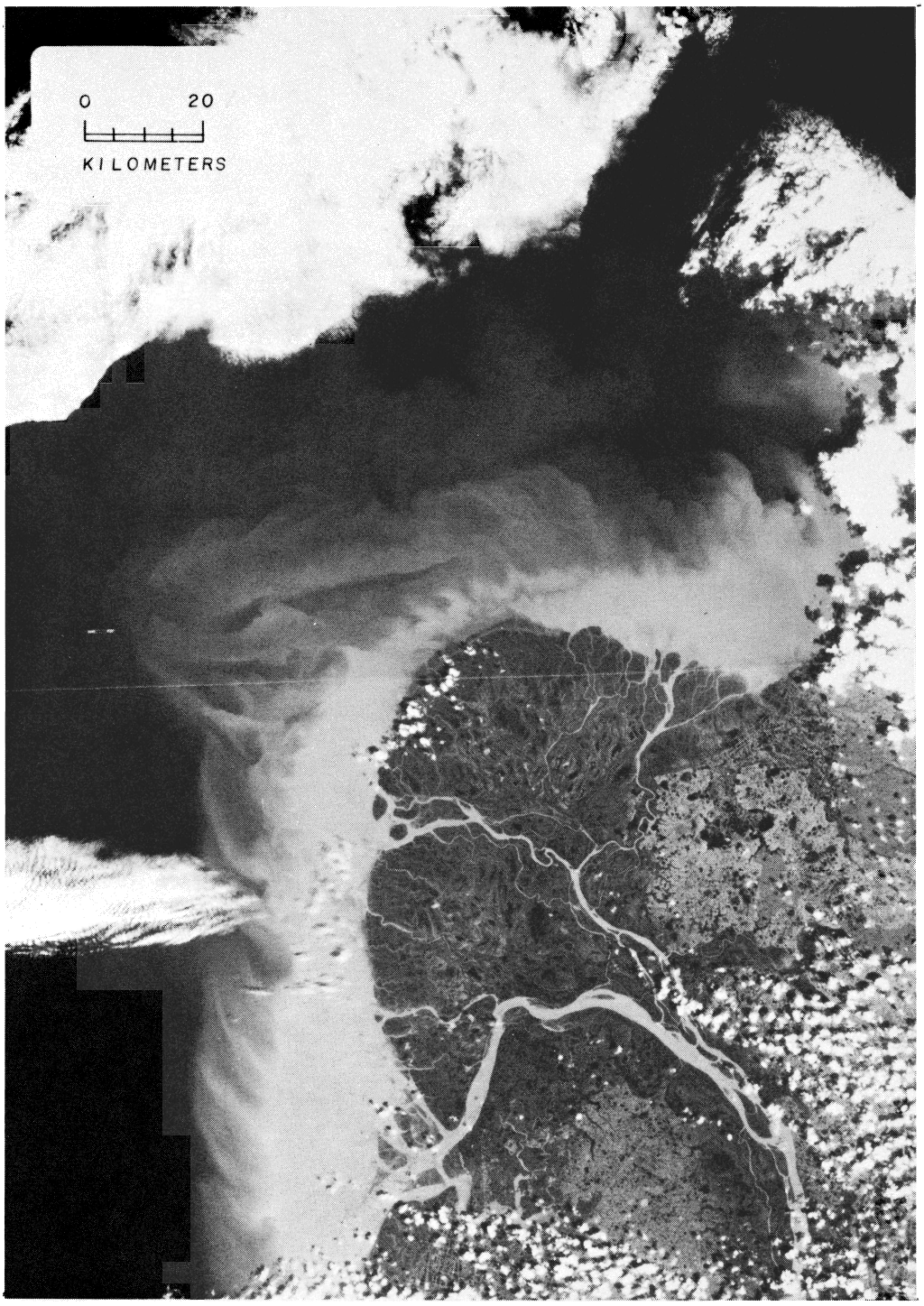

Figure 20-5. MSS Band 5 of LANDSAT images E-21640-21360-5 and E-21640-21363-5 taken on 20 July 1979, showing evidence of transport of suspended matter (appearing lighter in tone than the less turbid water) into Norton Sound.

the region, at least during periods of calm weather in the summer.

The near-bottom distribution of salinity, temperature, and total suspended matter also gives evidence of cyclonic movement of low-salinity (20-22°/oo), warm (~10 C) water to the northeast along the coast. This water mass can be traced as far north as Cape Darby. Near-bottom concentrations of suspended matter were highest near the mouth of the Yukon River and in the region about 20-30 km south-southwest of Nome. The near-bottom plume just seaward of the Yukon River extended to the northeast along the coast in a manner very similar to the surface plume. The near-bottom concentrations were

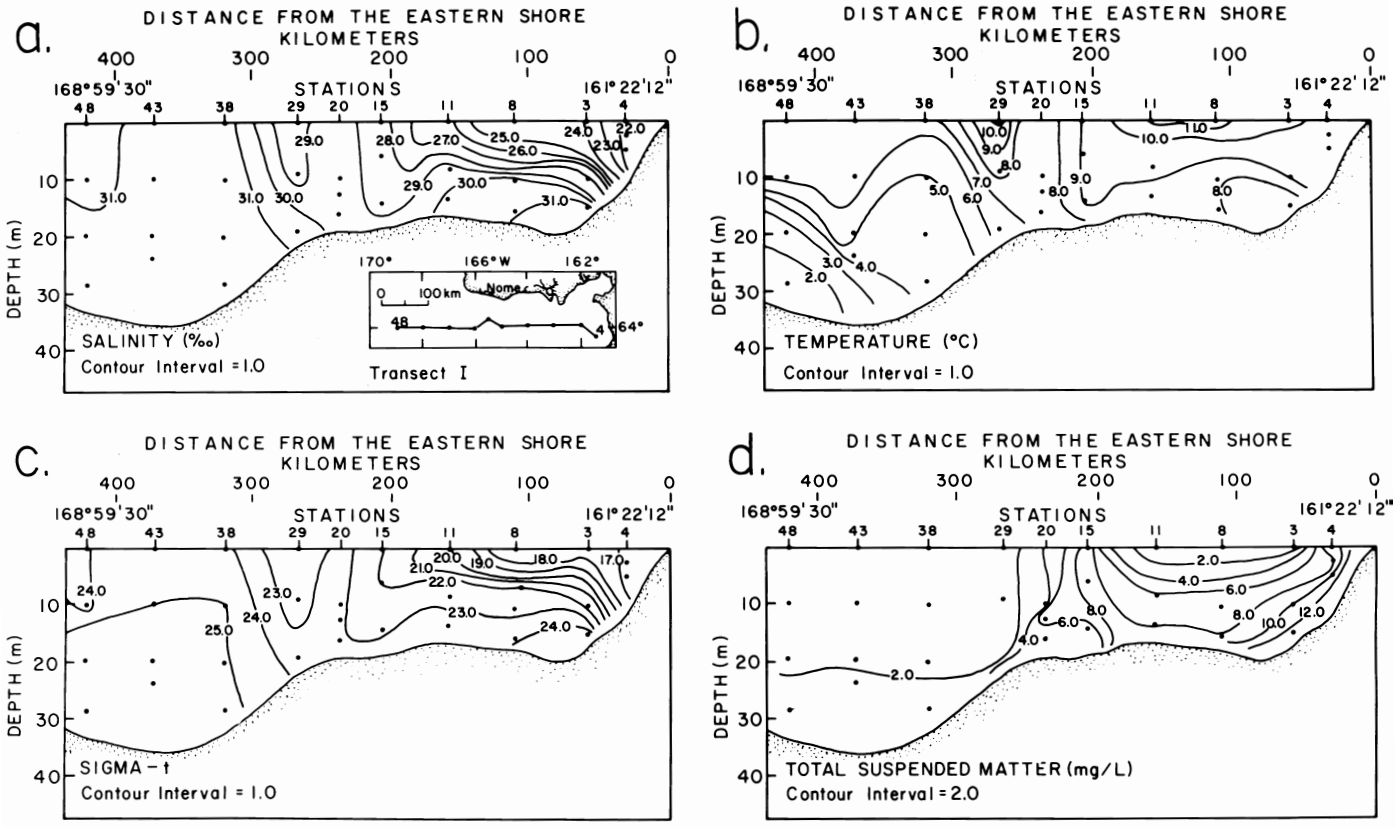

Figure 20-6. Vertical cross section of the distribution of: (a) salinity (b) temperature (c) sigma-t (d) total suspended matter for transect I in Norton Sound.

generally higher than surface concentrations, indicating that: (1) some fraction of the Yukon River material had settled to the near-bottom region during transit, and/or (2) a portion of the bottom sediments had been resuspended and remained in suspension.

Figs. 20-6 and 20-7 show cross sections of total suspended matter, salinity, temperature, and sigma-t for two east-west transects across the length of Norton Sound. Transect I is near the middle of the sound and Transect II is in the northern half, approximately 20-30 km from the coast. The two transects show very similar water mass characteristics. On the eastern side of the sound, both transects showed evidence of a two-layer system with the pycnocline varying in depth between 8 and 14 m (e.g., Stations 3 and 8 from Transect I and Stations 1, 9, and 10 from Transect II). Concentrations of suspended matter in this region showed a steady increase from about 6-8 m to the bottom. In the middle region (Stations 15, 20, and 29 of Transect I and Stations 22, 25, 27, and 39 of Transect II), the water column was virtually unstratified and concentrations of suspended matter increased to values greater than 30 mg/l in the near-bottom waters (e.g., Station 25 in Transect II). These water properties suggest that there is a tidally induced frontal zone with intense enough vertical mixing to break down the stability structure, with subsequent resuspension of sediments throughout the water column in some locations. This feature has the same characteristics as the anomalous plume of suspended matter described by Sharma et al. (1974) from data obtained in August 1973 at the same location. These data support the general conclusion of Cacchione and Drake (1979): during quiescent periods in the sound, resuspension of bottom sediments occurs as a result of increased tidal mixing during spring tide.

Further seaward, the water column was moderately stratified and concentrations of suspended matter decreased to values below 0.5 mg/l in surface waters. In near-bottom waters, however, concentrations of suspended matter were generally greater than 2.0 mg/l. The enriched concentrations of suspended matter near the bottom were probably caused by a combination of factors, including advective transport of particle-laden water to the northwest from

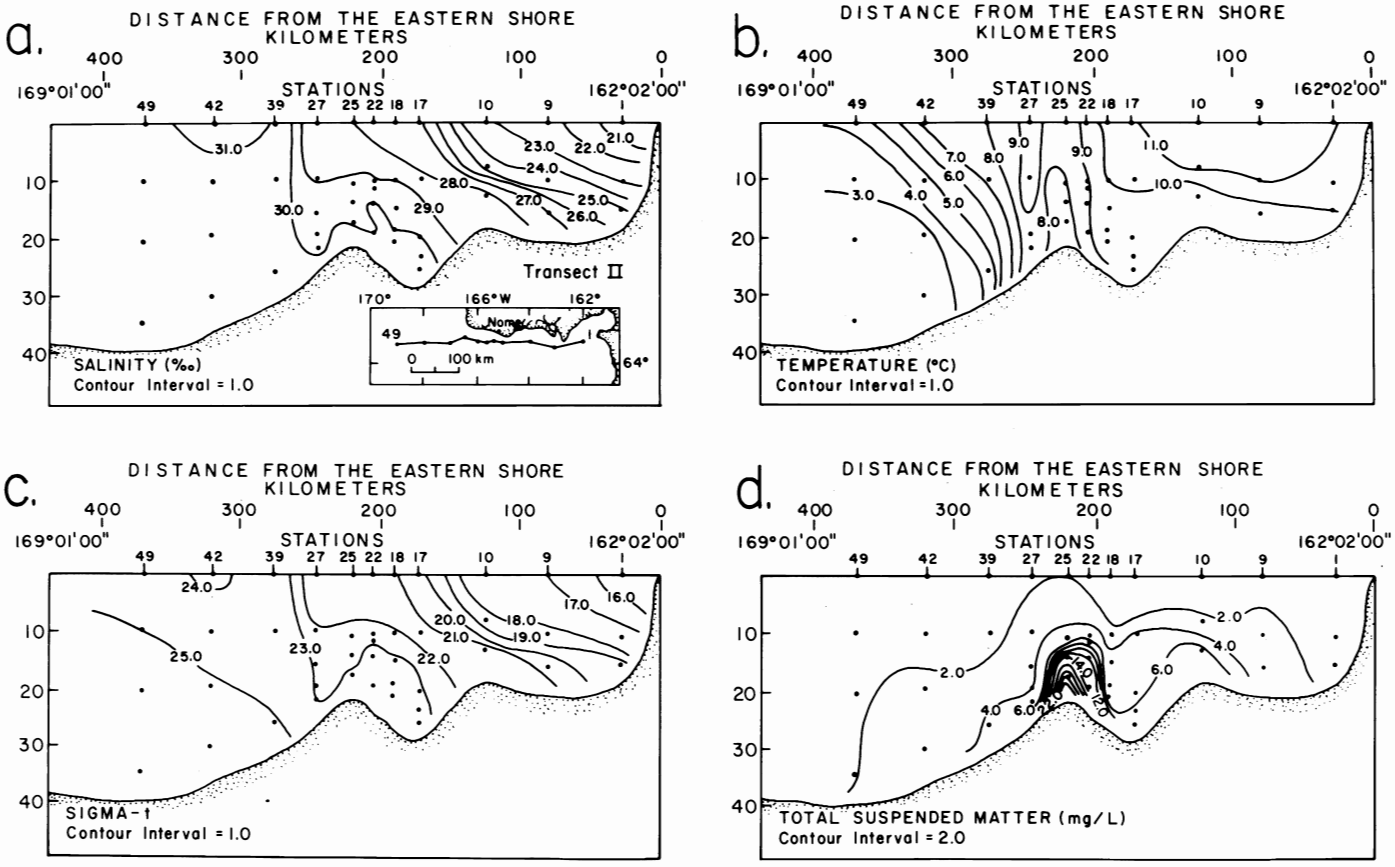

Figure 20-7 Vertical cross section of the distribution of: (a) salinity (b) temperature (c) sigma-t (d) total suspended matter for Transect II in Norton Sound.

within Norton Sound (Muench et al., Chapter 6, this volume) and local resuspension of bottom sediments.

Particulate elemental composition

In order to determine regional variations of the chemical composition of suspended material in Norton Sound, the particulate samples from the July 1979 cruise were analyzed for their major and trace element content by the methods described previously. The resulting data have been separated into five regions: Yukon River estuary with salinities of less than 15°/oo, Yukon River estuary with salinities between 15 and 25°/oo, eastern Norton Sound, central Norton Sound, and western Norton Sound/northeastern Bering Sea shelf. The averaged chemical data, along with published data for the Yukon River, are given in Tables 20-1 and 20-2. Table 20-3 shows C/N and element/Al ratios for the averaged data.

The elemental concentrations and elemental ratios illustrate some differences in composition between the suspended material discharged from the Yukon River and suspended matter in the sound. These differences can be viewed in terms of relative percentages of aluminosilicate and organic matter. Since most of the aluminum in marine particulate matter is in aluminosilicate material (Sackett and Arrhenius 1962), the Al concentrations in the suspended matter multiplied by 10 can be used to estimate percentages of aluminosilicate in the particulate matter. Similarly, Gordon (1970) suggested that particulate carbon multiplied by a factor of 1.8 may be used to estimate the amount of organic material in the suspended matter. On the basis of the particulate Al and particulate C concentrations, the composition of the suspended matter from the Yukon River estuary was determined to be approximately 88 percent aluminosilicate material and 6 percent organic matter. In like manner, samples from eastern and central Norton Sound are determined to contain about the same percentage of aluminosilicate material (88-92 percent). These results illustrate the predominance of the detrital

TABLE 20-1

Comparison of the elemental composition of suspended material from the Yukon River with the composition of suspended material collected from the near-shore regions seaward of the mouths of the Yukon River distributaries. (Samples collected 11 and 12 July 1979.[1])

Sample Description	No. of Samples	C[4] Wt. % ±1σ	N[4] Wt. % ±1σ	Mg Wt. % ±1σ	Al Wt. % ±1σ	Si Wt. % ±1σ	K Wt. % ±1σ	Ca Wt. % ±1σ	Ti Wt. % ±1σ	Cr ppm ±1σ	Mn ppm ±1σ	Fe Wt. % ±1σ	Ni ppm ±1σ	Cu ppm ±1σ	Zn ppm ±1σ
Yukon River Suspended Material															
Yukon River at Klakanak[2]										147	1079	5.4	109	320	
Yukon River at Pilot Station[3]		0.24-3.8								48	788-1308	3.1-4.3		24-148	49-142
Yukon River Estuary															
Surface Samples (0-15°/oo)	6	2.9 ±0.6	0.2 ±0.04	2.3 ±0.7	8.2 ±1.3	30.6 ± 1.9	2.2 ±0.3	1.5 ±0.2	0.50 ±0.06	110 ± 15	992 ± 131	5.5 ±0.8	59 ± 8	59 ± 8	171 ± 49
Yukon River Estuary															
Surface Samples (15-25°/oo)	6	4.2 ±1.2	0.4 ±0.8	3.1 ±0.8	9.3 ±1.8	31.5 ± 3.7	2.1 ±0.2	1.6 ±0.03	0.52 ±0.03	129 ± 15	1299 ± 192	5.81 ±0.4	60 ± 5	61 ± 10	193 ± 30

[1] Surface samples collected with precleaned polyethylene bottles. Standard deviations are given only for data obtained during a single sampling event wherever applicable.

[2] Data from Gibbs (1977)

[3] Water Resources Data (1976-77) U.S. Geological Survey

[4] Weight percentages of C and N were determined using two different filter types (Selas silver filters and Nuclepore filters) and, therefore, are subject to a greater number of errors than the data obtained for the inorganic elements, which were obtained from a single filter type.

TABLE 20-2

Summary of the elemental composition of suspended material collected from selected locations in Norton Sound and northeastern Bering Sea shelf. (Samples were collected 7-18 July 1979.[1])

Sample Description	No. of Samples	C[2] Wt. % ±1σ	N[2] Wt. % ±1σ	Mg Wt. % ±1σ	Al Wt. % ±1σ	Si Wt. % ±1σ	K Wt. % ±1σ	Ca Wt. % ±1σ	Ti Wt. % ±1σ	Cr ppm ±1σ	Mn ppm ±1σ	Fe Wt. % ±1σ	Ni ppm ±1σ	Cu ppm ±1σ	Zn ppm ±1σ
Eastern Norton Sound															
Surface	7	15.4 ± 5.8	2.4 ±0.9	3.1 ±0.5	9.2 ±1.4	30.1 ± 3.7	1.7 ±0.3	1.4 ±0.3	0.44 ±0.06	199 ± 59	2346 ± 845	5.3 ±0.6	52 ± 8	60 ± 9	201 ± 41
5 m above bottom	7	10.1 ± 6.2	1.1 ±0.8	2.9 ±0.5	9.1 ±1.3	31.0 ± 2.7	2.0 ±0.2	1.4 ±0.2	0.53 ±0.08	144 ± 38	2182 ± 682	5.7 ±0.4	57 ± 5	62 ±10	276 ±289
Central Norton Sound															
Surface	18	14.6 ± 8.6	1.9 ±1.1	3.3 ±0.7	9.0 ±1.7	30.8 ± 4.8	1.7 ±0.4	1.7 ±0.2	0.48 ±0.08	148 ± 36	2672 ±1104	5.4 ±0.8	59 ±21	61 ±12	246 ± 90
5 m above bottom	18	5.6 ± 3.6	0.7 ±0.5	3.0 ±0.6	8.8 ±1.2	32.4 ± 2.5	2.0 ±0.2	1.6 ±0.6	0.54 ±0.06	138 ± 27	1797 ± 287	5.8 ±0.6	57 ± 7	58 ± 6	196 ± 65
Western Norton Sound/northeastern Bering Sea Shelf															
Surface	18	25.6 ± 6.8	4.0 ±0.9	0.9 ±0.7	3.2 ±1.4	20.0 ± 7.9	0.5 ±0.2	1.4 ±0.4	0.23 ±0.10	100 ± 93	2160 ±1392	2.3 ±0.9	29 ±17	50 ±39	194 ±111
5 m above bottom	18	12.3 ± 6.9	1.3 ±0.4	1.9 ±0.5	5.1 ±1.2	31.8 ± 3.5	0.9 ±0.3	1.2 ±0.2	0.31 ±0.07	81 ± 17	1506 ± 761	3.4 ±0.7	30 ±13	36 ±11	137 ± 60

[1] Samples were collected with 10-l Niskin Bottles.

[2] Weight percentages of C and N were determined using two different filter types (Selas silver filters and Nuclepore filters) and, therefore, are subject to a greater number of errors than the data obtained for the inorganic elements, which were obtained from a single filter type.

TABLE 20-3
Average C/N and element/Al ratios for suspended materials from the Yukon River estuary, Norton Sound, and northeastern Bering Sea Shelf

Sample Description	C/N	C/Al	N/Al	Mg/Al	Si/Al	K/Al	Ca/Al	Ti/Al	Cr/Al $\times 10^{-3}$	Mn/Al $\times 10^{-3}$	Fe/Al	Ni/Al $\times 10^{-3}$	Cu/Al $\times 10^{-3}$	Zn/Al $\times 10^{-3}$
Yukon River Estuary (0-15°/co)	14.5	0.35	0.02	0.28	3.73	0.27	0.18	0.06	1.34	12.1	0.66	0.72	0.72	2.08
Yukon River Estuary (15-25°/oo)	10.5	0.45	0.04	0.33	3.39	0.23	0.17	0.06	1.38	14.0	0.62	0.64	0.66	2.07
Eastern Norton Sound														
Surface	6.4	1.71	0.27	0.34	3.34	0.19	0.16	0.05	2.21	26.1	0.59	0.58	0.66	2.23
5 m above bottom	9.2	1.11	0.12	0.32	3.41	0.22	0.15	0.06	1.58	24.0	0.63	0.63	0.68	3.03
Central Norton Sound														
Surface	7.7	1.62	0.21	0.37	3.42	0.19	0.19	0.05	1.64	29.7	0.60	0.65	0.67	2.73
5 m above bottom	8.0	0.63	0.08	0.34	3.68	0.23	0.18	0.06	1.57	20.4	0.66	0.65	0.66	2.23
Western Norton Sound-northeastern Bering Sea shelf														
Surface	6.4	8.0	1.30	0.28	6.35	0.16	0.44	0.07	3.12	67.5	0.72	0.91	1.56	6.06
5 m above bottom	9.5	2.4	0.25	0.37	6.23	0.17	0.24	0.06	1.59	29.5	0.66	0.59	0.67	2.68

material from the Yukon River in the central and eastern regions of the sound. This finding is supported by the chemical data for Si, K, Ca, Ti, Fe, Ni, and Cu, which are at about the same levels of concentration in eastern and central Norton Sound as they are in the Yukon River estuary. Only C, N, Mn, and Zn show enrichments offshore. For C and N these enrichments are attributed to a relative increase in the concentration of marine organic matter in offshore waters, which is probably due to increased light penetration away from the zone of high turbidity. This conclusion is supported by the C/N ratios (Table 20-3), which show a general decrease seaward, indicating a transition from organic matter dominated by terrestrial material (C/N ratios ranging between 12 and 15) to organic matter dominated by material of marine origin (C/N ratios ranging between 6 and 9) (Loder and Hood 1972). Mn and Zn enrichments can be attributed to a number of processes which are discussed in detail later.

In the western Norton Sound/northeastern Bering Sea shelf region, the suspended matter was depleted in particulate Mg, Al, K, Ti, Fe, Ni, and Cu and enriched in particulate C and N relative to the Yukon River estuarine samples. The depletions are attributed to a drop in the relative amount of aluminosilicate material in the suspended matter (<52 percent by weight) and an increase in the proportion of marine organic matter (>40 percent by weight), which contains less Mg, Al, K, Ti, Mn, Fe, Ni, and Cu than aluminosilicate material (Martin and Knauer 1973). It is important to note, however, that on the average the samples from this region contain about 88 percent more Mn than the Yukon River estuarine samples. Similarly, Zn concentrations in the suspended matter from this region are about the same as in the estuarine samples even though there is a significant drop in relative amount of aluminosilicate material in the suspended matter. These findings indicate that Mn and Zn concentrations in the suspended matter are controlled by distinctly different chemical processes.

In an attempt to determine the chemical nature and source of the enriched Mn and Zn in the offshore suspended matter, selected surface and near-bottom samples were treated with 25 percent (v/v) acetic acid to separate poorly structured oxyhydroxides from the more crystalline phases. This procedure has been shown to selectively dissolve trace elements precipitated in acid-soluble metal oxides and those adsorbed onto mineral surfaces without affecting highly oxidized ferromanganese minerals or the lattice structure of clays (Hirst and Nicholls 1958, Chester and Hughes 1967, and Bolger et al. 1978). The results of these experiments are given in Table 20-4. The data show higher amounts of weak-acid-soluble Mn in the offshore samples than in the estuarine samples, which are significant at the $p < 0.05$ level. These higher amounts, computed by taking the differences between the offshore and estuarine samples as a ratio to the estuarine samples, range between 134 percent and 351 percent and

TABLE 20-4
Partitioning of Mn and Zn between weak-acid-soluble (WAS) and weak-acid-insoluble (WAI) fractions of suspended material from Norton Sound and northeastern Bering Sea Shelf (Data presented as a percentage of total suspended matter)

Sample location	No. of samples	WAS Mn ±1σ	WAI Mn ±1σ	WAS Zn ±1σ	WAI Zn ±1σ
Yukon River Estuary	3	0.066 ±0.017	0.052 ±0.006	0.0059 ±0.0028	0.0140 ±0.0031
Eastern Norton Sound	5	0.155 ±0.038	0.040 ±0.011	0.0095 ±0.0031	0.0099 ±0.0021
Central Norton Sound	9	0.184 ±0.085	0.054 ±0.017	0.0108 ±0.0056	0.0114 ±0.0026
Western Norton Sound	9	0.298 ±0.092	0.074 ±0.041	0.0107 ±0.0053	0.0125 ±0.0070

account for all of the excess Mn in the suspended matter. Similarly, the data for Zn in the weak-acid-soluble fraction show enrichments ranging between 61 percent and 83 percent in the offshore samples which are significant at the $p < 0.20$ level. These results indicate that in the offshore waters Mn and Zn are being concentrated in the weak-acid-soluble fraction of the particulate matter, which in these samples probably consists of poorly structured oxyhydroxides of Mn. The probable sources of this material will be discussed below.

DISCUSSION

Probable source of excess Mn in the suspended matter

There are several possible sources of the excess Mn in the suspended matter of Norton Sound. These include (1) differential settling of particles of various sizes; (2) resuspension of Mn-enriched sediments; and (3) reductive dissolution of Mn within recent sediments followed by oxidative precipitation of Mn onto particulate phases in the water column. The first mechanism is unlikely in view of Gibbs's (1977) data for the chemical variations in the various size-fractions of Yukon River suspended material. The mean particle size distribution of suspended material in the sound would have to be about an order of magnitude smaller (i.e., a decrease from an average size of about 20 μm to about 2 μm) for the two-to-threefold increases in total Mn to occur. Unless some unusual chemical interactions were occurring in the estuary, this would necessarily be accompanied by a similar enrichment of total Fe and Cu in the suspended matter. No enrichments of that magnitude were observed in the Fe and Cu data. Furthermore, the particle-size data of Cacchione and Drake (1979) indicate that suspended matter in Norton Sound is primarily composed of fine-to-medium silt in the range between 4 and 32 μm. These data indicate that if differential settling occurs in Norton Sound, it is definitely not of the magnitude required to produce the observed Mn enrichments in the suspended matter.

The resuspension mechanism can also be refuted using a similar argument. While the distributions of suspended matter indicated that bottom sediments were being resuspended, the Mn content of the bulk sediments has been reported to be only in the range of 600-1,650 ppm (Larsen et al. in press). This means that the Mn content of the resuspended material would have to exceed the concentration observed within the sediments by a factor of about 2-4 to account for the observed Mn concentrations in the suspended matter. This would occur only if the clay size-fraction of the sediments were being preferentially resuspended. Since the particle-size data of Cacchione and Drake (1979) do not show any evidence for a decrease of this kind, this mechanism does not seem likely.

Reduction of Mn after burial in recent sediments with accompanying upward transport of dissolved

Mn into the overlying water, followed by precipitation onto suspended matter best explains the observed data. Efflux of Mn from rapidly accumulating sediments has been reported for several estuarine and coastal environments (Elderfield 1976, Graham et al. 1976, Aller 1977, Trefry 1977, Yeats et al. 1979, and Massoth et al. 1979). From studies of the sediments extending seaward of the Mississippi River, Trefry (1977) found that Mn fluxes from recent sediments varied directly with sedimentation rate. High Mn fluxes (i.e., ~2.7 $\mu g/cm^2/d$) were observed in sediments that accumulate at a rate of about 2.0 $g/cm^2/yr$, whereas low Mn fluxes (0.71 $\mu g/cm^2/d$) were observed in sediments that accumulate at a rate of 0.08 $g/cm^2/yr$. In Norton Sound modern sediments with accumulation rates ranging from 0.05 to 0.17 $g/cm^2/yr$ cover an area of approximately 22,000 km^2 (Nelson and Creager 1977). Assuming an average sedimentation rate of 0.1 $g/cm^2/yr$ for these sediments and using linear interpolation of Trefry's (1977) Mn flux data (i.e., 0.68 $\mu g/cm^2/d$), approximately 1.5×10^8 g Mn would be released daily into Norton Sound from this source. At this rate it would require approximately 21 days to account for all of the estimated excess Mn in the particulate matter (approximately 3.1×10^9 g Mn, assuming a total area of 45,000 km^2, an average depth of 16 m, an average concentration of suspended matter of 4.0 mg/l, and an average concentration of excess Mn of 1,079 ppm). If it is assumed that the rate of Mn oxidation is fast relative to an accumulation time of 21 days, then contact periods approximately equal to this time would be required for the chemical interactions to occur. Circulation in the sound is not completely understood, but studies conducted in summer indicate relatively sluggish circulation (Muench et al., Chapter 6, this volume). Net currents, with speeds varying between 10 and 15 km/d in surface waters and between 1 and 4 km/d in deep water, have been measured for short periods of time. Using a mean current of 8 km/d and a mean travel distance of 400 km, it is estimated that about 50 days are required for water to pass through the sound—a little more than twice the time required for the Mn from the sediment to accumulate on the suspended matter. Thus, if the underlying assumption that the kinetic rate of Mn oxidation in coastal waters is relatively rapid is correct, then the sediments could easily be the major source of the excess Mn in the suspended matter. The assumption of a rapid rate for Mn oxidation is supported by the recent findings of Wollast et al. (1979), to the effect that Mn oxidation in the Rhine and Scheldt estuaries is essentially complete within 10 days and the process is mediated by several strains of marine bacteria indigenous to coastal environments.

Implication for the geochemistry of Zn in Norton Sound

This discussion of the geochemical behavior of Mn in the sound is also important for understanding the chemical behavior of Zn in the suspended matter. As noted earlier, both Zn and Mn are enriched in the weak-acid-soluble fraction of the particulate matter. This is probably due to adsorption and/or coprecipitation of Zn on or in the newly formed Mn oxyhydroxides. Fig. 20-8 shows a plot of the relationship between total Zn and total Mn and for both surface and near-bottom samples. The plot of total Zn versus total Mn is roughly linear (r = 0.60), indicating an association between these two metals in the particulate matter. These results suggest that as the Mn oxyhydroxides form on the particulate matter, Zn is scavenged from solution. In similar fashion, the relationship between weak-acid-soluble Zn and weak-acid-soluble Mn is also linear (r = 0.39). This process effectively concentrates Zn and Mn in the suspended matter, which eventually either settles to the bottom of the sound or is transported to the northwest into the northeastern Bering Sea shelf and beyond.

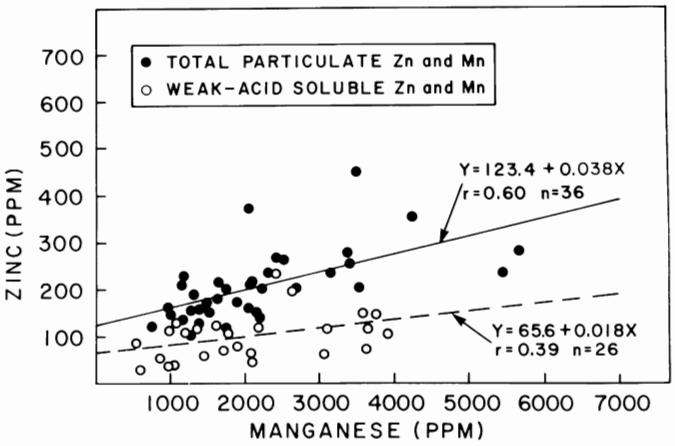

Figure 20-8. Plot of the relationships between total particulate Zn vs. total particulate Mn and weak-acid-soluble Zn vs. weak-acid-soluble Mn for selected surface and near-bottom samples from Norton Sound and northeastern Bering Sea shelf.

Implications for the geochemistry of suspended materials and sediments in regions beyond Norton Sound

The physical, chemical, and biological processes affecting the distribution and chemical composition

of suspended matter in Norton Sound and the northeastern Bering Sea shelf may also affect the composition of suspended materials and sediments in oceanic waters beyond the Bering Sea. As we stated earlier, the work of Nelson and Creager (1977) indicates that as much as one-third of the sediment load of the Yukon River bypasses the northern Bering Sea to accumulate in a thick deposit of Holocene sediment in the southern Chukchi Sea. These authors suggest that resuspension and transport of previously deposited sediments from Norton Sound during storms may contribute significantly to this phenomenon. Further support for this mechanism is indicated by the recent findings of Cacchione and Drake (1979) that more than 50 percent of the sediment transport in Norton Sound occurs during storm activity. Since the resuspended sediments in Norton Sound become enriched in Mn and Zn in oxygenated waters, it is reasonable to expect that the particulate matter will remain enriched in these metals until the particles are buried within the sediments and the recycling process is reinitiated in the reducing zone (Elderfield 1976). If it is further assumed, as suggested by Yeats et al. (1979), that the Mn precipitating in the water column will tend to be preferentially associated with small-sized particles, then the Mn and Zn content of the suspended material could be further enriched if some of the larger particles settle out. Therefore, Mn and Zn could be continually enriched in the particulate matter that is transported past the Bering Sea into the Chukchi Sea, where it forms a major fraction of the suspended matter and the recent sedimentary deposits. Thus, Mn and possible Zn recycling in the Chukchi Sea may be even more pronounced than in Norton Sound, because the incoming particulate materials are significantly enriched in these metals and the accumulation rates for recent sediments in the Chukchi Sea are as great as or greater than in Norton Sound (Naidu and Sharma 1972, Nelson and Creager 1977). If this is true, then Mn and Zn can undergo a number of recycling processes before they are ultimately buried in continental shelf, slope, or deep ocean sediments.

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