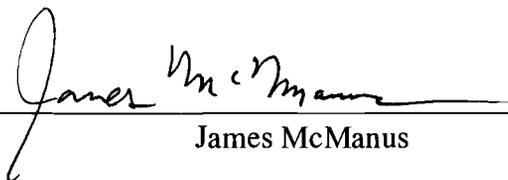


AN ABSTRACT OF THE DISSERTATION OF

Debbie Lee Colbert for the degree of Doctor of Philosophy in Oceanography
presented on July 1, 2004.

Title: Geochemical Cycling in a Pacific Northwest Estuary (Tillamook Bay,
Oregon, USA).

Abstract approved:



James McManus

This thesis investigates the behavior of major inorganic nutrients (P, N, Si), trace metals (Mn, Fe), and alkaline-earth metals (Ba) within Tillamook Bay over seasonal cycles and under a range of river discharge conditions from October 1997 through December 1999. Located in the Pacific Northwest region, Tillamook Bay is an ideal system for evaluating biogeochemical cycling along the river-estuary-ocean continuum and over seasonal cycles. The estuary experiences, on average, a 30-fold decrease in freshwater discharge from winter to summer due primarily to changes in precipitation. Additionally, the oceanography of this region is strongly influenced by the process of coastal upwelling.

Results presented here suggest that seasonal processes occurring at both the river and ocean end-members influence elemental estuarine behavior. Based on estuarine distributions and box model calculations, elemental behavior within the estuary is best explained by four factors: freshwater flushing time, biological uptake, interaction with suspended particulate material, and benthic regeneration. Freshwater flushing time, which is largely influenced by river discharge,

determines the amount of time for biological uptake, exchange with suspended particles, and interaction with the sediments. Superimposed on these estuarine processes is the seasonal influence of coastal upwelling on biogeochemical processes within the estuary.

The results of this research highlight the importance of estuarine processes in modifying the riverine flux of these elements to the ocean. This study also underscores the necessity of temporal sampling in evaluating processes controlling elemental distributions within estuaries and the delivery of land-derived material to the coastal ocean.

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Geochemical Cycling in a Pacific Northwest Estuary
(Tillamook Bay, Oregon, USA)

by
Debbie Lee Colbert

A DISSERTATION

submitted to

Oregon State University

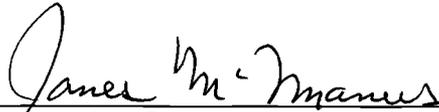
in partial fulfillment of
the requirement for the
degree of

Doctor of Philosophy

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Commencement June 2005

Doctor of Philosophy dissertation of Debbie Lee Colbert presented on July 1, 2004.

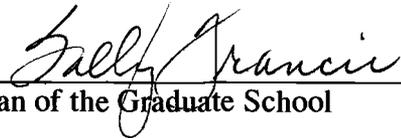
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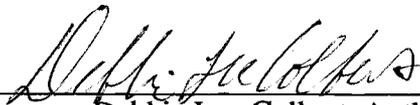


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I understand that my dissertation will become part of the permanent collection of Oregon State University libraries. My signature below authorizes release of my dissertation to any reader upon request.



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This work would not have been possible without funding from the Water and Watersheds Program of the U.S. Environmental Protection Agency (Grant R-825751-01). I also gratefully acknowledge funding from the NASA Space Grant Fellowship, P.F. Yerex and Nellie Buck Yerex Graduate Fellowship, and Richard Kobler Award.

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DEDICATION

This dissertation is dedicated to my mother and father:

Winona Passarello and Joseph E. Colbert.

One gave me the unconditional love that saw me through this challenge,
the other the stubbornness.

GEOCHEMICAL CYCLING IN A PACIFIC NORTHWEST ESTUARY (TILLAMOOK BAY, OREGON, USA)

1. INTRODUCTION

OVERVIEW

Estuaries host a complex mix of biogeochemical processes that can vary temporally and spatially within estuaries and often act as opposing or competing influences on elemental distributions (e.g., Hanor and Chan 1977; Morris et al. 1982; Balls 1992; Shiller 1997; Sin et al. 1999). This complex mix of processes, in turn, impacts the net transport of land-derived materials to the coastal ocean. Shifts in pH, ionic strength, and oxidation/reduction potential in estuaries and their associated sediments alter the adsorption characteristics of river particles and create new surfaces for scavenging, precipitation, and flocculation (Boyle et al. 1977; Mayer 1982; Morris et al. 1982; Fox et al. 1985; Millward 1995). Such biogeochemical processes can rearrange the physical partitioning of elements between the solid and dissolved states. Estuarine flushing rates, which are largely determined by river discharge, may further limit processes acting on land-derived materials within estuaries and ultimately how much material is delivered to the coastal ocean (Callaway and Specht 1982; Church 1986; Callaway et al. 1988; Balls 1994; Muller et al. 1994; Laslett and Balls 1995; Eyre and Twigg 1997).

While elemental cycling in estuaries has been the subject of extensive research (Sholkovitz 1976; Boyle et al. 1977; Hanor and Chan 1977; Li and Chan 1979; Correll et al. 1992; Eyre 1994; Howarth et al. 1996), few studies have

attempted to describe geochemistry along the river-estuary-ocean continuum, especially in areas subject to coastal upwelling (Callaway and Specht 1982; Mackas and Harrison 1997). Coastal processes such as upwelling can dramatically impact nutrient concentrations at the estuary-ocean interface (Stefansson and Richards 1963; Prego 1993; Nogueira et al. 1998; Perez et al. 2000). Wind-driven upwelling delivers nutrient-rich bottom waters to surface waters during spring and summer months (Strub et al. 1987; Chavez et al. 1991; Pennington and Chavez 2000). This nutrient source not only stimulates the growth of coastal phytoplankton communities (Chavez et al. 1991; Chavez 1996) but may also affect primary productivity within estuaries (Roson et al. 1995; Alvarez-Salgado et al. 1996; Perez et al. 2000) and ultimately carbon loading within estuaries (Perez 1993). While the influence of upwelling on nutrient biogeochemical budgets has been demonstrated for some estuarine systems, impacts on trace metals and alkaline-earth elements budgets have not been quantified.

The multiplicity of factors affecting the transformation and delivery of river-derived materials within estuaries makes it difficult to constrain their biogeochemical budgets. However, quantifying estuarine budgets provides necessary constraints for estimating the delivery of these materials to adjacent coastal waters.

SITE DESCRIPTION

Few studies have examined geochemical cycling of nutrients, trace elements, and other constituents in Pacific Northwest estuaries (Callaway and Specht 1982; De Angelis and Gordon 1985; Callaway et al. 1988; Sullivan et al.

2001; Klinkhammer and McManus 2001), particularly over seasonal timescales. The work described here focuses on a small ($\sim 34 \text{ km}^2$) Pacific Northwest estuary—the Tillamook Bay Estuary. This system is an ideal microcosm for evaluating biogeochemical cycling over the river-estuary-ocean continuum and the importance of seasonal variability, estuarine flushing rates, and coastal upwelling on elemental cycling. Tillamook Bay is located in the Pacific Northwest region roughly 60 km west of Portland, Oregon and approximately 80 km south of the Columbia River. The bay receives fresh water input from five rivers and exchanges ocean water through a single channel in the northwest corner of the Bay (Figure 1.1). Tillamook Bay experiences, on average, a 30-fold decrease in freshwater discharge from winter to summer caused primarily by changes in precipitation (Figure 1.2), resulting in estuarine flushing times of less than one day in winter and over a month in summer (Table 1.1).

Coastal upwelling also strongly influences the oceanography of the Pacific Northwest region in which Tillamook Bay is located. During the winter months from October to March the winds are dominantly from the south and southwest. During the summer months the winds reverse and come from the north and northwest due to prevailing high pressure off the coast of the Pacific Northwest (Strub et al. 1987; Strub et al. 1987). These north winds give rise to upwelling just off the Oregon Coast, which results in cool, nutrient-rich deep ocean water being brought to the surface (Huyer et al. 1979; Strub et al. 1987; Strub et al. 1987). This upwelled water is, in turn, responsible for the high ocean productivity of the region (Small and Menzies 1981).

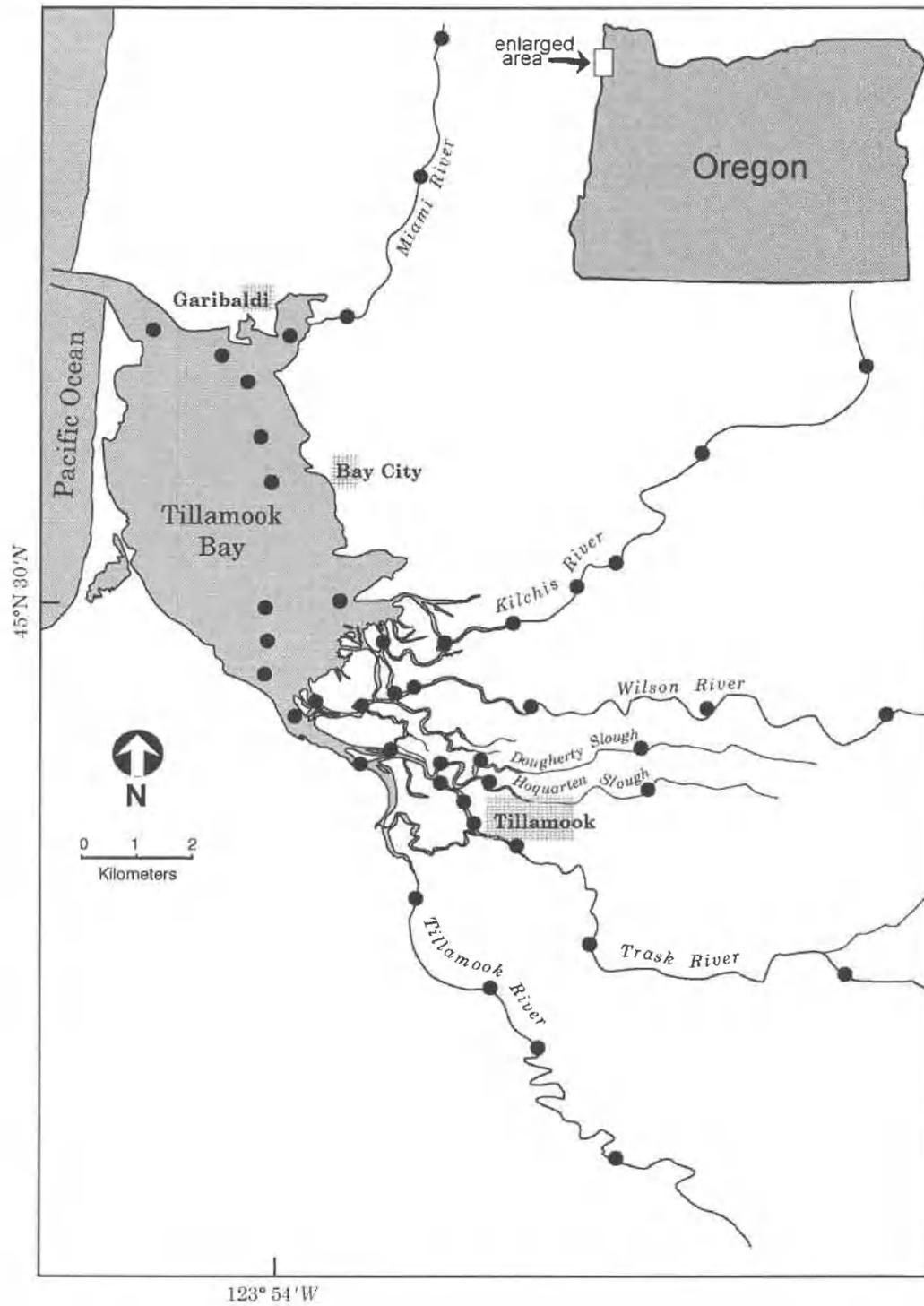


Figure 1.1. Map of the Tillamook Bay watershed identifying the location of sampling stations (●).

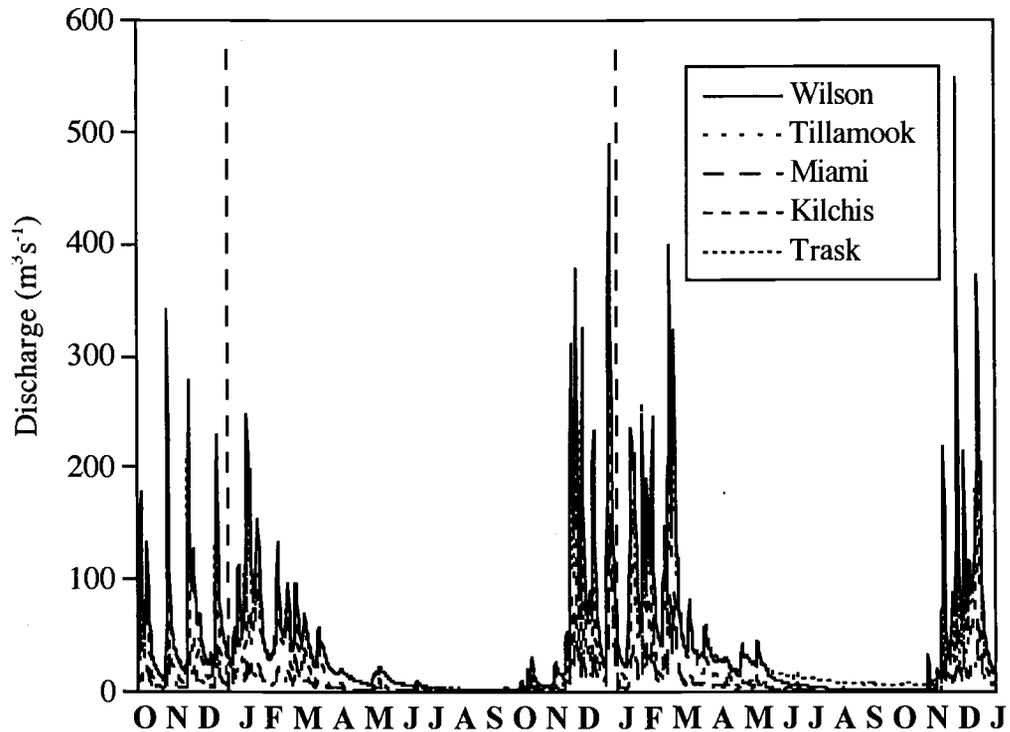


Figure 1.2. The record for daily streamflow measured for rivers entering Tillamook Bay between October 1997 through December 1999. Wilson and Trask River flow data are provided by USGS (<http://water.usgs.gov>). Data for Miami, Kilchis, and Tillamook Rivers between October 1997 through October 1998 are provided by Oregon Department of Environmental Quality (unpublished data). The daily flow record for the Miami, Kilchis, and Tillamook Rivers is not complete at the time of writing. Flows for these rivers for 1999 are calculated from mean daily flow in 1997 through 1998 records, normalized to flow measured in the Wilson River.

Table 1.1. Precipitation, estuarine flushing time, and river discharge data for Tillamook Bay and watershed (USGS: <http://water.usgs.gov>). River discharges shown in parentheses are estimated from 1997-1998 flow data normalized to Wilson River discharge data. Precipitation is reported as 7-day averages (Oregon Climate Service: <http://www.ocs.orst.edu>). Freshwater flushing times are calculated using the freshwater fraction method.

Sampling Dates	Discharge (m^3s^{-1})						Precipitation (in)	Flushing Time (d)
	Miami	Kilchis	Wilson	Trask	Tillamook	TOTAL		
10/11/97	14.84	49.41	91.47	84.11	23.17	263.00	0.81	1
11/29/97	12.09	47.71	69.10	58.91	15.05	205.97	0.63	3
1/10/98	9.48	26.03	50.69	47.01	10.40	143.61	0.35	2
2/7/98	7.90	36.42	32.85	31.72	6.23	115.12	0.30	3
3/22/98	8.36	26.19	37.95	32.85	10.15	115.50	0.29	5
4/11/98	3.53	4.21	17.56	19.03	3.36	47.69	0.17	7
5/23/98	4.42	8.37	19.51	18.75	7.19	58.24	0.34	7
6/24/98	2.25	0.67	5.92	6.74	1.91	17.49	0.12	17
7/12/98	1.66	4.15	3.96	4.67	0.56	15.00	0.00	27
8/26/98	0.66	2.01	1.93	2.72	0.45	7.77	0.00	34
10/17/98	2.23	5.10	12.26	7.93	1.95	29.47	0.32	12
11/29/98	(14.32)	(31.48)	81.84	67.40	(17.83)	(212.87)	1.14	2
1/2/99	(25.16)	(48.53)	80.43	75.61	(21.36)	(251.10)	1.08	1
2/27/99	(76.32)	(262.40)	308.69	224.29	(61.69)	(933.39)	1.55	1

Table 1.1. Continued.

Sampling Dates	Discharge (m^3s^{-1})						Precipitation (in)	Flushing Time (d)
	Miami	Kilchis	Wilson	Trask	Tillamook	TOTAL		
4/2/99	(7.66)	(22.03)	38.57	40.50	(7.70)	(116.40)	0.36	3
5/26/99	(5.27)	(3.13)	19.74	21.32	(6.00)	(55.46)	0.00	5
7/19/99	(1.53)	(0.30)	3.62	10.20	(0.27)	(15.91)	0.02	17
10/17/99	(0.31)	(0.66)	1.53	6.43	(0.38)	(9.31)	0.01	32
12/3/99	(23.57)	(88.12)	138.48	96.29	(28.97)	(375.43)	0.47	1

Recognizing that constraining elemental budgets and associated geochemical processes can be exasperated by anthropogenic loading of materials to estuarine and coastal waters, one of the initial objectives of this study was to ascertain the impact of anthropogenic activities on the estuary. The five major rivers that drain into Tillamook Bay drain part of the western slope of the northern Coast Range. The geologic rock formations contained within the Coast Range mountains consist primarily of Tertiary marine sediments and volcanic rocks that have accreted to the continent during plate subduction. While these rivers drain similar geologic terrain (Glenn 1978; McManus et al. 1998; Komar et al. in press), they differ markedly in the way each is influenced by local land use practices. The Trask River runs through the city of Tillamook whereas the Tillamook River, to the south, is heavily influenced by dairy farming activities. The rivers further to the north, the Wilson, Miami and Kilchis, experience progressively less urban and agricultural activities within their lower watersheds.

The Tillamook Watershed has undergone several changes in the extent and nature of anthropogenic activities within the watershed as a whole as well as within individual river basins. Dairy cowherd densities have increased significantly over the past decade (TBNEP 1998). Dairy farming activities within the watershed include confined animal feeding operations (CAFOs) and manure application. Each practice is associated with significant nutrient, suspended particulate matter (SPM), and organic carbon loading (Stewart 1997). The location and presumed impacts of these agricultural activities are not homogenous within the watershed. In fact, the Trask River alone accounts for 42% of the animal feeding operations with the

Wilson, Tillamook, Kilchis, and Miami Rivers accounting for 22%, 22%, 12% and 0% respectively (TBNEP 1998).

Tillamook County population has risen steadily since the 1990s (TBNEP 1998). This growth trend has significant implications for the amount of water delivered to the river system via wastewater treatment facilities, especially since winter storm events often lead treatment facilities to overflow or bypass normal treatment. In addition to discharging treated liquid waste into rivers and the estuary, wastewater treatment facilities dispose of wastewater solids by application to agricultural lands within the watershed. A total of 181 acres of biosolids are applied per year in the Tillamook Watershed, 99% of which are applied in the Tillamook River basin alone. Additional nutrient loading within the watershed occurs through failure of onsite septic systems. These septic systems are common throughout the watershed in areas outside the urban areas of Garibaldi, Bay City, and Tillamook. Failure rates among systems inspected have averaged between 6 to 7% since 1988 (TBNEP 1998). However, these failure rates may be conservative as failure rates increase during high precipitation events.

Similar to the agricultural and population growth trends for Tillamook County, the timber harvest industry is projected to increase in importance in the next 20-25 years as stands replanted after the Tillamook Burn fires (1933, 1939, 1945, and 1951) grow to harvestable age (TBNEP 1998). The patterns of land use described here highlight the range of human impacts within the watershed as well as the variability of those impacts among rivers.

RELATIONSHIPS BETWEEN ANTHROPOGENIC PROCESSES AND GEOCHEMISTRY

At the onset of this study, it was hypothesized that land use differences among catchment areas would be expressed as variations in water chemistry. However, despite contrasting land use patterns, there was surprisingly little river to river variability in the chemical composition of water entering the estuary. To evaluate the relationship between catchment characteristics and the geochemistry of river input to Tillamook Bay, each river catchment was digitized using ARC/INFO geographic information systems (GIS). The proportion of each land cover category (agricultural, forested, urban, and rural developed) was obtained by overlaying the GIS coverage of land cover category from the Tillamook Bay National Estuary Project (TBNEP) with the GIS coverage of the catchment boundary. Digitized catchment areas and each land use category as a proportion of the total land area are provided in Table 1.2. The number of confined animal feeding operations (CAFOs) located within each drainage area is reported in Table 1.2 and was estimated by overlaying the digitized GIS catchment boundaries with GIS coverage of CAFOs from the TBNEP.

Forested lands made up 92% of the total Tillamook Watershed area and accounted for 77% to 97% of the individual river drainage areas. Across the watershed, total catchment area and forested area were highly correlated ($r^2 = 0.99$, $n = 5$). Not surprisingly, the number of CAFOs and the extent of agricultural lands were also highly correlated across the watershed ($r^2 = 0.95$, $n = 5$). The Tillamook River catchment had the highest proportion of agricultural and rural residential

Table 1.2. Catchment area, land use, and number of confined animal feeding operations (CAFOs) for Tillamook Watershed and river drainages within the watershed based on digitized GIS coverages of land cover and permitted CAFOs obtained from the TBNEP.

Drainage	Catchment Area (km ²)	Proportion of total catchment area (%)					Number of CAFOs
		Agriculture	Forested	Rural Developed	Urban	Other	
Miami	93	4	95	2	0	0	2
Kilchis	167	1	96	1	0	2	3
Wilson	493	1	97	2	0	0	9
Trask	453	7	90	2	1	1	60
Tillamook	157	15	77	4	0	4	31
Watershed	1364	5	92	2	0	1	105

areas while the Trask River catchment had the only significant urban development though this was less than 1% of the catchment area.

For comparison with land use and catchment characteristics, average river concentrations of nutrients, metals, and other constituents were calculated using samples collected approximately monthly from October 1997 to December 1999 at stations distributed along the geographical extent of each river (Figure 1.1). Sample collection and analysis for each constituent is described in detail in subsequent chapters. For comparisons among rivers, average concentrations of each constituent were calculated by pooling all data from each river. Average river concentrations were compared to total catchment area and area of catchment composed of urban, agricultural, and forested lands and number of CAFOs. A statistical summary of these comparisons is provided in Table 1.3.

Despite some land use differences among rivers, there was little variability in the composition of water entering the estuary from the five rivers within the Tillamook Watershed. Only three of the 18 chemical constituents that were compared with land use and catchment characteristics displayed a significant relationship (i.e., $r^2 > 0.80$) (Table 1.3). pH levels were positively correlated with overall catchment size ($r^2 = 0.83$, $n = 5$), likely reflecting amount of time for precipitation-soil interactions. Phosphate concentrations within rivers were also positively correlated with total catchment area ($r^2 = 0.70$, $n = 5$) and with forested area within each catchment ($r^2 = 0.85$, $n = 5$). These relationships are consistent with riverine phosphorus generally being supplied from land drainage via soil leaching and mineral weathering (Meybeck 1993).

Within the Tillamook Watershed, nitrate concentrations exhibited a slightly negative correlation with total catchment area ($r^2 = 0.68$, $n = 5$). In a study of Oregon coastal streams, Wigington and others (1998) found a similar relationship between nitrate concentrations in streams and watershed size. They hypothesized that the primary source of nitrate in coastal streams was nitrogen fixation by alder stands. In the Tillamook Watershed, there was a strong negative correlation between river NO_3 concentrations and amount of forested area within each catchment ($r^2 = 0.83$; $n = 5$). While this relationship may reflect the extent of alder stands within forested areas, it cannot be teased out with available GIS data and warrants further study.

Other constituents did not display significant correlations with total catchment, land use, or number of CAFOs. In general, average concentrations of chemical constituents were also not significantly different among rivers (Tukey Multiple Run, $\alpha = 0.05$, $n = 5$). It is interesting to note that average concentrations of several constituents in the Tillamook River were significantly different from average concentrations of other rivers. Nitrite (NO_2^-), ammonium (NH_4^+), dissolved manganese (Mn), dissolved iron (Fe), and dissolved barium (Ba) concentrations were all significantly higher in the Tillamook River compared to other rivers (Tukey Multiple Run, $\alpha = 0.05$, $n = 5$). Mn content of suspended particulate material was also significantly higher in the Tillamook River water than other rivers (Tukey Multiple Run, $\alpha = 0.05$, $n = 5$). Conversely, silicic acid concentrations and pH values are significantly lower in the Tillamook River compared to other rivers (Tukey Multiple Run, $\alpha = 0.05$, $n = 5$). The unique chemical signature of Tillamook River water may result from a combination of

land use and geomorphology that cannot be deciphered by this dataset but warrants future study.

In general, land use and catchment characteristics did not exhibit a strong influence on the chemical signature of rivers within the Tillamook Watershed. As a result of this and the overall similarity in chemistry among rivers, input from the five rivers to the estuary could be modeled as a single river end-member in subsequent analyses.

SUMMARY

An initial goal of this study was to describe how anthropogenic activities modify riverine inputs to Tillamook Bay estuary and adjacent coastal ocean. Ultimately, I found that anthropogenic influence in this system is surprisingly small and, as I will show in later chapters, that natural oceanic variability may be leaving a larger fingerprint on the estuary. This thesis examines the distributions and partitioning of inorganic nutrients (P, N, Si), trace metals (Fe, Mn), and alkaline earth elements (Ba) in the Tillamook Bay estuary over seasonal cycles and river discharge conditions that can vary by a factor of 200. This study evaluates the importance of processes such as river discharge, freshwater flushing, internal estuarine processing, and coastal upwelling on elemental distributions in the Tillamook Bay estuary and, ultimately, their delivery to the coastal ocean. In Chapter 2, I describe the behavior of inorganic nutrients (P, N, Si) over seasonal cycles and under a range of river discharge conditions to evaluate the importance of processes such as freshwater flushing time, internal estuarine processing, and coastal upwelling in the Tillamook Bay estuary. In Chapter 3, I examine the

distributions of dissolved and particulate Mn and Ba in the Tillamook Bay estuary over seasonal cycles and quantify within-estuary material "processing" and the potential influence of within-estuary processes on seasonal fluxes to the coastal ocean. In Chapter 4, I describe dissolved and particulate Fe distributions within the Tillamook Bay estuary over seasonal cycles and under a range of river discharge conditions to quantify and identify the processes responsible for iron delivery to the coastal zone. In closing, Chapter 5 synthesizes my findings regarding biogeochemical processes affecting elemental distributions in the Tillamook Bay estuary, discusses the implications of these results, and suggests future work.

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2. NUTRIENT BIOGEOCHEMISTRY IN AN UPWELLING-INFLUENCED
ESTUARY OF THE PACIFIC NORTHWEST (TILLAMOOK BAY, OREGON,
USA)

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ABSTRACT

Located in the Pacific Northwest region, Tillamook Bay is a drowned river estuary which receives fresh water input from five rivers and exchanges ocean water through a single channel. Similar to other western U.S. estuaries, the bay exhibits a strong seasonal change in river discharge in which there is a pronounced winter maximum and summer minimum in precipitation and runoff. The behavior of major inorganic nutrients (P, N, Si) within the watershed are examined over seasonal cycles and under a range of river discharge conditions from October 1997 through December 1999. Monthly and seasonal sampling stations include transects extending from the mouth of each river to the mouth of the estuary as well as from 6-10 sites upstream along each of the five major rivers.

Few studies have examined nutrient cycling in Pacific Northwest estuaries. This study evaluates the distributions of inorganic nutrients to understand the net processes occurring within this estuary. Based on this approach, we hypothesize that nutrient behavior in the Tillamook Bay estuary can be explained by two dominant factors: freshwater flushing time and biological uptake and regeneration. Superimposed on these two processes is seasonal variability in nutrient concentrations of coastal waters via upwelling. Freshwater flushing time determines the amount of time for the uptake of nutrients by phytoplankton, exchange with suspended particles, and interaction with the sediments. Seasonal coastal upwelling controls the timing and extent of oceanic delivery of nutrients to the estuary. We suggest that benthic regeneration of nutrients is also an important process within the estuary that occurs seasonally and is dominated by the flushing characteristics of the estuary. Silicic acid, nitrate, and ammonium supply to the bay

appears to be dominated by riverine input. Phosphate supply is dominated by river input during periods of high river flow (winter months) with oceanic input via upwelling and tidal exchange important during other times (spring, summer, and fall months). Departures from conservative mixing indicate that internal estuarine sources of dissolved inorganic phosphorus and nitrogen (NH_4^+) are also significant over an annual cycle.

INTRODUCTION

Estuaries host a complex mix of biogeochemical processes that can vary temporally and spatially within estuaries and often act as opposing or competing influences on nutrient distributions within estuaries (Balls 1992; Sin et al. 1999). This complex mix of processes, in turn, impacts the net transport of land-derived nutrients to the coastal ocean. For example, phosphorus may be added to or removed from an estuarine water column via particle interaction (Fox et al. 1985; Froelich 1988; Lebo 1990), biological processes (Meybeck et al. 1988; Conley et al. 1995), or benthic exchange (Callender 1982; Callender and Hammond 1982; Zwolsman 1994). In addition to biological removal and regeneration (Kemp and Boynton 1984), nitrogen transformation through nitrification (Balls et al. 1996) and denitrification (Seitzinger 1988; Eyre and Twigg 1997) makes nitrogen processing within estuaries more difficult to quantify than phosphorus. Dissolved silica often displays conservative mixing behavior in estuaries (Balls 1992) but can exhibit removal via chemical precipitation (Liss and Spencer 1970; Morris et al. 1981) or biological uptake (Anderson 1986; Balls 1994) and input via regeneration from bottom sediments (Callender and Hammond 1982; D'Elia et al. 1983).

Freshwater flushing time may control the extent to which nutrient compositions are modified by internal processes by limiting the amount of time for nutrient uptake by phytoplankton, exchange with suspended particles, and interaction with the sediments. For example, Balls (1994) demonstrated that flushing time was a dominant feature controlling the degree of nutrient modification in nine estuaries feeding the North Sea. Other studies have also concluded that the distribution of dissolved nutrients is a function of freshwater flushing time (Callaway and Specht 1982; Nielsen et al. 1995; Eyre and Twigg 1997; Sin et al. 1999). In this manner, estuarine flushing rates, which are largely determined by river discharge, may set limits on how long processes can act on nutrients delivered by rivers and ultimately how much nutrient is delivered to the coastal ocean.

The multiplicity of factors affecting the transformation and delivery of nutrients within estuaries makes it difficult to constrain their biogeochemical budgets. However, developing estuarine budgets is fundamental to estimating the delivery of land-derived nutrients to adjacent coastal waters. Attempts to constrain nutrient budgets can be further exasperated by anthropogenic loading of nutrients to estuarine and coastal waters. Input from agricultural and urban runoff and from sewage outfalls can elevate phosphorus and nitrogen concentrations in estuarine and coastal waters (Correll et al. 1992; Wahl et al. 1997; Carpenter et al. 1998; Moreau et al. 1998). Such changes in nutrient loading can further lead to environmental perturbations such as water column hypoxia, toxic algal blooms, and shifts in coastal phytoplankton communities (Pearl 1988; Turner and Rabalais 1994; Justic et al. 1995; Justic et al. 1995; Humborg et al. 2000). For these reasons,

nutrient cycling in estuaries has been the subject of extensive research (e.g. Correll et al. 1992; Eyre 1994; Howarth et al. 1996; Wahl et al. 1997; Dauer et al. 2000).

While most studies address nutrient cycling from the perspective of processes occurring within the estuary or from the perspective of anthropogenic perturbations to estuaries, several studies have also considered the influence of the coastal ocean on estuarine cycling (Cloern 1979; De Angelis and Gordon 1985; Prego 1993; Alvarez-Salgado et al. 1996; Mackas and Harrison 1997; Nogueira et al. 1998). However, few studies have attempted to describe nutrient geochemistry along the river-estuary-ocean continuum, especially in areas subject to coastal upwelling (Callaway and Specht 1982; Mackas and Harrison 1997). Coastal processes such as upwelling can dramatically impact nutrient concentrations at the estuary-ocean interface (Hutchings et al. 1995). Under eastern boundary upwelling regimes, wind driven upwelling delivers nutrient-rich bottom waters to surface waters during spring and summer months (Strub et al. 1987; Chavez et al. 1991; Pennington and Chavez 2000). This nutrient source not only stimulates the growth of coastal phytoplankton communities (Chavez et al. 1991; Chavez 1996), but may also affect primary productivity within estuaries (Roson et al. 1995; Alvarez-Salgado et al. 1996; Perez et al. 2000).

Here, we examine the behavior of major inorganic nutrients (P, N, Si) over seasonal cycles and under a range of river discharge conditions to evaluate the importance of processes such as freshwater flushing time and coastal upwelling on nutrient cycles in the Tillamook Bay estuary. Our approach to describing the distributions of these elements within the estuary relies on traditional, descriptive data as there is limited information available for this and other Pacific Northwest

estuaries. Nevertheless, this approach can be used to gain an understanding of net processes such as biological uptake or regeneration and benthic inputs that may be occurring within the estuary. Moreover, Tillamook Bay is an ideal microcosm to evaluate the effect of freshwater flushing time on the distribution of nutrients within an estuary. It experiences, on average, a 30-fold decrease in freshwater discharge from winter to summer due primarily to changes in precipitation. Additionally, the oceanography of this region is strongly influenced by the process of coastal upwelling. The contribution of nutrient fluxes to the estuary via coastal upwelling is compared to riverine input to demonstrate the relative importance of these processes on nutrient concentrations in the estuary.

METHODS

Site Description

Tillamook Bay is located in the Pacific Northwest region roughly 60 km west of Portland, Oregon and approximately 80 km south of the Columbia River. Tillamook Bay is a drowned river estuary which receives fresh water input from five rivers and exchanges ocean water through a single channel in the northwest corner of the Bay (Figure 2.1). The five rivers feeding the bay drain similar geologic terrain (Glenn 1978; McManus et al. 1998). Approximately 10 km long and 3.4 km wide, the Bay averages only 2 meters in depth over a total area of 34

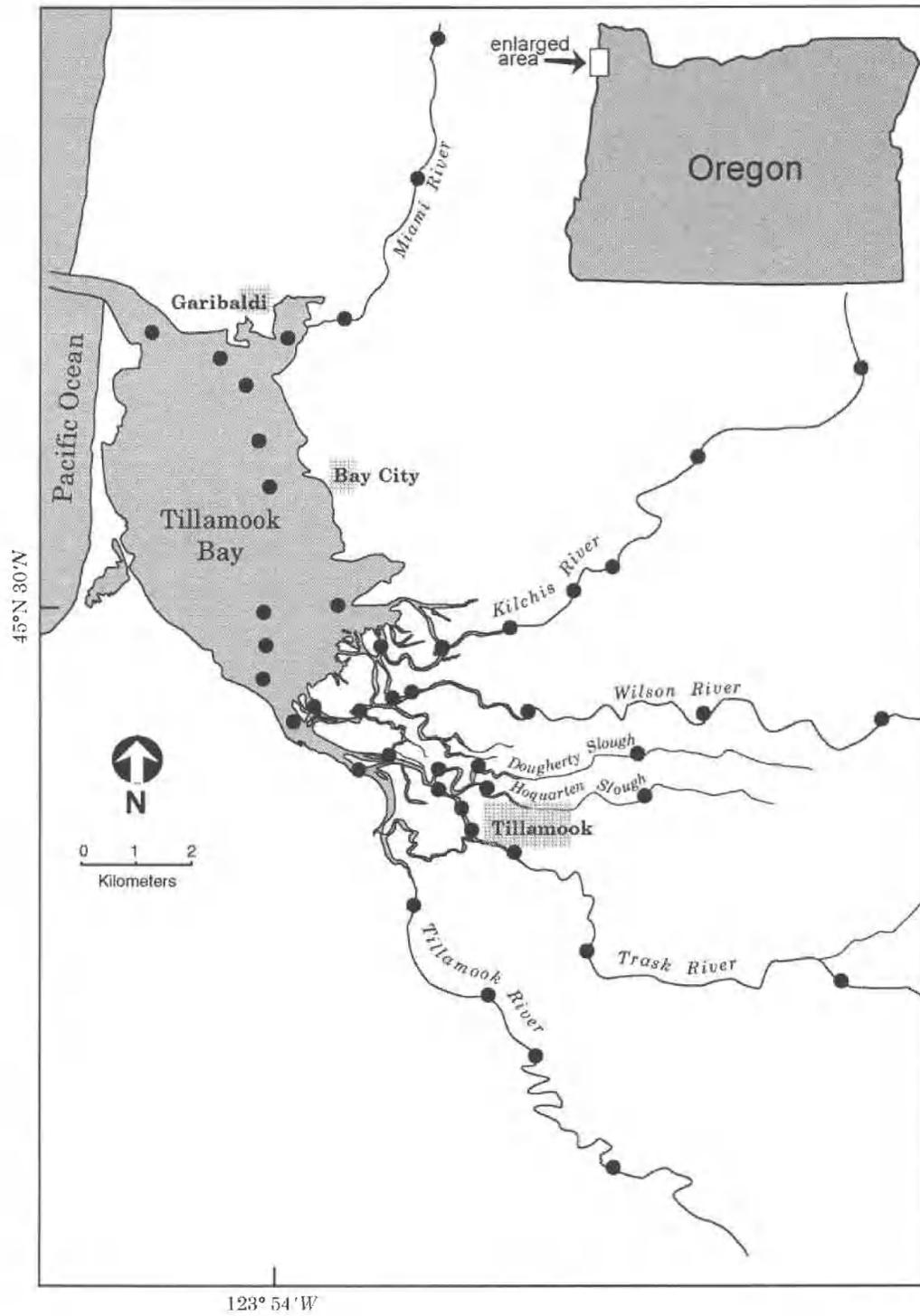


Figure 2.1. Map of the Tillamook Bay watershed identifying the location of sampling stations (●).

km². The total catchment area is 1400 km² (Komar 1997). At low tide, approximately 50% of the estuary bottom is exposed as intertidal mud flats (TBNEP 1998). Despite large freshwater inflows, especially during rainy winter months, heavy tidal fluxes dominate the system, and extreme diurnal tides reach 4.1 m. Average tidal range is 1.7 m. Tidal effects extend from a minimum of 0.6 km for the Miami River up to 11 km for the Tillamook River (Komar 1997). The tidal prisms for the mean and diurnal ranges of tides are estimated as $4.63 \times 10^7 \text{ m}^3$ and $6.20 \times 10^7 \text{ m}^3$, respectively (Johnson 1972).

Tillamook Bay exhibits a strong seasonal change in river discharge in which there is a pronounced winter maximum and summer minimum in precipitation and runoff (Figure 2.2). The two largest rivers, the Wilson and Trask, contribute 69% of all freshwater discharge into the bay while the Miami, Kilchis, and Tillamook account for 6, 19, and 6%, respectively.

Sample Collection and Analysis

Water samples were collected approximately monthly from October 1997 to December 1999 (Figure 2.2). Samples were collected at stations located along transects from the mouth of each river to the mouth of the estuary to encompass a range in salt contents from fresh to ocean water (Figure 2.1). Additional stations were distributed along the geographical extent of each river.

All sample collection was conducted from small boats and from vehicles using river access roads and bridges. Vehicle and boat sampling were coordinated so that all samples were collected during a 4-hour window at high tide. Bulk water samples for dissolved phases were collected approximately monthly at each station

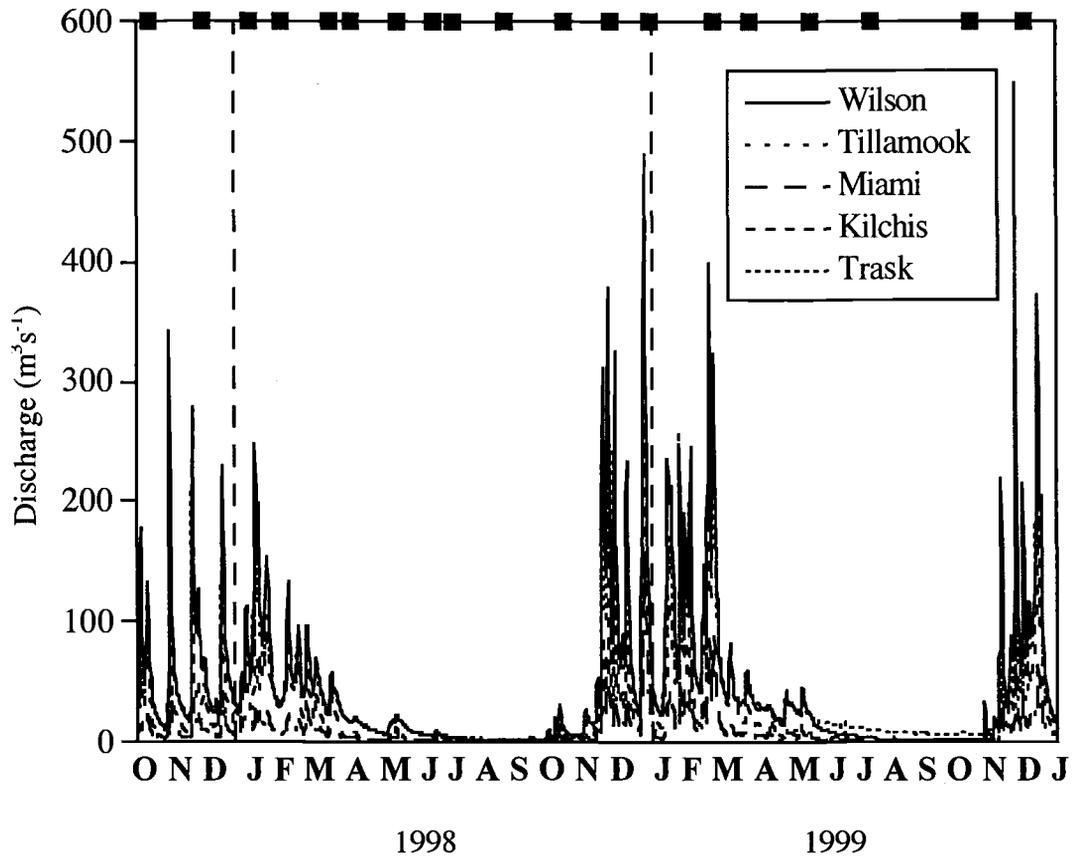


Figure 2.2. The record for daily streamflow measured for rivers entering Tillamook Bay between October 1997 through December 1999. Filled squares identify times when samples were collected as part of this study. Wilson and Trask River flow data are provided by USGS (<http://water.usgs.gov>). Data for Miami, Kilchis, and Tillamook Rivers between October 1997 through October 1998 are provided by Oregon Department of Environmental Quality (unpublished data). The daily flow record for the Miami, Kilchis, and Tillamook Rivers is not complete at the time of writing. Flows for these rivers for 1999 are calculated from mean daily flow in 1997 through 1998 records, normalized to flow measured in the Wilson River.

from one meter below the surface using a modified 5-liter Niskin sampling bottle. Water samples for particulate analysis were collected seasonally in 10-liter carboys using a submerged pump and large diameter polyethylene tubing. During July and

December 1999, samples were also collected approximately every 120 minutes at the mouth of the estuary, the head of the estuary, and the mouth of each river over a 30-hour period for a total of nine to ten samples at each location.

A dissolved organic carbon (DOC) sample was collected at each station into an acid-cleaned syringe directly from the Niskin sampling bottle. Each syringe was rinsed three times with sample water prior to sample collection. Fifteen milliliters of sample were filtered ($0.45\ \mu\text{m}$ pore size, Acrodisc[®], Gelman Sciences) and discarded prior to filtering 10-ml of sample into an acid-cleaned borosilicate glass vial with a teflon-lined cap. DOC samples were frozen until analysis by high temperature combustion (Shimadzu TOC-5000A).

Within six hours of collection, bulk water samples were filtered through $0.45\ \mu\text{m}$ membrane filters (Acrodisc[®], Gelman Sciences). Dissolved inorganic phases of nitrogen (NH_4^+ , NO_2^- , N+N), phosphorous (SRP), and silicon (silicic acid) were determined within 12 hours of filtration using standard analytical techniques adapted for an autoanalyzer (Strickland and Parsons 1972; Gordon et al. 1995). N+N is the total of the nitrate and nitrite concentrations. Detection limits were calculated as three times the standard deviation of the blank and were $0.01\ \mu\text{M PO}_4^{3-}$, $0.02\ \mu\text{M NH}_4^+$, $0.09\ \mu\text{M H}_4\text{SiO}_4$, $0.08\ \mu\text{M N+N}$, and $0.01\ \mu\text{M NO}_2^-$ ($n = 20$). Chloride concentration was determined using conductivity detection with a DIONEX ED40 Electrochemical Detector. The detection limit for chlorinity was $0.22\ \mu\text{M}$ ($n = 5$). The salinity (S) was calculated from the chloride concentration (chlorinity) by the expression: $S = 1.81 \times \text{chlorinity}$ (Knauss 1978).

Suspended particulate material (SPM) in seasonal samples was determined by pressure filtration (nitrogen gas, 10-15 psi) of a known volume of water through

pre-weighed polycarbonate membrane filters (1.0 μm pore size, 90 mm diameter, Poretics). Filters were oven-dried for a minimum of 24 hours at 50° C and re-weighed for the calculation of SPM concentration (mg l^{-1}). Filters were digested using the hot HF/HNO₃ method described by Collier and Edmond (1984). Aluminum, iron, and phosphorus content of the SPM were analyzed by inductively coupled plasma atomic emission spectrometry (ICP AES) (Varian Liberty 150).

Particulate organic carbon (POC) and nitrogen (PON) contents of seasonal samples were obtained by vacuum filtering water through glass fiber filters (1.2 μm pore size, 25 mm diameter, Whatman GF/F) with each filter pre-combusted at 450° C for four hours. Particulate carbon and nitrogen contents were determined by combustion in a Carlo-Erba NA-1500 elemental analyzer. Prior to analysis, filters were fumed with concentrated hydrochloric acid (~8 hr) to remove carbonate, oven-dried (24 hr at ~50° C), and packed in solvent cleaned tin boats.

Data Analysis

The average river end-member concentrations for each sampling date are reported as a flow-weighted average using the concentration measured at the station closest to the estuary on each river but with salinity less than 0.09 psu. This treatment of the river input to the estuary means that the contribution of an element from each river to the estuary is weighted by its contribution to the total freshwater flow into the estuary. The contribution from the Miami River is not included in the average end-member calculations because the Miami River discharges into the northern end of the estuary and contributes only 6.8% to the total freshwater input into the estuary. In addition, freshwater input from the Miami River had no

obvious affect on the salinity distributions within the estuary presumably because the circulation patterns of the estuary deliver Miami River water to the ocean without significant interaction within the main body of the estuary (Komar 1997; McManus et al. 1998).

Freshwater flushing times (Table 2.1) are calculated using the freshwater fraction method (Dyer 1997). The freshwater fraction method is described by the equation $T = VQ^{-1} [(S_s - S_n) S_s^{-1}]$ where T is flushing time, V is estuarine volume for that sampling date, Q is river discharge, S_s is salinity of coastal seawater (NE Pacific surface waters 44°49.1' N 126°03.0' W: 32.64 psu, Wheeler, unpublished data), and S_n is the mean salinity observed in the estuary. Mean salinity of the estuary (S_n) is calculated from the salinity measured at stations within the estuary.

Table 2.1. Freshwater flushing times are calculated using the freshwater fraction method. Departures from conservative mixing within the estuary for each nutrient are also shown. Loss of a constituent within the estuary is indicated by a negative value while a source within the estuary is indicated by a positive value. Note that the values are percent deviations from conservative mixing.

Date	Flushing Time (d)	PO ₄ ⁻³	N+N	H ₄ SiO ₄	NH ₄ ⁺	NO ₃ ⁻	NO ₂ ⁻
1/10/98	2	11	-3	-4	160		
4/11/98	7	9	2	1	23		
5/23/98	7	35	6	-3	15		
6/24/98	17	47	-27	-10	75		
7/12/98	27	-3	-30	-8	-12		
10/17/98	12	-15	5	-10	38	4	61
1/2/99	1	10	-1	-4	51	-1	-1
4/2/99	3	17	-1	-6	13	-1	1
5/26/99	5	-13	-24	-11	-10	-24	-34
7/19/99	17	-30	-38	-19	-47	-38	-2
10/17/99	32	27	-21	-20	158	-21	44

Estimates of estuary volume for each sampling date are calculated using the tidal prism reported by Johnson (1972) and corrected for daily tidal height change. River discharge data on each sampling date is first used to estimate flushing time. This estimate of flushing time is then used to calculate a mean river discharge over this time period, and a flushing time is calculated from this mean discharge. These estimates of flushing time assume that the estuary is well mixed throughout the year. However, the circulation patterns of Tillamook Bay have not been extensively studied. Burt and McAllister (1959) described Tillamook Bay as stratified during the high discharge of winter shifting to a well-mixed estuary during the spring, summer, and fall months. Therefore, winter estimates of flushing time may be underestimated. Spring and summer estimates of flushing times would also be expected to be smaller than calculated here because of upwelling decreased flushing time (Duxbury 1979).

Mixing diagrams represent the distribution of a constituent along a salinity gradient. While these diagrams are descriptive representations of static measurements, they are useful in evaluating net processes such as phytoplankton accumulation and nutrient loss or production within an estuary. The limited data available for the Tillamook Bay estuary and Pacific Northwest estuaries, in general, make these diagrams particularly useful in identifying processes that may be operating within these systems.

Departures from conservative mixing are estimated using the methods described by Fisher and others (1988) in which a best fit high order polynomial is fitted to each of the observed distributions. The difference between the fitted and conservative mixing curves is then expressed as the percent loss or gain relative to

the conservative mixing line. Table 2.1 reports the maximum loss or gain calculated and represents the net result of all processes occurring within the estuary.

Nutrient fluxes are estimated using a steady state box-model approach described in detail by Gordon et al. (1996). The estuary is modeled as a single box with input from the five rivers and exchange with the coastal ocean. Estuary volumes are obtained from Choi (1975). Coastal ocean nutrient concentrations (44.65° N 124.18°W) are obtained from Wheeler (unpublished data). The box-model approach assumes that nutrient input from groundwater and precipitation and evaporative losses are negligible relative to river and ocean input. The model also assumes that the estuary is well-mixed with depth.

RESULTS AND DISCUSSION

River Water Composition

N + N concentrations ($\text{NO}_3^- + \text{NO}_2^-$, hereinafter referred to as NO_3^-) in the rivers feeding Tillamook Bay range from 23.8 to 76.2 μM . These values are 15 times greater than concentrations reported for average pristine rivers (1.6 μM , Meybeck and Helmer 1989). Average riverine nitrate concentrations are within the range reported for Oregon Coast streams (5 - 172 μM , Wigington et al. 1998) and similar to some Pacific Northwest rivers (Yaquina Bay: 22.3 - 88.1 μM , Karentz and McIntire 1977) but elevated relative to other Pacific Northwest rivers (Fraser River: 2 - 15 μM , Drinnan and Clark 1980; as cited in Mackas and Harrison 1997). Strong seasonal variability is observed in the flow-weighted average NO_3^- at the

river end-member, reaching maximum concentrations during winter-spring (Figure 2.3). Seasonality of nitrate has been observed in other rivers (Edwards 1973; Kemp and Boynton 1984; Eyre 1994; Markich and Brown 1998; Moreau et al. 1998) and is typically attributed to external inputs via land runoff. Seasonality of nitrate reflects leaching of excess nitrate from the soils in conjunction with seasonal changes in precipitation and river runoff (Edwards 1973; Eyre 1994).

Riverine phosphate concentrations feeding Tillamook Bay (0.15 - 1.01 μM) are similar to phosphate concentrations reported for average pristine rivers (0.11 μM , Meybeck and Helmer 1989) and other Pacific Northwest rivers (Yaquina Bay: 0.1 - 0.6 μM , Karentz and McIntire 1977). Average flow-weighted river end-member concentrations of phosphate exhibit a similar, but less-pronounced seasonal cycle as nitrate with maximum concentrations during winter months (Figure 2.3). While riverine phosphorus is generally supplied from land drainage, the low solubility of phosphate minerals results in little leaching of phosphate from soils (Edwards 1973; Eyre 1994). In the Tillamook watershed, high phosphate concentrations in the rivers during high runoff, winter months may reflect delivery of phosphate from agricultural lands in the catchment.

Silicic acid concentrations in the five rivers (200 - 250 μM) are approximately 20% higher than average world rivers (179 μM , Meybeck and Helmer 1989). Riverine H_4SiO_4 concentrations are also higher than concentrations reported in rivers feeding other Pacific Northwest estuaries (Yaquina Bay: 37.6 - 214 μM , Karentz and McIntire 1977; Callaway and Specht 1982). Flow-weighted average silicic acid concentrations at the river end-member are relatively constant (Figure 2.3), varying less than 6% among seasons.

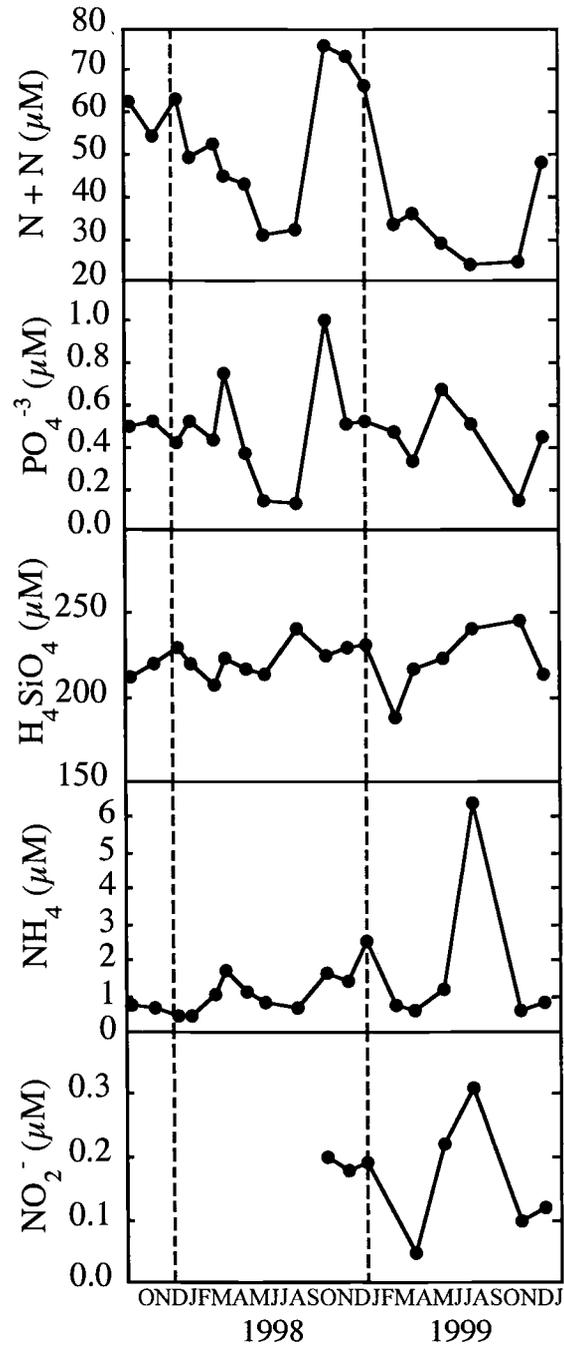


Figure 2.3. Seasonal distributions of river end-member for nitrate (N+N), phosphate, silicic acid, ammonium, and nitrite.

Flow-weighted river ammonium concentrations do not vary seasonally but peak during the summer of 1999 (Figure 2.3). Seasonal patterns in nitrite concentrations are not resolvable because of the limited number of analyses (Figure 2.3). Dissolved organic carbon data, available for the 1999 sampling efforts only, indicate seasonal variability with average river end-member concentrations in summer ($259 \mu\text{M}$) three times higher than those observed in winter ($92 \mu\text{M}$).

Estuary

Estuarine nutrient distributions can best be described in terms of seasonal changes in river hydrology. We group our monthly results into four seasons based on average river discharge (Figure 2.2) and on calculated freshwater flushing times for sampling dates (Table 2.1) during the course of our study. Freshwater flushing rates average 10 days, varying from one to 34 days during our study period (Table 2.1). Winter months, which include December, January, and February, are characterized by high average monthly river discharges (mean = $282 \text{ m}^3 \text{ s}^{-1}$) and rapid flushing (< 2 days). The spring months of March, April, and May exhibit reduced river discharge rates (mean = $93 \text{ m}^3 \text{ s}^{-1}$) and increased flushing times (mean = 5 days). Low discharge (mean = $16 \text{ m}^3 \text{ s}^{-1}$) and slow freshwater flushing times (mean = 24 days) characterize summer conditions in June through September during both years. Fall months of October and November typically experience the onset of high precipitation with dramatic increases in river discharge (mean = $137 \text{ m}^3 \text{ s}^{-1}$) and decreases in freshwater flushing times (mean = 10 days) compared to summer months. Profiles of PO_4^{3-} , NO_3^- , H_4SiO_4 , NH_4^+ , NO_2^- , and DOC, all plotted versus salinity for representative sampling periods, are presented in Figure 2.4.

Other data, summarized in Table 2.1, are available from the corresponding author upon request.

Nutrient behavior in the Tillamook Bay estuary can be explained by two dominant factors: freshwater flushing time and biological uptake/regeneration. Superimposed on these two processes is seasonal variability in nutrient concentrations of coastal waters caused by upwelling. Freshwater flushing time determines the amount of time for the uptake of nutrients by phytoplankton, exchange with suspended particles, and interaction with the sediments. Seasonal coastal upwelling controls the timing and extent of oceanic delivery of nutrients to the estuary, which, in turn, affects the magnitude and timing of the biological response within the estuary. We attribute seasonal differences in nutrient concentrations in the Tillamook estuary to this combination of flushing time, biological activity, and coastal upwelling.

Winter

Freshwater flushing time switches the estuary between nutrient concentrations dominated by flow and concentrations dominated by biological drawdown and release. During winter months, fast flushing times prevent the development of significant phytoplankton populations within the estuary. Other estuarine studies have concluded that light is the dominant factor influencing phytoplankton productivity (Cloern 1979; Edmond et al. 1981; Cole and Cloern 1987; Small et al. 1990). However, in Tillamook Bay, the residence time of water during winter months (mean = 1.7 days) is fast relative to average growth rates (Chrysophyta average divisions $d^{-1} = 1.88$, Tang 1996). Therefore, phytoplankton

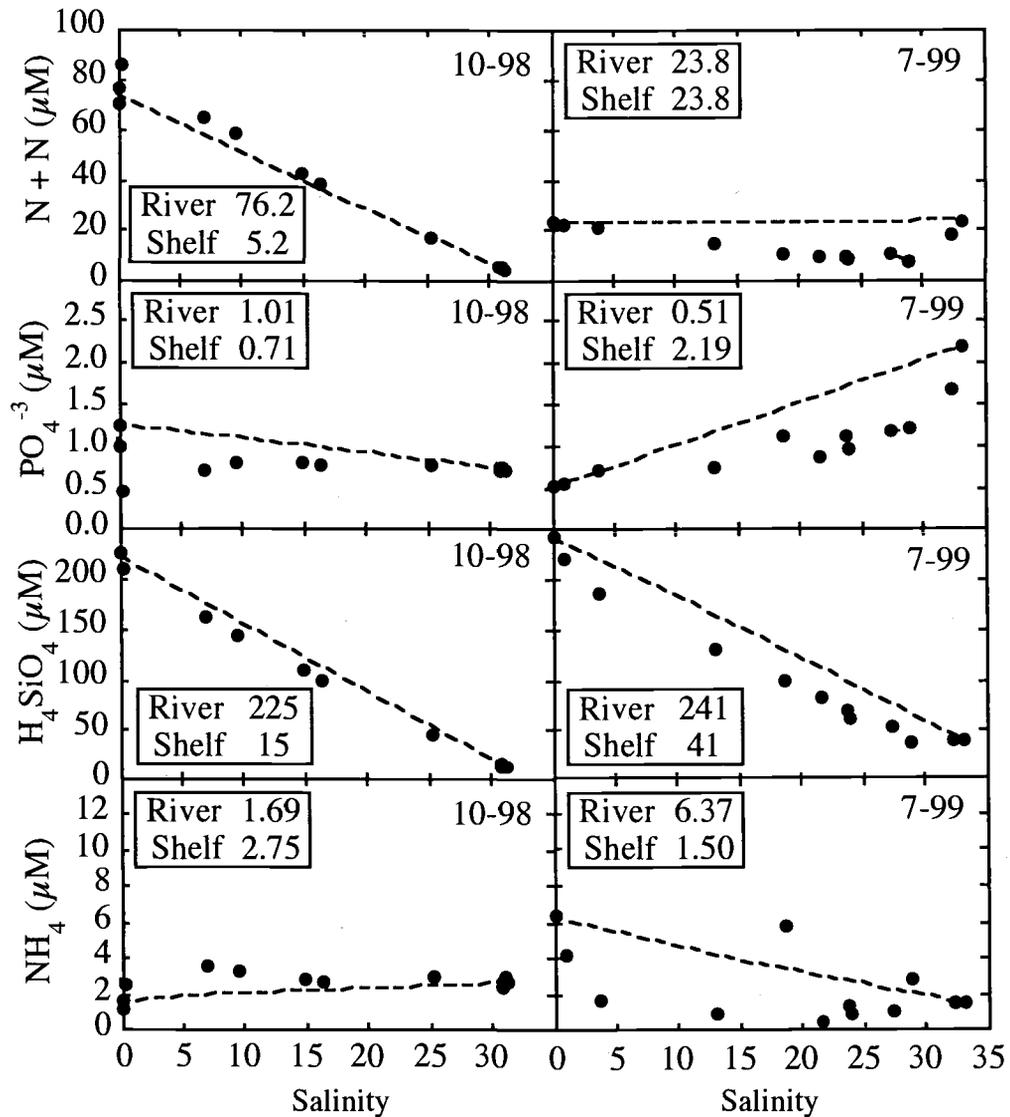


Figure 2.4. Example nutrient concentration versus salinity plots from two representative sampling periods. Dashed lines indicate theoretical mixing between river and ocean end-members. Dashed lines in N:P plot indicate average ratios predicted from fresh plankton, i.e., "Redfield ratios" (Richards 1958; Redfield et al. 1963). Average river end-member and shelf concentrations are indicated on each plot. (na indicates data not available)

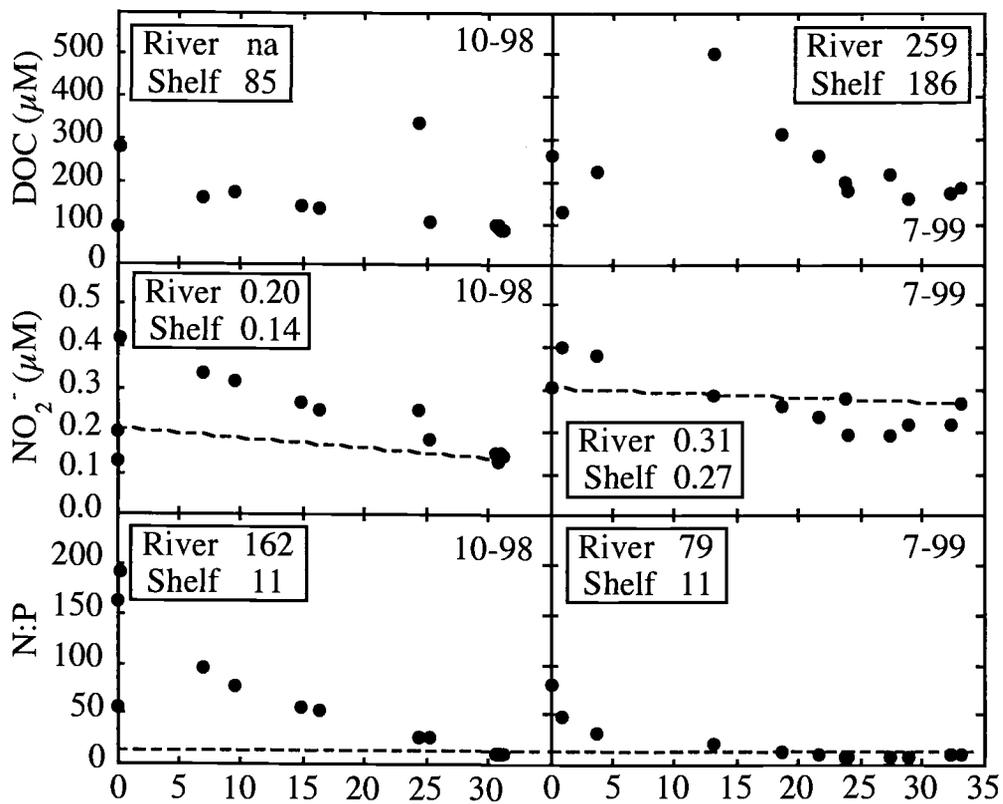


Figure 2.4. Continued.

are unlikely to significantly impact estuarine nutrient distributions during winter months even under acceptable light and high nutrient conditions. Any phytoplankton occurring within the estuary are rapidly flushed out under high flow conditions, preventing phytoplankton uptake from significantly affecting nutrient distributions in the estuary. This process is borne out by the conservative mixing behavior of nitrate and dissolved silicon during winter months of our study along with low phytoplankton biomass within the estuary during the winter (Table 2.2).

Table 2.2. Spatial and seasonal distribution of phytoplankton biomass ($\mu\text{g l}^{-1}$) in Tillamook Bay (TBNEP, unpublished data).

Location	Fall 1997	Winter 1998	Spring 1998	Summer 1998
Upper Estuary	0.0	0.0	0.1	0.3
Lower Estuary	0.0	0.0	42.3	18.4
Mouth of Estuary	0.0	0.0	80.1	28.7

This pattern has been observed in other estuarine systems under high flow conditions (e.g. Balls 1994; Sin et al. 1999). Consistent with this hypothesis, the near-crustal mineral content (e.g. % weight Fe, Figure 2.5) and soil-like C:N ratio (Figure 2.6b) of suspended material indicate that terrestrial sources, not phytoplankton, dominate the particulate signal under winter conditions. This pattern has also been observed in the Columbia River estuary (Sullivan et al. 2001). The combined evidence supports the hypothesis that during periods of high flow, estuarine nutrient distributions are dominated by the high flushing rates.

While biological uptake did not significantly affect nutrient concentrations during winter months, remineralization of organic carbon is important for some

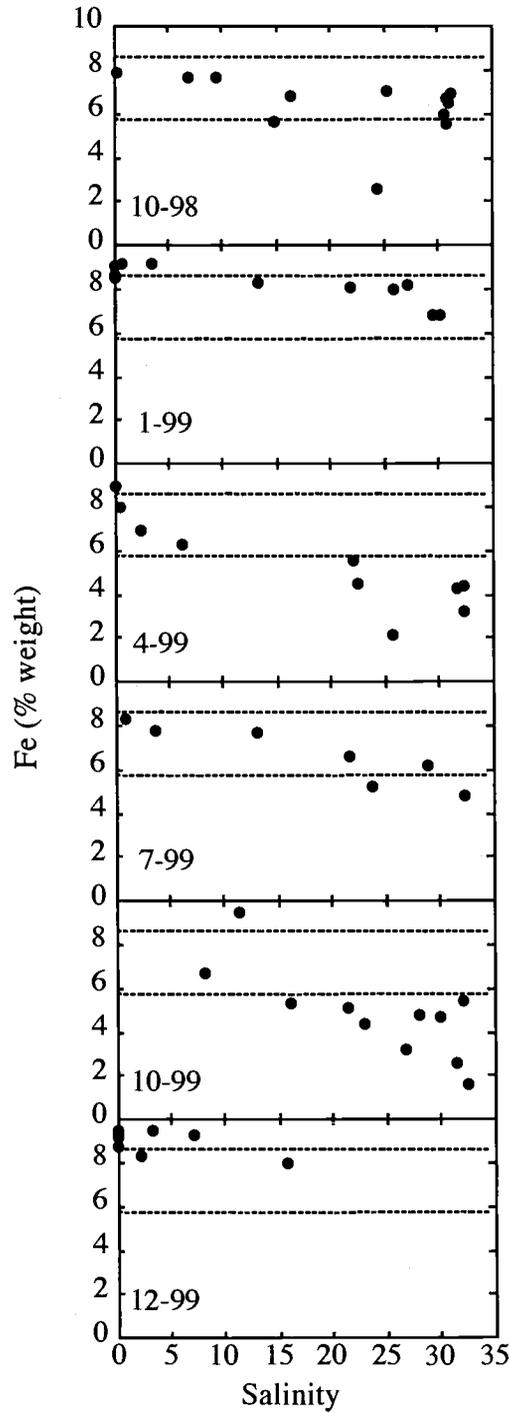


Figure 2.5. Particulate iron concentrations (% weight) for suspended material versus salinity for each sampling date. Dashed lines indicate average iron abundance in basalt (8.56%) and continental crust (5.63%) reported by Taylor (1964).

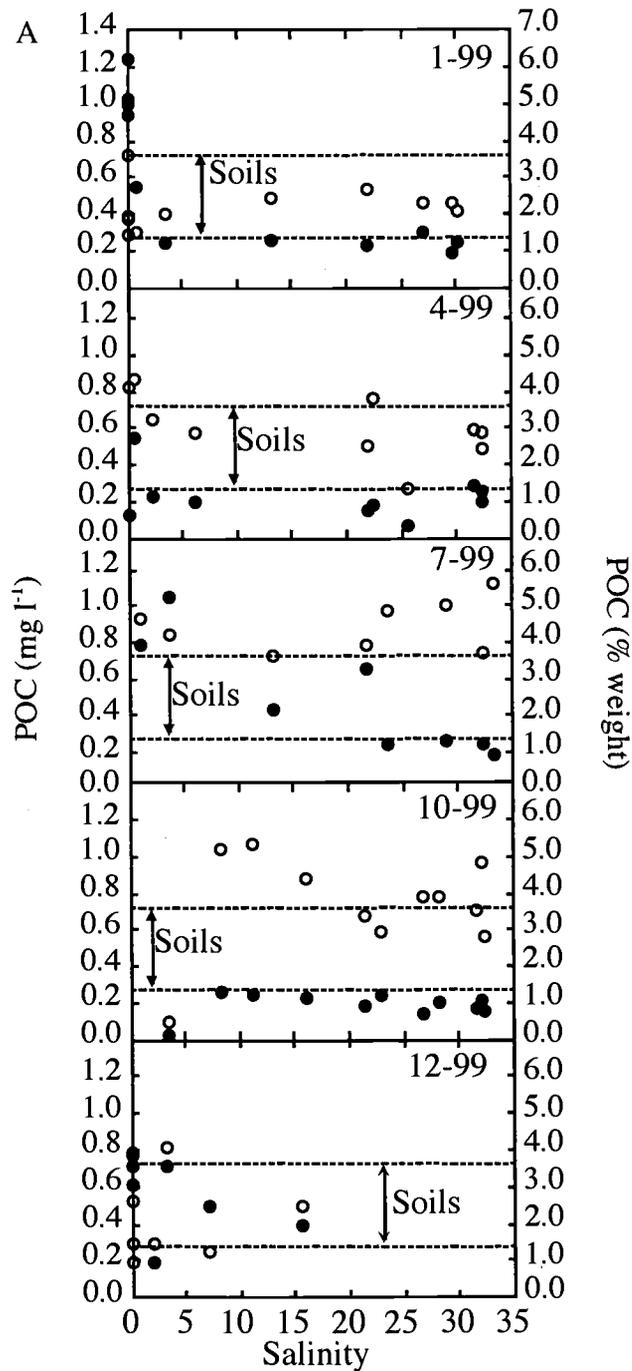


Figure 2.6. a) POC concentration (●) and % weight POC (○) of suspended material versus salinity for each sampling date. Dotted lines indicate the range in % weight POC for Oregon soils (Prahel et al. 1994). b) Particulate organic carbon to nitrogen ratios of suspended material versus salinity for each sampling date. Dotted lines indicate C:N measured for Oregon soils (Prahel et al. 1994), and dashed line indicates average Redfield ratios (Richards 1958; Redfield et al. 1963).

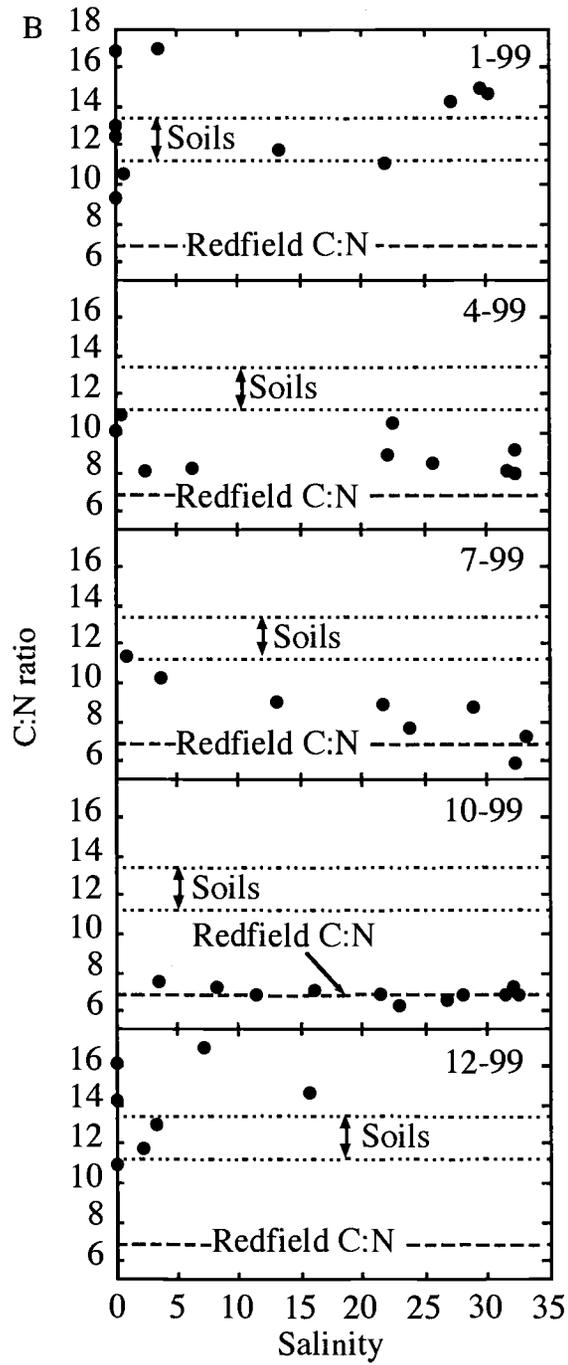


Figure 2.6. Continued.

nutrients. Particulate materials, derived from the rivers and upper reaches of the estuary, undergo decomposition and regeneration of dissolved inorganic nutrients (Kemp and Boynton 1984). During winter months, concentrations of PO_4^{-3} and NH_4^+ are elevated over concentrations predicted by mixing between river water and seawater (Table 2.1). In 1998, the elevated concentrations of dissolved phosphate and ammonium represent an excess of 11% and 160%, respectively, over conservative mixing predictions (Table 2.1). The ratio of excess $\text{NH}_4^+:\text{PO}_4^{-3}$ (NH_4^+ excess: PO_4^{-3} excess ~ 15) is consistent with regeneration of these nutrients at values close to Redfield predictions for fresh phytoplankton (N:P = 16, Richards 1958; Redfield et al. 1963), suggesting that excess NH_4^+ and PO_4^{-3} are produced during the remineralization of organic carbon within the estuary.

While the excess ammonium and phosphate in January 1998 (Table 2.1) is distributed evenly along the longitudinal extent of the bay, the source of excess ammonium and phosphate in January 1999 is most apparent at the upper estuary and coincides with POC (Figure 2.6a) and DOC maxima and a pH minimum at the upper estuary. In 1999, there is also a pronounced winter maximum (January) in SPM concentrations at the river end-member that is not apparent in the 1998 data. The suspended load entering the estuary in 1999 (42.8 mg l^{-1}) is an order of magnitude larger than observed in January 1998 (3.5 mg l^{-1}). The regeneration ratio of NH_4^+ to PO_4^{-3} in winter 1999 (Table 2.1: NH_4^+ excess: PO_4^{-3} excess ~ 5) is less than half that predicted for RKR material. This difference between winters may indicate an additional source of phosphate or a sink for ammonium within the estuary. The percent source estimates within the estuary (Table 2.1) indicate that the enrichment of phosphate within the estuary is relatively constant between years.

However, excess ammonium within the estuary is significantly lower in January 1999 than 1998. Ammonium concentrations reach $12 \mu\text{M}$ at the upper estuary during January 1999 (not shown). These high ammonium concentrations may support nitrifying bacteria, resulting in the coincident upper estuary source of nitrite and nitrate observed during this period. However, similar to the flushing effect predicted for phytoplankton, the high flushing rates of winter would likely prevent nitrifying bacteria in the water column from producing this signal. While our data cannot constrain the source of this nitrite signal, it suggests that remineralization and nitrification may be occurring in the sediments during winter months.

Spring and Summer

Because river discharge rates within Tillamook Bay decrease progressively from winter through summer, longer water residence times occur. Under reduced flushing rates of spring and summer, the affect of biological uptake becomes evident within the estuary. Phytoplankton biomass estimates available for the 1997 through 1998 sampling effort are consistent with this observation (TBNEP unpublished data). Phytoplankton biomass measured at the middle and lower estuary are approximately forty times higher in spring and summer relative to winter months (Table 2.2).

Reduced freshwater flushing times and increased biomass accumulation within the estuary affect the suspended particulate composition in the bay with a seasonal progression from a lithogenic signature in winter (Figure 2.7) to a biogenic signature in summer (Figure 2.8). Particulate C:N of suspended material

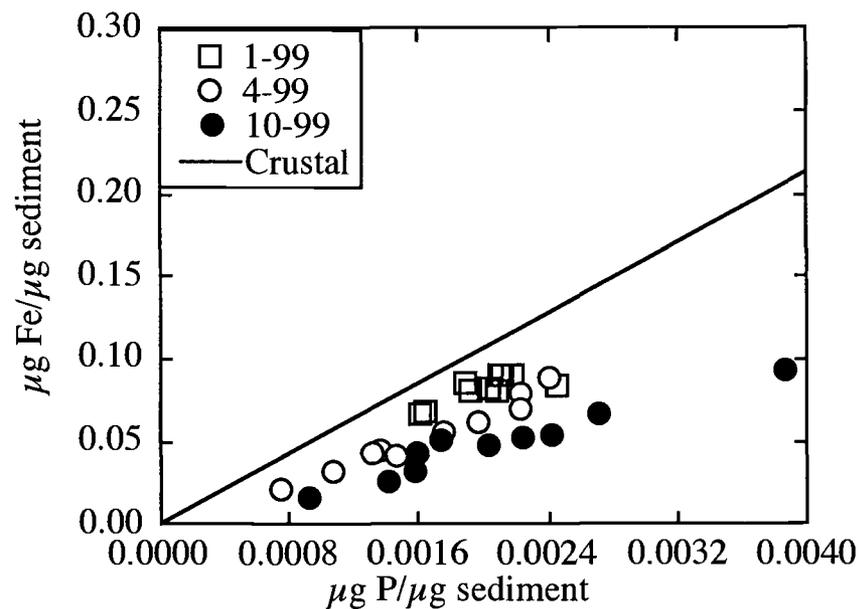


Figure 2.7. Particulate iron concentrations as a function of particulate phosphorus concentrations for different sampling periods. Average crustal iron to phosphorus ratio is indicated by the solid line (Taylor 1964).

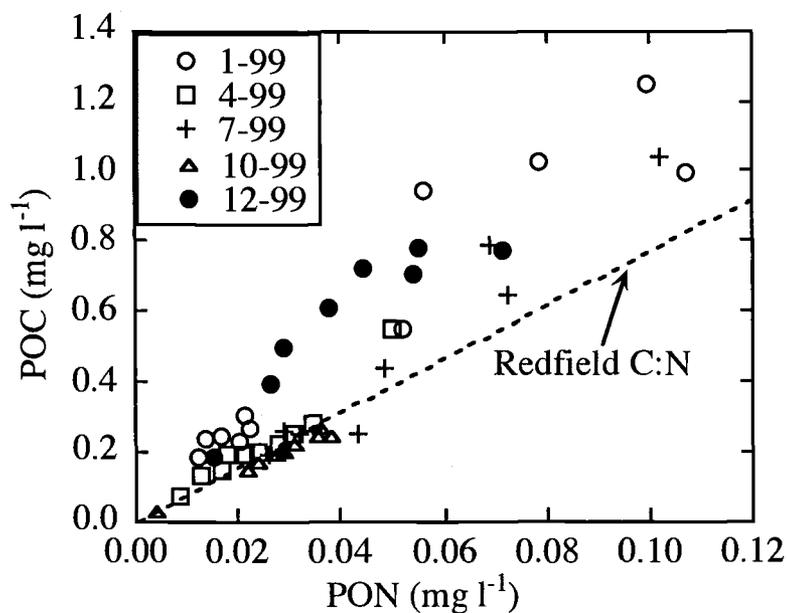


Figure 2.8. Particulate organic carbon as a function of particulate nitrogen along the spatial gradient of the estuary. Dashed line indicates Redfield C:N ratio (Richards 1958; Redfield et al. 1963).

within the bay shift from a soil dominated signature (average C:N = 13.7 ± 2.4) in winter months to a phytoplankton dominated signature in summer (average C:N = 8.6 ± 1.7) (Figure 2.8).

Biological uptake within the estuary during this period also affects estuarine nutrient distributions. During 1998 and 1999, there is significant removal of all nutrients within the estuary as spring progresses (Table 2.1). This process is apparent in the nitrate and silicic acid distributions within the bay during spring and summer (Figure 2.4). The removal of nitrate and silicic acid, in particular, from the water column indicates uptake by diatoms. The diatom genus *Chaetoceros* dominated species composition (>55%) in vertical tows conducted in the spring of 1998 (TBNEP, unpublished data). The shift from conservative mixing of silicic acid under fast flushing conditions (winter) to removal caused by diatom uptake under slow flushing conditions (summer) has been observed in other estuaries (Wollast and De Broeu 1971; Anderson 1986; Balls 1994).

Development of a significant phytoplankton community during spring and summer is caused, in part, by delivery of nutrient-rich water via coastal upwelling. The upwelling indices reported for 125°W 45°N indicate active coastal upwelling during our spring and summer sampling efforts of 1998 and 1999 (www.pfeg.noaa.gov/las/main.html). The transition from winter to spring/summer conditions along the West Coast of North America is associated with an abrupt switch from northward to southward winds (Strub et al. 1987; Strub et al. 1987). This seasonal shift to southward winds drives the alongshore flow and offshore Ekman transport at the surface that results in upwelling of denser, nutrient-rich water along the shelf (Huyer et al. 1979; Strub et al. 1987; Strub et al. 1987). Fresh

water from the Columbia River plume which is diverted south during spring and summer may help to maintain the upwelling front closer to the coast north of 42°N (Strub et al. 1987).

Stefansson and Richards (1963) found that an important process adding nutrients to the surface waters off Washington and Oregon coasts is wind-induced upwelling during the spring and summer, especially the region south of Tillamook Head. Other studies have found that tidal exchange can transport nutrient-rich upwelled water into West Coast estuaries, resulting in spring and summer phytoplankton blooms (Cloern 1979; Prego 1993; Harrison et al. 1994; Harrison and Kedong 1998). With only a few exceptions (May, 1998 and October, 1999, data not shown), phosphate concentrations in Tillamook Bay exhibit lower concentrations at the river end-member than the seawater end-member, suggesting that oceanic input to the bay is important for this nutrient (e.g., Figure 2.4). Box model calculations indicate that the coastal ocean supplies PO_4^{-3} to the estuary throughout the year (Table 2.3). Phosphate supply to the estuary is dominated by river input only during winter months with fluxes up to three times higher than ocean-supplied phosphate during these seasons. During spring and summer, phosphate flux from the ocean to the estuary is, on average, three times the riverine flux of phosphate to the estuary.

The differences in the primary sources delivering nitrate and phosphate to the estuary are evident in the spatial patterns of potential nutrient limitation within the estuary. The low phosphate along with the high nitrogen concentrations within the rivers result in N:P ratios well above the Redfield ratio at the river end-member during all seasons (Figure 2.9). These high ratios suggest that P limitation occurs at

Table 2.3. Box model calculations of seasonal fluxes of nutrients (10^6 mol yr^{-1}) from the Tillamook Bay estuary to the coastal ocean (F_E). Seasonal riverine fluxes (F_Q) and oceanic fluxes (F_O) into the estuary (mol s^{-1}) are shown for phosphate.

Season	Estuary to ocean flux ¹ F_E				Ocean to estuary flux ² F_O	River flux ³ F_Q
	PO_4^{-3}	N+N	H_4SiO_4	NH_4^+	PO_4^{-3}	PO_4^{-3}
winter	5.2	143	416	8.1	2.3	4.5
spring	2.6	49	166	1.7	2.9	1.5
summer	0.8	9	28	0.5	2.1	0.5
fall	0.8	14	33	1.0	0.8	0.6

¹ $F_E = V_R * Y_R$ where V_R is the net water exchange and equal to freshwater inflow ($-V_Q$) and Y_R is the average of the estuarine and ocean nutrient concentrations using ocean nutrient concentrations at $44.65^\circ \text{ N } 124.18^\circ \text{ W}$ from Wheeler, unpublished data.

² $F_O = V_X * [Y_O - Y_E]$ where V_X is the calculated mixing volume between the ocean and estuary, Y_E is the mean phosphate concentration in the estuary, and Y_O is the ocean phosphate concentration at $44.65^\circ \text{ N } 124.18^\circ \text{ W}$ from Wheeler, unpublished data. Assuming conservation of salt and volume within the estuary, $V_X = V_Q (S_O + S_E - 2S_Q) (2(S_O - S_E))^{-1}$ where S_O , S_E , and S_Q are ocean ($44.65^\circ \text{ N } 124.18^\circ \text{ W}$), average estuary, and flow-weighted river end-member salinities, respectively.

³ $F_Q = V_Q * Y_Q$ where V_Q is the total freshwater discharge into the estuary and Y_Q is the average flow-weighted river end-member phosphate concentration.

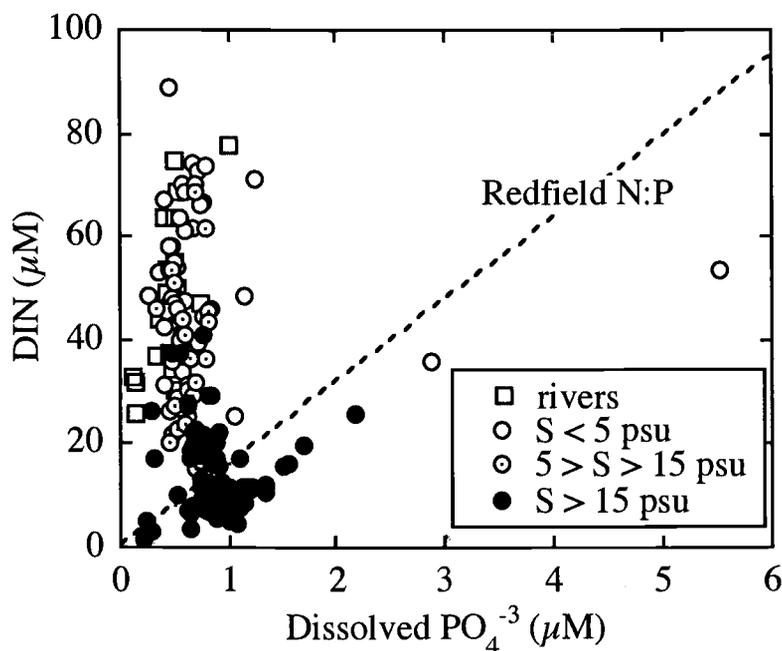


Figure 2.9. Dissolved inorganic nitrogen as a function of dissolved soluble reactive phosphate along the spatial gradient of the estuary during the two-year study. Dashed line indicates Redfield N:P ratio.

the freshwater end-member. However, N:P ratios indicate a shift to potential N limitation in the lower estuary during all seasons (Figure 2.9). This observation is consistent with evidence that marine phytoplankton are generally nitrogen limited while freshwater phytoplankton are limited by phosphorus (Ryther and Dunstan 1971; Hecky and Kilham 1988). The position of the transition zone from potential P limitation to potential N limitation varies according to river discharge volume

with the location of the shift from P to N limitation shifting toward the upper estuary as river discharge decreases. Other studies have suggested that the limiting nutrient for plankton biomass varies spatially within estuaries (Eyre 1994; O'Donohue and Dennison 1997; Sin et al. 1999).

In general, compositional ratios of suspended material exhibit similar trends along the salinity gradient in Tillamook Bay. There appears to be a spatial transition within the estuary from land-derived sediment at the upper estuary to mineral-depleted, biogenic-enriched particles at the ocean end-member (Figures 2.5 and 2.6). Phytoplankton biomass also varies along the salinity gradient with the highest concentration of phytoplankton occurring at the lower estuary during spring and summer (Table 2.2). This evidence suggests that, while phytoplankton are potentially N-limited in the outer estuary, significant populations can be sustained under these conditions. At the river end-member and upper estuary, P limitation may be severe enough to prevent phytoplankton growth. However, other factors such as light availability cannot be eliminated as the limiting growth factor in this area of the estuary.

Fall

By late summer and early fall, biological uptake in the water column cannot solely account for observed nutrient distributions within the estuary. Under these slow freshwater flushing conditions, phosphate (October 1999) and ammonium (October 1998 and 1999) exhibit positive deviations from the theoretical dilution line, likely reflecting release from the sediments (Table 2.1; Figure 2.4). The relatively shallow depths within the estuary (mean depth ~ 2 m, Komar 1997)

would be expected to produce short residence times for detrital material. Therefore, most of the microbial regeneration of nutrients is likely to occur on or in the sediments. Maximum PO_4^{-3} and NH_4^+ concentration peaks are located at the upper estuary where there are extensive mudflats. With the onset of fall conditions, an upper estuary source of PO_4^{-3} , NO_3^- , NH_4^+ , and NO_2^- is apparent in the data while H_4SiO_4 data suggests removal throughout the estuary. The upper estuary sources of NO_3^- , PO_4^{-3} , NH_4^+ , and NO_2^- are most pronounced during October 1999. The onset of fall rains are delayed in 1999 resulting in an unseasonably dry October with only two-thirds the discharge feeding the estuary as in the previous October and one-tenth the discharge of October 1997 (USGS: <http://water.usgs.gov>). In addition, N:P ratios at the upper and lower estuary are near ~16, while the mid-estuary displays values well above that value (Figure 2.4). Particulate C:N ratios do not vary within the estuary, and the average C:N of 6.9 is close to that predicted for phytoplankton (Figure 2.6b).

Seasonal patterns of benthic regeneration of phosphate and ammonium are consistent with observations in other estuarine systems (Jensen et al. 1990; Balls 1992; Hopkinson et al. 1999). These studies have found that phosphate fluxes from sediments reflect changes in redox potential while ammonium regeneration is dependent on temperature-driven benthic metabolism (Callender 1982; Kemp and Boynton 1984; Sin et al. 1999).

Benthic release of phosphate has been described in a number of estuarine systems (Callender 1982; Callender and Hammond 1982; Kemp and Boynton 1984; Chambers et al. 1995; Conley et al. 1995). Within aerobic water columns, phosphorus is adsorbed by Fe and Mn oxides and hydroxides to form insoluble

precipitates that settle out of the water column. Regeneration of this phosphate occurs under reducing conditions within sediments (Callender 1982; Callender and Hammond 1982; Chambers et al. 1995). In the Tillamook estuary, enhanced carbon loading along with slow flushing rates and high temperatures in late summer and early fall likely results in a shallow redox boundary in sediments. High remineralization rates within the sediment would lead, in turn, to low sediment oxygen concentrations which facilitate the reduction of iron and manganese oxides and the subsequent release of PO_4^{3-} from the sediments (Kemp and Boynton 1984). This potential flux of phosphate is consistent with dissolved manganese distributions within the estuary, which indicate a benthic source of Mn during the fall months (Colbert and McManus submitted). In this phosphate limited area of the upper estuary, benthic input of phosphate to the overlying water could represent a significant source of this nutrient for phytoplankton growth.

Ammonium release from estuarine sediments can be associated with microbial degradation of organic carbon in the sediment (Jensen et al. 1990). In temperate estuaries, seasonal patterns of benthic ammonium regeneration generally exhibit strong summer maximum which correlate well with water temperature (Madden et al. 1988; Sin et al. 1999). Balls (1992) observed an ammonium maximum in the Forth and Tay estuaries in Scotland during summer months that they attributed to a benthic source. Madden and others (1988) found that regeneration of ammonium was the primary source of ammonium to the Fourleague Bay water column in summer. Calculated and measured benthic fluxes for ammonium are comparable in Tillamook Bay. The ammonium fluxes necessary to account for the observed enrichment within the estuary in October 1998 and 1999

are estimated using the excess concentrations above conservative mixing (Table 2.1), estuary volumes and surface areas, and flushing times of the estuary (Table 2.1). Calculated fluxes range from 4.9 to 5.6 mmol NH_4^+ m^{-2} d^{-1} . Ammonium fluxes estimated by pore water concentration profiles derived from peeper deployments in late August 1998 (0.2 and 1.8 mmol NH_4^+ m^{-2} d^{-1} with $\phi = 0.9$, $D_s = 0.9 \times 10^{-5}$ $\text{cm}^2 \text{sec}^{-1}$) are consistent with these flux estimates, suggesting that benthic exchange is a significant seasonal source of ammonium to the estuary.

The phosphate and ammonium distributions observed during late summer and early fall are consistent with benthic regeneration of these nutrients. Alternatively, the upper estuary source signal for PO_4^{3-} and NH_4^+ could be produced by wind-driven resuspension or tidally induced resuspension of sediments in the upper estuary. Under low flow conditions, tidally induced resuspension of sediments has been shown to occur in macrotidal estuaries that narrow rapidly towards their head as does the Tillamook Estuary (Balls 1992). This hypothesis is supported by the dramatic decrease in organic carbon (Figure 2.6b) and organic nitrogen content (not shown) of the particulate material in the upper estuary. However, low SPM concentrations in this area do not support this hypothesis. Thus, we conclude that benthic regeneration dominates this signature, but recognize that other processes may be influencing these properties.

Nutrient Fluxes to Coastal Waters

The processes outlined above have a pronounced effect on the net flux of the nutrients to the coastal ocean. The box model approach allows for the quantification of fluxes from the estuary to the coastal ocean (Gordon et al. 1996).

When river discharges reach an annual maximum during winter, substantial quantities of nutrients are exported to the adjacent coastal ocean (Table 2.3). Dissolved inorganic nitrogen ($N + N, NH_4^+$), silicic acid, and phosphate fluxes decrease from this winter maximum through spring and reach the lowest annual fluxes during summer with fluxes increasing again in fall as precipitation and discharge increase. This pattern suggests that nutrient fluxes are primarily regulated by changes in river discharge volume. However, the spring and fall nutrient fluxes are not consistent with this hypothesis. Average spring nutrient fluxes are 1.2 to 5.1 times higher than average fluxes calculated for fall months while river discharge rates are generally higher during fall (average = $137 \text{ m}^3 \text{ s}^{-1}$) than spring (average = $93 \text{ m}^3 \text{ s}^{-1}$) (Figure 2.2). We attribute this inconsistency to limitations in our data as fall fluxes could only be calculated on two sampling dates. These two dates (October 1998 and 1999) have an average discharge of $19 \text{ m}^3 \text{ s}^{-1}$ which is not representative of the high river discharge rates typically observed during this season. For this reason, average fall fluxes from the estuary may be underestimated.

Interannual Differences

Because upwelling is an important process affecting geochemistry in Tillamook Bay, it is likely that El Niño/Southern Oscillation (ENSO) events could have a potentially significant impact on the development of spring and summer primary productivity signals. Coastal upwelling is dampened during El Niño periods and enhanced during La Niña events. ENSO induced changes in upwelling intensity may, in part, explain differences in nitrate and phosphate concentrations

observed at the ocean end-member during spring/summer 1998 and spring/summer 1999 as these years include portions of El Niño and La Niña periods, respectively (McPhaden 1999). Ocean end-member concentrations for each sampling event are defined as the concentration measured at the mouth of the estuary during an incoming tide, at or near high tide. Ocean end-member phosphate and nitrate concentrations are significantly different between sampling years (t-test assuming equal variances, $\alpha = 0.05$). These differences are most pronounced during spring and summer conditions with phosphate and nitrate concentrations two to four times higher at the ocean end-member during this period in 1999 than 1998.

The affect of ENSO events on estuarine geochemistry is further manifested by its effect on the delivery of nutrients at the river end-member via changes in the quantity and timing of precipitation and, in turn, river discharge (Kahya and Dracup 1993; Rajagopalan and Lall 1998). During winter, spring, and summer months of 1999, river discharge (Figure 2.2) and precipitation are twice that of 1998, resulting in higher riverine nutrient fluxes during 1999 than 1998. In this manner, ENSO induced changes in offshore upwelling intensity and precipitation likely affect the biogeochemistry of nutrients in this estuary.

CONCLUSION

Patterns of dissolved nutrient concentrations over the two and a half year study suggest that estuarine nutrient behavior is dominated by two factors: freshwater flushing time and biological uptake and regeneration. Benthic regeneration of nutrients (PO_4^{3-} , NH_4^+) contributes nutrients seasonally according to the flushing characteristics of the estuary. Nutrient supply to the coastal ocean is

primarily regulated by river discharge volume. However, seasonal coastal upwelling is also an important process, supplying biologically important nutrients such as phosphate to the estuary.

Because upwelling is an important process affecting geochemistry in Tillamook Bay, it is likely that El Niño/Southern Oscillation (ENSO) events could have a potentially significant impact on the development of spring and summer primary productivity signals. The effect of changes in offshore upwelling intensity and precipitation during these oscillation events on nutrient biogeochemistry of this estuary and other Pacific Northwest estuaries warrants further investigation.

An important aspect of nutrient supply to estuaries is the potential for eutrophication due to excessive nutrient loading. Eutrophication of Tillamook Bay does not seem likely in its current condition. Fluxes of nutrients to the estuary are highest during winter and spring when freshwater flushing times are fastest. Additionally, the low phosphate loading rates relative to the dissolved inorganic nitrogen supply at the upper estuary prevents the development of a significant phytoplankton signal throughout the year (Table 2). Furthermore, seasonal increases in phytoplankton biomass at the outer estuary are not due to anthropogenic loading of nutrients but rather oceanic delivery of nutrients via coastal upwelling (Table 3). The role of upwelling and the low potential for eutrophication via anthropogenic loading has been observed in other estuaries as well (Prego 1993; Mackas and Harrison 1997).

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SOURCES OF UNPUBLISHED MATERIAL

- Oregon Department of Environmental Quality, Northwest Region, Portland, Oregon.
- Tillamook Bay National Estuary Project, Tillamook Bay National Estuary Project Citizen Plankton Monitoring Program, Garibaldi, Oregon.
- P.A. Wheeler. College of Oceanic & Atmospheric Sciences, Oregon State University, 104 Ocean Admin Building, Corvallis, Oregon.

3. IMPORTANCE OF SEASONAL VARIABILITY AND COASTAL
PROCESSES ON ESTUARINE MANGANESE AND BARIUM CYCLING

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ABSTRACT

Dissolved and particulate manganese (Mn) and barium (Ba) within the Tillamook Bay estuary are examined over seasonal cycles and under a range of river discharge conditions from January through December 1999. Based on estuarine distributions and box model calculations, Mn and Ba behavior within the estuary is best quantified by considering two dominant factors: interaction with suspended particulate material (adsorption/desorption reactions) and input from benthic sources. Seasonal differences in elemental concentration patterns are dominated by variations in the relative importance of these two variables. While Mn exhibits estuarine behavior typical for these elements, Ba shows an uncharacteristic lower estuary source. We hypothesize that this source results from the benthic dissolution of ocean-derived particulate Ba.

The flux of dissolved Mn and Ba from the river to the coastal ocean are related to river discharge rates with the high fluxes observed under winter conditions. These winter flux maxima occur despite estuarine removal processes that also occur under winter conditions. During all other seasons, box model calculations indicate that the total (dissolved plus particulate) riverine fluxes of Mn and Ba to the coastal ocean are enhanced due to internal estuarine processes — i.e., by transport across the sediment-water interface. On an annual basis, dissolved Mn and Ba fluxes to the coastal ocean are enriched by 390 and 170%, respectively, over what is expected from riverine inputs alone. The results of this research underscore the importance of estuarine processes in modifying the riverine flux of these elements to the ocean and the necessity of temporal sampling in evaluating processes controlling elemental distributions and delivery to the coastal ocean.

Measurements of both the dissolved and particulate phases are also essential for describing and modeling these elemental budgets.

INTRODUCTION

The importance of estuaries in modifying the riverine flux of trace and alkaline-earth elements to the oceans is well documented (Hanor and Chan 1977; Morris et al. 1982; Shiller 1997). Changes in pH, ionic strength, and redox potential alter the adsorption potential of suspended particles, creating surfaces for scavenging, precipitation, and flocculation (Morris et al. 1982; Millward 1995). Such geochemical processes can, in turn, affect the partitioning between the particulate and dissolved phases of elements such as Mn (Callaway et al. 1988), and Ba (Li and Chan 1979).

The variety of hydrodynamic and physico-chemical conditions occurring in estuaries gives rise to a range of element behavior among estuarine systems (Owens et al. 1997) and temporally within a given estuary (Stecher and Kogut 1999). For example, dissolved manganese can behave conservatively (Moore et al. 1979; Muller et al. 1994), exhibit mid-estuarine maxima (Callaway et al. 1988; Laslett and Balls 1995), or undergo removal at low salinities (Morris and Bale 1979; Yan et al. 1990). Within the water column, dissolved Mn sources include release via bacterial reduction of Mn oxides (Klinkhammer and McManus 2001) and addition from anthropogenic sources (Klinkhammer and Bender 1981; Owens and Balls 1997). Mid-estuary peaks in dissolved Mn have been attributed to benthic sources either as diagenetic remobilization from bottom sediments (Laslett and Balls 1995), injection of sediment pore fluids into the water column (Morris et

al. 1982; Morris et al. 1987; Paucot and Wollast 1997), or desorption from resuspended particles (Callaway et al. 1988). Removal of dissolved Mn at low salinities has been attributed to suspended particulate interactions (Morris and Bale 1979; Yan et al. 1990) and flocculation processes (Church 1986). The extent to which these biogeochemical processes influence estuarine Mn distributions may, in turn, depend on estuarine flushing time (Callaway et al. 1988; Muller et al. 1994; Laslett and Balls 1995), which can vary seasonally with river discharge.

While manganese cycling exhibits a broad range of behavior in estuarine systems, barium distributions have typically exhibited non-conservative behavior in estuaries with barium production generally occurring at low salinities (Hanor and Chan 1977; Edmond et al. 1978; Li and Chan 1979). Desorption of Ba from riverine particles occurs as seawater cations substitute into clay matrices at the freshwater-saltwater boundary (Hanor and Chan 1977; Coffey et al. 1997). However, this riverine particulate source does not adequately account for Ba enrichment observed in some estuaries (Carroll et al. 1993; Coffey et al. 1997; Moore 1997; Shaw et al. 1998). In these systems, excess barium is attributed to seasonal salt intrusion with release of barium from barium-rich sediments stored in upper estuaries (Carroll et al. 1993) or from coastal aquifers (Moore 1997; Shaw et al. 1998). These studies suggest that additional Ba sources within estuaries may be important for constructing geochemical budgets for this element, especially over seasonal cycles. Barium cycling within estuaries is further complicated by seasonal removal of Ba in association with phytoplankton production (Guay and Falkner 1998; Stecher and Kogut 1999; Nozaki et al. 2001) and via adsorption onto Fe and Mn oxyhydroxides (Ingri and Widerlund 1994; Coffey et al. 1997).

The variety of Mn and Ba behaviors highlights the need for further understanding how these elements are affected by seasonal changes in estuary hydrodynamics as well as how these elements interact with each other. Furthermore, few studies have examined trace and alkaline-earth element distributions within Pacific Northwest estuaries (Callaway et al. 1988; Klinkhammer and McManus 2001), especially over seasonal timescales. We measured dissolved and particulate Mn and Ba in the Tillamook Bay estuary and five rivers feeding the estuary from January through December 1999. Our goal was to examine the distributions and partitioning of these elements in the estuary over a range of river discharge conditions and quantify their input to the coastal ocean.

METHODS

Study Area

Tillamook Bay estuary is located 80 km south of the Columbia River. The bay receives freshwater input from five rivers: the Miami, Kilchis, Wilson, Trask, and Tillamook (Figure 3.1). The estuary encompasses an area of 34 km² with an average depth of two meters (Komar 1997). Mixed semidiurnal tides occur within the estuary with up to 50% of the bay exposed as intertidal mud flats during low tides (TBNEP 1998). The study area is described in detail in Colbert and McManus (2003). River discharge rates vary seasonally due to changes in precipitation with a 30-fold decrease in discharge from winter to summer recorded during the study period (Table 3.1). Estuarine flushing times range from a

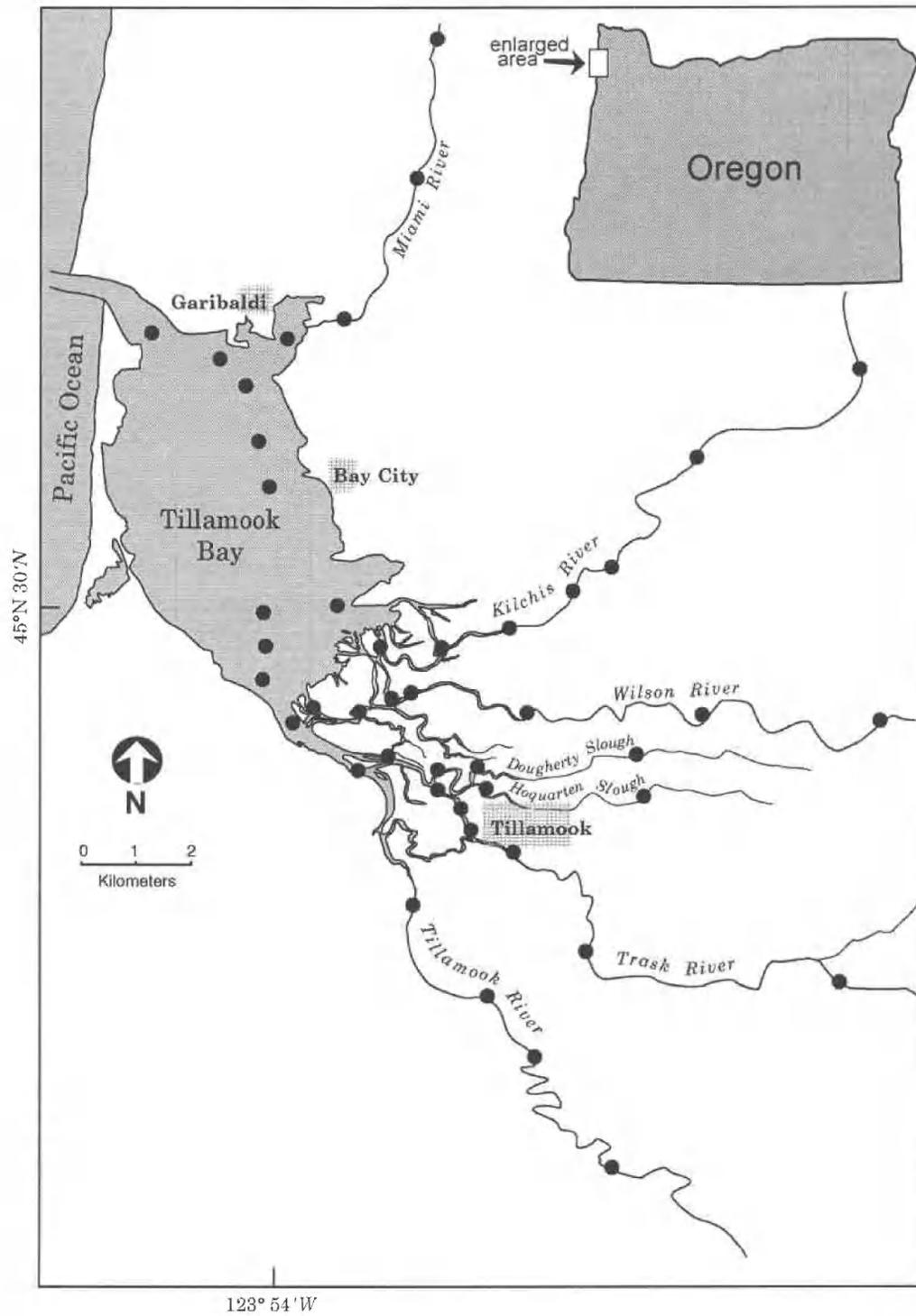


Figure 3.1. Map of study area with sampling stations indicated (●).

Table 3.1. Summary of sampling dates with river discharge (USGS: <http://water.usgs.gov>) and precipitation. Precipitation is reported as 7-day averages (Oregon Climate Service). River discharges shown in parentheses were estimated from 1997-1998 flow data normalized to Wilson River discharge data. Estuarine flushing times are calculated using the freshwater fraction method of Dyer (1997).

Sampling Dates	Discharge (m^3s^{-1})						Precipitation (in)	Flushing Time (d)
	Miami	Kilchis	Wilson	Trask	Tillamook	TOTAL		
1/2/99	na (25.2)	na (48.5)	80.4	75.6	na (21.4)	na (251.1)	1.08	1
4/2/99	na (7.7)	na (22.0)	38.6	40.5	na (7.7)	na (116.4)	0.36	3
7/19/99	na (1.5)	na (0.3)	3.6	10.2	na (0.3)	na (15.9)	0.02	17
10/17/99	na (0.3)	na (0.7)	1.5	6.4	na (0.4)	na (9.3)	0.01	32
12/3/99	na (23.6)	na (88.1)	138.5	96.3	na (29.0)	na (375.4)	0.47	1

maximum of 32 days in summer to a minimum of 1 day in winter (Table 3.1).

Estuarine flushing times (T) are calculated using the freshwater fraction method of Dyer (1997) and are described in detail in Colbert and McManus (2003).

Sampling Methods

Riverine and estuarine samples were collected on six occasions from January through December 1999 within four hours after high tide by small boat or from docks and bridges. Sampling stations were located on each river and ranged from a maximum of 13 stations on the Trask River to a minimum of four stations on the Miami River. Sampling stations also included a transect of eight stations along the major channel of the estuary (Figure 3.1). During July and December 1999, samples were collected approximately every 120 minutes at the mouth of each river and at the mouth, mid-point, and head of the estuary for a 30-hour period. Trace element clean techniques were employed during field collection and sample preparation (Bruland et al. 1979).

At each station, bulk samples for dissolved elements were collected at one meter below the surface using a modified 5-liter Niskin sampling bottle. During July and December 1999, samples were also collected one meter above the sediment interface at the mouth of the estuary. Within six hours of collection, these samples were vacuum-filtered through acid cleaned 0.45 μm membrane filters (Acrodisc[®], Gelman Sciences) in a class 100 laminar flow hood (Environmental Air Control). Samples were acidified to pH < 2 with triple-distilled nitric acid and stored until analysis. Samples were also filtered for salinity measurement.

Water samples for particulate phases were pumped through large diameter polyethylene tubing into an acid-cleaned 10-liter carboy. Samples were vacuum - filtered onto pre-weighed polycarbonate filters (1.0 μM , 90 mm diameter, Poretics). Filters were then oven-dried (50°C, 24 hours), re-weighed, and combusted at 550°C for five hours. Particulate material was digested using the hot HF/HNO₃ method of Collier and Edmond (1984). Suspended particulate material (SPM) (mg l^{-1}) was calculated by difference between loaded and unloaded filter weights divided by the volume of water sample filtered.

Surface sediment was collected at nine river stations on June 16, 2001 (Figure 3.2), according to the collection procedures described by McManus et al. (1998). Sediment samples were freeze-dried and homogenized. An aliquot of each sediment sample was weighed (0.089 - 0.108 g) and combusted at 550°C for five hours. Sediment was then digested using the hot HF/HNO₃ method described by Collier and Edmond (1984).

Analytical Methods

Samples for dissolved Mn and Ba analysis were diluted prior to analysis with 18 M Ω cm⁻¹ water (MQ water) from a Milli-Q[®] deionization system (Millipore Corp.) acidified with triple-distilled nitric acid (HNO₃). July and December 1999 samples were analyzed for dissolved manganese and barium concentrations by ICP-MS (VG Elemental PQ ExCell) at the W.M. Keck Collaboratory at Oregon State University. All other dissolved Mn and Ba analyses were performed by HR ICP-MS (VG Elemental AXIOM). Certified reference samples (NIST1643c and NIST1643d, National Institute of Standards and

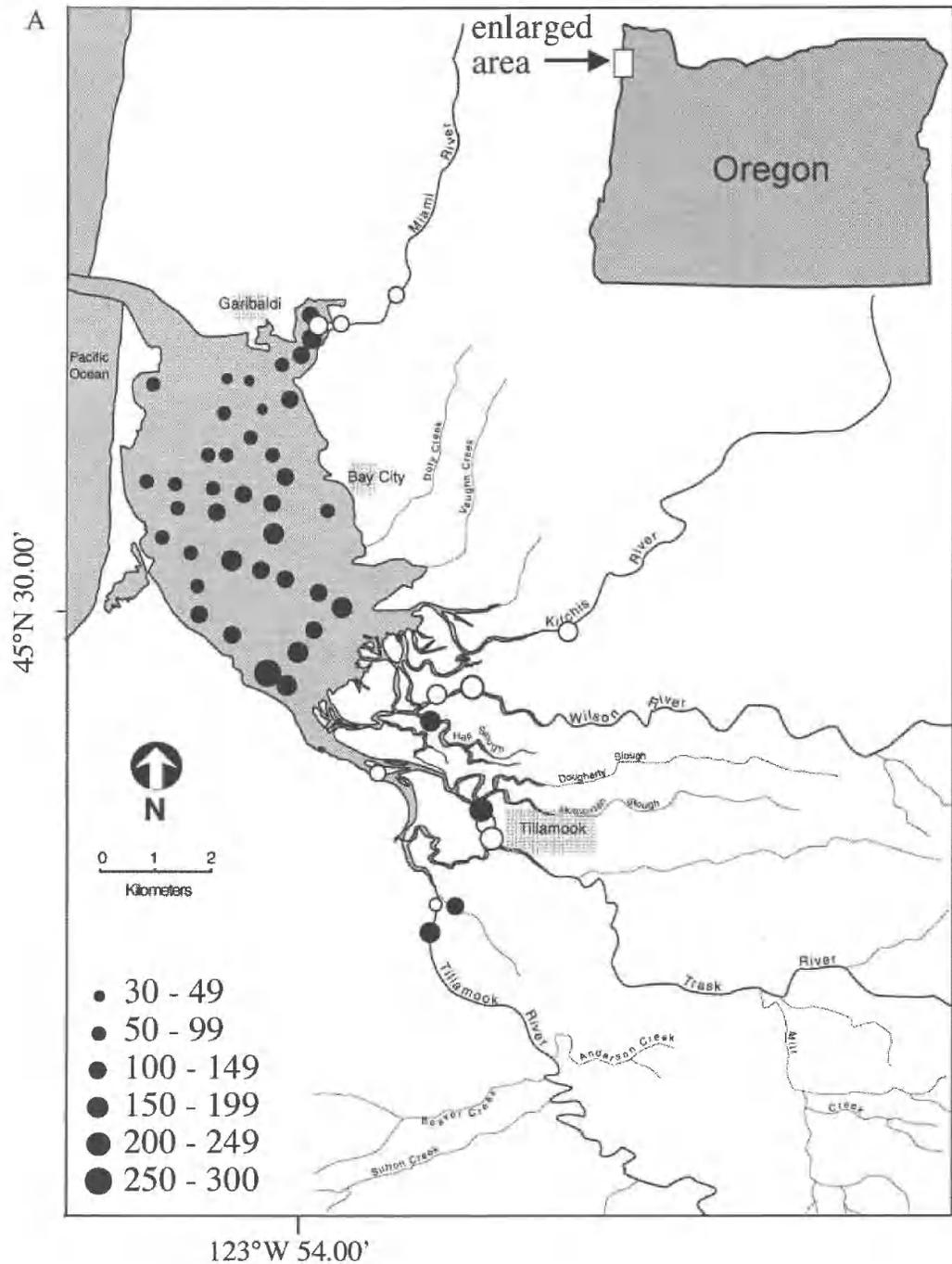


Figure 3.2. Surface sediment distributions of $Mn:Al \times 10^4$ (a) and $Ba:Al \times 10^4$ (b) collected on June 16, 2001 (open circles) and from McManus et al. (1998) (filled circles).

Table 3.2. Detection limits and blanks for dissolved elements and results of the analyses of certified standard reference materials.

Metal	Blank (nM)	Detection Limit (nM)	Certified Reference Material	Mean \pm s.d. (nM)	n	Certified value (nM)
Mn	0.17	0.17	NIST1643c	590 \pm 51	7	630 \pm 39
			NIST 1643d	690 \pm 60	5	680 \pm 15
Ba	0.36	0.11	NIST 1643c	330 \pm 17	2	360 \pm 22

Technology) were analyzed to assess analytical accuracy (Table 3.2). Detection limits were defined as three times the standard deviation of the blank (Table 3.2). The blank was determined by analyzing MQ water acidified with triple-distilled nitric acid (HNO₃).

Following digestion, particulate and surface sediment samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP-AES) (Varian Liberty 150) for Al, Mn, and Ba content. The standard reference materials for basalt (BCR-1, United States Geological Survey) and estuarine sediment (NIST-1646a, National Institute of Standards and Technology) were analyzed to verify the accuracy of particulate analyses. Measured Al, Mn, and Ba concentrations of these reference materials were within 5%, 7%, and 7%, respectively, of certified values (n = 8).

Chloride concentrations were measured using conductive detection by a DIONEX ED40 Electrochemical Detector. Detection limit for chloride was 0.22 μ M (n = 5). Salinity was calculated as 1.81 times the chloride content (Knauss 1978).

Data Analysis

Average river end-member concentrations for each sampling date are calculated as the flow-weighted average of all rivers using the river concentration farthest down stream with a salinity less than 0.09 psu. That is, the contribution of an element from each river is weighted by its contribution to the total freshwater flow. The contribution from the Miami River is not included in the average end-member calculations because the Miami River discharges into the northern end of

the estuary and contributes < 7% to the total freshwater input into the estuary. In addition, freshwater input from the Miami River had no obvious affect on the estuary's salinity distribution. The negligible impact is not surprising given the Miami's small volume contribution and the fact that the estuary's circulation pattern will lead to the rapid removal of this river's material (Komar 1997; Komar et al. in press).

Each of the observed estuarine distributions is fitted with a best fit high order polynomial to estimate departures from conservative mixing. Internal sources or sinks of trace elements are calculated by difference between the conservative end-member mixing line and the line fitted to observations. The net gain or loss calculated by this method is reported in Table 3.3 as the percent deviation from a conservative mixing line. Departures from conservative mixing could not be calculated for December 1999, as the entire salinity gradient was not sampled during this month.

Table 3.3. Departures from conservative mixing within the estuary for each element. Loss of a constituent within the estuary is indicated by a negative value while a source within the estuary is indicated by a positive value. Note that the values are percent deviations from conservative mixing.

Date	Dissolved		Particulate			Total	
	Mn	Ba	SPM	Mn	Ba	Mn	Ba
1/2/99	62	80	-53	-55	-55	-38	-12
4/2/99	125	47	26	-2	17	43	37
7/19/99	371	234	32	9	10	76	157
10/17/99	1004	331	2	41	35	402	279

Estuarine Box Model

Estuary mass balances for Mn and Ba are modeled after an approach described elsewhere (Klinkhammer and Bender 1981; Yang and Sanudo-Wilhelmy 1998) (Figure 3.3). Briefly, mass balances for each element and sampling event are modeled using river input from the southern rivers (Kilchis, Wilson, Trask, and Tillamook Rivers), input from the northern river (Miami River) and exchange with the coastal ocean. As indicated above, mass balances are not calculated for

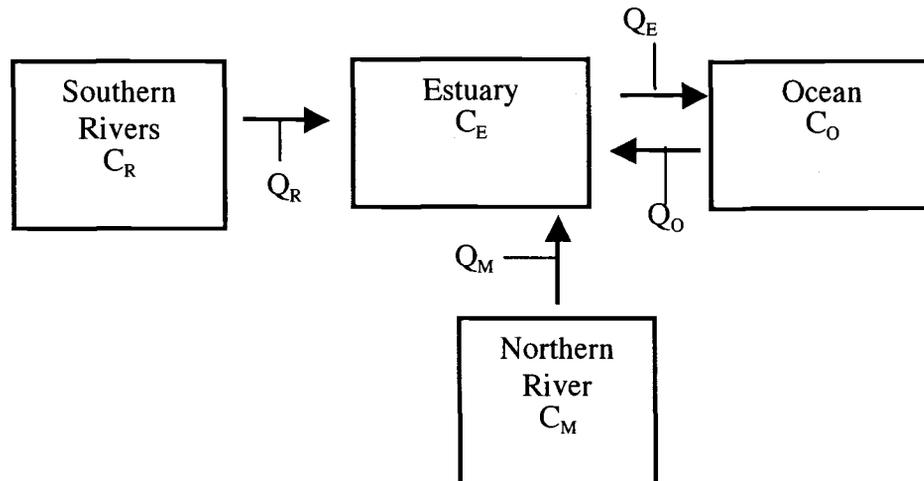


Figure 3.3. Box model of the Tillamook Bay estuary where Q_R is the total discharge from the southern rivers (Kilchis, Wilson, Trask, and Tillamook Rivers), Q_M is the discharge from the Miami River, Q_E is the flow from the estuary, and Q_O is the exchange from the ocean. Concentration for the southern rivers (C_R), the northern river (C_M), average estuary (C_E), and ocean end-member as measured (C_O) at the station at the mouth of the estuary are also indicated.

December 1999. The concentrations measured at the station located at the estuary mouth are designated as the ocean end-member. River flux is calculated as the average river end-member concentration (Table 3.4) times the river discharge rates

Table 3.4. Average flow-weighted river end-member reported (Mn, Ba, SPM, salinity) as the concentration at the farthest down stream station with salinity less than 0.09 psu. Average particulate river end-members for July and December 1999 are concentrations at the upper estuary with lowest salinity (1.05 and 0.04, respectively, for July and December).

Date	Mn (uM)	Ba (nM)	Mn (ppm)	Ba (ppm)	Al (%wt)	Ti (%wt)	Salinity	SPM (mg ^l ⁻¹)
1/2/99	0.19	8.26	1390	389	8.0	1.3	0.01	41.2
4/2/99	0.07	6.22	1360	357	6.9	1.1	0.01	4.1
7/19/99	0.20	9.06	1967	294	8.1	1.3	0.04	16.9
10/17/99	0.07	7.35	2063	250	6.1	0.9	0.06	4.2
12/3/99	0.10	7.48	1174	362	9.0	1.3	0.03	36.3

(Table 3.1) for the southern rivers (F_R) and for the northern river (F_M). Assuming conservation of salts within the estuary, the estuary can be described by the following equations $Q_E \times S_E = Q_O \times S_O$ and $Q_E = Q_R + Q_M + Q_O$, where Q_O is ocean exchange, Q_R is the river discharge from the southern rivers, Q_M is the river discharge from the northern river, S_O is the salinity measured at the ocean end-member, and S_E is the average salinity within the estuary. Combining these equations, ocean exchange (Q_O) is described by the equation $Q_O = (Q_R + Q_M) \times ((S_O \times S_E^{-1}) - 1)^{-1}$. The flux of each element from the ocean to the estuary (F_O) is calculated as the concentration at the ocean end-member times the calculated ocean exchange (Q_O). The flux from the estuary (F_E) to the ocean is equal to the total input from the rivers and the ocean ($Q_E = Q_R + Q_M + Q_O$) times the average concentration of each element within the estuary. The average estuarine concentration is calculated from the volume-weighted concentrations measured at estuary stations, not including the ocean end-member station.

Errors associated with model inputs (F_R , F_M , F_O , Total F_{in}) and outputs (F_E) were propagated using the methods described by Taylor (1982) and included uncertainties in SPM concentrations, salinity, streamflow, particulate and dissolved Mn and Ba concentrations, and estuarine volume. Generally, error terms were less than 30% of the calculated flux values. However, during winter (January 1999), the error associated with the calculated flux of Mn and Ba from the estuary (F_E) is as much as 500% of the calculated flux values. Due to the large uncertainty in F_E , the modeled “imbalance” between Mn and Ba fluxes into (Total F_{in}) and out of the estuary (F_E) during January 1999 falls within the calculated error. During other

months, the flux “imbalance” exceeds the flux error, indicating that an additional source or sink is required to balance the model.

We recognize the limitations of this type of box model approach in a small shallow estuary system. However, we use these results as a semi-quantitative numerical approach for constraining the primary input and output terms from which major imbalances can be gleaned, especially when combined with other evidence presented (e.g., estuarine distributions, calculated deviations from conservative mixing predictions). We have also demonstrated that this model balances the budget of conservative-behaving elements (e.g., H_4SiO_4 , NO_2+NO_3 ; Colbert and McManus, 2003).

RESULTS

On average, river discharge rates during winter months (January and December, 1999) are $313 \text{ m}^3 \text{ s}^{-1}$, and average estuarine flushing time is one day (Table 3.1). River discharge rates decrease through spring (April 1999, $116 \text{ m}^3 \text{ s}^{-1}$) and summer (July 1999, $16 \text{ m}^3 \text{ s}^{-1}$), reaching a minimum of $9 \text{ m}^3 \text{ s}^{-1}$ during fall (October 1999). Similarly, estuarine flushing times increases from winter through spring and summer, reaching a maximum of 32 days in fall. As a result of seasonal changes in river discharge rates and estuarine flushing, there is considerable spatial and temporal variability in the average riverine end-member concentration and the estuarine distributions of dissolved and particulate Mn and Ba.

River Water Composition

While there is some variability in riverine dissolved Mn and Ba (Table 3.4; Figures 3.4a-b), dissolved concentrations are not related to seasonal changes in river discharge rates ($R^2 < 0.12$, $n = 5$). Dissolved concentrations are also not significantly correlated with changes in SPM concentrations ($R^2 < 0.23$, $n = 5$) or SPM metal concentrations ($R^2 < 0.04$, $n = 5$).

The suspended Al concentrations vary from 9% of the suspended load during winter months to 6.1% in the fall (Table 3.4), indicating a progressive decrease in detrital particles from winter to fall. The average river end-member feeding Tillamook Bay varies seasonally in SPM concentration and metal content (Table 3.4). Average riverine SPM concentrations range from 4.1 to 41.2 mg l⁻¹ and are positively correlated with river flow ($R^2 = 0.81$, $n = 5$). Suspended particulate Mn content is inversely correlated with river discharge rates (Mn: $R^2 > 0.70$, $n = 5$) while particulate Ba content is positively correlated with river discharge rates (Ba: $R^2 > 0.74$, $n = 5$). Average annual transport of the total Mn and Ba to the estuary is dominated by the particulate phase with 75 and 76% of these elements transported in the particulate load, respectively.

Estuary

Dissolved Mn exhibits non-conservative excesses across the salinity gradient, (Figure 3.4a). The estuary is a net source of dissolved Mn, with an added Mn flux that is ~60 to 1000% over that expected if the element behaved conservatively (Table 3.3). These dissolved Mn excesses increase progressively from winter through fall of 1999, and maximum concentrations are positively

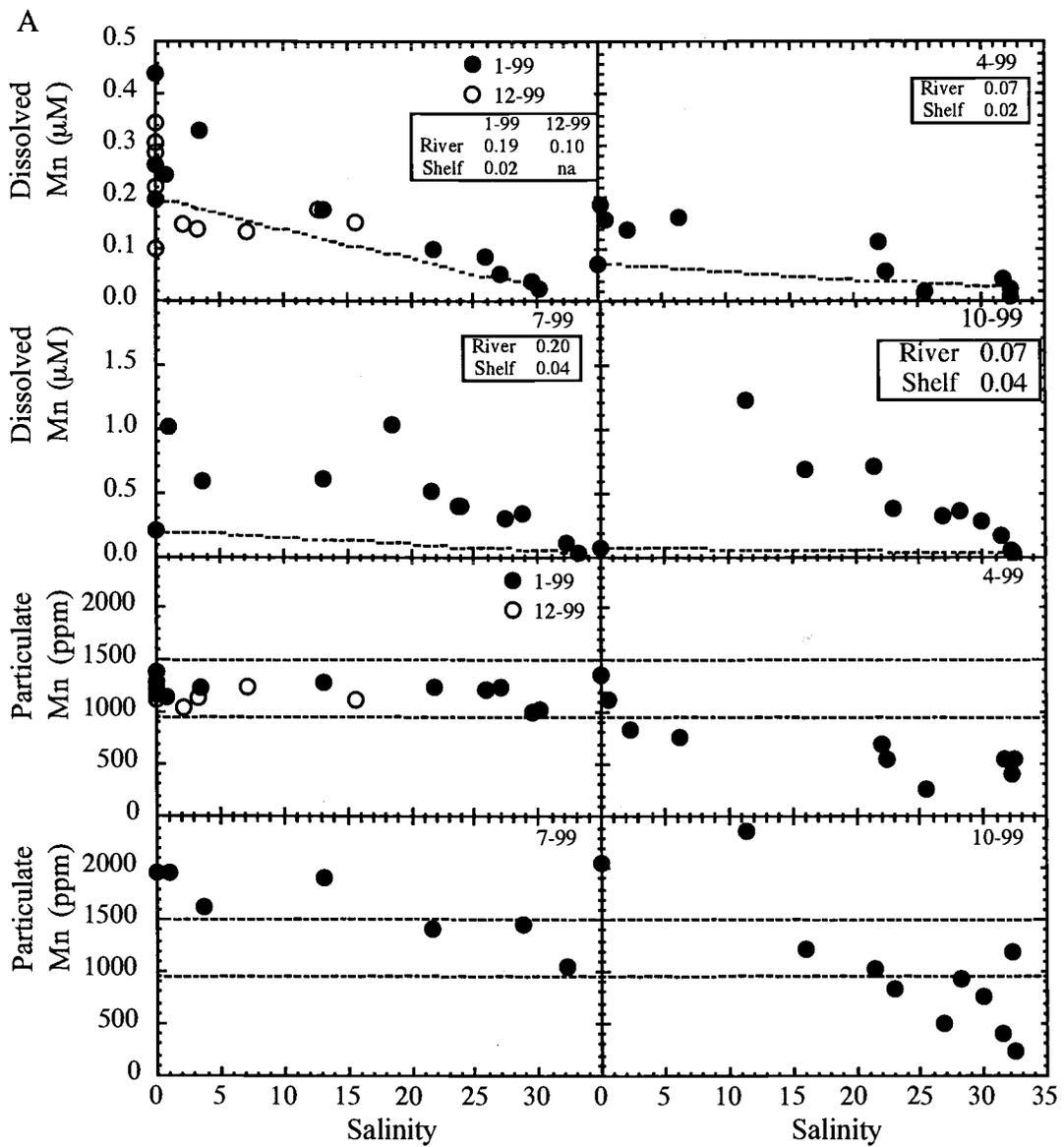


Figure 3.4. Concentrations versus salinity for each sampling date: a) dissolved and suspended particulate Mn; b) dissolved and suspended particulate Ba; c) SPM concentrations (Colbert and McManus 2003); d) suspended particulate Al. Distributions for winter months are combined for January 1999 (filled circles) and December 1999 (open circles). Average river end-member and shelf concentrations are indicated for dissolved elements. Average basalt (upper) and continental crustal (lower) abundances are indicated in plots of all suspended particulate phases (Taylor 1964).

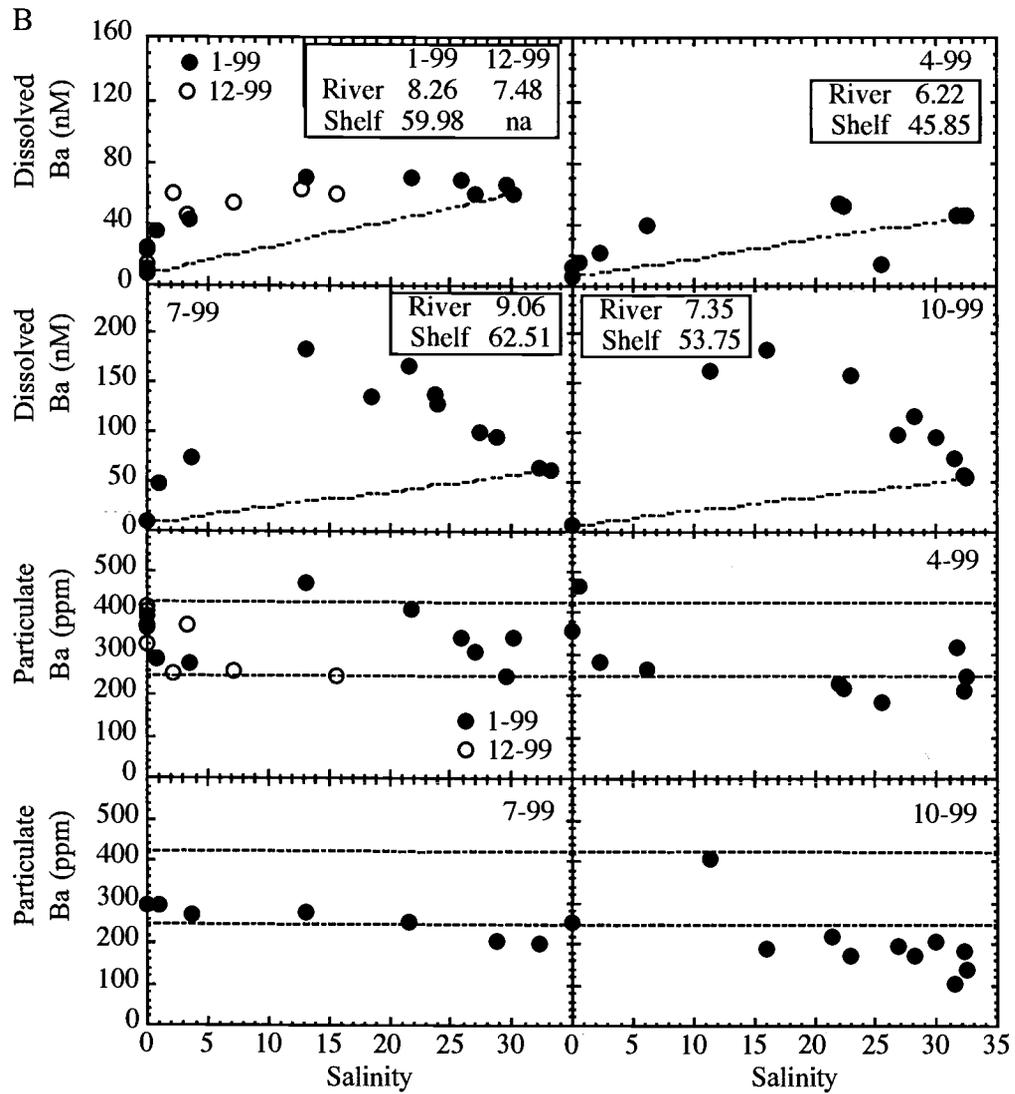


Figure 3.4. Continued.

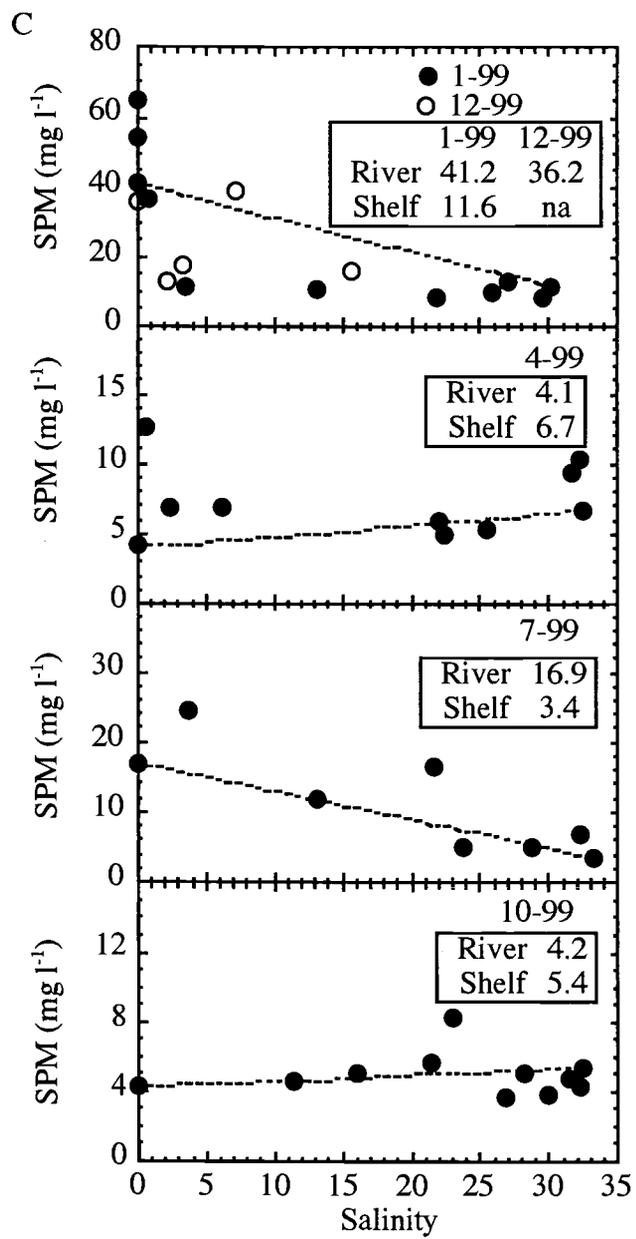


Figure 3.4. Continued.

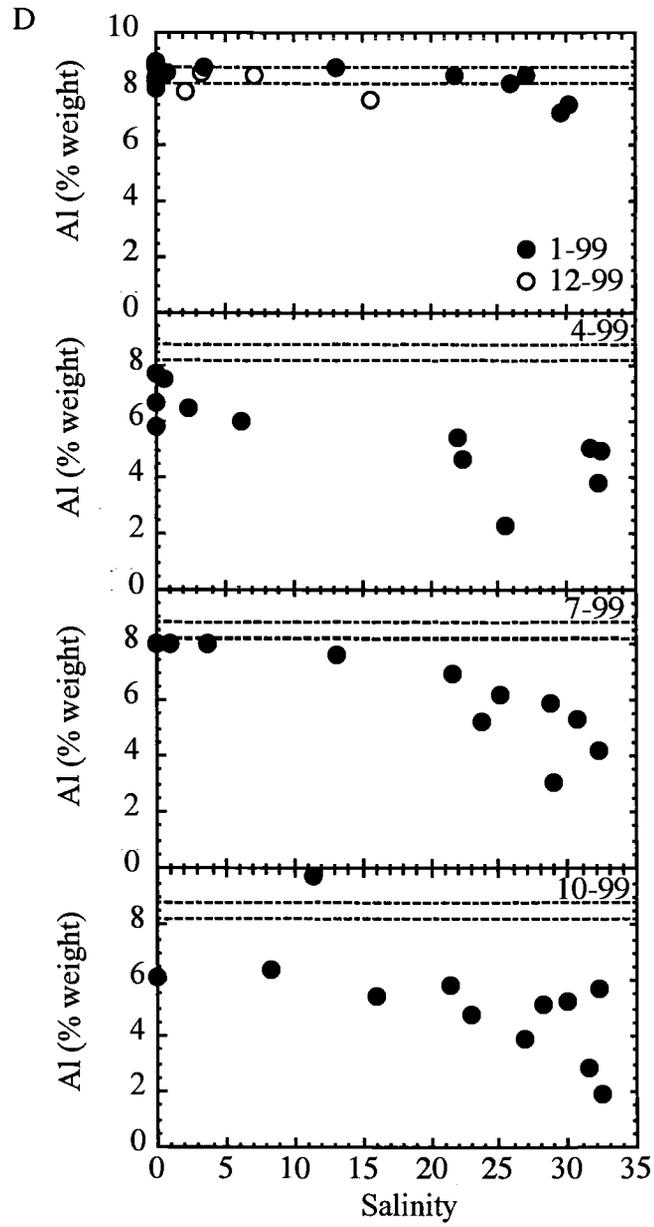


Figure 3.4. Continued.

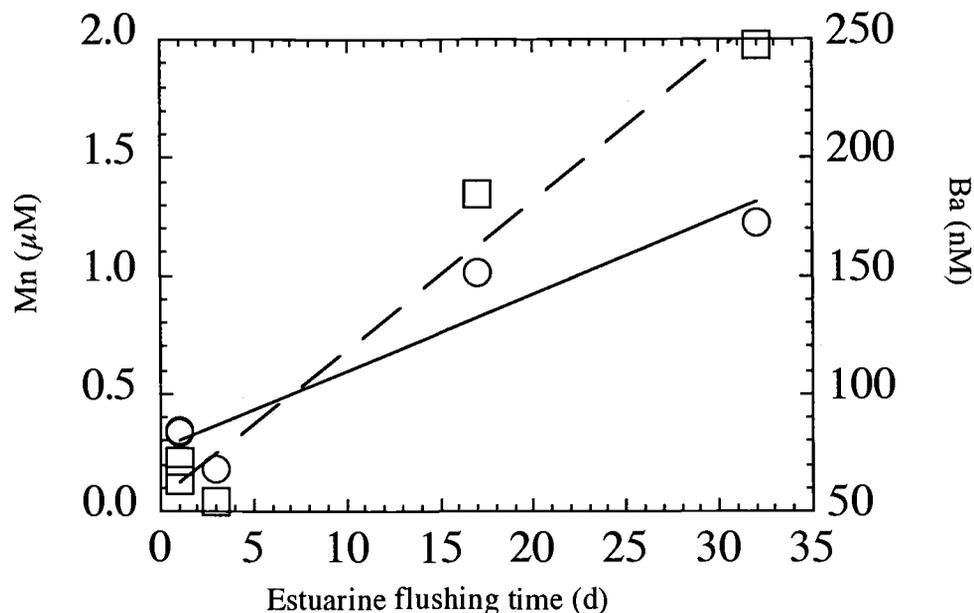


Figure 3.5. Maximum estuarine concentrations of Mn (○) and Ba (□) versus estuarine flushing time for each sampling event. The regression lines for Mn (solid: $y = 0.26 + 0.03x$; $R^2 = 0.91$) and Ba (dashed line: $y = 56 + 6.3x$; $R^2 = 0.96$) are also plotted.

correlated with estuarine flushing time (Figure 3.5: $R^2 = 0.91$, $n = 5$). Particulate Mn concentration varies seasonally with higher average concentrations observed in summer and fall than observed in winter and spring (Figure 3.4a).

Dissolved Ba is produced within the estuary during all sampling efforts (Figure 3.4b) with an excess barium flux of ~50 to 330% over that anticipated from conservative behavior (Table 3.3). The peak in Ba production varies horizontally within the estuary over seasonal cycles with maximum Ba concentrations occurring at increasing salinities from winter to fall. Maximum Ba concentrations within the estuary are positively correlated with estuarine flushing time (Figure 3.5: $R^2 = 0.96$,

n = 5) with maximum Ba production occurring under low discharge conditions (Figure 3.4b). Ba content of suspended material decreases from winter to fall (Figure 3.4b).

We estimate an effective river end-member (EREM) for dissolved Ba by extrapolating the linear region of the dissolved Ba versus salinity relationship to the zero salinity intercept (Guay and Falkner 1998; Stecher and Kogut 1999). The difference between the EREM and the measured dissolved Ba concentration can be used to estimate the particulate Ba load necessary to produce the observed signal. This approach assumes that cation exchange is the dominant excess Ba source, and is thus termed "desorbed Ba." This desorbed signal, in turn, can be compared to the actual riverine suspended particulate Ba concentrations to verify if the particulate input is sufficient to account for the observed Ba concentration ("desorbable Ba"). Based on these comparisons, the production of dissolved Ba via desorption from suspended riverine material can account for the Ba excesses in the estuary during winter months (Table 3.5). However, at all other times the Ba content of suspended riverine material is insufficient to account for the dissolved Ba excess (Table 3.5).

SPM concentrations are relatively constant throughout the estuary but exhibit an upper estuary maximum during winter months (Figure 3.4c). There is a ~50% loss of the suspended load in the upper estuary during January 1999 while suspended material excesses occur during all other months (Table 3.3). The location of these SPM excesses varies horizontally within the estuary with excess SPM most pronounced at the upper estuary during April 1999, and transitioning to mid-estuary by July 1999 (Figure 3.4c). The Al concentration in the suspended load decreases progressively from crustal values under winter, high flow conditions

Table 3.5. Dissolved Ba concentrations observed at the river end-member and calculated effective river end-member (EREM).^a

Sampling Date	Riverine Ba (nM)	EREM Ba (nM)	Desorbed Ba (nM)	Desorbable Ba (nM)
1/2/99	8	80	72	117
4/2/99	6	69	63	11
7/19/99	9	254	245	36
10/17/99	7	387	379	8
12/3/99	7	58	50	96

^a EREM was estimated graphically by extrapolating the linear portion of the dissolved Ba versus salinity data to the zero salinity intercept. Desorbed Ba is calculated as the difference between the EREM and the observed river Ba concentrations. Desorbable Ba is the average particulate Ba content of the suspended riverine load times the average SPM concentration of the rivers.

to below crustal values under the low river discharge conditions of fall (Figure 3.4d). The mean annual percentage of total estuarine Mn and Ba present in the solid phase is 97 and 40%, respectively. The percent of Mn and Ba associated with suspended particles reaches minimums of ~50 and <20% in July 1999 and 25 and <15% in October 1999, respectively.

Surface sediment Mn in the rivers and upper estuary is similar to average crustal abundance for basalt ($\text{Mn:Al} \times 10^4 = 171$) and continental crust ($\text{Mn:Al} \times 10^4 = 115$) (Taylor 1964) and is depleted relative to Al toward the mouth of the estuary (Figure 3.2a). Average surface sediment Ba in the rivers and upper estuary is also similar to the crustal abundance for basalt ($\text{Ba:Al} \times 10^4 = 28$) and continental crust ($\text{Ba:Al} \times 10^4 = 52$) (Taylor 1964) but is enriched toward the mouth of the estuary (Figure 3.2b).

Box Model

Based on box model calculations (Figure 3.3), total budgets for Mn and Ba are not sufficiently balanced with missing sinks and sources accounting for up to 77% of the total budgets (Table 3.6). During January 1999, sources of Mn to the estuary exceed calculated outputs by ~6% (Table 3.6). Although uncertainties in the mass balance calculation may explain this deficit, ~50% of the suspended load is removed in the upper estuary ($S < 4$), and there is a concurrent loss of ~50% or more of the particulate Mn and Ba within the estuary (Table 3.3). A sedimentation rate for January 1999 (R_s) is calculated using the loss of suspended material (L) within the estuary (Table 3.3), the volume of the estuary ($V = 7.0 \times 10^{10}$ l), the area of the estuary ($A = 34$ km²), the calculated flushing time ($T = 1$ day), and a dry sediment density (ρ) of 2.65 g cm⁻³ (as referenced in Yang and Sanudo-Wilhelmy 1998) as described in the equation $R_s = (L \times V_E) \times (T \times A \times \rho)^{-1}$. The sedimentation rate calculated by this method is 0.4 cm y⁻¹ and compares well with sedimentation rates reported for the estuary (0.05 to 0.68 cm y⁻¹; McManus et al. 1998). Sediment burial (F_s) is described by the equation $F_s = R_s \times [(1-\phi) \times \rho \times C_p] \times A_E$ where R_s is the calculated sedimentation rate, ϕ is the porosity (0.9), ρ is dry sediment density (2.65 g cm⁻³), C_p is the average estuarine suspended particulate concentration for each element, and A_E is the surface area of the estuary (34 km²). When these sediment burial rates are incorporated into the Mn and Ba budgets for January, the modeled sources and sinks are nearly balanced (within 10%) (Table 3.6). This agreement is particularly surprising as it is during this period that the uncertainties in modeled fluxes are the highest.

Table 3.6. Mass balance results for total Mn and Ba in the Tillamook Estuary.^b

	Date	F _R	F _M	F _O	Total F _{in}	F _E	Imbalance	%	F _S	F _{Re}	F _D
Mn	1/2/99	15.4	0.54	2.7	19	-18	-1.1	-6	-1.4		
	4/2/99	1.0	0.03	0.55	1.6	-2.4	0.78	33		0.31	0.85
	7/19/99	0.64	0.03	0.28	0.94	-1.9	0.99	51		0.12	1.1
	10/17/99	0.11	0.00	0.14	0.26	-1.2	0.89	77		0	0.64
Ba	1/2/99	3.9	0.16	2.5	6.5	-6.8	0.28	4	-0.39		
	4/2/99	0.25	0.02	0.92	1.2	-1.6	0.37	24		0.12	0.43
	7/19/99	0.09	0.01	0.21	0.30	-0.71	0.41	57		0.05	0.51
	10/17/99	0.02	0.00	0.21	0.23	-0.71	0.48	68		0	0.30

^b All fluxes are in g s^{-1} with losses from the estuary indicated as a negative flux. Flux from the southern rivers (F_R) is equal to the average flow-weighted concentration of the southern rivers (C_R) times the total river discharge (Q_R) from those rivers. Flux from the northern river (F_M) is equal to the Miami River concentration (C_M) times Miami River flow (Q_M). Flux from the ocean to the estuary (F_O) is equal to the concentration at the mouth (C_O) times the calculated ocean exchange (Q_O). Flux from the estuary to the ocean (F_E) is the average estuary concentration (C_E) times the total input from rivers and exchange from the ocean (Q_R + Q_M + Q_O). For January 1999, F_S is the burial amount calculated from loss of SPM within the estuary (R_S = 0.38 m y^{-1}) during January 1999. Resuspension rates (F_{Re}) are calculated based on the observed SPM excesses, average surface sediment Mn and Ba concentrations within the estuary (Figure 3.2: McManus et al. 1998), and estuarine volume and flushing time during each sampling event (Table 3.1). Input from benthic flux (F_D) is calculated using the excess concentrations above conservative mixing (Table 3.3), estuary volumes, and flushing time of the estuary (Table 3.1). Imbalance column indicates the input needed to balance the total output.

During all other sampling events, there is net production of suspended material within the estuary (Table 3.3). From this "excess" of suspended material we calculate an input rate for each element (F_{Re}) (Table 3.3). For this calculation we use the average surface sediment Mn and Ba concentrations within the estuary (Figure 3.2: McManus et al. 1998), the estuarine volume (April: 6.7×10^{10} l; July: 6.5×10^{10} l; October: 5.9×10^{10} l) and the flushing time during each sampling event (Table 3.1). This calculation represents an extreme case in that we are assuming that all of the excess SPM is caused by resuspension of bottom sediments—i.e., there is no internal estuarine production of particles. Despite this end-member assumption, resuspended material cannot balance the internal budgets.

A dissolved flux from the sediments could be an additional elemental source to the estuary, and is consistent with the observed dissolved excesses (Figure 3.4a-4b). If we assume that the observed excess dissolved concentrations were driven by input from the sediment (Table 3.3), we can calculate a benthic flux from the estuary volumes, surface area (34 km^2), and flushing time of the estuary (Table 3.1). With this additional elemental source (F_D), mass balances for Mn and Ba for April and July 1999 agree within 15%. If both the resuspension and benthic flux terms are included in the box model, the sources of Mn and Ba to the estuary exceed calculated outputs by ~10 to 20% for April and July 1999. However, the October 1999 budgets for Mn and Ba could accommodate additional dissolved sources with missing sources accounting for up to 26% of the total budget.

The highest total riverine fluxes of Mn and Ba (dissolved plus particulate) are related to river discharge rates with the highest fluxes occurring under winter conditions (Table 3.6: $F_R + F_M$). Fluxes from the estuary to the coastal ocean are

five times higher during the winter than any other season (Table 3.6: F_E). However, internal sources of Mn and Ba significantly increase the fluxes to the coastal ocean during spring, summer and fall. Internal sources of dissolved Mn and Ba are most pronounced under the low river flow conditions of July and October 1999 (Table 3.6: F_D & F_{Re}).

DISCUSSION

River Water Composition

Average dissolved Mn concentrations at the river end-member of Tillamook Bay ($0.07 - 0.24 \mu\text{M}$) are similar to average world river concentrations ($0.15 \mu\text{M}$: Martin and Whitfield 1983) and within the range reported for other rivers (Bewers and Yeats 1978; Laslett and Balls 1995). Average dissolved Ba concentrations ($6.2 - 12.9 \text{ nM}$) at the river end-member are 30 times lower than average world river concentrations (437 nM : Martin and Whitfield 1983) and are considerably lower than many other river systems, e.g., the Ganges-Brahmaputra river system ($382-613 \text{ nM}$, Carroll et al. 1993), Eurasian rivers ($24-160 \text{ nM}$, Guay and Falkner 1998), and the Mississippi River ($60-64 \text{ nM}$, Hanor and Chan 1977).

Estuary

Based on Mn and Ba distributions and on the calculated sources and sinks for these metals, their estuarine behavior is dominated by two factors: interaction with suspended river-derived particulate material and input from benthic sources. We attribute seasonal concentration differences to changes in the relative

importance of these two variables. Suspended sediment interactions include precipitation reactions (i.e., possible removal) as well as desorption or remineralization from riverine particulate material. Benthic input of Mn and Ba includes the dissolved advective and diffusive flux from the sediments and the potential contribution from resuspension of surface sediment from within the estuary.

Manganese

Dissolved manganese distributions in Tillamook Bay (Figure 3.4a) resemble those found in numerous other estuaries (Yaquina Estuary: Callaway et al. 1988; St. Lawrence, Newport, Rhine and Scheldt estuaries, Tamar estuary, Severn estuary, and the Forth: Laslett and Balls 1995). During all seasons, dissolved Mn exhibits non-conservative production across the salinity gradient (Figure 3.4a). The apparent excesses in dissolved Mn vary seasonally, progressively increasing from winter through fall. Manganese particulate content also varies seasonally with higher average concentrations observed in summer and fall than in winter and spring (Figure 3.4a). We attribute these seasonal differences in dissolved and particulate Mn distributions in Tillamook Bay to a combination of suspended particulate interactions, namely remineralization of organic material and sedimentation, and diffusive flux from the sediments.

Under high flow conditions of winter (mean discharge = $313 \text{ m}^3 \text{ s}^{-1}$), the source of dissolved manganese within the Tillamook estuary is concentrated at the river water-salt water interface (Figure 3.4a). Surveys of the Seine River estuary and mixing studies indicate release of Mn from SPM in the mixing zone of river

and estuarine waters due to sharp increases in turbidity and salinity over seasonal cycles (Ouddane et al. 1997). Consistent with these studies, in Tillamook Bay the upper estuary source of dissolved Mn coincides with high SPM loads ($< 65 \text{ mg l}^{-1}$, Figure 3.4c) and sharp increases in salinity at the river water – ocean water interface during winter months. However, the dissolved Mn enrichment in the presence of elevated SPM is also consistent with Mn-oxides being reduced at the low salinity region of the estuary, a location dominated by intertidal mudflats. While non-conservative behavior of Mn in the upper estuary of the Scheldt estuary is attributed to dissolution of oxy-hydroxides under low water column oxygen conditions (Paucot and Wollast 1997), production of dissolved Mn from the dissolution of oxy-hydroxides does not necessitate low dissolved oxygen concentrations. For example, Klinkhammer et al. (1997) found that the non-conservative distribution of dissolved Mn in the Columbia River estuary and its associated plume is due to Mn-oxide reduction during the oxidation of humic ligands. This reduction occurs in suboxic interiors of suspended aggregates by microbes using Mn-oxides as electron acceptors (Klinkhammer and McManus 2001). Vojak et al. (1985) found that microbial oxidation of manganese in estuarine waters is enhanced by high particulate loads such as those observed at the upper estuary of Tillamook Bay under high discharge, winter months. Consistent with this idea, distributions of dissolved phosphate and ammonium within the Tillamook estuary during the winter of 1999 indicate significant organic carbon remineralization within the water column at low salinities (Colbert and McManus 2003).

Under high flow conditions of winter, we observe a net loss relative to conservative behavior of 38 g m^{-2} of particulate Mn within the estuary compared to conservative mixing predictions ($\sim 55\%$ loss shown in Table 3.3). As described above, a potential “sink” for particulate Mn could be the reduction of suspended Mn-oxides. Reduction of Mn-oxides should leave a dissolved Mn signature within the estuary. Consistent with this idea, we observe an 8 g m^{-2} excess of dissolved Mn within the estuary ($\sim 62\%$ excess shown in Table 3.3). Assuming that all of the “excess” dissolved Mn observed at the upper estuary is released from the reduction of Mn-oxides, this production of dissolved Mn can only account for $\sim 20\%$ of the loss of particulate Mn observed in the estuary (Table 3.3). Box model calculations and sediment burial rates indicate that the remaining loss of particulate Mn is due to sedimentation of suspended particulate material at the upper estuary (Table 3.6), as observed for particulate Fe (data not shown). Therefore, winter Mn distributions within Tillamook Bay result from production of dissolved Mn from the remineralization of organic carbon and loss of particulate Mn from sedimentation of suspended material. This combination of processes results from the high delivery rates of terrestrial material during high river discharge.

While excesses in dissolved Mn are expected under high flow conditions, excesses are also observed under the reduced SPM concentrations of spring, summer, and fall (Table 3.3). Other studies attribute production of dissolved Mn to resuspension of bottom sediments (Morris et al. 1982; Morris et al. 1987; Paucot and Wollast 1997) or a benthic flux driven by the reductive dissolution of sedimentary Mn (Laslett and Balls 1995). We observed “excess” particles within the estuary compared to conservative mixing (i.e. SPM source – Table 3.3), which

are coincident with excesses in particulate Mn within the estuary during summer (<10%) and fall (~40%) (Table 3.3). However, inputs from suspended material (F_{Re}) are insufficient to account for the Mn excesses observed during spring, summer, or fall (Table 3.6). Therefore, budgets for Mn in the estuary can only be balanced by considering an additional input, i.e., a benthic input (F_D) calculated from the observed dissolved Mn excesses and estuarine volume, area, and flushing time (Table 3.6).

Based on these constraints, we calculate a Mn flux of 30 to 50 $\mu\text{mol Mn m}^{-2} \text{d}^{-1}$, which is generally smaller than, but similar to those in other estuaries (Scheldt Estuary calculated flux of 200 $\mu\text{mol m}^{-2} \text{d}^{-1}$: Duinker et al. 1979; Narragansett Bay chamber flux of 20-730 $\mu\text{mol m}^{-2} \text{d}^{-1}$: Elderfield et al. 1981; Chesapeake Bay microcosm experiment flux of 36-400 $\mu\text{mol m}^{-2} \text{d}^{-1}$: Hunt 1983; Yaquina Estuary calculated flux of 100-400 $\mu\text{mol m}^{-2} \text{d}^{-1}$: Callaway et al. 1988). Input of dissolved Mn via diffusive flux is also consistent with the strong linear correlation between maximum dissolved Mn concentrations within the estuary and estuarine flushing times (Figure 3.5) as increased water residence times would allow buildup of the dissolved Mn signal in the water column from the benthic flux.

The upper estuary dissolved Mn source (Figure 3.4a) coincides with the location of mudflats and Mn-rich surface sediment within the estuary (Figure 3.2a). Mn-oxides are typically reduced in tidal mudflats (Panutrakul and Baeyens 1991; Caetano et al. 1997) such as those characterizing the upper estuary. In the Tillamook estuary, high sediment loading rates during winter are followed by reduced estuarine flushing during spring, summer, and fall. This reduction in circulation may lead to low sediment oxygen concentrations that facilitate the

reduction of Fe and Mn-oxides within the sediment. Regeneration of Mn as the soluble form Mn (II) occurs under reducing conditions within sediments (Froelich et al. 1979). Unstable Mn (II) ions may persist in oxic waters since the rate of Mn (II) oxidation is slow (Hem 1963; Morris et al. 1982; as referenced in Ouddane et al. 1997). Particulate Mn content within the water column is significantly enriched at the upper estuary during spring and summer (Figure 3.4a). This seasonal enrichment may be supported by the diffusive flux of reduced Mn and subsequent oxidation to Mn-oxides which form coatings on suspended particles within the estuary (Dehairs et al. 1989; Millward et al. 1996; Owens et al. 1997).

It is clear that the processes influencing dissolved and particulate Mn distributions vary seasonally. Remineralization of river-derived organic material increases dissolved Mn concentrations during winter months while a benthic source dominates during reduced estuarine flushing conditions. The particulate Mn budgets are dominated by sedimentation of river-derived particles during winter and by the oxidation of sediment-derived dissolved Mn during the other seasons.

Barium

As in the case of Mn, production of dissolved barium within the estuary plays a central role in its cycling. Dissolved Ba excesses range from ~50 to over 300% (Table 3.3; Figure 3.4b). Barium production has been observed in numerous other estuaries (Hanor and Chan 1977; Edmond et al. 1978; Li and Chan 1979) and is generally attributed to desorption of Ba from suspended riverine particulates as seawater cations substitute for Ba in clay matrices (Hanor and Chan 1977). Within the Tillamook estuary, dissolved Ba production via desorption from suspended

riverine material can account for the Ba excesses in the estuary during winter months (Table 3.5). This calculation, however, assumes that all of the particulate Ba is available for desorption — an assumption that is highly unlikely. Moreover, previous studies that discuss the importance of this mechanism typically describe desorption as occurring at low salinities (Hanor and Chan 1977; Edmond et al. 1978; Li and Chan 1979), in contrast, our observed dissolved Ba excesses are at high salinities. Outside of winter months, our data indicate that there must be a lower estuary source for dissolved Ba that is not supported by riverine inputs (dissolved or particulate).

As with our study, Carroll and others (1993) observed high barium production in the Ganges-Brahmaputra mixing zone that could not be supported by desorption of Ba from riverine particles alone. They hypothesized that an additional Ba source was the storage of sediments in fresh water sections of the river mouth during high discharge, followed by reworking and desorption of Ba during low discharge. Moore (1997) measured Ba fluxes from the Ganges-Brahmaputra and found that reworking of sediments could not account for the Ba signals observed by Carroll et al. (1993) as there was insufficient storage of sediment during high discharge periods to account for the Ba signal during low discharge periods. Sediment Ba concentrations in surface sediments of rivers feeding Tillamook Bay are also not sufficient to support the observed excesses in dissolved Ba (Figure 3.2b).

The central dilemma regarding Ba is that outputs far exceed known external inputs, but there is clearly internal Ba production that could bring the budget nearly in balance. Thus there must be a source for which we simply do not have an

accurate accounting. We must reconcile our hypothesis with two fundamental observations (1) that the dissolved Ba excess is centered at much higher salinities than that typically identified in estuaries (Figure 3.4b) and (2) that sedimentary Ba is highest at the lower extremes of the estuary (Figure 3.2b). We propose that enrichment of sediment Ba concentrations are associated with ocean-derived material deposited at the lower estuary (McManus et al. 1998). We choose this hypothesis because Ba concentrations of bed sediments are noted to increase along a zonal gradient from the upper estuary toward the mouth of the estuary (Figure 3.2b) while, in contrast, Mn contents decrease (Figure 3.2a). Certainly, the difference in these sediment distributions can be caused by dilution of estuarine sediments with marine particles, or some type of particle recycling process. However, these distributions are also consistent with an oceanic source of lower estuarine sediment, which is precisely the conclusion of Komar and others (in press) based on the estuary's sediment budget. In addition, as mentioned above, the dissolved Ba maxima occurs through the mid to lower estuary during summer and fall suggesting a lower estuary dissolved source (Figure 3.4b). We note here the possibility that the source of dissolved Ba could be resuspension of this surface sediment followed by its dissolution or a direct dissolved benthic flux or both of these processes. Production of suspended material during April, July, and October 1999 is coincident with excesses in particulate Ba within the estuary during these months (Table 3.3). However, resuspension of surface sediment is insufficient to balance the Ba budget (Table 3.6; Table 3.3).

Assuming that the dissolved Ba is derived from a benthic source, we calculate a lower estuary benthic Ba efflux that ranges from 5 to 9 $\mu\text{mol m}^{-2} \text{d}^{-1}$.

There are no reported estuarine barium fluxes for comparison with these estimates; however, these fluxes were similar to coastal Ba fluxes measured in the Southern California borderland basins ($0.7 - 4.1 \mu\text{mol m}^2 \text{d}^{-1}$) and slightly elevated relative to central California margin sites ($0.6 - 1.3 \mu\text{mol m}^2 \text{d}^{-1}$) (McManus et al. 1999). Thus, the idea of a benthic efflux of this magnitude would hardly be surprising. Input of dissolved Ba via a sedimentary efflux is also consistent with the strong linear correlation between maximum dissolved Ba concentrations within the estuary and estuarine flushing times (Figure 3.5), as increasing water residence times would allow buildup of the dissolved Ba signal in the water column from benthic flux.

We suggest that the benthic efflux of dissolved Ba is the source of the observed excesses within the estuary and that the dissolved flux is supplied by regeneration of solid Ba that originates seaward of the estuary. The oceanic source of solid Ba may be derived from biogenic material formed in the near-shore water column. Barite may precipitate inside sulfate-rich microenvironments formed by assemblages of decaying diatoms (Alldredge and Gotschalk, 1989; Bishop, 1988). This barite would sink rapidly with the associated biogenic detritus and could be delivered to the estuary. The benthic efflux of dissolved Ba would then result from the deposition and benthic dissolution of ocean-derived particulate Ba.

We recognize that other sources may also be contributing to the dissolved Ba budget. For instance, seasonal intrusion of saltwater into aquifers can support elevated Ba concentrations in estuarine and coastal systems (Moore 1997; Shaw et al. 1998). However, the dissolved Ba maximum in this previous work occurs at much lower salinities than where our maximum occurs. Thus, while investigations

into the seasonal groundwater discharge in the Tillamook watershed are certainly warranted, our interpretation of an oceanic Ba source is consistent with the available data.

Annual Budgets

The processes outlined here have a pronounced affect on Mn and Ba fluxes to the coastal ocean. Mn and Ba fluxes from the estuary to the adjacent coastal waters depend primarily on river discharge rates with maximum annual fluxes occurring in winter and decreasing through spring, summer, and fall (F_E , Table 3.6). When river discharge reaches a winter maximum, substantial quantities are exported. However, the high suspended load transported during high discharge months is significantly reduced by sedimentation at the river water-salt water interface (F_s , Table 3.6). Reductions in river discharge rates from spring through fall facilitate the development of a benthic source signal, significantly increasing Mn and Ba fluxes from the estuary to the coastal ocean. The transport across the sediment-water interface during months of reduced river discharge results in dissolved Mn and Ba fluxes to the coastal ocean that are enriched by 390 and 170%, respectively, over what is expected from riverine inputs alone (F_D , Table 3.6).

CONCLUSIONS

Our goal was to examine the seasonal distributions and partitioning of Mn and Ba in the Tillamook Bay estuary. This study describes mechanisms operating within the estuary and highlights the need for further study of Pacific Coast

estuaries. To first order, the Ba distributions, are consistent with other studies but point to processes that have not been identified elsewhere—i.e., an important oceanic source. The processes outlined here have a pronounced affect on elemental fluxes to the coastal ocean. Elemental fluxes from the estuary to the adjacent coastal waters depend primarily on river discharge rates (Table 3.6). When river discharge reaches a winter maximum, substantial quantities are exported. However, the high suspended load transported during high discharge months is significantly reduced by sedimentation at the river water-salt water interface. Reductions in discharge rates from spring through fall facilitate the development of a benthic source signal, significantly increasing Mn and Ba fluxes from the estuary to the coastal ocean.

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4. IRON CYCLING IN A PACIFIC NORTHWEST ESTUARY: IMPORTANCE
OF SEASONALITY AND PARTICULATE PHASES FOR COASTAL IRON
DELIVERY

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ABSTRACT

We measured dissolved and particulate iron (Fe) within the Tillamook Bay estuary to quantify and identify the processes responsible for iron delivery to the Oregon coastal zone. Measurements were made under a range of river discharge conditions, which are driven by seasonal variations in precipitation. In general, riverine iron is dominated by particulate phases (~98%). Total (dissolved plus particulate) riverine iron export to the coastal ocean is more than a factor of ten higher during winter than during any other time period. These winter flux maxima occur despite estuarine removal processes that also occur under winter conditions. During all other seasons, box model calculations indicate that the total Fe transport to the coastal ocean may be enhanced by internal estuarine processes, thus leading to greater iron export than predicted simply from riverine delivery. Results presented here suggest that although rivers deliver most of their iron to the ocean in particle phases during winter months, some of this particulate material is trapped in the estuary and processed within the estuary over seasonal timescales. This internal processing of particulate iron may deliver more bioavailable iron to the coastal zone during these periods. Although much of the primary production within the estuary may be occurring during summer periods, it is clear that most of the coastal iron is delivered during the less-productive periods. Therefore, we speculate that processing of this iron on the near-shore seabed will likely release bio-reactive iron to the overlying water column later in the year.

INTRODUCTION

The variety of hydrodynamic and physico-chemical conditions occurring in estuaries gives rise to a range of elemental behavior among estuarine systems (Owens et al. 1997) and temporally within a given estuary (Stecher and Kogut 1999). Iron distributions within estuaries are controlled largely by flocculation of colloidal materials at low salinities (Sholkovitz 1976; Boyle et al. 1977; Mayer 1982; Church 1986; Forsgren et al. 1996). At the freshwater-saltwater interface, river-derived iron oxide-organic colloids are neutralized by seawater cations and are rapidly removed from solution (Boyle et al. 1977). As a result, riverine iron fluxes to coastal waters are dramatically reduced. For example, Flegal and others (1991) documented a loss of 70% of the dissolved Fe flux within the San Francisco Bay estuary. Likewise, removal of 50-95% of the riverine flux of dissolved iron has been observed in U.S. East Coast estuaries (Boyle et al. 1977; Church 1986).

While Fe behavior is relatively consistent among estuaries, seasonal changes in Fe transport and flux can occur (Yang and Sanudo-Wilhelmy 1998), but are not well quantified. Such variations could dramatically affect the amount of iron delivered to the coastal ocean where iron concentrations can be limiting to coastal phytoplankton populations (Hutchins and Bruland 1998; Hutchins et al. 1998; Zhang 2000). Furthermore, because Fe oxides are known to influence the precipitation and regeneration of other elements (Ingri and Widerlund 1994), seasonal changes in their reactivity may also influence the estuarine distribution and transport of other elements.

Few studies have examined iron distributions within Pacific Northwest

estuaries (Callaway et al. 1988), especially over seasonal timescales. We measured dissolved and particulate Fe in the Tillamook Bay estuary and the five rivers feeding the estuary from January through December 1999. Our goal was to examine the distributions and partitioning of iron in the Tillamook Bay estuary over seasonal cycles and under a range of river discharge conditions. Furthermore, we quantified seasonal changes in loading rates from the rivers to the estuary and, ultimately, fluxes to the coastal ocean.

METHODS

Study Area

Tillamook Bay estuary is located 80 km south of the Columbia River. The bay receives freshwater input from five rivers (Figure 4.1), encompasses an area of 34 km², and has an average depth of two meters (Komar et al. in press). The study area is described in greater detail elsewhere (Colbert and McManus 2003). River discharge rates vary seasonally with a 30-fold decrease in discharge from winter to summer recorded during the study (Table 4.1) and calculated estuarine flushing times ranging from a maximum of 32 days in summer to a minimum of 1 day in winter (Table 4.1).

Sampling and Analytical Methods

Riverine and estuarine samples were collected on six occasions from January through December 1999 within four hours after high tide by small boat or from docks and bridges. Samples were collected at 4 - 13 stations on each river

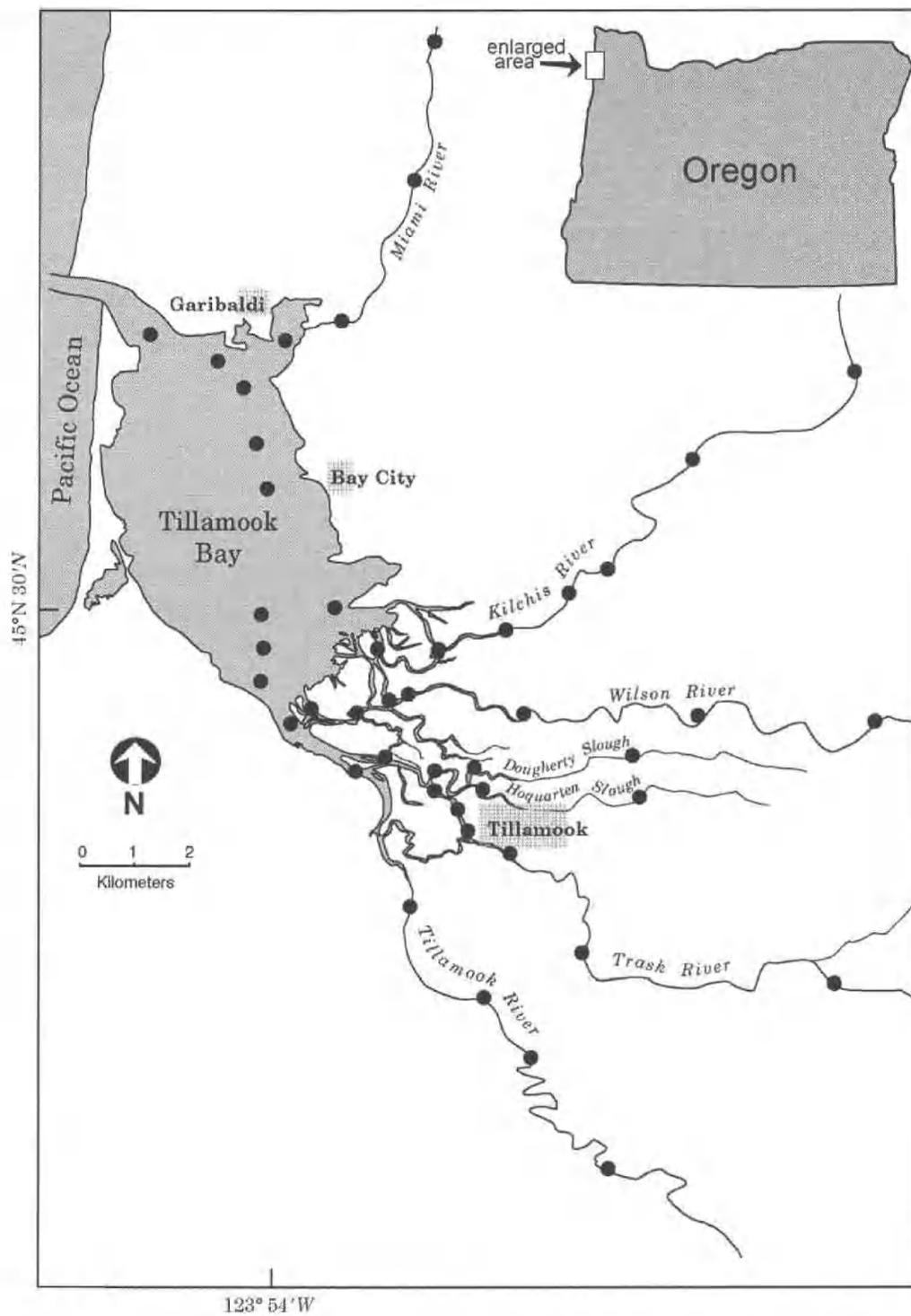


Figure 4.1. Map of study area with sampling stations indicated (●). The bay receives freshwater input from five rivers: Miami, Kilchis, Wilson, Trask, and Tillamook.

Table 4.1. Summary of sampling dates with river discharge (USGS: <http://water.usgs.gov>) and precipitation. Precipitation is reported as 7-day averages (Oregon Climate Service). River discharges shown in parentheses were estimated from 1997-1998 flow data normalized to Wilson River discharge data. Estuarine flushing times are calculated using the freshwater fraction method of Dyer (1997).

Sampling Dates	Discharge ($\text{m}^3 \text{s}^{-1}$)						Precipitation (in)	Flushing Time (d)
	Miami	Kilchis	Wilson	Trask	Tillamook	TOTAL		
1/2/99	na (25.2)	na (48.5)	80.4	75.6	na (21.4)	na (251.1)	1.08	1
4/2/99	na (7.7)	na (22.0)	38.6	40.5	na (7.7)	na (116.4)	0.36	3
7/19/99	na (1.5)	na (0.3)	3.6	10.2	na (0.3)	na (15.9)	0.02	17
10/17/99	na (0.3)	na (0.7)	1.5	6.4	na (0.4)	na (9.3)	0.01	32
12/3/99	na (23.6)	na (88.1)	138.5	96.3	na (29.0)	na (375.4)	0.47	1

and at eight stations along a transect of the major channel of the estuary (Figure 4.1). During July and December 1999, samples were collected approximately every 120 minutes at the mouth of each river and at the mouth, mid-point, and head of the estuary for a 30-hour period. Trace element clean techniques were employed during field collection and sample preparation. All sample bottles were made of polypropylene, polyethylene, or Teflon[®] and were also stored and handled according to trace metal clean techniques (Bruland et al. 1979).

At each station, samples for dissolved elements were collected at one meter below the surface using a modified 5-liter Niskin sampling bottle. During July and December 1999, samples were also collected one meter above the sediment-water boundary at the mouth of the estuary. Within six hours of collection, these samples were vacuum-filtered through acid cleaned 0.45 μm membrane filters (Acrodisc[®], Gelman Sciences) in a class 100 laminar flow hood (Environmental Air Control) and acidified to $\text{pH} < 2$ with triple-distilled nitric acid. Chloride concentrations were measured on filtered samples using conductive detection by a DIONEX ED40 Electrochemical Detector. Detection limit for chloride was $0.22 \mu\text{mol L}^{-1}$ ($n = 5$). Salinity was calculated as 1.81 times the chloride content (Knauss 1978).

Dissolved iron concentrations for July and December 1999 samples were analyzed by flow injection with spectrophotometric detection (Measures et al. 1995). Iron concentrations of all other samples were analyzed by high resolution inductively coupled plasma mass spectrometry (HR ICP MS) (VG Elemental AXIOM). Certified reference samples (NIST1643c and NIST1643d, National Institute of Standards and Technology) were analyzed to assess analytical accuracy. Measurements of dissolved Fe concentrations were within 10% ($n = 7$) and 20% (n

= 4) of NIST1643c and NIST1643d standards, respectively. Detection limit for dissolved Fe, defined as three times the standard deviation of the blank, was 2.5 nmol L⁻¹.

For suspended particulate collection, water was pumped through large diameter polyethylene tubing into an acid-cleaned 10-liter carboy. This water was vacuum-filtered onto pre-weighed polycarbonate filters (1.0 μm , 90 mm diameter, Poretics). Filters were then oven-dried (50°C, 24 hours), re-weighed, and combusted at 550°C for five hours. Particles were digested using the hot HF/HNO₃ method of Collier and Edmond (1984). Suspended particulate material (SPM) (mg L⁻¹) was calculated by difference between loaded and unloaded filter weights divided by the volume of water sample filtered.

Following digestion, suspended and surface sediment samples were analyzed by inductively coupled plasma atomic emission spectrometry (ICP AES) (Varian Liberty 150) for Al, Ti, and Fe content. The standard reference materials for basalt (BCR-1, United States Geological Survey) and estuarine sediment (NIST-1646a, National Institute of Standards and Technology) were analyzed to verify procedural accuracy. Measured Fe concentrations of these reference materials were within 8% of certified values ($n = 8$).

Surface sediment was collected at 42 stations from September 30 to October 3, 1996 and at nine river stations on June 16, 2001 (Figure 4.2). Sediment samples were freeze-dried and homogenized. An aliquot of each sediment sample was weighed (0.089 - 0.108 g) and combusted at 550°C for five hours. Sediment was then digested using the hot HF/HNO₃ method described by Collier and Edmond (1984).

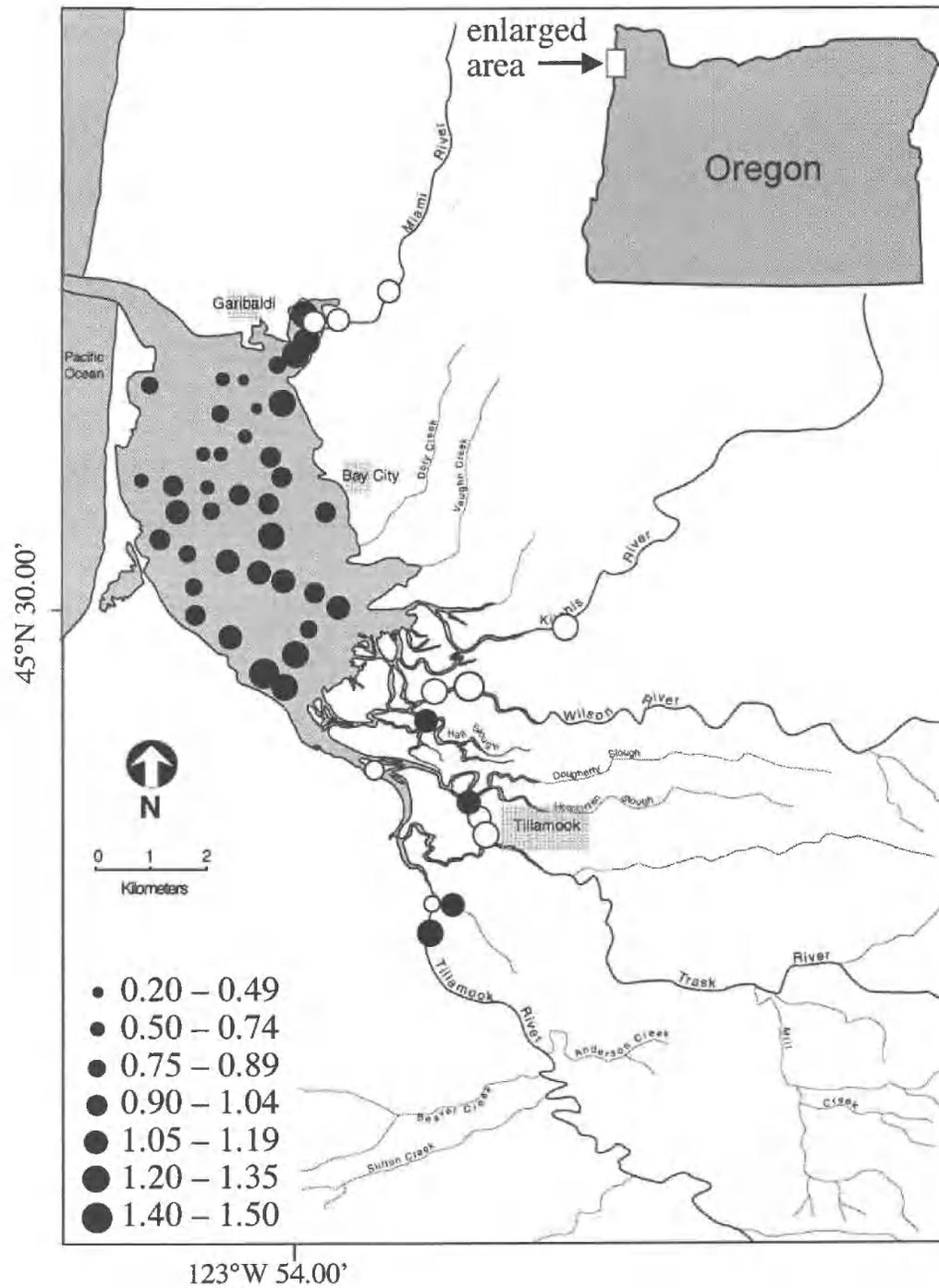


Figure 4.2. Surface sediment distributions of Fe:Al collected in 1998 (filled circles) and 2001 (open circles).

Data Analysis

Average river end-member concentrations for each sampling date are calculated as the flow-weighted average of all rivers using the river concentration farthest down stream with salinity less than 0.09 psu and are provided in Table 4.2. This calculation is described in detail in Colbert and McManus (2003). Briefly, each of the observed estuarine distributions is fitted with a best-fit high order polynomial to estimate departures from conservative mixing. Internal sources and sinks of Fe and suspended particulate material (SPM) are calculated by difference between the conservative end-member mixing line and the line fitted to observations. The net gain or loss calculated by this method is reported in Table 4.3. Departures from conservative mixing could not be calculated for December 1999, as the entire salinity gradient was not sampled during this month.

Table 4.2. Average flow-weighted river end-member reported as the concentration at the farthest down stream station with salinity less than 0.09 psu. Average particulate river end-members for July and December 1999 are concentrations at the upper estuary with lowest salinity (1.05 and 0.04, respectively, for July and December).

Date	Fe (uM)	Fe (%wt)	Salinity	SPM (mg l ⁻¹)
1/2/99	0.25	8.6	0.01	41.2
4/2/99	0.19	7.8	0.01	4.1
7/19/99	0.60	8.2	0.04	16.9
10/17/99	0.20	6.5	0.06	4.2
12/3/99	0.26	9.6	0.03	36.3

Table 4.3. Departures from conservative mixing within the estuary. Loss within the estuary is indicated by a negative value while a source within the estuary is indicated by a positive value. Note that the values are percent deviations from conservative mixing.

Date	Dissolved		Particulate			Total (Net)
	Fe	SPM	Fe	Al	Ti	Fe
1/2/99	-75	-53	-51	-48	-54	-51
4/2/99	-23	26	20	18	17	19
7/19/99	-59	32	14	21	16	12
10/17/99	-30	2	63	71	71	59

Estuarine flushing times (T) are calculated using the freshwater fraction method of Dyer (1997) where $T = V/Q \times (S_s - S_n)/S_s$ and V is estuarine volume for that sampling date, Q is river discharge, S_n is the mean salinity observed in the estuary, and S_s is salinity of coastal seawater (NE Pacific surface waters 44°49.1' N 126°03.0' W: 32.6 psu, Wheeler, unpublished data). Estuary volumes are calculated using the tidal prism reported by Johnson (1972) and corrected for tidal height change for each sampling event. Further details of these calculations are described in Colbert and McManus (2003).

Estuarine Box Model

Mass balances within the Tillamook estuary are modeled after the methods of Klinkhammer and Bender (1981) and Yang and Sanudo-Wilhelmy (1998) (Figure 4.3). Mass balances for each sampling event are modeled using river input from the southern rivers, input from the northern river, and exchange with the

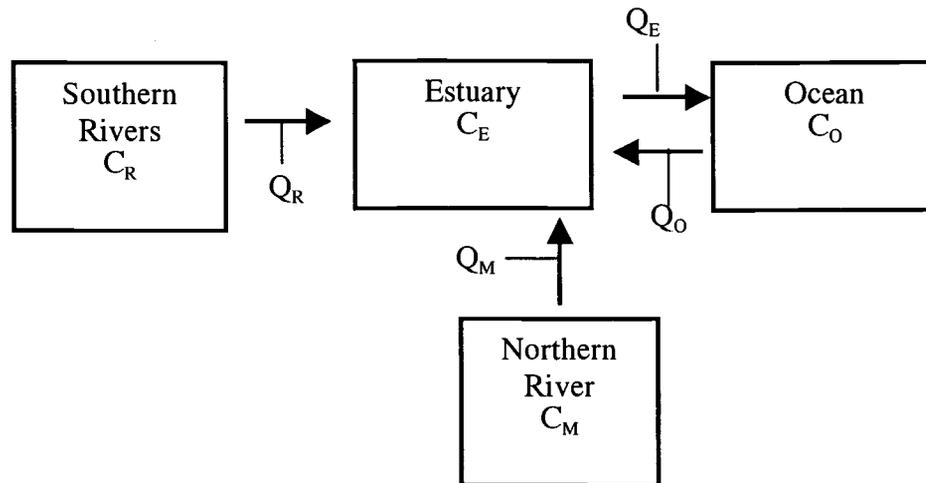


Figure 4.3. Box model of the Tillamook Bay estuary where Q_R is the total discharge from the southern rivers (Kilchis, Wilson, Trask, and Tillamook Rivers), Q_M is the discharge from the Miami River, Q_E is the flow from the estuary, and Q_O is the exchange from the ocean. Concentration for the southern rivers (C_R), the northern river (C_M), average estuary (C_E), and ocean end-member as measured (C_O) at the station at the mouth of the estuary are also indicated.

coastal ocean. Mass balances are not calculated for December 1999. During all other months, Fe concentration measured at the station located at the mouth of the estuary is designated as the ocean end-member. Assuming conservation of salts within the estuary, the estuary is described by the following equations $Q_E \times S_E = Q_O \times S_O$ and $Q_E = Q_R + Q_M + Q_O$, where Q_O is ocean exchange, Q_R is the river discharge from the southern rivers, Q_M is the river discharge from the northern river, S_O is the salinity measured at the ocean end-member, and S_E is the average salinity within the estuary. Combining these equations, ocean exchange (Q_O) is described by the equation $Q_O = (Q_R + Q_M) \times ((S_O \times S_E^{-1}) - 1)^{-1}$.

RESULTS

The sampling events of this study encompass the seasonal changes in river discharge rates and estuarine flushing times that occur in the Tillamook Bay estuary (Table 4.1). On average, river discharge rates during winter months (January and December, 1999) are $313 \text{ m}^3 \text{ s}^{-1}$, and average estuarine flushing time is one day. Spring discharge (April 1999, $116 \text{ m}^3 \text{ s}^{-1}$) is 2.5 times less than winter rates with a concurrent increase in flushing time to 3 days. River discharge is $16 \text{ m}^3 \text{ s}^{-1}$ during the summer sampling event (July 1999), and estuarine flushing time is 17 days. River discharge reached a minimum under fall conditions (October 1999) at $9 \text{ m}^3 \text{ s}^{-1}$ with an estuarine flushing time of 32 days. As a result of seasonal changes in river discharge rates and estuarine flushing, there is considerable spatial and temporal variability in the average riverine end-member concentration (Table 4.2) and the estuarine distributions of dissolved and particulate Fe (Figure 4.4a).

River Water Composition

Average dissolved Fe concentrations in the rivers feeding Tillamook Bay range from 0.19 to $0.60 \mu\text{M}$. These values are within the range observed in the Sacramento River ($0.09 - 1.7 \mu\text{M}$; Flegal et al. 1991) but generally lower than concentrations observed in U.S. East Coast rivers ($0.3 - 11.9 \mu\text{M}$; Boyle et al. 1977) and average world rivers ($0.72 \mu\text{M}$; Martin and Whitfield 1983). The flow-weighted dissolved Fe concentration is highest at the river end-member during summer (Table 4.2, Figure 4.4a). However, there is no relationship ($r^2 = 0.12$, $n = 5$) observed between river discharge rate and dissolved Fe at the river end-member.

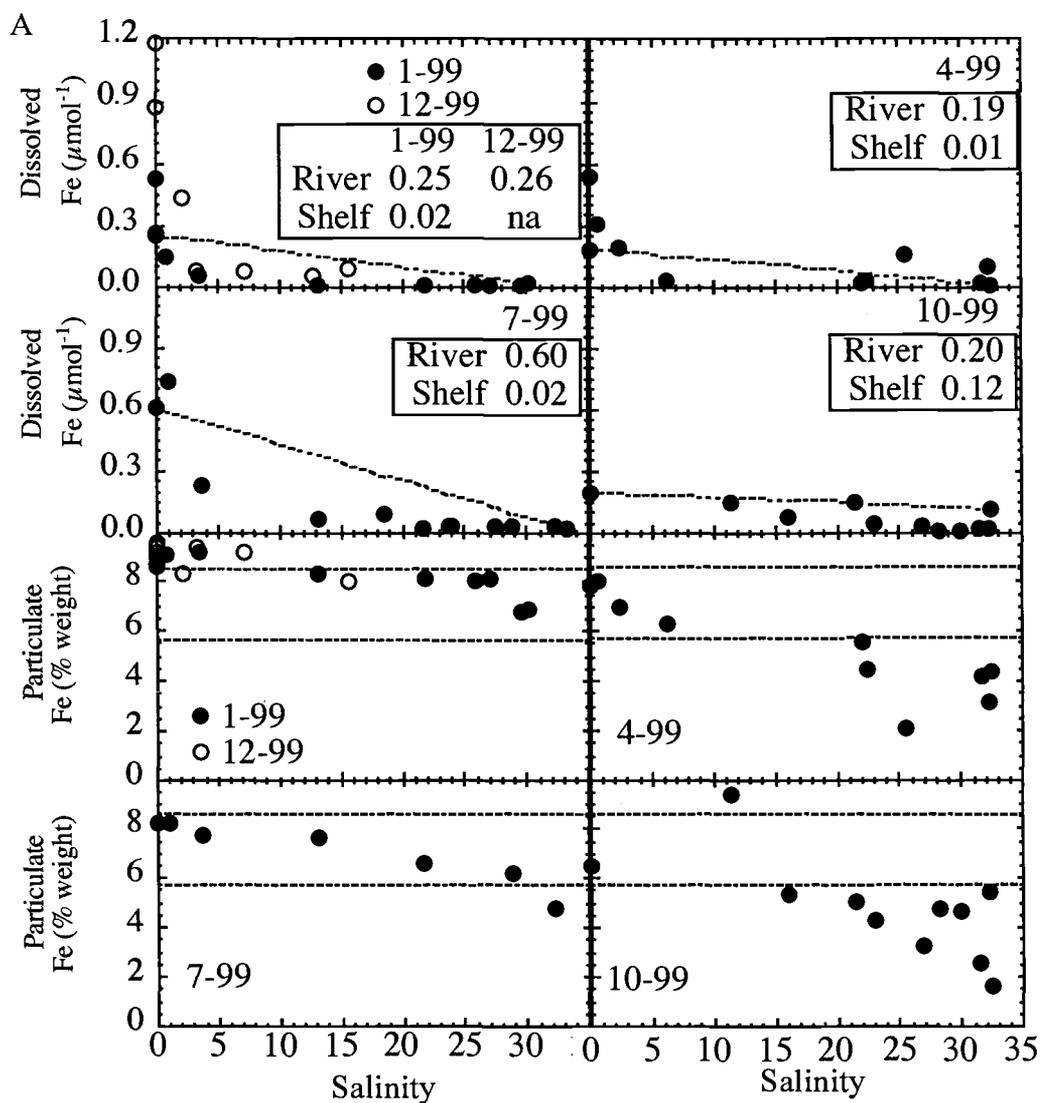


Figure 4.4. Concentrations versus salinity for each sampling date: a) dissolved and suspended particulate Fe; b) SPM concentrations (Colbert and McManus 2003); c) suspended particulate Al; and d) particulate Fe:Al. Distributions for winter months are combined for January 1999 (filled circles) and December 1999 (open circles). Average river end-member and shelf concentrations are indicated for dissolved elements. Average basalt (upper) and continental crustal (lower) abundances are indicated in plots of all suspended particulate phases (Taylor 1964).

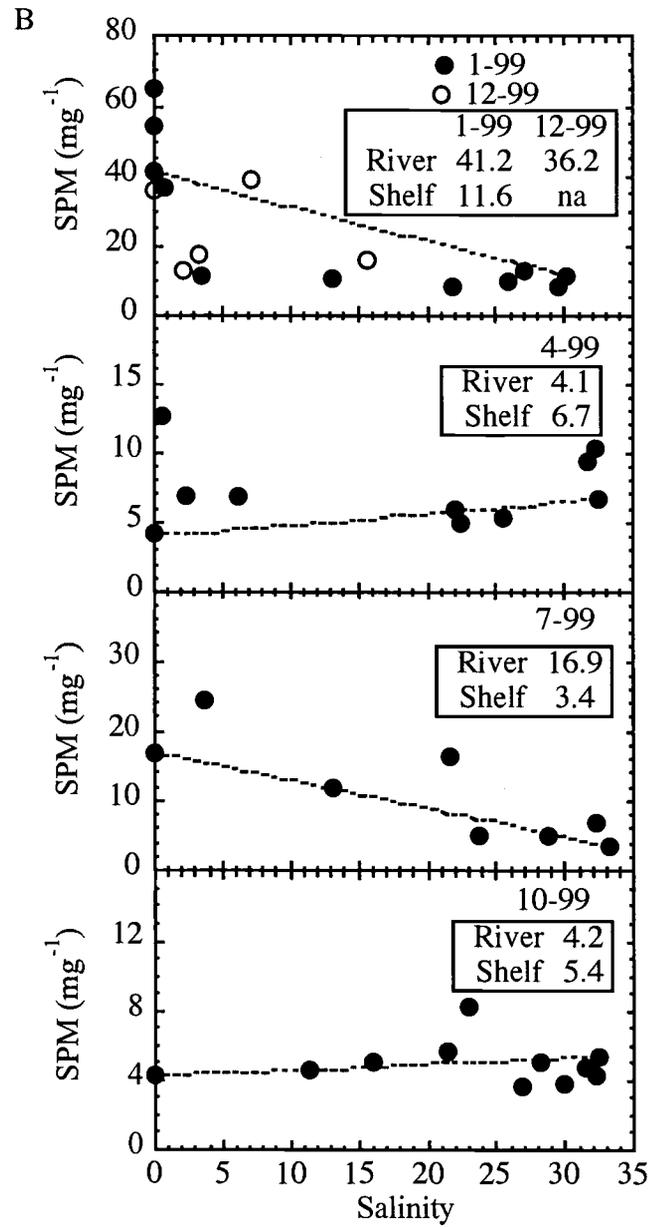


Figure 4.4. Continued.

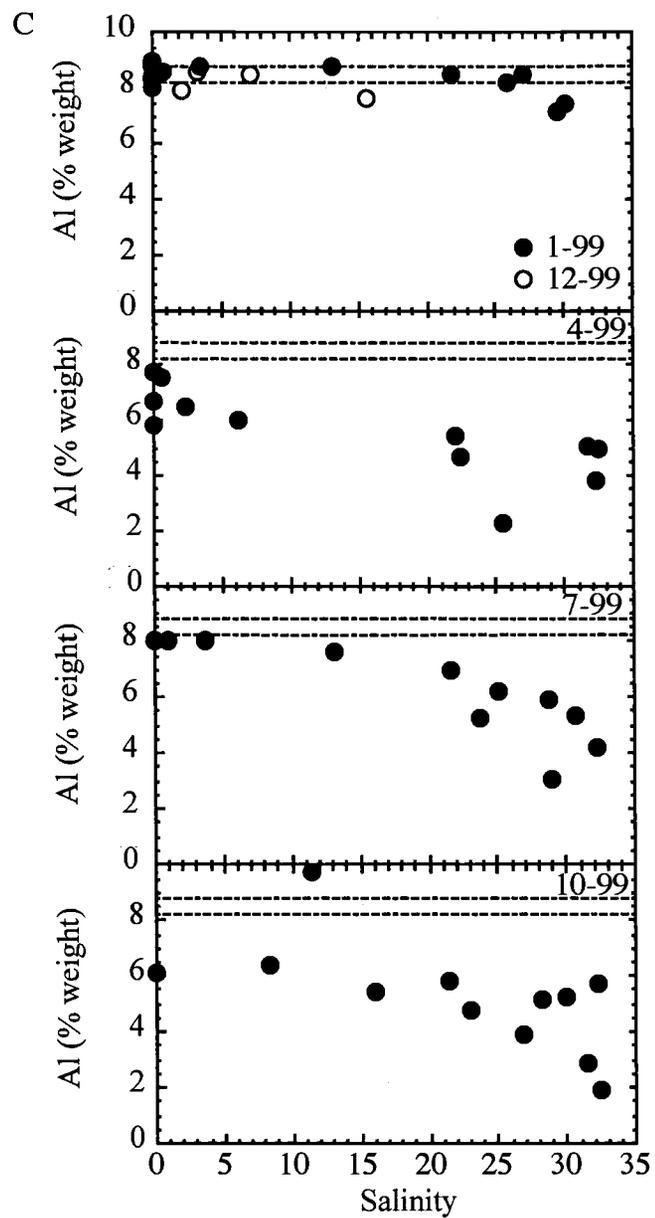


Figure 4.4. Continued.

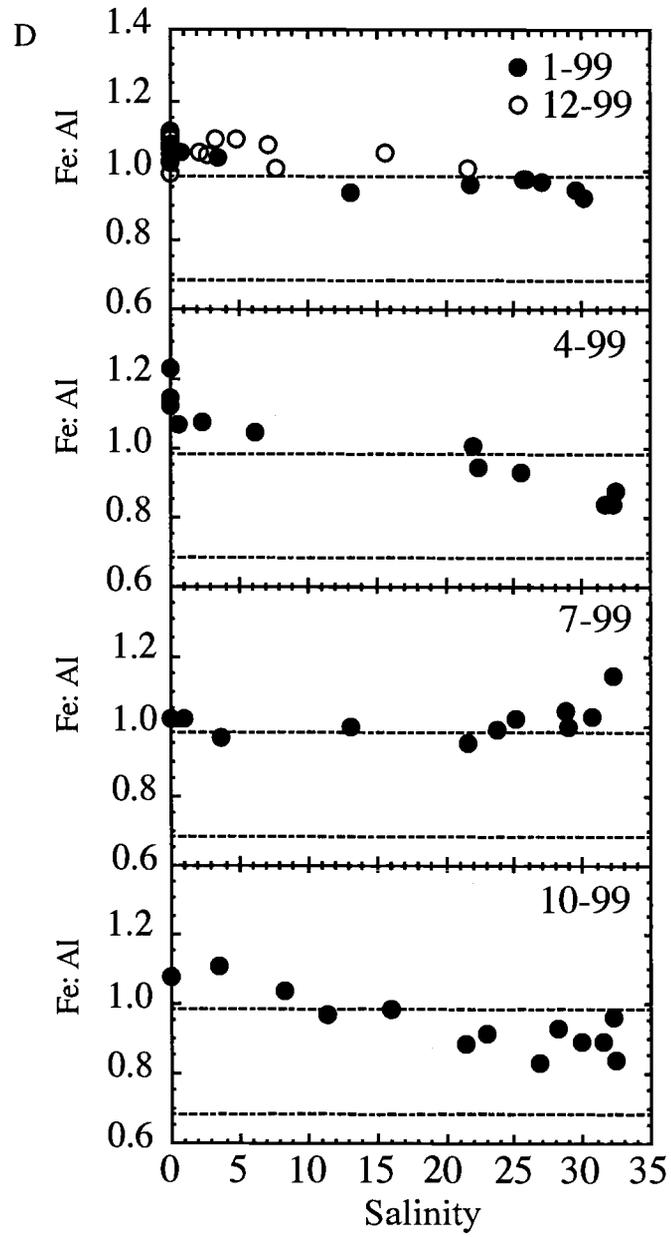


Figure 4.4. Continued.

Dissolved Fe concentrations are also not significantly correlated with changes in SPM concentrations ($r^2 = 0.07$, $n = 5$).

Average seasonal SPM concentrations range from 4.1 to 41.2 mg l⁻¹ (Table 4.2) and are positively correlated with river flow ($r^2 = 0.81$, $n = 5$). Average annual transport of the total Fe from the rivers to the estuary is dominated by the particulate phase with 98% transported in the particulate load. Particulate Fe content is positively correlated with river discharge rates ($r^2 = 0.67$, $n = 5$). Total riverine Fe fluxes (dissolved plus particulate) are also related to river discharge rates with the highest fluxes occurring under winter conditions (Table 4.4: $F_R + F_M$). The concentration of Al in the suspended load varies from 9% of the suspended load during winter months to 6.1% in the fall, indicating a progressive decrease in detrital particles from winter to fall.

Table 4.4. Mass balance results for total Fe in the Tillamook Estuary.^a

Date	F_R	F_M	F_O	Total F_{in}	F_E	Imbalance	%
1/2/99	800	20	160	980	-930	50	5
4/2/99	36	1.2	35	72	-92	-20	-22
7/19/99	21	0.74	6.7	28	-34	-6.2	-18
10/17/99	2.6	0.04	4.1	6.7	-8.7	-2.0	-23

^a All fluxes are in g s⁻¹ with losses from the estuary indicated as a negative flux. Flux from the southern rivers (F_R) is equal to the average flow-weighted concentration of the southern rivers (C_R) times the total river discharge (Q_R) from those rivers. Flux from the northern river (F_M) is equal to the Miami River concentration (C_M) times Miami River flow (Q_M). Flux from the ocean to the estuary (F_O) is equal to the concentration at the mouth (C_O) times the calculated ocean exchange (Q_O). Flux from the estuary to the ocean (F_E) is the average estuary concentration (C_E) times the total input from rivers and exchange from the ocean ($Q_R + Q_M + Q_O$).

Estuary

SPM concentrations are relatively constant throughout the estuary but exhibit an upper estuary maximum during winter months (Figure 4.4b). There is a 52% loss of the suspended load in the upper estuary during January 1999 while excesses of suspended material of 2 to 32% over conservative mixing occur during all other months (Table 4.3). The location of these apparent excesses in SPM varies horizontally within the estuary with excess SPM most pronounced at the upper estuary during April 1999, and transitioning to mid-estuary by July 1999 (Figure 4.4b).

In general, dissolved Fe distributions within the estuary are relatively consistent among seasons (Figure 4.4a). All sampling events are characterized by removal of dissolved Fe at the upper estuary ($S < 7$) with losses ranging between 20 and 75% (Table 4.3). Iron content of suspended particles varies seasonally with average concentrations within the estuary decreasing from winter through fall (Figure 4.4a). Suspended particulate Fe exhibits the highest concentrations at the fresh water—salt water boundary and decreases longitudinally toward the mouth of the estuary, dropping below crustal abundances near the mouth of the estuary during spring, summer, and fall (Figure 4.4a). Similarly, percent weight of Al progressively decreases from the river end-member toward the mouth of the estuary, falling below crustal predictions during spring, summer, and fall (Figure 4.4c). These trends are further illustrated in the Fe:Al of suspended particles within the estuary. Fe:Al is enriched above crustal abundances at the upper estuary and decreases toward the mouth of the estuary (Figure 4.4d). This pattern is also consistent with Fe:Al of surface sediment within the estuary. Surface sediment

Fe:Al in the rivers and upper estuary is enriched relative to average crustal abundances for basalt (Fe:Al = 0.98) and continental crust (Fe:Al = 0.68) (Taylor 1964) and is depleted toward the mouth of the estuary (Figure 4.2).

Box Model

If we consider our first order model, estuarine inputs and outputs balance within 25% for each seasonal snap-shot (Table 4.4). However, there are imbalances that are either caused by non-steady state behavior or internal estuarine processes. During January 1999, it appears that ~50% of the suspended load is removed in the upper estuary ($S < 4$), and there is a concurrent loss of ~50% or more of the particulate Al, Ti, and Fe within the estuary (Table 4.3). Thus, the estuary is a net sink for particulate material during this particular period, despite the fact that this season dominates the export of iron to the coastal zone (Table 4.4: F_E). Based on the measured water column loss of SPM, we calculate a sedimentation rate for January 1999 (R_S). For this calculation we use the loss of suspended material (L) within the estuary (Table 4.3), the volume of the estuary ($V = 7.0 \times 10^{10}$ l), the area of the estuary ($A = 34 \text{ km}^2$), the calculated flushing time ($T = 1$ day), a dry sediment density (ρ) of 2.65 g cm^{-3} (as referenced in Yang and Sanudo-Wilhelmy 1998), and the relationship: $R_S = (L \times V) \times (T \times A \times \rho)^{-1}$. The sedimentation rate calculated by this method is 0.4 cm y^{-1} and compares well with sedimentation rates reported for the estuary (0.05 to 0.68 cm y^{-1} : Glenn 1978; Komar et al. in press). Sediment burial (Table 4.5: F_S) is described by the equation $F_S = R_S \times [(1-\phi) \times \rho \times C_p] \times A$ where R_S is the calculated sedimentation rate, ϕ is the porosity (0.9), ρ is dry sediment density (2.65 g cm^{-3}), and C_p is the average

estuarine suspended particulate concentration for each element. By taking into account this removal term for iron, the small imbalance for January becomes even smaller (i.e., Table 4.5: total inputs = 980, total outputs = 1020). While the agreement seems shocking for such a simple model, we should point out here that the budgetary discrepancies for Al, Ba, and Mn were also less than 10% (Colbert and McManus submitted). Thus, it would appear that during the high sediment discharge of winter some of the riverine sediment is being trapped within the estuary despite the short residence time of water within the system.

Table 4.5. Calculated burial rates (F_S), resuspension rates (F_{Re}), and benthic flux (F_D).^a

Date	F_S	F_{Re}	F_D	Net Budget ^b		
				In	Out	Imbalance
1/2/99	-94	na	na	980	-1020	-40
4/2/99	na	26	na	98	-92	6
7/19/99	na	10	na	38	-34	4
10/17/99	na	0.17	2.4	9.3	-8.7	0.6

^a For January 1999, F_S is the burial amount calculated from loss of SPM within the estuary ($R_S = 0.38 \text{ m y}^{-1}$) during January 1999. Resuspension rates (F_{Re}) are calculated based on the observed SPM excesses, average surface sediment Fe concentration within the estuary (Figure 4.7: McManus et al. 1998), and estuarine volume and flushing time during each sampling event (Table 4.1). Input from benthic flux (F_D) is calculated using the excess concentration above conservative mixing (Table 4.3), estuary volumes, and flushing time of the estuary (Table 4.1).

^bNet budget includes the terms from Table 4.4. Imbalance column indicates the input needed to balance the total output. na indicates not applicable.

During all other sampling events, there is net production of suspended material within the estuary (Table 4.3). This “production” of particles could be caused by either water column particle production (primary production or particle coagulation) or sediment resuspension. For simplicity, we ignore water column production and assume that the “production” is actually a resuspension signature. Part of the rationale for this is that most of the iron that enters and leaves the estuary is as particles rather than in the dissolved form. Furthermore, regardless of the particle source the point here is that whatever process is generating the particulate iron is internal to the estuary, rather than being an external process. We thus calculate a resuspension rate (Table 4.5: F_{Re}) based on the observed SPM excesses (Table 4.3), the average surface sediment Fe concentration within the estuary (Figure 4.2), estuarine volume (April: 6.7×10^{10} l; July: 6.5×10^{10} l; October: 5.9×10^{10} l) and flushing time during each sampling event (Table 4.1). With this additional particulate iron input, the iron budget during April and July 1999 is balanced (Table 4.5).

While excesses in particulate Fe are also observed during October 1999, if we treat those excesses as resuspension of typical estuarine sediment, we can only account for 9% of the missing source during this period (Table 4.5). However, the resuspended material is particularly iron-rich during this period (Figure 4.4d). We suggest that there is an upper estuary source of iron to the water column. This source likely comes from reductive dissolution of iron oxides and (rapid) reoxidation of that iron, thereby generating a particulate source of iron (Table 4.3). Sediment regeneration of Fe may thus account for this additional “source” of particulate Fe to the water column. To quantify this additional source, we use the

excess particulate Fe (Fe excess) within the estuary (Table 4.3, Figure 4.4d), the volume of the estuary ($V = 5.9 \times 10^{10}$ l), the area of the estuary ($A = 34$ km²), the calculated flushing time ($T = 32$ days), and the relationship: $F_D = (\text{Fe excess} \times V) \times (A)^{-1} \times (T)^{-1}$. The calculated diffusive flux of iron is 0.11 mmol m⁻² d⁻¹. The addition of this iron source brings the budget closer to a net balance (Table 4.5).

DISCUSSION

Based on seasonal Fe distributions and our model calculations, estuarine iron behavior is dominated by two factors: interaction with suspended river-derived particulate material and input from benthic (dissolved or particulate) sources. The importance of these two factors varies seasonally, and influences the annual estuarine iron budget. This seasonal variability, as we suggest below, holds an important key for Fe delivery to the coastal ocean.

The highest removal rates of dissolved iron (Table 4.3) are observed under the high SPM concentrations of winter (Figure 4.4b), consistent with studies suggesting that flocculation and precipitation of dissolved iron increases with increasing SPM concentrations (Aston and Chester 1973; Forsgren et al. 1996). During this period, the near-crustal mineral content (Figure 4.4) of suspended material within the estuary indicates that terrestrial sources dominate the particulate signal. Based on box model calculations (Table 4.4) and a sedimentation rate calculated from the percent loss of SPM within the estuary (Table 4.5), loss of iron within the estuary can be supported entirely by the sedimentation of suspended particulate iron. Enrichment of sediment iron concentrations at the upper estuary (Figure 4.2) is consistent with the flocculation and precipitation of dissolved iron

and the burial of particulate iron at the river water-salt water boundary. Therefore, it appears that during high discharge, high turbidity months, the dominant processes controlling the dissolved iron distributions are flocculation and precipitation at the upper estuary and sedimentation of suspended particles. However, despite this net loss of Fe within the estuary, the bulk of the particulate Fe is exported to the coastal ocean (Table 4.4: F_E).

In contrast to the high turbidity conditions of winter, during other seasons there is an excess of particulate iron (~10 to 60%) over that expected from conservative mixing within the estuary (Table 4.3). While enrichment of particulate Fe might be attributed to flocculation of dissolved Fe at the low salinity interface of the estuary, our calculations suggest that removal of this dissolved iron accounts for <10% of the observed particulate enrichment within the estuary. Therefore, an additional input of particulate iron is necessary to account for the source of particulate iron within the estuary during April, July and October 1999 (Table 4.2). During April and July, we attribute this particulate source signal to resuspension of bottom sediments within the estuary. Tidally induced resuspension of sediments has been shown to occur in macrotidal estuaries which narrow rapidly towards their heads (Balls 1992) as occurs in the Tillamook Estuary. Resuspension rates (F_{Re}) calculated from excess SPM within the estuary for April and July 1999 can account for the observed enrichment of particulate iron during these months (Table 4.5). We note here the small imbalance in the net budget for these months (Table 4.5), and suggest that this much uncertainty is reasonable given our model assumptions and the non-steady state nature of estuarine processes. More specifically, this discrepancy most likely stems from the assumption that all of the

excess SPM during spring and summer months is due to resuspension. Nutrient distributions and phytoplankton biomass data indicate that there is significant biological production in Tillamook Bay during spring and summer months which contributes to the observed excesses in suspended concentrations during these times (Colbert and McManus 2003). Therefore, resuspension rates calculated here represent an upper limit and likely overestimate this input in the strictest sense. However, what is clear from our work is that, during these months, there is a significant source of particulate iron to the estuarine water column, and this source could result in as much as 30% more Fe delivered to the coastal ocean than predicted from riverine sources alone (Table 4.5).

Under the slow estuarine flushing conditions observed during October 1999 (Table 4.1), excess SPM within the estuary cannot adequately account for the enrichment of particulate iron within the estuary (Table 4.4), and an additional source of iron is necessary to balance its budget. We propose that the most likely source of this Fe is sediment regeneration. Iron reduction within sediments can occur under low sediment oxygen conditions as iron oxides and hydroxides are used as terminal electron acceptors in the breakdown of organic material within the sediment (Froelich et al. 1979). Reduction of Fe-oxides within the sediment would support a flux of dissolved iron as Fe (II) from the sediment to the overlying water column. Iron (II) is, however, rapidly reoxidized (Davidson and Seed 1983; Caetano et al. 1997). Therefore, any dissolved iron flux from the sediment will likely result in an enrichment of particulate iron within the estuary (Caetano et al. 1997), as occurs in the upper estuary during fall (Figure 4.4a). The location of the upper estuary Fe enrichment is coincident with extensive intertidal mudflats at the

upper estuary. Based on the observed enrichment of particulate iron within the estuary and the volume, area, and flushing time of the estuary, the calculated diffusive flux of iron is $0.11 \text{ mmol m}^{-2} \text{ d}^{-1}$. This flux is similar to measured and calculated fluxes reported for other estuaries and coastal areas (Humber Plume: $0.05 - 29 \text{ m}^{-2} \text{ d}^{-1}$; Millward et al. 1996; Galveston Bay: $0.01-0.06 \text{ mmol m}^{-2} \text{ d}^{-1}$; Warnken et al. 2001). This dissolved iron effluxing into the water column from porewaters will likely be scavenged onto particles supporting a particulate Fe source similar to the particulate source predicted in other coastal and estuarine areas (Millward et al. 1996; Warnken et al. 2001). Similar to April and July 1999, our calculations suggest that this internal source of Fe delivers 30% more Fe to the coastal ocean than flux from the rivers alone.

What arises from this work is a view of iron cycling whereby seasonal variations in physio-biochemical processes conspire to deliver reactive iron to the coastal zone at the most opportune time. Although during high flow periods much of the *annual* iron load is delivered to the coastal zone, some of that iron is stored in the estuary until the lower flow periods of spring through fall when it is reworked by internal biogeochemical processes to support enhanced Fe delivery to the coastal ocean. These lower flow periods coincide with the periods of highest biological production (e.g., Colbert and McManus 2003). Parenthetically, production in this particular west coast estuary is bolstered by the input of reactive phosphorus from the ocean—i.e., the oceanic phosphorus source is larger than the riverine source (Colbert and McManus 2003). Thus, coastal upwelling supplements nutritional supply for estuary carbon production. This carbon, of course, as it decomposes supplies the fuel for estuary benthic diagenesis, that will

mobilize reduced iron (e.g., see Froelich et al. 1979) within the sediments where it can diffuse or be advected into the overlying water. Once exposed to the oxic water column this reduced iron will rapidly reprecipitate and may make its way to the coastal zone as a fresh (reactive) micronutrient source. By contrast, the low production (e.g., Colbert and McManus 2003) and short residence time of winter do not foster this relationship.

If we extend this particular view of estuarine iron behavior to the coastal zone we might expect that the particles from the winter export maximum are reprocessed on the Oregon shelf or slope and could be redelivered to the surface ocean in either the dissolved phase or as a recently precipitated iron oxide phase once upwelling in the coastal zone initiates. More specifically, we speculate that oxygen penetration into the sediments is sufficiently shallow (scale of millimeters) that diagenetic reactions within the sediments will dissolve particulate iron after which it can diffuse to the sediment-water boundary. Because of the availability of dissolved oxygen within the oceanic water column, we would anticipate that this iron will predominantly be present as a particulate phase. Consistent with the idea of an important sedimentary iron source, Chase and others (2002) found that shelf sediments are an important source of Fe to coastal Oregon waters. While the source of this sediment-derived Fe was not apparent, these authors note an iron enrichment at middepth (~100 m) in offshore waters. These authors suggest that this sub surface iron may be an important source to nearshore surface water, and biological production, via upwelling. They also suggest the possibility that the Columbia River may contribute to the shelf sediment source of Fe. However, we suggest that other, smaller estuaries may also be a significant source of Fe to the

coastal shelf, particularly because fresh water from the Columbia River plume is diverted south during spring and summer and may help to maintain the upwelling front closer to the coast north of 42°N (Strub et al. 1987).

This view of iron processing along the shelf and slope is also consistent with other studies on coastal iron supply (e.g., Johnson et al. 1999; Johnson et al. 2001). We recognize the possibility of regional differences in iron sources (as pointed out in Chase et al. 2002). However, the implication here as well as in other studies is that sedimentary dissolution of solid-phase iron at the sea floor is pivotal for supporting coastal production (e.g., Johnson et al. 1999; Johnson et al. 2001). In essence, the processing of iron along the seafloor in coastal regions may supply a significant iron pool to the overlying water column. This iron, which is constantly undergoing dissolution-precipitation cycles related to changes in reductant supply (i.e., organic carbon), could be delivered to the water column either in the dissolved phase or as fresh Fe-rich particles. Furthermore, because of the tight couple between iron and carbon cycling, there is the potential for a positive feedback between carbon delivery to the seafloor and iron delivery to the water column (e.g., Johnson et al. 1999; Johnson et al. 2001).

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5. CONCLUSION

This thesis evaluates the distributions of major inorganic nutrients (P, N, Si), trace metals (Mn, Fe), and alkaline-earth metals (Ba) in the Tillamook Bay estuary to describe the net processes occurring within this estuary over seasonal cycles. What arises from this work is a view of the estuary in which seasonal processes occurring at both the river and ocean end members influence elemental estuarine behavior. River discharge sets freshwater flushing time and delivery of land-derived materials to the estuary. Freshwater flushing time, in turn, determines the amount of time for the biological uptake of materials, exchange with suspended particles, and interaction with the sediments. Seasonal coastal upwelling controls the timing and extent of oceanic delivery of nutrients to the estuary. Biogeochemical processes occurring at the river water – salt water interface result in seasonal trapping of material within the estuary which later supply materials for sediment regeneration via resuspension and diffusive flux.

During winter months, fast flushing times prevent the development of significant phytoplankton populations within the estuary. This process is borne out by the conservative mixing behavior of nitrate and dissolved silicon during winter months along with low phytoplankton biomass within the estuary during the winter. Consistent with this hypothesis, the near-crustal mineral content (e.g. % weight Fe) and soil-like C:N ratio of suspended material indicate that terrestrial sources, not phytoplankton, dominate the particulate signal under winter conditions.

High river discharge conditions of winter are also associated with elevated SPM concentrations at the upper estuary. The fate of this material is manifested in

the elemental distributions within the estuary. Some of this particulate material undergoes decomposition and results in elevated concentrations of dissolved inorganic nutrients (PO_4^{3-} , NH_4^+) and dissolved Mn at low salinities. However, box model calculations and sediment burial rates indicate that some of the suspended load transported during high discharge months is significantly reduced by sedimentation at the river water – salt water interface. Sedimentation of this suspended material results in loss of particulate Mn and Fe from the water column. Enrichment of sediment Fe and Mn concentrations at the upper estuary is also consistent with the flocculation and precipitation of these materials at the river water-salt water interface.

As river discharge rates decrease progressively from winter through summer, longer water residence times occur. Under reduced flushing rates of spring and summer, the effect of biological uptake becomes evident within the estuary, and there is significant removal of all nutrients within the estuary as spring progresses. Development of a significant phytoplankton community during spring and summer is caused, in part, by delivery of nutrient-rich water via coastal upwelling. Meanwhile, tidally induced resuspension of sediments during this period results in elevated Mn and Fe concentrations at the upper estuary.

Under slow freshwater flushing conditions of late summer and early fall, internal estuary processes dominate elemental distributions within the estuary. Enhanced carbon loading along with slow flushing rates and high temperatures in late summer and early fall likely results in a shallow redox boundary in sediments. Decomposition of organic material within the sediment results in the release of

PO_4^{3-} and NH_4 from the sediment. High remineralization rates within the sediment leads, in turn, to low sediment oxygen concentrations which facilitate the reduction of iron and manganese oxides and the subsequent release of Mn, and Fe from the sediments. The slow flushing time within the estuary allows the build up of these dissolved signals in the water column.

The seasonal processes outlined here have a pronounced effect on elemental fluxes to the coastal ocean. Elemental fluxes from the estuary to the adjacent coastal waters depend primarily on river discharge rates. When river discharge reaches a winter maximum, substantial quantities are exported. During all other months, box model calculations indicate that total fluxes of dissolved constituents to the coastal ocean are significantly enhanced due to internal estuarine processes.

In conclusion, the results of this research underscore the importance of estuarine processes in modifying the riverine flux of these elements to the ocean and the necessity of temporal sampling in evaluating processes controlling elemental distributions and delivery to the coastal ocean. This study relied on traditional, descriptive data to tease out biogeochemical processes affecting the distributions of these elements within the estuary. Additional research quantifying the rates of processes identified here would provide a clearer picture of temporal processes affecting elemental distributions and cycling within this system. Additional data characterizing the fate of estuarine-derived Fe along the shelf, estuarine processing of organic material, and oceanic Ba sources to the estuary will strengthen our understanding of this and other Pacific Northwest estuaries. Pore water and/or benthic flux chamber studies, in particular, are needed to better constrain the processes described here.

This study also highlights the need for further study of geochemical cycles in Pacific Coast estuaries. Because upwelling is an important process affecting geochemistry in Tillamook Bay, it is likely that El Niño/Southern Oscillation (ENSO) events could have a potentially significant impact on the development of spring and summer primary productivity signals. Coastal upwelling is dampened during El Niño periods and enhanced during La Niña events. The effect of ENSO events on estuarine geochemistry is further manifested by its effect on the delivery of materials at the river end-member due to changes in the quantity and timing of precipitation and, in turn, river discharge. In this manner, changes in offshore upwelling intensity and precipitation due to ENSO events would likely affect biogeochemistry of this estuary and other Pacific Northwest estuaries and warrants further investigation.

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APPENDIX A: STATION LOCATIONS

Station	Latitude	Longitude
MR101	45° 36.65' N	123° 52.03' W
MR103	45° 34.47' N	123° 52.46' W
MR104	45° 33.63' N	123° 53.52' W
KR201	45° 32.24' N	123° 47.10' W
KR202	45° 31.06' N	123° 49.80' W
KR203.7	45° 29.84' N	123° 50.65' W
WR301	45° 28.37' N	123° 44.27' W
WR302	45° 28.62' N	123° 48.51' W
WR303	45° 28.72' N	123° 50.70' W
WR304.5	45° 28.78' N	123° 52.97' W
WR305	45° 28.65' N	123° 53.11' W
TR400	45° 26.83' N	123° 42.62' W
TR401	45° 26.58' N	123° 46.58' W
TR402	45° 25.80' N	123° 49.45' W
TR404	45° 27.25' N	123° 51.52' W
TR405	45° 27.37' N	123° 51.65' W
TR406	45° 27.75' N	123° 51.98' W
TR407	45° 28.08' N	123° 52.47' W
TR408	45° 27.89' N	123° 50.68' W
TR409	45° 27.87' N	123° 51.49' W
TR410	45° 27.90' N	123° 51.98' W
TR411	45° 27.53' N	123° 50.67' W
TR412	45° 27.80' N	123° 51.45' W
TI501	45° 24.50' N	123° 49.47' W
TI502	45° 25.79' N	123° 50.67' W
TI504	45° 27.16' N	123° 52.73' W
TI506	45° 27.95' N	123° 52.78' W
TB601	45° 28.47' N	123° 53.74' W
TB602	45° 28.90' N	123° 54.18' W
TB603	45° 29.52' N	123° 54.10' W
TB604	45° 29.92' N	123° 54.04' W
TB606	45° 31.29' N	123° 54.01' W
TB607	45° 32.04' N	123° 54.06' W
TB608	45° 32.88' N	123° 54.57' W
TB609	45° 33.22' N	123° 54.91' W

Station	Latitude	Longitude
TB610	45° 33.18' N	123° 54.23' W
TB612	45° 33.63' N	123° 56.15' W
TB613	45° 32.88' N	123° 56.20' W
TB614	45° 32.04' N	123° 56.58' W
TB615	45° 31.25' N	123° 56.58' W
TB616	45° 30.50' N	123° 56.30' W
TB617	45° 29.58' N	123° 54.91' W

APPENDIX B: SURFACE WATER CHEMISTRY

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
10/12/97	MR101	5.5	0.17	0.26	209	85.5	---	4.10	0.01	0.00	---	---	---	---	---
10/12/97	MR102	3.7	0.14	0.17	205	82.0	---	4.33	0.01	0.01	---	---	---	---	---
10/12/97	MR103	1.7	0.15	0.22	206	77.6	---	4.47	0.01	0.01	---	---	---	---	---
10/12/97	MR104	0.0	0.16	0.30	212	76.6	---	6.16	0.01	0.01	---	---	---	---	---
10/12/97	KR201	7.0	0.20	0.33	198	52.2	---	3.12	0.01	0.00	---	---	---	---	---
10/12/97	KR202	4.0	0.33	0.12	210	61.7	---	3.26	0.01	0.01	---	---	---	---	---
10/12/97	KR203	2.9	0.35	0.18	210	61.8	---	3.29	0.01	0.01	---	---	---	---	---
10/12/97	KR204	1.0	0.38	0.25	214	63.8	---	3.72	0.01	0.01	---	---	---	---	---
10/11/97	KR206	-1.5	0.45	0.12	200	67.9	---	37.2	0.07	0.04	---	---	---	---	---
10/11/97	KR207	-1.0	0.52	0.90	197	62.0	---	16.7	0.03	0.01	---	---	---	---	---
10/12/97	KR209	-0.5	1.04	9.74	190	165	---	91.4	0.17	0.14	---	---	---	---	---
10/12/97	WR301	8.5	0.32	0.24	226	53.4	---	2.80	0.01	0.02	---	---	---	---	---
10/12/97	WR302	3.8	0.36	0.16	229	56.1	---	3.08	0.01	0.02	---	---	---	---	---
10/12/97	WR303	2.1	0.37	0.25	229	56.4	---	2.46	0.00	0.01	---	---	---	---	---
10/11/97	WR304	0.0	0.38	0.28	215	55.6	---	3.47	0.01	0.02	---	---	---	---	---
10/11/97	WR305	-2.0	5.52	12.9	159	40.7	---	22.0	0.04	0.10	---	---	---	---	---
10/11/97	WR307	-1.0	0.52	0.23	211	54.8	---	4.77	0.01	0.02	---	---	---	---	---
10/12/97	TR401	7.0	0.37	0.25	248	59.3	---	3.92	0.01	0.02	---	---	---	---	---
10/12/97	TR402	4.2	0.37	0.37	247	62.2	---	4.16	0.01	0.02	---	---	---	---	---
10/12/97	TR403	2.2	0.37	0.26	247	62.2	---	3.33	0.01	0.02	---	---	---	---	---
10/12/97	TR404	1.4	0.47	0.47	245	67.4	---	3.96	0.01	0.02	---	---	---	---	---
10/12/97	TR405	1.2	0.44	0.55	245	66.8	---	147	0.26	0.03	---	---	---	---	---
10/11/97	TR406	0.6	0.52	0.84	229	67.5	---	9.09	0.02	0.02	---	---	---	---	---
10/11/97	TR407	0.0	0.67	1.33	225	71.1	---	5.87	0.01	0.03	---	---	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
10/12/97	TR408	2.0	0.54	2.10	265	75.7	---	148	0.27	0.03	---	---	---	---	---
10/11/97	TR409	1.0	0.66	1.44	221	61.8	---	5.23	0.01	0.02	---	---	---	---	---
10/11/97	TR410	0.5	1.20	3.28	208	78.5	---	9.35	0.02	0.03	---	---	---	---	---
10/12/97	TR411	2.0	0.52	2.11	265	75.7	---	5.86	0.01	0.03	---	---	---	---	---
10/11/97	TR412	1.0	1.64	5.92	203	125	---	11.4	0.02	0.04	---	---	---	---	---
10/12/97	TI501	7.0	0.34	0.75	177	67.4	---	5.46	0.01	0.02	---	---	---	---	---
10/11/97	TI503	3.5	0.27	1.50	160	65.1	---	6.52	0.01	0.02	---	---	---	---	---
10/11/97	TI504	2.0	0.36	1.18	143	63.9	---	6.62	0.01	0.03	---	---	---	---	---
10/11/97	TI505	1.0	0.51	1.20	157	60.8	---	6.94	0.01	0.03	---	---	---	---	---
10/11/97	TI506	0.0	0.57	1.60	173	68.5	---	8.06	0.01	0.04	---	---	---	---	---
10/11/97	TB601	---	0.60	1.05	226	67.4	---	9.16	0.02	0.03	---	---	---	---	---
10/11/97	TB605	---	0.48	0.27	180	57.7	---	24.9	0.04	0.04	---	---	---	---	---
11/29/97	MR101	5.5	0.18	0.14	191	74.3	---	3.79	0.01	0.00	---	---	---	---	---
11/29/97	MR103	1.7	0.19	0.21	191	71.5	---	4.33	0.01	0.01	---	7.0	---	---	---
11/29/97	MR104	0.0	0.19	0.49	194	69.8	---	10.6	0.02	0.02	---	6.8	---	---	---
11/29/97	KR201	7.0	0.19	0.29	180	45.9	---	3.04	0.01	0.00	---	7.2	---	---	---
11/29/97	KR202	4.0	0.31	0.13	189	53.0	---	3.14	0.01	0.00	---	7.1	---	---	---
11/29/97	KR204	1.0	0.31	0.26	189	53.9	---	3.23	0.01	0.01	---	7.1	---	---	---
11/29/97	KR205	0.0	0.30	0.19	191	54.2	---	3.18	0.01	0.01	---	7.1	---	---	---
11/29/97	KR206	-1.5	0.39	0.83	182	52.7	---	918	1.66	1.2	---	7.4	---	---	---
11/29/97	KR207	-1.0	0.29	0.21	190	53.7	---	3.53	0.01	0.01	---	7.2	---	---	---
11/29/97	KR208	-2.0	0.49	0.98	189	52.7	---	592	1.07	0.80	---	7.2	---	---	---
11/29/97	WR301	8.5	0.31	0.10	214	41.7	---	2.43	0.00	0.02	---	---	---	---	---
11/29/97	WR302	3.8	0.41	0.33	215	45.5	---	2.67	0.00	0.02	---	7.2	---	---	---
11/29/97	WR303	2.1	0.43	0.33	218	46.7	---	3.35	0.01	0.02	---	7.2	---	---	---
11/29/97	WR304	0.0	0.62	0.46	219	47.2	---	60.5	0.11	0.01	---	7.3	---	---	---
11/29/97	WR305	-2.0	1.16	1.32	216	47.4	---	421	0.76	0.58	---	7.2	---	---	---
11/29/97	WR306	-0.2	0.69	0.43	221	47.3	---	3.08	0.01	0.02	---	7.2	---	---	---
11/29/97	WR307	-1.0	0.59	0.31	219	46.7	---	58.7	0.11	0.02	---	7.2	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
11/29/97	TR401	7.0	0.59	0.72	243	52.4	---	3.63	0.01	0.02	---	7.1	---	---	---
11/29/97	TR402	4.2	0.42	0.49	242	55.3	---	48.4	0.09	0.02	---	7.2	---	---	---
11/29/97	TR404	1.4	0.43	0.63	245	57.8	---	17.4	0.03	0.02	---	7.1	---	---	---
11/29/97	TR405	1.2	0.62	2.60	244	60.7	---	87.5	0.16	0.02	---	7.0	---	---	---
11/29/97	TR406	0.6	0.49	0.88	241	56.7	---	3.70	0.01	0.02	---	7.3	---	---	---
11/29/97	TR407	0.0	0.48	1.12	244	59.4	---	32.9	0.06	0.02	---	7.2	---	---	---
11/29/97	TR408	2.0	0.42	3.24	305	122	---	7.70	0.01	0.03	---	6.6	---	---	---
11/29/97	TR409	1.0	0.79	5.68	257	117	---	20.2	0.04	0.04	---	6.7	---	---	---
11/29/97	TR410	0.5	0.68	1.42	233	59.5	---	4.19	0.01	0.02	---	7.1	---	---	---
11/29/97	TR411	2.0	0.72	4.44	242	94.2	---	8.33	0.02	0.03	---	6.8	---	---	---
11/29/97	TR412	1.0	0.60	2.75	244	83.4	---	7.38	0.01	0.03	---	6.9	---	---	---
11/29/97	TI501	7.0	0.29	1.04	166	67.0	---	48.0	0.09	0.02	---	6.8	---	---	---
11/29/97	TI502	3.9	0.25	1.56	158	62.2	---	6.46	0.01	0.03	---	6.3	---	---	---
11/29/97	TI505	1.0	0.51	1.52	226	67.3	---	98.9	0.18	0.03	---	6.8	---	---	---
11/29/97	TI506	0.0	0.42	1.55	215	65.5	---	6.46	0.01	0.03	---	6.9	---	---	---
11/29/97	TB601	---	0.53	1.69	195	52.4	---	2326	4.20	3.2	---	7.4	---	---	---
11/29/97	TB602	---	0.45	1.87	182	51.8	---	2806	5.07	3.9	---	7.4	---	---	---
11/29/97	TB603	---	0.58	1.71	170	42.5	---	4153	7.50	6.0	---	7.8	---	---	---
11/29/97	TB604	---	0.58	1.47	153	38.0	---	4743	8.57	7.0	---	7.8	---	---	---
1/10/98	MR101	5.5	0.17	0.08	211	82.7	---	4.05	0.01	0.00	---	7.2	---	---	---
1/10/98	MR103	1.7	0.19	0.11	210	76.8	---	5.72	0.01	0.01	---	7.0	---	---	---
1/10/98	MR104	0.0	0.20	0.38	211	75.0	---	154	0.28	0.20	---	6.9	---	---	---
1/10/98	KR201	7.0	0.25	0.07	197	51.3	---	4.51	0.01	0.00	---	7.3	---	---	---
1/10/98	KR202	4.0	0.40	0.11	210	62.0	---	3.36	0.01	0.01	---	7.2	---	---	---
1/10/98	KR203.7	1.4	0.37	0.16	215	68.1	---	4.07	0.01	0.01	---	7.0	---	---	---
1/10/98	KR205	0.0	0.37	0.11	214	67.3	---	7.76	0.01	0.01	---	7.2	---	---	---
1/10/98	KR206	-1.5	0.52	0.82	187	49.7	---	2967	5.36	4.2	---	7.7	---	---	---
1/10/98	KR207	-1.0	0.38	0.44	208	65.4	---	525	0.95	0.71	---	7.1	---	---	---
1/10/98	WR301	8.5	0.36	0.12	229	53.5	---	3.65	0.01	0.02	---	7.5	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
1/10/98	WR302	3.8	0.42	0.83	232	58.4	---	3.97	0.01	0.02	---	7.2	---	---	---
1/10/98	WR303	2.1	0.40	0.27	232	58.9	---	5.00	0.01	0.02	---	7.2	---	---	---
1/10/98	WR304	0.0	0.44	0.25	231	58.7	---	7.64	0.01	0.02	---	7.3	---	---	---
1/10/98	WR305	-2.0	0.50	0.59	212	54.3	---	1449	2.62	1.9	---	7.5	---	---	---
1/10/98	WR306	-0.2	0.67	1.04	229	58.3	---	31.2	0.06	0.02	---	7.2	---	---	---
1/10/98	WR307	-1.0	0.44	0.28	232	56.7	---	59.2	0.11	0.08	---	7.2	---	---	---
1/10/98	TR401	7.0	0.43	0.16	250	58.0	---	4.94	0.01	0.02	---	7.3	---	---	---
1/10/98	TR402	4.2	0.44	0.27	252	61.1	---	3.96	0.01	0.02	---	7.2	---	---	---
1/10/98	TR404	1.4	0.43	0.54	250	63.8	---	33.0	0.06	0.02	---	7.1	---	---	---
1/10/98	TR406	0.6	0.46	0.78	249	62.7	---	13.8	0.02	0.02	128	7.3	---	---	---
1/10/98	TR407	0.0	0.46	0.81	250	64.4	---	12.7	0.02	0.03	---	7.2	---	---	---
1/10/98	TR408	2.0	0.49	2.61	247	118	---	13.8	0.02	0.03	---	6.7	---	---	---
1/10/98	TR409	1.0	0.49	2.24	245	110	---	11.3	0.02	0.04	---	6.8	---	---	---
1/10/98	TR410	0.5	0.48	0.97	249	69.8	---	4.84	0.01	0.03	---	7.1	---	---	---
1/10/98	TR411	2.0	0.49	0.95	250	70.3	---	4.56	0.01	0.02	---	7.1	---	---	---
1/10/98	TR412	1.0	0.49	1.33	242	102.2	---	6.94	0.01	0.03	---	6.9	---	---	---
1/10/98	TI501	7.0	0.23	0.40	182	68.9	---	6.55	0.01	0.02	---	7.0	---	---	---
1/10/98	TI502	3.9	0.19	0.85	175	67.2	---	7.38	0.01	0.03	---	6.4	---	---	---
1/10/98	TI504	2.0	0.39	2.53	215	65.7	---	69.4	0.13	0.05	---	6.9	---	---	---
1/10/98	TI506	0.0	---	---	---	---	---	---	---	---	---	6.9	---	---	---
1/10/98	TB601	---	0.47	1.59	189	52.2	---	3379	6.10	4.8	75	7.6	---	---	---
1/10/98	TB602	---	0.51	1.50	182	49.6	---	3993	7.21	5.8	78	7.7	---	---	---
1/10/98	TB603	---	0.55	1.02	131	38.1	---	7202	13.0	11	104	8.2	---	---	---
1/10/98	TB604	---	0.55	1.06	137	38.9	---	6945	12.5	10	78	8.0	---	---	---
1/11/98	TB606	---	0.64	0.94	60	17.6	---	13551	24.5	20	143	8.1	---	---	---
1/11/98	TB607	---	0.63	0.49	20	6.6	---	17029	30.8	26	108	8.1	---	---	---
1/11/98	TB608	---	0.64	0.30	9	3.3	---	18233	32.9	27	120	8.1	---	---	---
1/11/98	TB609	---	0.67	0.69	21	7.3	---	16735	30.2	25	133	8.1	---	---	---
1/11/98	TB610	---	0.55	1.00	113	36.4	---	8354	15.1	13	119	8.0	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
1/11/98	TB613	---	0.65	0.57	19	6.0	---	16858	30.5	25	101	8.1	---	---	---
1/11/98	TB614	---	0.75	0.96	41	11.9	---	15109	27.3	23	116	8.1	---	---	---
1/11/98	TB615	---	0.69	1.15	62	17.9	---	13459	24.3	20	132	8.1	---	---	---
1/11/98	TB616	---	0.67	1.16	63	18.3	---	13446	24.3	20	128	8.0	---	---	---
1/11/98	TB617	---	0.63	1.16	96	26.7	---	10579	19.1	16	132	8.0	---	---	---
2/7/98	MR101	5.5	0.32	0.09	208	72.4	---	4.01	0.01	0.01	---	7.2	---	---	---
2/7/98	MR102	3.7	0.22	0.22	205	70.3	---	4.42	0.01	0.01	---	7.1	---	---	---
2/7/98	MR103	1.7	0.21	0.24	208	69.4	---	4.79	0.01	0.01	---	7.0	---	---	---
2/7/98	MR104	0.0	0.20	0.57	210	68.5	---	413	0.75	0.62	---	7.1	---	---	---
2/7/98	KR201	7.0	0.29	0.17	186	186	---	3.25	0.01	0.01	---	7.3	---	---	---
2/7/98	KR202	4.0	0.37	0.16	199	199	---	3.30	0.01	0.01	---	7.2	---	---	---
2/7/98	KR203.7	1.4	0.28	0.12	206	55.7	---	3.45	0.01	0.01	---	7.0	---	---	---
2/7/98	KR205	0.0	0.41	0.19	201	54.4	---	3.84	0.01	0.01	---	7.1	---	---	---
2/7/98	KR206	-1.5	0.74	1.06	188	40.9	---	2333	4.22	3.4	---	7.5	---	---	---
2/7/98	KR207	-1.0	0.49	0.85	181	47.9	---	2036	3.68	3.0	---	7.3	---	---	---
2/7/98	WR301	8.5	0.35	0.04	220	39.1	---	2.55	0.00	0.02	---	7.5	---	---	---
2/7/98	WR302	3.8	0.50	0.18	223	44.6	---	2.74	0.00	0.02	---	7.2	---	---	---
2/7/98	WR303	2.1	0.51	0.23	222	44.4	---	2.71	0.00	0.02	---	7.3	---	---	---
2/7/98	WR304	0.0	0.93	0.18	223	44.8	---	2.96	0.01	0.02	---	7.2	---	---	---
2/7/98	WR305	-2.0	0.79	0.95	167	35.2	---	4643	8.39	6.9	---	7.5	---	---	---
2/7/98	WR306	-0.2	0.96	0.32	221	45.1	---	3.47	0.01	0.02	---	7.2	---	---	---
2/7/98	WR307	-1.0	0.79	0.68	196	39.3	---	1999	3.61	3.0	---	7.4	---	---	---
2/7/98	TR401	7.0	0.38	0.10	249	45.0	---	3.02	0.01	0.02	---	7.4	---	---	---
2/7/98	TR402	4.2	0.38	0.56	250	47.8	---	3.10	0.01	0.02	---	7.3	---	---	---
2/7/98	TR404	1.4	0.45	0.43	247	50.7	---	3.30	0.01	0.03	---	7.2	---	---	---
2/7/98	TR406	0.6	0.33	1.08	249	47.7	---	4.17	0.01	0.03	---	7.3	---	---	---
2/7/98	TR407	0.0	0.17	1.66	216	44.8	---	1874	3.39	2.8	---	7.4	---	---	---
2/7/98	TR408	2.0	0.49	3.66	277	108	---	17.1	0.03	0.06	---	7.0	---	---	---
2/7/98	TR409	1.0	0.43	1.78	245	57.8	---	47.3	0.09	0.10	---	7.2	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
2/7/98	TR410	0.5	0.36	1.51	230	48.9	---	580	1.05	1.01	---	7.2	---	---	---
2/7/98	TR411	2.0	0.49	1.44	243	53.2	---	21.8	0.04	0.06	---	7.3	---	---	---
2/7/98	TR412	1.0	0.40	1.48	243	60.1	---	20.1	0.04	0.05	---	7.1	---	---	---
2/7/98	TI501	7.0	0.14	0.69	172	62.7	---	6.89	0.01	0.02	---	7.1	---	---	---
2/7/98	TI502	3.9	0.16	1.19	165	56.4	---	5.77	0.01	0.03	---	6.9	---	---	---
2/7/98	TI504	2.0	0.36	2.59	204	47.7	---	1373	2.48	2.1	---	7.3	---	---	---
2/7/98	TI506	0.0	0.46	2.25	190	44.6	---	2615	4.72	3.9	---	7.2	---	---	---
2/7/98	TB601	---	0.63	1.31	126	30.2	---	8109	14.6	12	---	7.8	---	---	---
2/7/98	TB602	---	0.70	1.14	90	21.6	---	11078	20.0	17	---	7.9	---	---	---
2/7/98	TB603	---	0.66	1.11	88	21.2	---	11232	20.3	17	---	7.9	---	---	---
2/7/98	TB604	---	0.62	1.06	111	26.1	---	9198	16.6	14	---	8.0	---	---	---
3/22/98	MR101	5.5	0.13	0.16	193	62.2	---	3.66	0.01	0.00	---	7.2	---	---	---
3/22/98	MR103	1.7	0.19	0.22	195	60.0	---	4.32	0.01	0.01	---	7.1	---	---	---
3/22/98	MR104	0.0	0.17	0.28	200	60.2	---	5.45	0.01	0.01	---	6.9	---	---	---
3/22/98	KR201	7.0	0.15	0.16	179	38.4	---	2.89	0.01	0.01	---	---	---	---	---
3/22/98	KR202	4.0	0.26	0.10	186	44.5	---	2.89	0.01	0.00	---	7.3	---	---	---
3/22/98	KR203.7	1.4	0.27	0.15	188	47.5	---	2.96	0.01	0.01	---	7.3	---	---	---
3/22/98	KR205	0.0	0.29	0.29	188	48.7	---	3.06	0.01	0.01	---	7.0	---	---	---
3/22/98	KR206	-1.5	0.34	0.35	185	48.8	---	388	0.70	0.51	---	7.1	---	---	---
3/22/98	KR209	-0.5	0.49	5.64	136	97.8	---	12.8	0.02	0.02	---	6.1	---	---	---
3/22/98	WR301	8.5	0.30	0.02	210	36.1	---	2.43	0.00	0.02	---	7.4	---	---	---
3/22/98	WR302	3.8	0.39	0.19	212	40.7	---	2.54	0.00	0.02	---	7.3	---	---	---
3/22/98	WR303	2.1	0.48	0.56	212	44.7	---	2.74	0.00	0.02	---	7.2	---	---	---
3/22/98	WR305	-2.0	0.83	0.86	212	45.2	---	7.17	0.01	0.02	---	7.1	---	---	---
3/22/98	WR306	-0.2	1.24	1.49	206	43.1	---	5.49	0.01	0.00	---	7.0	---	---	---
3/22/98	WR307	-1.0	0.73	0.57	209	44.3	---	4.39	0.01	0.00	---	7.1	---	---	---
3/22/98	TR401	7.0	0.37	0.30	237	44.0	---	2.76	0.00	0.02	---	7.5	---	---	---
3/22/98	TR402	4.2	0.37	0.37	233	45.8	---	2.87	0.01	0.02	---	7.4	---	---	---
3/22/98	TR404	1.4	0.48	1.08	224	47.0	---	2.97	0.01	0.02	---	7.0	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
3/22/98	TR406	0.6	0.53	1.72	226	48.4	---	3.38	0.01	0.02	---	7.1	---	---	---
3/22/98	TR407	0.0	0.55	1.97	234	66.6	---	5.92	0.01	0.01	---	7.0	---	---	---
3/22/98	TR408	2.0	0.64	5.70	360	159	---	10.9	0.02	0.01	---	6.9	---	---	---
3/22/98	TR409	1.0	0.75	4.50	330	154	---	27.8	0.05	0.02	---	6.8	---	---	---
3/22/98	TR410	0.5	0.79	3.84	262	160	---	14.2	0.03	0.02	---	6.8	---	---	---
3/22/98	TR411	2.0	0.50	8.14	160	178	---	7.48	0.01	0.01	---	6.4	---	---	---
3/22/98	TR412	1.0	0.50	6.18	182	176	---	9.24	0.02	0.01	---	6.6	---	---	---
3/22/98	TI501	7.0	0.24	0.84	153	51.4	---	4.51	0.01	0.02	---	7.0	---	---	---
3/22/98	TI502	3.9	0.19	1.16	141	44.3	---	7.40	0.01	0.02	---	6.8	---	---	---
3/22/98	TI504	2.0	0.19	2.09	164	46.7	---	7.23	0.01	0.03	---	6.5	---	---	---
3/22/98	TI506	0.0	0.26	1.95	189	46.4	---	7.10	0.01	0.03	---	6.7	---	---	---
3/22/98	TB601	---	0.51	2.88	217	45.8	---	697	1.26	1.2	---	7.2	---	---	---
3/22/98	TB602	---	0.35	2.08	200	43.9	---	3421	6.18	5.0	---	7.2	---	---	---
3/22/98	TB603	---	0.49	2.40	218	45.5	---	1798	3.25	2.7	---	7.2	---	---	---
3/22/98	TB604	---	0.48	1.50	167	36.1	---	8824	15.9	13	---	7.5	---	---	---
4/11/98	MR101	5.5	0.14	0.47	214	69.1	---	3.88	0.01	0.00	---	7.2	---	---	---
4/11/98	MR103	1.7	0.11	0.17	211	60.1	---	4.60	0.01	0.01	---	7.2	---	---	---
4/11/98	MR104	0.0	0.17	0.44	214	61.0	---	15.7	0.03	0.02	---	7.1	---	---	---
4/11/98	KR201	7.0	0.20	0.33	190	40.4	---	2.98	0.01	0.01	---	7.3	---	---	---
4/11/98	KR202	4.0	0.28	0.44	199	46.0	---	3.12	0.01	0.00	---	7.5	---	---	---
4/11/98	KR203.7	1.4	0.23	0.53	203	51.4	---	3.39	0.01	0.01	---	7.2	---	---	---
4/11/98	KR206	-1.5	0.66	1.37	135	27.9	---	11197	20.2	17	---	7.7	---	---	---
4/11/98	KR207	-1.0	0.76	0.73	202	45.6	---	661	1.19	1.2	---	7.3	---	---	---
4/11/98	KR209	-0.5	0.20	1.34	181	86.0	---	2027	3.66	3.0	---	6.8	---	---	---
4/11/98	WR301	8.5	0.35	0.22	221	35.6	---	5.98	0.01	0.02	---	7.7	---	---	---
4/11/98	WR302	3.8	0.24	0.44	222	40.1	---	2.87	0.01	0.02	---	7.3	---	---	---
4/11/98	WR303	2.1	0.25	0.26	223	41.7	---	2.77	0.01	0.02	---	7.2	---	---	---
4/11/98	WR304	0.0	1.19	0.46	222	41.8	---	3.87	0.01	0.02	---	7.1	---	---	---
4/11/98	WR305	-2.0	0.76	0.72	227	43.9	---	187	0.34	0.30	---	7.4	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
4/11/98	WR307	-1.0	0.69	0.72	198	41.1	---	1134	2.05	1.6	---	7.5	---	---	---
4/11/98	TR401	7.0	0.33	0.44	243	36.8	---	2.98	0.01	0.02	---	7.6	---	---	---
4/11/98	TR402	4.2	0.31	0.48	244	38.8	---	2.97	0.01	0.02	---	7.5	---	---	---
4/11/98	TR404	1.4	0.29	0.49	245	40.2	---	3.11	0.01	0.02	---	7.3	---	---	---
4/11/98	TR406	0.6	0.38	1.82	244	43.2	---	3.38	0.01	0.02	---	7.2	---	---	---
4/11/98	TR407	0.0	0.54	3.34	235	46.5	---	42.4	0.08	0.08	---	7.3	---	---	---
4/11/98	TR408	2.0	0.44	2.98	338	145	---	12.6	0.02	0.03	---	7.0	---	---	---
4/11/98	TR409	1.0	0.43	1.57	246	52.0	---	5.46	0.01	0.01	---	7.2	---	---	---
4/11/98	TR410	0.5	0.62	2.40	232	47.9	---	39.2	0.07	0.06	---	7.2	---	---	---
4/11/98	TR411	2.0	0.34	10.5	217	117	---	9.44	0.02	0.02	---	6.6	---	---	---
4/11/98	TR412	1.0	0.48	1.97	246	60.7	---	9.05	0.02	0.01	---	7.2	---	---	---
4/11/98	TI501	7.0	0.15	0.51	175	49.7	---	4.91	0.01	0.02	---	7.2	---	---	---
4/11/98	TI502	3.9	0.14	2.01	170	50.4	---	6.09	0.01	0.02	---	6.9	---	---	---
4/11/98	TI504	2.0	0.24	1.09	186	44.9	---	9.19	0.02	0.03	---	6.9	---	---	---
4/11/98	TI506	0.0	0.50	1.25	215	43.6	---	685	1.24	0.92	---	7.4	---	---	---
4/11/98	TB601	---	0.59	0.91	229	46.6	---	131	0.24	0.23	---	7.3	---	---	---
4/11/98	TB602	---	0.64	1.14	179	35.0	---	5941	10.7	8.9	89	7.7	---	---	---
4/11/98	TB603	---	0.74	1.89	102	18.6	---	17143	31.0	26	92	7.8	---	---	---
4/11/98	TB604	---	0.72	1.68	87	15.7	---	14700	26.6	22	93	7.9	---	---	---
4/11/98	TB606	---	0.52	1.01	56	9.3	---	12084	21.8	18	81	8.1	---	---	---
4/11/98	TB607	---	0.22	0.02	17	1.3	---	19155	34.6	29	112	8.2	---	---	---
4/11/98	TB608	---	0.27	0.28	23	2.6	---	14261	25.8	22	---	8.2	---	---	---
4/11/98	TB609	---	0.28	0.53	22	2.4	---	14249	25.7	22	100	8.2	---	---	---
4/11/98	TB610	---	0.32	0.76	69	16.2	---	10766	19.4	16	90	8.1	---	---	---
4/11/98	TB614	---	0.22	0.11	18	1.4	---	14575	26.3	22	95	8.2	---	---	---
5/23/98	MR101	5.5	0.06	0.41	205	65.5	---	---	---	---	---	7.2	---	---	---
5/23/98	MR103	1.7	0.04	0.43	203	58.0	---	---	---	---	---	7.0	---	---	---
5/23/98	MR104	0.0	0.05	0.62	211	57.1	---	11.1	0.02	0.02	---	6.8	---	---	---
5/23/98	KR201	7.0	0.07	0.35	183	40.7	---	---	---	---	---	7.4	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
5/23/98	KR203.7	1.4	0.14	0.88	199	49.8	---	2.06	0.00	0.00	---	7.1	---	---	---
5/23/98	KR207	-1.0	0.11	0.75	197	50.0	---	6.39	0.01	0.00	---	6.9	---	---	---
5/23/98	WR301	8.5	0.13	0.74	216	33.1	---	---	---	---	---	7.5	---	---	---
5/23/98	WR302	3.8	0.16	0.71	219	38.4	---	---	---	---	---	7.2	---	---	---
5/23/98	WR303	2.1	0.16	0.46	218	38.2	---	---	---	---	---	7.1	---	---	---
5/23/98	WR304	0.0	0.63	0.78	217	38.8	---	1.69	0.00	0.01	---	7.0	---	---	---
5/23/98	WR305	-2.0	0.72	1.50	216	38.1	---	63.0	0.11	0.09	---	7.0	---	---	---
5/23/98	WR306	-0.2	0.70	0.70	217	38.5	---	---	---	---	---	7.1	---	---	---
5/23/98	WR307	-1.0	0.70	1.04	215	37.8	---	26.7	0.05	0.05	---	7.1	---	---	---
5/23/98	TR401	7.0	0.23	0.87	245	38.6	---	---	---	---	---	7.5	---	---	---
5/23/98	TR402	4.2	0.23	1.09	245	40.5	---	---	---	---	---	7.2	---	---	---
5/23/98	TR404	1.4	0.88	4.50	243	46.6	---	---	---	---	---	7.1	---	---	---
5/23/98	TR405	1.2	0.33	1.52	244	42.4	---	---	---	---	---	7.1	---	---	---
5/23/98	TR406	0.6	0.70	4.46	233	44.8	---	---	---	---	---	7.0	---	---	---
5/23/98	TR407	0.0	0.54	2.35	212	43.9	---	148	0.27	0.24	---	7.0	---	---	---
5/23/98	TR408	2.0	2.38	13.0	265	68.6	---	---	---	---	---	6.8	---	---	---
5/23/98	TR409	1.0	0.71	4.92	243	44.4	---	---	---	---	---	7.0	---	---	---
5/23/98	TR410	0.5	0.58	2.94	220	43.8	---	---	---	---	---	6.9	---	---	---
5/23/98	TR411	2.0	2.72	13.0	260	79.3	---	---	---	---	---	6.7	---	---	---
5/23/98	TR412	1.0	0.70	4.96	243	44.4	---	---	---	---	---	7.0	---	---	---
5/23/98	TI501	7.0	0.07	0.40	177	49.0	---	---	---	---	---	7.1	---	---	---
5/23/98	TI502	3.9	0.06	1.41	176	47.5	---	---	---	---	---	6.4	---	---	---
5/23/98	TI504	2.0	0.37	2.12	201	45.3	---	57.2	0.10	0.11	---	6.8	---	---	---
5/23/98	TI506	0.0	0.57	1.70	193	39.6	---	1243	2.25	1.79	---	7.3	---	---	---
5/23/98	TB601	---	0.51	1.74	208	45.3	---	146	0.26	0.28	---	7.0	---	---	---
5/23/98	TB602	---	0.55	1.76	205	42.5	---	451	0.81	0.64	---	7.1	---	---	---
5/23/98	TB603	---	0.48	1.04	171	34.7	---	2924	5.28	4.3	---	7.4	---	---	---
5/23/98	TB604	---	0.46	0.68	134	25.4	---	5811	10.5	8.6	---	7.7	---	---	---
5/23/98	TB606	---	0.51	0.90	139	26.4	---	5368	9.698	7.9	---	7.7	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
5/23/98	TB607	---	0.49	0.66	114	21.2	---	7632	13.8	11	---	7.8	---	---	---
5/23/98	TB608	---	0.45	0.70	105	19.6	---	8036	14.5	12	---	7.9	---	---	---
5/23/98	TB609	---	0.28	1.44	103	25.0	---	8411	15.2	12	---	7.9	---	---	---
5/23/98	TB612	---	0.24	0.75	38	4.4	---	13177	23.8	20	---	8.1	---	---	---
6/24/98	MR101	5.5	0.13	0.41	218	62.5	---	---	---	---	---	7.2	---	---	---
6/24/98	MR103	1.7	0.07	0.26	193	47.0	---	---	---	---	---	7.1	---	---	---
6/24/98	MR104	0.0	0.07	0.89	204	49.4	---	23.9	0.043	0.03	---	6.9	---	---	---
6/24/98	KR201	7.0	0.21	0.60	193	37.5	---	---	---	---	---	7.3	---	---	---
6/24/98	KR203.7	1.4	0.15	0.46	203	46.5	---	---	---	---	---	7.2	---	---	---
6/24/98	KR206	-1.5	0.70	1.12	123	15.1	---	6572	11.9	9.8	---	7.5	---	---	---
6/24/98	KR209	-0.5	0.08	1.10	112	38.7	---	---	---	---	---	6.8	---	---	---
6/24/98	WR301	8.5	0.15	0.64	221	28.3	---	---	---	---	---	7.8	---	---	---
6/24/98	WR302	3.8	0.14	1.02	218	33.1	---	---	---	---	---	7.3	---	---	---
6/24/98	WR303	2.1	0.12	0.74	219	34.4	---	3.21	0.01	0.02	---	7.1	---	---	---
6/24/98	WR305	-2.0	1.16	2.14	196	25.9	---	---	---	---	---	7.2	---	---	---
6/24/98	TR400	10.0	0.09	1.16	230	20.7	---	---	---	---	---	8.6	---	---	---
6/24/98	TR401	7.0	0.08	0.67	218	21.8	---	---	---	---	---	8.2	---	---	---
6/24/98	TR402	4.2	0.08	0.71	213	25.4	---	---	---	---	87	7.1	---	---	---
6/24/98	TR404	1.4	0.15	1.17	220	26.1	---	---	---	---	---	7.1	---	---	---
6/24/98	TR405	1.2	0.20	1.62	220	26.3	---	---	---	---	76	7.0	---	---	---
6/24/98	TR406	0.6	0.46	3.84	220	27.6	---	---	---	---	---	7.2	---	---	---
6/24/98	TR407	0.0	0.65	4.15	203	26.7	---	735	1.33	0.95	---	7.2	---	---	---
6/24/98	TR408	2.0	1.32	3.24	332	18.8	---	---	---	---	---	7.0	---	---	---
6/24/98	TR409	1.0	1.17	3.48	238	38.4	---	---	---	---	---	7.0	---	---	---
6/24/98	TR410	0.5	0.59	2.97	210	27.5	---	---	---	---	---	7.1	---	---	---
6/24/98	TR411	2.0	1.50	6.02	217	130	---	---	---	---	---	6.6	---	---	---
6/24/98	TR412	1.0	1.11	4.29	234	40.4	---	---	---	---	---	7.0	---	---	---
6/24/98	TI501	7.0	0.26	0.39	180	34.9	---	---	---	---	---	7.7	---	---	---
6/24/98	TI502	3.9	0.07	0.40	182	29.2	---	---	---	---	---	7.0	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
6/24/98	TI504	2.0	0.52	1.71	162	21.2	---	---	---	---	---	7.3	---	---	---
6/24/98	TI506	0.0	0.54	1.95	158	20.8	---	3683	6.65	5.4	---	7.4	---	---	---
6/24/98	TB601	---	0.69	1.26	113	13.6	---	7640	13.8	11	107	7.6	---	---	---
6/24/98	TB602	---	0.74	0.60	97	11.0	---	9698	17.5	15	---	7.7	---	---	---
6/24/98	TB603	---	0.79	0.62	76	7.9	---	12304	22.2	19	---	7.8	---	---	---
6/24/98	TB604	---	0.81	2.23	74	6.8	---	12371	22.3	19	525	7.8	---	---	---
6/24/98	TB606	---	0.90	1.16	34	6.7	---	16733	30.2	26	---	7.9	---	---	---
6/24/98	TB607	---	0.92	1.30	37	7.3	---	15972	28.9	24	---	7.9	---	---	---
6/24/98	TB608	---	0.89	0.76	21	6.8	---	17711	32.0	27	---	8.0	---	---	---
6/24/98	TB609	---	0.89	0.79	22	6.9	---	18052	32.6	27	---	8.0	---	---	---
6/24/98	TB610	---	0.90	1.82	39	7.8	---	15810	28.6	24	---	7.9	---	---	---
6/24/98	TB612	---	0.80	0.62	21	6.1	---	17616	31.8	27	83	8.0	---	---	---
7/12/98	KR203.7	1.4	0.17	0.50	218	47.9	---	2.95	0.01	0.01	---	7.0	---	---	---
7/12/98	WR303	2.1	0.05	0.68	222	30.7	---	3.32	0.01	0.03	---	7.4	---	---	---
7/12/98	WR304	0.0	2.69	1.48	215	31.8	---	82.8	0.15	0.14	---	7.2	---	---	---
7/12/98	WR305	-2.0	0.96	2.00	187	23.2	---	---	---	---	---	7.4	---	---	---
7/12/98	TR407	0.0	0.70	1.09	138	17.2	---	6381	11.5	8.7	---	7.5	---	---	---
7/12/98	TR408	2.0	1.07	2.66	275	29.8	---	99.8	0.18	0.14	---	7.2	---	---	---
7/12/98	TR411	2.0	1.15	2.15	228	80.5	---	109	0.20	0.16	---	7.0	---	---	---
7/12/98	TI506	0.0	0.93	0.66	96	10.1	---	12686	22.9	19.7	---	7.7	---	---	---
7/12/98	TB601HT	---	0.84	0.41	71	6.8	---	11408	20.6	17.4	125	7.9	---	---	---
7/12/98	TB602HT	---	0.80	0.70	66	6.2	---	12113	21.9	18.1	104	7.9	---	---	---
7/12/98	TB603HT	---	0.89	1.12	63	6.5	---	13056	23.6	19.3	101	7.9	---	---	---
7/12/98	TB604HT	---	0.86	1.05	57	6.5	---	13604	24.6	19.8	131	7.8	---	---	---
7/12/98	TB606HT	---	0.82	1.03	22	6.4	---	16488	29.8	23.8	83	8.0	---	---	---
7/12/98	TB607HT	---	1.01	0.92	19	9.6	---	17545	31.7	25.0	84	8.0	---	---	---
7/12/98	TB608HT	---	0.97	1.29	34	8.2	---	15979	28.9	22.7	102	8.0	---	---	---
7/12/98	TB609HT	---	0.86	1.46	20	6.5	---	17360	31.4	24.7	116	8.0	---	---	---
7/12/98	TB610HT	---	0.88	1.86	49	6.4	---	14937	27.0	21.1	102	8.0	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
7/12/98	TB612HT	---	1.04	0.81	17	10.0	---	17726	32.0	25.2	75	8.0	---	---	---
7/12/98	TB613HT	---	0.87	1.38	20	7.1	---	17503	31.6	25.9	117	8.0	---	---	---
7/12/98	TB614HT	---	0.79	0.49	18	6.5	---	17444	31.5	25.8	105	8.0	---	---	---
7/12/98	TB615HT	---	0.92	1.02	34	5.4	---	16427	29.7	24.2	110	7.9	---	---	---
7/12/98	TB616HT	---	0.89	0.91	50	4.7	---	15289	27.6	22.5	116	7.9	---	---	---
7/12/98	TB617HT	---	0.85	0.67	45	5.7	---	15481	28.0	22.7	115	8.0	---	---	---
7/12/98	TB601LT	---	0.58	2.39	209	27.9	---	1088	1.97	1.1	139	7.2	---	---	---
7/12/98	TB602LT	---	0.57	2.34	207	27.6	---	1075	1.94	1.3	129	7.2	---	---	---
7/12/98	TB603LT	---	0.63	2.71	205	27.6	---	1262	2.28	1.5	126	7.2	---	---	---
7/12/98	TB604LT	---	0.64	2.26	204	27.8	---	1546	2.79	1.8	118	7.2	---	---	---
7/12/98	TB606LT	---	0.81	1.48	146	18.1	---	4580	8.27	6.9	114	7.4	---	---	---
7/12/98	TB607LT	---	0.89	1.27	68	8.0	---	12554	22.7	20	106	7.7	---	---	---
7/12/98	TB608LT	---	0.96	1.63	44	7.1	---	13711	24.8	21	102	7.8	---	---	---
8/26/98	MR101	5.5	0.27	0.60	246	67.1	---	---	---	---	---	7.3	---	---	---
8/26/98	MR103	1.7	0.16	0.40	240	53.5	---	---	---	---	---	7.1	---	---	---
8/26/98	MR104	0.0	0.20	1.07	247	50.6	---	292	0.53	0.48	---	6.9	---	---	---
8/26/98	KR201	7.0	0.19	0.28	193	36.5	---	---	---	---	---	7.4	---	---	---
8/26/98	KR202	4.0	0.13	0.47	216	42.2	---	---	---	---	---	7.2	---	---	---
8/26/98	KR203.7	1.4	0.14	0.35	241	49.0	---	4.31	0.01	0.00	---	6.9	---	---	---
8/26/98	KR209	-0.5	0.19	1.19	108	12.0	---	---	---	---	---	7.1	---	---	---
8/26/98	WR301	8.5	0.04	0.71	219	19.8	---	---	---	---	---	7.6	---	---	---
8/26/98	WR302	3.8	0.08	0.76	237	31.3	---	---	---	---	---	7.0	---	---	---
8/26/98	WR303	2.1	0.10	0.76	237	27.1	---	---	---	---	---	7.2	---	---	---
8/26/98	WR304	0.0	1.31	2.01	125	16.5	---	5988	10.8	11	---	7.7	---	---	---
8/26/98	WR305	-2.0	0.90	1.05	79	7.9	---	---	---	---	---	7.7	---	---	---
8/26/98	WR306	-0.2	0.78	1.88	127	15.6	---	---	---	---	---	7.7	---	---	---
8/26/98	TR400	10.0	0.23	0.57	249	13.7	---	---	---	---	---	8.5	---	---	---
8/26/98	TR401	7.0	0.15	0.93	241	18.0	---	---	---	---	---	7.6	---	---	---
8/26/98	TR402	4.2	0.12	0.84	250	20.3	---	---	---	---	---	7.4	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
8/26/98	TR404	1.4	1.04	8.93	218	23.0	---	---	---	---	---	7.3	---	---	---
8/26/98	TR405	1.2	0.61	4.89	219	21.8	---	---	---	---	---	7.3	---	---	---
8/26/98	TR406	0.6	0.79	1.00	86	10.1	---	---	---	---	---	7.6	---	---	---
8/26/98	TR407	0.0	0.97	0.75	61	5.5	---	13384	24.2	20	---	7.7	---	---	---
8/26/98	TR408	2.0	0.62	3.44	184	11.7	---	---	---	---	---	7.2	---	---	---
8/26/98	TR409	1.0	0.53	3.12	146	19.1	---	---	---	---	---	7.4	---	---	---
8/26/98	TR410	0.5	0.80	0.93	86	10.0	---	---	---	---	---	7.6	---	---	---
8/26/98	TR411	2.0	0.30	1.65	125	61.5	---	---	---	---	---	7.2	---	---	---
8/26/98	TR412	1.0	0.53	2.82	140	18.8	---	---	---	---	---	7.4	---	---	---
8/26/98	TI501	7.0	0.37	0.77	200	32.3	---	---	---	---	---	7.3	---	---	---
8/26/98	TI502	3.9	0.24	3.88	193	36.0	---	---	---	---	---	6.8	---	---	---
8/26/98	TI504	2.0	0.28	2.77	134	22.9	---	---	---	---	---	7.2	---	---	---
8/26/98	TI506	0.0	1.01	0.91	52	4.3	---	14462	26.1	21	---	7.7	---	---	---
8/26/98	TB601	---	1.05	1.00	54	4.3	---	14372	26.0	21	---	---	---	---	---
8/26/98	TB602	---	1.09	0.96	49	3.7	---	15127	27.3	22	---	---	---	---	---
10/17/98	MR101	5.5	0.15	0.36	217	114.7	0.03	3.83	0.01	0.01	---	7.2	0.02	0.00	2.9
10/17/98	MR103	1.7	0.12	0.21	215	94.7	0.04	4.32	0.01	0.01	---	6.9	0.20	0.03	16
10/17/98	KR202	4.0	0.25	0.30	206	79.2	0.03	3.18	0.01	0.01	113	7.2	0.03	0.01	2.5
10/17/98	KR203.7	1.4	0.25	0.27	210	80.5	0.04	2.98	0.01	0.01	---	7.2	0.06	0.01	4.1
10/17/98	WR302	3.8	0.29	0.56	227	70.1	0.06	2.40	0.00	0.03	---	7.1	0.11	0.03	5.8
10/17/98	WR303	2.1	0.31	0.37	227	69.8	0.06	2.42	0.00	0.03	---	7.3	0.31	0.10	6.6
10/17/98	WR304	0.0	1.81	0.95	226	70.1	0.17	8.14	0.01	0.03	147	7.1	0.37	0.16	8.1
10/17/98	WR305	-2.0	1.24	1.29	225	70.2	0.13	23.8	0.04	0.05	89	7.0	0.21	0.04	11
10/17/98	TR401	7.0	0.27	0.44	240	75.3	0.09	4.32	0.01	0.03	---	7.3	0.55	0.30	17
10/17/98	TR404	1.4	0.30	1.35	243	80.4	0.26	5.93	0.01	0.04	---	7.2	0.52	0.23	17
10/17/98	TR406	0.6	0.46	3.66	241	81.2	0.33	6.02	0.01	0.04	---	7.1	0.94	0.50	18
10/17/98	TR407	0.0	0.62	4.28	234	83.7	0.44	55.1	0.10	0.10	150	7.2	---	---	---
10/17/98	TR409	1.0	0.78	8.11	237	128	1.33	220	0.40	0.34	---	6.8	---	---	---
10/17/98	TR410	0.5	0.63	4.73	237	91.1	0.60	81.9	0.15	0.14	---	7.0	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
10/17/98	TR412	1.0	0.54	9.92	237	146	1.55	210	0.38	0.31	---	6.7	---	---	---
10/17/98	TI502	3.9	0.21	2.13	191	82.6	0.27	10.4	0.02	0.04	---	6.5	1.64	0.94	79
10/17/98	TI506	0.0	0.47	2.61	210	86.4	0.42	127	0.23	0.23	279	7.0	1.66	0.73	27
10/17/98	TB601	---	0.71	3.61	163	65.2	0.34	3869	6.99	5.2	158	7.5	0.37	0.37	45
10/17/98	TB602	---	0.80	3.30	144	58.2	0.32	5302	9.58	7.2	172	7.6	0.27	0.34	43
10/17/98	TB603	---	0.82	2.82	110	42.9	0.27	8156	14.7	11	140	7.8	0.09	0.26	51
10/17/98	TB604	---	0.77	2.75	100	38.2	0.25	9071	16.4	12	136	7.8	0.05	0.24	51
10/17/98	TB606	---	0.76	3.04	47	17.6	0.18	13973	25.2	20	103	8.0	0.15	0.21	81
10/17/98	TB607	---	0.74	2.71	16	5.7	0.13	17005	30.7	24	99	8.0	0.02	0.07	51
10/17/98	TB608	---	0.71	2.75	15	5.2	0.14	17245	31.2	25	85	8.0	0.04	0.05	49
10/17/98	TB609	---	0.74	3.00	14	5.3	0.15	17168	31.0	25	88	8.0	0.13	0.06	50
10/17/98	TB612	---	0.71	2.40	15	5.6	0.14	17095	30.9	24	91	8.0	0.02	0.05	52
10/17/98	TB614	---	0.75	2.99	16	5.9	0.15	16968	30.7	24	96	8.1	0.02	0.06	50
10/17/98	TB615	---	0.78	3.29	50	18.6	0.25	13535	24.5	19	336	8.0	0.01	0.17	50
11/29/98	MR101	5.5	0.11	0.23	215	90.8	0.02	---	---	---	56	7.0	---	---	---
11/29/98	MR103	1.7	0.12	1.16	211	83.5	0.02	---	---	---	---	6.7	---	---	---
11/29/98	MR104	0.0	0.15	0.51	212	83.9	0.04	---	---	---	---	6.6	---	---	---
11/29/98	KR201	7.0	0.15	0.29	206	55.6	0.01	---	---	---	60	7.2	---	---	---
11/29/98	KR202	4.0	0.26	0.33	217	66.1	0.01	---	---	---	---	7.0	---	---	---
11/29/98	KR203.7	1.4	0.26	0.34	221	71.8	0.02	---	---	---	---	---	---	---	---
11/29/98	KR205	0.0	0.27	0.30	224	74.6	0.01	---	---	---	62	6.9	---	---	---
11/29/98	KR206	-1.5	0.39	1.08	222	79.6	0.12	---	---	---	---	6.9	---	---	---
11/29/98	WR301	8.5	0.26	0.18	239	56.9	0.00	---	---	---	68	7.3	---	---	---
11/29/98	WR302	3.8	0.32	0.16	243	61.8	0.02	---	---	---	---	7.1	---	---	---
11/29/98	WR303	2.1	0.31	0.37	242	62.3	0.02	---	---	---	---	7.1	---	---	---
11/29/98	WR304	0.0	0.55	0.24	240	62.7	0.02	---	---	---	---	7.1	---	---	---
11/29/98	WR304.5	-1.0	0.52	0.63	233	62.9	0.04	---	---	---	---	7.0	---	---	---
11/29/98	WR305	-2.0	0.45	0.43	234	63.2	0.04	---	---	---	85	7.1	---	---	---
11/29/98	WR306	-0.2	0.48	0.42	234	63.5	0.07	---	---	---	---	7.0	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
11/29/98	TR400	10.0	0.31	0.19	247	63.4	0.03	---	---	---	---	7.4	---	---	---
11/29/98	TR401	7.0	0.30	0.37	244	67.7	0.03	---	---	---	192	7.1	---	---	---
11/29/98	TR404	1.4	0.65	2.10	237	85.9	0.33	---	---	---	---	6.9	---	---	---
11/29/98	TR405	1.2	0.66	2.44	241	85.0	0.34	---	---	---	---	6.9	---	---	---
11/29/98	TR406	0.6	0.64	2.42	245	84.9	0.39	---	---	---	---	6.9	---	---	---
11/29/98	TR407	0.0	0.60	1.87	240	90.5	0.32	---	---	---	469	6.8	---	---	---
11/29/98	TR409	1.0	0.23	3.65	261	96.9	0.38	---	---	---	---	6.6	---	---	---
11/29/98	TR410	0.5	0.54	3.53	241	105	0.52	---	---	---	---	6.7	---	---	---
11/29/98	TR411	2.0	3.27	27.9	202	247	1.61	---	---	---	---	6.4	---	---	---
11/29/98	TR412	1.0	0.70	5.59	229	184	0.98	---	---	---	---	6.5	---	---	---
11/29/98	TI504	2.0	0.42	3.03	178	79.5	0.31	---	---	---	---	6.4	---	---	---
11/29/98	TI506	0.0	1.59	11.1	201	87.0	0.84	---	---	---	257	6.5	---	---	---
11/29/98	TB601	---	1.55	6.14	216	88.3	0.84	---	---	---	188	---	---	---	---
11/29/98	TB602	---	1.38	5.68	203	84.8	0.74	---	---	---	---	---	---	---	---
11/29/98	TB603	---	0.92	4.86	196	70.6	0.49	---	---	---	107	6.6	---	---	---
11/29/98	TB604	---	0.76	3.49	193	65.1	0.37	---	---	---	90	6.6	---	---	---
11/29/98	TB609	---	0.54	2.12	54	18.1	0.32	---	---	---	---	6.8	---	---	---
1/2/99	MR101	5.5	0.21	0.26	219	83.9	0.02	4.06	0.01	0.01	182	7.2	0.07	0.01	5.4
1/2/99	MR103	1.7	0.22	0.13	217	78.8	0.02	4.43	0.01	0.01	55	7.1	---	---	---
1/2/99	MR104	0.0	0.24	0.33	218	79.1	0.03	5.13	0.01	0.02	51	7.0	0.32	0.17	19
1/2/99	KR201	7.0	0.29	0.52	200	47.7	0.01	2.03	0.00	0.01	175	7.4	---	---	---
1/2/99	KR202	4.0	0.41	0.31	214	61.1	0.02	3.04	0.01	0.01	84	7.2	0.15	0.02	2.4
1/2/99	KR203.7	1.4	0.39	0.18	218	69.0	0.02	2.63	0.00	0.01	98	6.9	0.14	0.03	3.4
1/2/99	KR206	-1.5	0.48	1.47	214	71.7	0.13	132	0.24	0.28	52	7.1	---	---	---
1/2/99	WR301	8.5	0.41	0.43	235	50.7	0.01	2.29	0.00	0.02	53	7.5	---	---	---
1/2/99	WR302	3.8	0.42	0.44	237	57.0	0.02	1.74	0.00	0.02	85	7.3	---	---	---
1/2/99	WR303	2.1	0.41	0.20	237	57.4	0.01	3.06	0.01	0.02	61	7.2	0.16	0.06	3.8
1/2/99	WR304	0.0	0.51	0.64	237	57.6	0.04	4.20	0.01	0.02	60	---	0.16	0.08	4.2
1/2/99	WR304.5	-1.0	0.49	0.67	237	57.6	0.04	2.63	0.00	0.02	52	7.2	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
1/2/99	WR305	-2.0	0.47	0.53	237	57.6	0.04	3.77	0.01	0.02	159	7.2	0.12	0.08	4.1
1/2/99	TR400	10.0	0.48	0.32	258	53.0	0.01	2.12	0.00	0.02	92	7.5	---	---	---
1/2/99	TR401	7.0	0.44	0.25	251	57.9	0.01	17.5	0.03	0.02	71	7.4	0.17	0.05	4.8
1/2/99	TR402	4.2	0.43	0.50	255	62.8	0.03	1.90	0.00	0.02	---	7.2	---	---	---
1/2/99	TR404	1.4	0.64	4.80	249	66.7	0.30	2.37	0.00	0.02	---	7.1	0.20	0.20	7.9
1/2/99	TR405	1.2	0.63	4.68	250	66.8	0.30	2.36	0.00	0.02	94	7.1	---	---	---
1/2/99	TR407	0.0	0.62	4.78	252	74.3	0.39	4.41	0.01	0.02	122	7.0	0.15	0.29	8.7
1/2/99	TR411	2.0	0.71	11.7	205	287	2.31	10.2	0.02	0.05	263	6.4	---	---	---
1/2/99	TI501	7.0	0.35	1.49	181	74.4	0.12	3.90	0.01	0.02	93	7.0	---	---	---
1/2/99	TI502	3.9	0.28	4.03	176	72.3	0.26	4.86	0.01	0.02	---	6.6	0.67	0.40	44
1/2/99	TI504	2.0	0.57	7.36	172	65.6	0.43	7.97	0.01	0.03	---	6.5	1.21	0.64	36
1/2/99	TI506	0.0	0.68	12.2	182	61.9	0.51	6.82	0.01	0.03	---	6.6	0.53	0.44	25
1/2/99	TB601	---	0.71	5.94	242	66.9	0.36	4.31	0.01	0.02	99	7.1	0.26	0.20	8.1
1/2/99	TB602	---	0.80	6.69	232	66.9	0.41	5.15	0.01	0.03	407	7.0	0.25	0.26	9.1
1/2/99	TB603	---	0.69	4.66	220	65.8	0.39	419	0.76	0.64	80	7.1	0.14	0.25	37
1/2/99	TB604	---	0.68	3.59	205	58.0	0.31	1984	3.58	2.9	70	7.3	0.06	0.33	45
1/2/99	TB606	---	0.82	2.23	131	41.3	0.25	7333	13.2	10	74	7.8	0.01	0.18	74
1/2/99	TB607	---	0.92	1.13	56	20.8	0.33	14338	25.9	20	80	8.0	0.01	0.09	72
1/2/99	TB608	---	0.92	0.63	34	15.0	0.34	16374	29.6	23	78	8.0	0.01	0.04	68
1/2/99	TB609	---	0.88	0.94	47	19.2	0.48	14979	27.1	21	82	8.0	0.01	0.05	62
1/2/99	TB610	---	0.84	1.27	76	28.0	0.44	12138	21.9	17	87	8.0	0.01	0.10	74
1/2/99	TB612	---	0.94	0.49	25	12.2	0.51	16706	30.2	24	126	8.1	0.02	0.02	62
2/27/99	MR101	5.5	0.16	0.12	150	34.5	---	4.41	0.01	0.01	---	7.0	---	---	---
2/27/99	MR103	1.7	0.19	0.24	152	36.7	---	4.22	0.01	0.01	---	6.9	---	---	---
2/27/99	MR104	0.0	0.24	0.80	157	42.7	---	6.87	0.01	0.02	---	6.0	---	---	---
2/27/99	KR202	4.0	0.23	0.27	138	20.6	---	10.4	0.02	0.01	---	6.0	---	---	---
2/27/99	WR301	8.5	0.37	0.18	180	25.3	---	2.45	0.00	0.01	71	7.3	---	---	---
2/27/99	WR302	3.8	0.42	0.25	181	27.5	---	2.63	0.00	0.01	126	7.2	---	---	---
2/27/99	WR303	2.1	0.44	0.40	181	28.2	---	2.19	0.00	0.01	87	7.2	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
2/27/99	TR401	7.0	0.45	0.22	203	33.5	---	4.51	0.01	0.01	77	7.3	---	---	---
2/27/99	TR402	4.2	0.44	0.45	209	39.8	---	2.97	0.01	0.02	---	7.0	---	---	---
2/27/99	TR404	1.4	0.55	0.92	209	41.4	---	3.03	0.01	0.02	186	7.2	---	---	---
2/27/99	TR405	1.2	0.55	0.75	209	41.1	---	2.96	0.01	0.02	71	7.2	---	---	---
2/27/99	TR411	2.0	0.70	11.2	124	167.4	---	10.2	0.02	0.03	---	6.5	---	---	---
2/27/99	TI501	7.0	0.42	0.95	117	42.8	---	3.73	0.01	0.01	---	6.8	---	---	---
2/27/99	TI502	3.9	0.33	1.34	132	47.8	---	6.64	0.01	0.01	148	6.8	---	---	---
2/27/99	TI504	2.0	0.58	2.78	189	44.7	---	5.13	0.01	0.02	94	7.0	---	---	---
4/2/99	MR101	5.5	0.16	0.04	200	52.7	0.03	5.26	0.01	0.01	37	7.2	0.04	0.01	4.3
4/2/99	MR103	1.7	0.17	0.31	201	52.9	0.04	6.00	0.01	0.01	51	7.0	---	---	---
4/2/99	MR104	0.0	0.18	0.13	207	54.1	0.04	6.04	0.01	0.01	33	7.0	0.11	0.03	11
4/2/99	KR201	7.0	0.19	0.13	181	26.9	0.02	4.07	0.01	0.01	29	7.3	0.03	0.00	1.6
4/2/99	KR202	4.0	0.30	0.05	193	35.3	0.03	4.48	0.01	0.01	40	7.2	0.04	0.00	1.9
4/2/99	KR206	-1.5	0.52	0.72	195	35.1	0.07	567	1.02	0.84	66	7.3	---	---	---
4/2/99	WR301	8.5	0.28	0.14	213	25.9	0.03	3.22	0.01	0.02	39	7.4	---	---	---
4/2/99	WR303	2.1	0.31	0.09	218	33.8	0.03	3.45	0.01	0.02	42	7.2	0.16	0.03	4.2
4/2/99	WR305	-2.0	0.57	0.57	217	33.4	0.06	4.67	0.01	0.02	59	7.1	0.74	0.05	5.3
4/2/99	WR304.5	-1.0	0.56	0.46	217	33.4	0.03	3.50	0.01	0.02	57	7.1	---	---	---
4/2/99	TR401	7.0	0.29	0.13	233	30.3	0.03	3.46	0.01	0.02	49	7.4	0.15	0.02	5.6
4/2/99	TR402	4.2	0.29	0.12	233	36.1	0.03	4.32	0.01	0.02	47	7.2	---	---	---
4/2/99	TR404	1.4	0.31	0.38	232	38.0	0.06	3.54	0.01	0.02	49	7.2	0.15	0.09	7.9
4/2/99	TR405	1.2	0.31	0.53	231	37.0	0.06	3.79	0.01	0.02	51	7.1	---	---	---
4/2/99	TR406	0.6	0.37	1.40	232	37.9	0.08	4.07	0.01	0.02	68	7.2	---	---	---
4/2/99	TR407	0.0	0.37	1.25	232	37.7	0.08	3.93	0.01	0.02	53	7.2	0.39	0.09	8.4
4/2/99	TR409	1.0	0.63	3.91	230	103	0.58	10.0	0.02	0.04	135	6.9	0.23	0.09	8.0
4/2/99	TR410	0.5	0.39	1.25	232	41.0	0.10	4.42	0.01	0.02	58	7.1	---	---	---
4/2/99	TR411	2.0	0.60	5.97	159	239	0.55	9.56	0.02	0.04	156	6.4	---	---	---
4/2/99	TR412	1.0	0.63	3.95	220	126	0.65	10.8	0.02	0.04	148	6.8	---	---	---
4/2/99	TI501	7.0	0.16	0.39	164	50.4	0.07	5.81	0.01	0.02	75	7.0	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
4/2/99	TI502	3.9	0.15	0.57	162	50.0	0.06	6.51	0.01	0.02	91	6.8	0.54	0.18	41
4/2/99	TI504	2.0	0.33	1.28	198	44.6	0.13	21.8	0.04	0.05	120	6.9	0.50	0.36	23
4/2/99	TI506	0.0	0.44	1.15	210	44.5	0.15	16.3	0.03	0.04	96	7.0	1.04	0.26	17
4/2/99	TB601	---	0.41	0.73	202	41.8	0.11	53.7	0.10	0.10	88	7.0	0.54	0.18	13
4/2/99	TB602	---	---	---	---	---	---	329	0.59	0.50	81	7.2	0.31	0.16	16
4/2/99	TB603	---	0.51	0.81	196	36.3	0.12	1296	2.34	1.9	68	7.4	0.19	0.14	22
4/2/99	TB604	---	0.62	0.91	172	29.3	0.11	3466	6.26	4.9	69	7.6	0.04	0.16	41
4/2/99	TB606	---	0.84	1.18	75	16.7	0.21	12192	22.0	17	75	8.0	0.02	0.12	56
4/2/99	TB607	---	0.87	1.27	37	10.6	0.29	12444	22.5	17	74	8.1	0.03	0.06	54
4/2/99	TB608	---	0.93	1.20	17	7.4	0.32	17909	32.4	26	73	8.0	0.01	0.02	48
4/2/99	TB609	---	0.93	1.16	20	8.0	0.32	17536	31.7	25	82	8.1	0.02	0.04	47
4/2/99	TB610	---	0.85	1.02	56	15.1	0.25	14161	25.6	20	86	8.1	0.16	0.02	14
4/2/99	TB612	---	0.89	0.47	14	6.9	0.30	17887	32.3	25	74	8.1	0.10	0.01	47
5/26/99	MR101	5.5	0.18	0.29	214	56.1	0.04	4.40	0.01	0.01	---	---	---	---	---
5/26/99	MR103	1.7	0.19	0.31	214	50.9	0.05	6.04	0.01	0.01	---	---	---	---	---
5/26/99	MR104	0.0	0.21	0.52	220	51.9	0.05	5.92	0.01	0.01	---	---	---	---	---
5/26/99	KR201	7.0	0.24	0.53	194	29.3	0.04	4.77	0.01	0.01	---	---	---	---	---
5/26/99	KR202	4.0	0.38	0.39	209	39.5	0.05	3.61	0.01	0.01	---	---	---	---	---
5/26/99	KR203.7	1.4	0.36	0.37	214	44.0	0.06	3.83	0.01	0.01	---	---	---	---	---
5/26/99	KR206	-1.5	0.56	0.71	192	29.3	0.14	873	1.58	1.3	---	---	---	---	---
5/26/99	WR301	8.5	0.21	0.39	209	17.7	0.07	2.42	0.00	0.02	---	---	---	---	---
5/26/99	WR302	3.8	0.25	0.38	215	24.2	0.06	2.48	0.00	0.02	---	---	---	---	---
5/26/99	WR303	2.1	0.26	0.36	216	24.5	0.07	2.92	0.01	0.02	---	---	---	---	---
5/26/99	WR304	0.0	1.10	0.73	215	24.8	0.23	3.33	0.01	0.02	---	---	---	---	---
5/26/99	WR305	-2.0	1.06	0.64	214	24.7	0.22	3.77	0.01	0.02	---	---	---	---	---
5/26/99	WR306	-0.2	1.13	1.02	213	24.2	0.22	3.73	0.01	0.02	---	---	---	---	---
5/26/99	TR400	10.0	0.30	0.21	243	22.8	0.08	3.42	0.01	0.02	---	---	---	---	---
5/26/99	TR401	7.0	0.26	0.48	239	25.3	0.09	2.71	0.00	0.03	---	---	---	---	---
5/26/99	TR402	4.2	0.28	0.67	241	27.3	0.12	2.66	0.00	0.03	---	---	---	---	---

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
5/26/99	TR404	1.4	0.27	0.69	241	28.6	0.13	2.91	0.01	0.03	---	---	---	---	---
5/26/99	TR405	1.2	0.31	1.14	241	28.5	0.15	2.91	0.01	0.02	---	---	---	---	---
5/26/99	TR406	0.6	0.35	1.72	241	28.8	0.17	2.93	0.01	0.02	---	---	---	---	---
5/26/99	TR407	0.0	0.43	1.81	239	30.1	0.23	5.35	0.01	0.03	---	---	---	---	---
5/26/99	TR408	2.0	0.37	0.78	294	81.4	1.71	8.38	0.02	0.03	---	---	---	---	---
5/26/99	TR409	1.0	0.71	2.11	229	68.2	1.31	16.7	0.03	0.04	---	---	---	---	---
5/26/99	TR410	0.5	0.47	1.80	239	29.9	0.28	6.40	0.01	0.03	---	---	---	---	---
5/26/99	TR411	2.0	0.27	7.98	223	146	2.07	10.6	0.02	0.03	---	---	---	---	---
5/26/99	TR412	1.0	0.64	3.17	230	69.6	1.35	21.4	0.04	0.05	---	---	---	---	---
5/26/99	TI501	7.0	0.20	0.70	178	37.9	0.08	4.83	0.01	0.02	---	---	---	---	---
5/26/99	TI502	3.9	0.13	0.90	173	35.3	0.09	6.78	0.01	0.02	---	---	---	---	---
5/26/99	TI504	2.0	0.40	1.13	208	30.4	0.20	24.3	0.04	0.05	---	---	---	---	---
5/26/99	TI506	0.0	0.41	0.99	210	30.2	0.19	22.8	0.04	0.05	---	---	---	---	---
5/26/99	TB601	---	0.54	0.99	208	28.0	0.18	446	0.81	0.72	---	---	---	---	---
5/26/99	TB602	---	0.62	0.94	198	24.4	0.18	1099	1.99	1.6	---	---	---	---	---
5/26/99	TB603	---	0.71	1.27	176	21.6	0.16	2781	5.02	3.8	---	---	---	---	---
5/26/99	TB604	---	0.77	1.08	152	17.5	0.15	4709	8.51	6.4	---	---	---	---	---
5/26/99	TB605.5	---	0.80	0.59	98	10.7	0.15	9503	17.2	13	---	---	---	---	---
5/26/99	TB606	---	0.87	0.74	73	9.4	0.18	12009	21.7	17	---	---	---	---	---
5/26/99	TB607	---	0.97	1.03	60	9.0	0.21	13380	24.2	19	---	---	---	---	---
5/26/99	TB608	---	1.22	1.22	39	10.3	0.31	16121	29.1	23	---	---	---	---	---
5/26/99	TB609	---	1.34	1.02	27	10.6	0.35	17335	31.3	25	---	---	---	---	---
5/26/99	TB610	---	0.90	0.83	87	16.1	0.19	11167	20.2	15	---	---	---	---	---
5/26/99	TB612	---	1.34	0.92	17	9.8	0.39	18209	32.9	26	---	---	---	---	---
10/17/99	MR101	5.5	0.38	0.21	245	60.2	0.05	5.08	0.01	0.01	---	7.0	0.02	0.00	2.9
10/17/99	MR103	1.7	0.20	0.22	223	42.4	0.08	6.06	0.01	0.02	---	7.0	---	---	---
10/17/99	MR104	0.0	0.27	0.70	243	48.8	0.07	42.2	0.08	0.06	---	6.8	0.40	0.23	13
10/17/99	KR201	7.0	0.23	0.16	200	37.3	0.05	4.15	0.01	0.01	---	7.2	---	---	---
10/17/99	KR202	4.0	0.24	0.13	209	41.1	0.08	3.74	0.01	0.01	---	7.1	0.02	0.01	2.3

Sampling Date	Sample ID	River Mile	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
10/17/99	KR203.7	1.4	0.25	0.14	241	43.9	0.07	4.08	0.01	0.01	---	6.7	0.05	0.02	4.1
10/17/99	WR301	8.5	0.16	0.36	212	20.6	0.06	4.17	0.01	0.04	---	7.4	---	---	---
10/17/99	WR302	3.8	0.01	0.36	232	35.1	0.11	3.81	0.01	0.04	---	6.9	0.14	0.12	6.6
10/17/99	WR303	2.1	0.01	0.60	233	33.3	0.10	4.10	0.01	0.04	---	6.9	0.15	0.13	7.0
10/17/99	WR305	-2.0	2.88	4.54	185	31.1	0.36	1950	3.52	2.81	---	7.1	1.07	1.70	89
10/17/99	TR401	7.0	0.10	0.63	240	18.4	0.09	4.01	0.01	0.04	---	7.2	0.11	0.06	6.9
10/17/99	TR402	4.2	0.17	0.70	251	20.6	0.10	4.41	0.01	0.04	---	7.0	---	---	---
10/17/99	TR404	1.4	0.78	7.47	239	24.3	0.36	518	0.94	0.74	---	7.0	0.52	1.13	38
10/17/99	TR405	1.2	1.17	9.86	237	26.1	0.48	612	1.11	0.88	---	7.0	0.58	0.92	28
10/17/99	TR406	0.6	1.26	8.89	243	25.8	0.47	347	0.63	0.53	---	7.0	0.37	2.23	99
10/17/99	TR407	0.0	0.98	9.38	205	25.1	0.41	1950	3.52	2.8	---	7.1	---	---	---
10/17/99	TR408	2.0	0.62	7.83	228	35.3	0.54	1596	2.88	2.2	---	7.0	---	---	---
10/17/99	TR409	1.0	0.54	9.16	213	33.8	0.50	1548	2.80	2.2	---	7.0	---	---	---
10/17/99	TR410	0.5	0.98	8.61	225	25.5	0.40	1138	2.06	1.6	---	7.0	---	---	---
10/17/99	TR411	2.0	0.21	12.1	190	81.6	1.55	1391	2.51	1.9	---	6.8	---	---	---
10/17/99	TR412	1.0	0.55	9.39	213	33.6	0.51	1543	2.79	2.2	---	7.0	---	---	---
10/17/99	TI501	7.0	0.34	0.96	200	30.8	0.09	7.76	0.01	0.03	---	6.9	2.16	0.20	28
10/17/99	TI502	3.9	0.12	8.50	177	27.5	0.34	1364	2.46	1.9	---	6.7	---	---	---
10/17/99	TI506	0.0	0.68	7.21	158	22.0	0.29	4585	8.28	6.9	---	7.4	0.24	1.81	138
10/17/99	TB601	---	0.59	5.54	129	17.9	0.24	6283	11.4	8.5	---	7.4	0.15	1.23	169
10/17/99	TB602	---	0.65	3.94	100	13.3	0.19	8879	16.0	12.7	---	7.6	0.08	0.69	190
10/17/99	TB603	---	1.01	2.63	69	8.0	0.15	11868	21.4	16.5	---	7.7	0.15	0.72	257
10/17/99	TB604	---	1.00	2.35	60	6.7	0.14	12691	22.9	17.6	---	7.7	0.05	0.38	164
10/17/99	TB606	---	1.10	2.23	36	5.4	0.13	15563	28.1	21.7	---	7.9	0.01	0.37	122
10/17/99	TB607	---	1.15	2.32	29	6.2	0.14	16557	29.9	23.4	---	7.8	0.01	0.29	100
10/17/99	TB608	---	1.35	2.45	25	9.7	0.17	17439	31.5	24.4	---	7.9	0.03	0.17	78
10/17/99	TB609	---	1.01	2.78	49	8.7	0.15	14855	26.8	21.0	---	7.7	0.03	0.32	101
10/17/99	TB610	---	1.52	2.29	24	13.1	0.19	17805	32.2	24.9	---	7.9	0.02	0.06	59
10/17/99	TB612	---	1.56	2.31	24	14.0	0.19	17933	32.4	25.5	---	7.8	0.11	0.04	56

APPENDIX C: PARTICULATE CHEMISTRY

Sampling Date	Sample ID	River Mile	SPM (mg ^l ⁻¹)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)	P (ppm)
1/10/98	KR205	0.0	0.5	---	---	---	---	---	---	---	---
1/10/98	KR206	-1.5	5.0	---	---	---	---	---	---	---	---
1/10/98	KR207	-1.0	1.4	---	---	---	---	---	---	---	---
1/10/98	WR304	0.0	3.6	---	---	---	---	---	---	---	---
1/10/98	WR305	-2.0	6.3	---	---	---	---	---	---	---	---
1/10/98	WR307	-1.0	6.7	---	---	---	---	---	---	---	---
1/10/98	TR407	0.0	5.1	---	---	---	---	---	---	---	---
1/10/98	TB601	---	5.9	---	---	---	---	---	---	---	---
1/10/98	TB602	---	4.2	---	---	---	---	---	---	---	---
1/10/98	TB603	---	5.3	---	---	---	---	---	---	---	---
1/10/98	TB604	---	11.0	---	---	---	---	---	---	---	---
1/11/98	TB606	---	24.8	---	---	---	---	---	---	---	---
1/11/98	TB607	---	12.2	---	---	---	---	---	---	---	---
1/11/98	TB608	---	6.6	---	---	---	---	---	---	---	---
1/11/98	TB609	---	14.3	---	---	---	---	---	---	---	---
1/11/98	TB610	---	8.8	---	---	---	---	---	---	---	---
1/11/98	TB613	---	26.6	---	---	---	---	---	---	---	---
1/11/98	TB614	---	9.2	---	---	---	---	---	---	---	---
1/11/98	TB615	---	23.1	---	---	---	---	---	---	---	---
1/11/98	TB616	---	18.3	---	---	---	---	---	---	---	---
1/11/98	TB617	---	9.6	---	---	---	---	---	---	---	---
4/11/98	MR104	0.0	1.5	---	---	---	---	---	---	---	---
4/11/98	KR206	-1.5	15.4	---	---	---	---	---	---	---	---
4/11/98	KR207	-1.0	3.1	---	---	---	---	---	---	---	---
4/11/98	WR304	0.0	1.5	---	---	---	---	---	---	---	---
4/11/98	WR305	-2.0	5.5	---	---	---	---	---	---	---	---
4/11/98	WR307	-1.0	9.1	---	---	---	---	---	---	---	---

Sampling Date	Sample ID	River Mile	SPM (mg l ⁻¹)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)	P (ppm)
4/11/98	TR408	2.0	3.3	---	---	---	---	---	---	---	---
4/11/98	TI506	0.0	7.2	---	---	---	---	---	---	---	---
4/11/98	TB601	---	5.1	---	---	---	---	---	---	---	---
4/11/98	TB602	---	6.6	---	---	---	---	---	---	---	---
4/11/98	TB603	---	10.7	---	---	---	---	---	---	---	---
4/11/98	TB604	---	8.9	---	---	---	---	---	---	---	---
4/11/98	TB606	---	14.3	---	---	---	---	---	---	---	---
4/11/98	TB607	---	11.2	---	---	---	---	---	---	---	---
4/11/98	TB608	---	10.3	---	---	---	---	---	---	---	---
4/11/98	TB609	---	5.7	---	---	---	---	---	---	---	---
4/11/98	TB610	---	4.6	---	---	---	---	---	---	---	---
4/11/98	TB614	---	6.7	---	---	---	---	---	---	---	---
7/12/98	WR304	0.0	1.9	3.4	0.5	4.2	2676	2460	---	---	---
7/12/98	WR305	-2.0	5.6	---	---	---	---	---	---	---	---
7/12/98	TR407	0.0	8.6	---	---	---	---	---	---	---	---
7/12/98	TI506	0.0	12.5	---	---	---	---	---	---	---	---
7/12/98	TB601HT	---	5.0	---	---	---	---	---	---	---	---
7/12/98	TB602HT	---	5.7	---	---	---	---	---	---	---	---
7/12/98	TB603HT	---	8.4	2.6	0.4	2.5	300	151	---	---	---
7/12/98	TB604HT	---	4.6	---	---	---	---	---	---	---	---
7/12/98	TB606HT	---	4.4	---	---	---	---	---	---	---	---
7/12/98	TB607HT	---	4.3	---	---	---	---	---	---	---	---
7/12/98	TB608HT	---	3.4	---	---	---	---	---	---	---	---
7/12/98	TB609HT	---	5.4	---	---	---	---	---	---	---	---
7/12/98	TB610HT	---	2.5	---	---	---	---	---	---	---	---
7/12/98	TB612HT	---	2.5	4.2	0.7	4.4	841	2010	---	---	---
7/12/98	TB613HT	---	3.1	---	---	---	---	---	---	---	---
7/12/98	TB614HT	---	4.1	---	---	---	---	---	---	---	---
7/12/98	TB615HT	---	3.4	---	---	---	---	---	---	---	---
7/12/98	TB616HT	---	7.5	---	---	---	---	---	---	---	---
7/12/98	TB617HT	---	6.4	---	---	---	---	---	---	---	---
7/12/98	TB601LT	---	7.4	---	---	---	---	---	---	---	---

Sampling Date	Sample ID	River Mile	SPM (mg l ⁻¹)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)	P (ppm)
7/12/98	TB602LT	---	6.3	---	---	---	---	---	---	---	---
7/12/98	TB603LT	---	7.4	---	---	---	---	---	---	---	---
7/12/98	TB604LT	---	12.0	---	---	---	---	---	---	---	---
7/12/98	TB606LT	---	15.0	---	---	---	---	---	---	---	---
7/12/98	TB607LT	---	51.3	---	---	---	---	---	---	---	---
7/12/98	TB608LT	---	11.6	---	---	---	---	---	---	---	---
10/17/98	MR103	1.7	1.5	5.3	0.9	5.8	1135	1534	---	---	2175
10/17/98	KR203.7	1.4	1.7	2.2	0.4	2.7	607	570	---	---	1063
10/17/98	WR303	2.1	3.7	---	---	---	---	---	---	---	---
10/17/98	WR304	0.0	5.5	6.2	1.1	6.9	2628	730	---	---	2377
10/17/98	WR305	-2.0	5.6	---	---	---	---	---	---	---	---
10/17/98	TR404	1.4	3.1	5.9	0.9	6.8	2563	908	---	---	2596
10/17/98	TR407	0.0	8.8	6.3	1.0	6.9	2646	1738	---	---	2087
10/17/98	TI502	3.9	4.0	6.9	0.8	8.7	4431	1680	---	---	2762
10/17/98	TI506	0.0	9.4	6.8	0.9	7.9	2336	1891	---	---	2639
10/17/98	TB601	---	8.2	7.3	1.0	7.7	1353	1929	---	---	2569
10/17/98	TB602	---	5.7	7.2	1.0	7.6	1395	648	---	---	2401
10/17/98	TB603	---	4.6	5.9	0.8	5.6	1015	5432	---	---	1684
10/17/98	TB604	---	6.7	6.9	1.0	6.8	1089	2719	---	---	2158
10/17/98	TB606	---	4.4	7.3	1.1	7.1	1053	2380	---	---	2210
10/17/98	TB607	---	2.2	6.5	1.0	6.6	782	3192	---	---	2134
10/17/98	TB608	---	2.7	6.9	1.1	6.9	829	1080	---	---	2618
10/17/98	TB609	---	3.2	6.5	1.0	6.5	792	1064	---	---	2228
10/17/98	TB612	---	1.9	5.6	0.8	5.6	747	4008	---	---	2178
10/17/98	TB614	---	1.9	5.8	0.9	5.9	717	3060	---	---	2334
10/17/98	TB615	---	4.2	2.4	0.3	2.6	364	383	---	---	1062
1/2/99	MR104	0.0	9.9	7.8	1.3	8.0	1229	379	0.27	4.1	1741
1/2/99	KR202	4.0	6.8	6.9	1.5	8.6	1441	267	0.26	4.9	1835
1/2/99	KR206	-1.5	9.0	0.8	0.2	1.0	138	25	0.21	3.4	---
1/2/99	WR303	2.1	59.1	7.6	1.3	7.9	1119	347	0.07	1.3	1715
1/2/99	WR304	0.0	54.5	8.3	1.3	8.4	1246	364	---	---	---
1/2/99	WR305	-2.0	66.9	7.6	1.3	8.0	1144	341	0.08	1.4	---

Sampling Date	Sample ID	River Mile	SPM (mg l ⁻¹)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)	P (ppm)
1/2/99	TR404	1.4	69.6	8.6	1.3	8.7	1241	395	0.10	1.2	1839
1/2/99	TR407	0.0	57.0	8.5	1.3	8.7	1275	433	0.15	1.8	2035
1/2/99	TI504	2.0	13.5	8.1	1.0	8.9	2223	612	0.48	5.5	3375
1/2/99	TI506	0.0	27.4	8.0	1.1	8.5	1495	404	0.39	3.6	2450
1/2/99	TB601	---	64.9	8.4	1.3	8.6	1217	369	0.15	1.9	1878
1/2/99	TB602	---	54.5	8.8	1.3	9.0	1282	392	0.14	1.9	2100
1/2/99	TB603	---	36.7	8.6	1.2	9.1	1144	284	0.14	1.5	2118
1/2/99	TB604	---	11.8	8.8	1.3	9.1	1253	275	0.12	2.0	2176
1/2/99	TB606	---	10.8	8.8	1.2	8.3	1295	471	0.21	2.4	2032
1/2/99	TB607	---	9.9	8.2	1.2	8.0	1212	339	---	---	1945
1/2/99	TB608	---	8.1	7.1	1.0	6.7	1003	249	0.15	2.3	1605
1/2/99	TB609	---	13.1	8.5	1.2	8.2	1232	307	0.16	2.3	1916
1/2/99	TB610	---	8.5	8.5	1.2	8.1	1250	410	0.24	2.7	2080
1/2/99	TB612	---	11.6	7.5	1.0	6.8	1029	340	0.14	2.1	1637
4/2/99	MR104	0.0	1.7	7.2	1.2	8.8	1342	475	0.65	6.6	2704
4/2/99	KR206	-1.5	9.4	7.2	1.1	7.9	977	255	0.35	3.5	---
4/2/99	WR303	2.1	3.6	6.9	1.3	7.9	1072	349	0.27	3.2	---
4/2/99	WR305	-2.0	3.2	7.8	1.4	8.9	1320	380	0.40	4.1	2409
4/2/99	WR304.5	-1.0	4.7	6.4	1.4	7.7	1132	312	0.28	2.8	---
4/2/99	TR402	4.2	3.2	7.1	1.2	7.9	1462	716	0.48	4.7	---
4/2/99	TR406	0.6	3.5	7.1	1.1	8.1	1714	429	0.48	5.1	2461
4/2/99	TR407	0.0	2.8	6.9	1.0	7.6	1660	416	0.74	7.1	2580
4/2/99	TR410	0.5	2.7	---	---	---	---	---	---	---	---
4/2/99	TI506	0.0	3.5	6.7	1.0	8.2	2323	375	---	---	3705
4/2/99	TB602	---	12.6	7.5	1.1	8.0	1120	462	0.39	4.3	2229
4/2/99	TB603	---	6.9	6.5	1.0	6.9	846	283	0.40	3.2	2223
4/2/99	TB604	---	6.8	6.0	0.9	6.3	753	264	0.35	2.9	1974
4/2/99	TB606	---	6.0	5.5	0.8	5.5	682	227	0.28	2.5	1748
4/2/99	TB607	---	5.0	4.7	0.6	4.5	558	218	0.36	3.8	1369
4/2/99	TB608	---	6.7	5.0	0.6	4.4	558	244	0.32	2.9	1320
4/2/99	TB609	---	9.4	5.1	0.6	4.2	541	315	0.37	3.0	1464
4/2/99	TB610	---	5.3	2.3	0.3	2.1	272	184	0.16	1.4	754

Sampling Date	Sample ID	River Mile	SPM (mg l ⁻¹)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)	P (ppm)
4/2/99	TB612	---	10.4	3.8	0.4	3.2	396	209	0.30	2.4	1080
10/17/99	MR104	0.0	2.3	4.6	0.8	5.1	958	190	0.63	6.4	1834
10/17/99	WR303	2.1	1.2	4.2	0.7	4.5	1349	221	3.02	18.3	3552
10/17/99	WR305	-2.0	6.2	5.6	0.9	6.3	2314	229	0.06	0.5	---
10/17/99	TR404	1.4	8.0	---	---	---	---	---	0.73	5.4	---
10/17/99	TR406	0.6	5.4	7.3	1.1	7.7	2346	278	---	---	3025
10/17/99	TR407	0.0	6.1	---	---	---	---	---	0.59	5.0	---
10/17/99	TR410	0.5	5.8	---	---	---	---	---	---	---	---
10/17/99	TI501	7.0	3.6	4.0	0.5	6.5	3736	321	2.40	20.4	5862
10/17/99	TI506	0.0	5.1	6.4	0.8	6.7	1568	259	0.71	5.2	2714
10/17/99	TB601	---	4.6	9.7	1.4	9.4	2357	410	0.78	5.4	3869
10/17/99	TB602	---	5.0	5.4	0.7	5.3	1209	189	0.62	4.4	2250
10/17/99	TB603	---	5.6	5.8	0.8	5.1	1021	219	0.49	3.4	1736
10/17/99	TB604	---	8.2	4.7	0.7	4.3	835	174	0.46	2.9	1598
10/17/99	TB606	---	5.1	5.1	0.7	4.8	924	173	0.57	3.9	2041
10/17/99	TB607	---	3.8	5.2	0.8	4.7	771	205	---	---	2133
10/17/99	TB608	---	4.7	2.9	0.4	2.6	409	104	0.51	3.5	1411
10/17/99	TB609	---	3.7	3.9	0.5	3.2	496	193	0.59	3.9	1579
10/17/99	TB610	---	4.3	5.7	0.7	5.4	1192	183	0.67	4.8	2433
10/17/99	TB612	---	5.4	1.9	0.2	1.6	228	138	0.40	2.8	931

APPENDIX D: WATER CHEMISTRY OF SAMPLES FROM 24 HOUR EXPERIMENTS

Sample Date & Time	Sample ID	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
7/19/99 12:55	MR104-1	0.19	0.69	226	43.4	0.09	33.3	0.06	0.05	201	6.9	0.79	0.20	20
7/19/99 15:54	MR104-2	0.20	0.76	226	44.2	0.11	16.3	0.03	0.02	24	7.0	0.54	0.10	15
7/19/99 18:25	MR104-3	0.17	0.66	227	44.0	0.11	50.7	0.09	0.02	274	6.9	0.36	0.06	13
7/19/99 20:55	MR104-4	0.17	1.00	228	45.7	0.11	34.5	0.06	0.02	191	6.7	0.33	0.06	13
7/19/99 23:33	MR104-5	0.18	0.83	224	45.4	0.09	42.4	0.08	0.03	156	6.9	0.60	0.11	16
7/20/99 2:30	MR104-6	0.19	1.07	223	47.5	0.09	114	0.21	0.06	166	7.1	0.70	0.12	16
7/20/99 5:30	MR104-7	0.17	1.22	225	49.2	0.06	102	0.18	0.02	165	6.8	0.39	0.08	15
7/20/99 7:30	MR104-8	0.17	0.54	226	49.4	0.06	129	0.23	0.02	215	6.8	0.38	0.07	15
7/20/99 10:25	MR104-9	0.18	0.78	228	48.6	0.07	21.7	0.04	0.03	174	7.2	0.32	0.07	13
7/20/99 12:35	MR104-10	0.19	1.40	227	46.5	0.08	21.1	0.04	0.03	172	7.4	0.56	0.12	16
7/19/99 13:35	KR203.7-1	0.32	0.79	218	39.2	0.10	45.2	0.08	0.07	298	7.0	0.06	0.02	4.6
7/19/99 15:54	KR203.7-2	0.25	0.61	215	38.0	0.10	27.7	0.05	0.01	154	7.0	0.07	0.02	4.0
7/19/99 16:25	KR203.7-3	0.27	0.74	217	38.0	0.12	24.9	0.04	0.02	175	7.0	0.07	0.01	4.0
7/19/99 21:05	KR203.7-4	0.29	1.13	217	38.6	0.12	44.2	0.08	0.01	171	7.0	0.07	0.02	4.2
7/19/99 23:33	KR203.7-5	0.26	0.85	218	40.4	0.12	14.5	0.03	0.01	182	7.2	0.07	0.02	4.2
7/20/99 3:12	KR203.7-6	0.24	0.83	218	41.5	0.10	59.8	0.11	0.02	333	6.8	0.07	0.02	4.8
7/20/99 5:42	KR203.7-7	0.24	0.82	218	42.1	0.08	104	0.19	0.01	172	6.8	0.07	0.02	4.7
7/20/99 7:45	KR203.7-8	0.23	1.26	219	42.0	0.08	69.4	0.13	0.05	130	6.8	0.08	0.02	7.0
7/20/99 10:40	KR203.7-9	0.27	0.92	220	41.2	0.08	7.15	0.01	0.01	165	6.9	0.06	0.02	4.5
7/20/99 12:54	KR203.7-10	0.26	0.63	218	39.9	0.08	52.8	0.10	0.06	152	7.1	0.07	0.02	4.8
7/19/99 13:50	WR303-1	0.20	1.23	232	27.9	0.18	26.4	0.05	0.03	136	7.4	0.27	0.10	6.2
7/19/99 16:35	WR303-2	0.19	0.68	231	27.6	0.19	5.24	0.01	0.03	275	7.1	0.19	0.09	6.3
7/19/99 19:03	WR303-3	0.20	0.80	233	27.0	0.20	14.9	0.03	0.03	170	7.3	1.02	0.12	7.5
7/19/99 21:16	WR303-4	0.20	1.41	233	27.9	0.21	31.1	0.06	0.03	242	7.4	0.14	0.07	6.2
7/20/99 0:22	WR303-5	0.21	1.14	235	28.6	0.20	17.6	0.03	0.03	172	6.8	0.21	0.08	6.9
7/20/99 3:27	WR303-6	0.21	1.17	235	29.2	0.18	63.0	0.11	0.03	195	7.1	0.20	0.10	6.9
7/20/99 5:52	WR303-7	0.20	1.16	236	30.2	0.19	10.8	0.02	0.03	193	7.0	0.17	0.10	7.2

Sample Date & Time	Sample ID	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
7/20/99 8:00	WR303-8	0.20	1.12	234	30.6	0.18	119	0.21	0.03	160	7.0	0.20	0.09	6.9
7/20/99 10:50	WR303-9	0.19	1.50	235	30.3	0.20	4.55	0.01	0.03	185	7.0	0.18	0.09	6.8
7/20/99 13:05	WR303-10	0.20	1.07	234	29.4	0.19	22.8	0.04	0.03	143	7.5	0.22	0.10	6.8
7/19/99 14:02	TR405-1	0.35	2.51	243	20.8	0.32	35.6	0.06	0.04	272	7.3	0.58	0.22	8.3
7/19/99 16:45	TR405-2	0.70	6.81	242	21.6	0.34	76.4	0.14	0.04	244	7.3	0.59	0.21	8.5
7/19/99 19:20	TR405-3	0.68	2.33	204	21.6	0.30	1341	2.42	1.7	162	7.6	0.74	0.62	67
7/19/99 21:30	TR405-4	1.10	13.1	237	22.4	0.43	207	0.37	0.24	298	7.6	0.76	0.33	19
7/20/99 0:35	TR405-5	0.43	4.15	244	22.0	0.35	11.2	0.02	0.04	229	7.2	0.75	0.21	10
7/20/99 3:40	TR405-6	0.60	6.57	243	21.6	0.33	58.1	0.10	0.03	211	7.2	0.65	0.15	8.8
7/20/99 6:04	TR405-7	0.53	5.59	242	22.4	0.37	61.6	0.11	0.04	325	7.5	0.66	0.17	8.3
7/20/99 8:15	TR405-8	1.16	15.3	241	23.8	0.46	154	0.28	0.19	186	7.2	0.64	0.35	15
7/20/99 11:05	TR405-9	0.76	11.0	248	22.0	0.38	4.08	0.01	0.03	349	7.3	0.72	0.20	9
7/20/99 13:20	TR405-10	1.02	16.3	248	22.0	0.36	11.1	0.02	0.04	---	7.2	0.61	0.22	10
7/19/99 14:12	TI504-1	0.19	1.71	187	23.5	0.31	356	0.64	0.49	324	7.1	2.23	1.91	64
7/19/99 16:59	TI504-2	0.53	2.78	206	22.8	0.35	656	1.18	0.96	249	7.3	1.10	0.76	61
7/19/99 19:30	TI504-3	0.64	0.60	167	19.3	0.33	3805	6.87	5.55	221	7.5	0.20	0.61	152
7/19/99 21:40	TI504-4	0.58	2.25	199	21.9	0.35	1351	2.44	1.88	346	7.6	0.29	0.62	74
7/20/99 0:47	TI504-5	0.44	2.86	195	22.4	0.29	662	1.20	0.89	302	7.1	1.74	1.00	76
7/20/99 3:51	TI504-6	0.40	3.57	202	21.6	0.25	441	0.80	0.39	481	7.0	2.89	1.07	44
7/20/99 6:12	TI504-7	0.54	3.78	200	22.3	0.27	988	1.78	1.21	231	7.3	1.34	0.79	80
7/20/99 8:25	TI504-8	0.74	3.84	204	22.6	0.33	1203	2.17	1.47	177	7.4	2.67	0.74	64
7/20/99 11:15	TI504-9	0.46	3.73	194	22.0	0.26	805	1.45	1.05	260	7.2	2.07	1.07	73
7/20/99 13:28	TI504-10	0.36	2.70	191	22.9	0.32	381	0.69	0.53	298	7.0	3.70	1.45	57
7/19/99 14:45	TB601-1	0.56	4.11	219	22.5	0.40	582	1.05	0.77	127	7.3	0.73	1.01	49
7/19/99 17:10	TB601-2	0.70	1.64	186	21.1	0.38	2046	3.70	2.83	227	7.6	0.23	0.58	76
7/19/99 19:40	TB601-3	0.87	0.42	83	10.2	0.24	11954	22	16.6	261	7.8	0.02	0.52	174
7/19/99 21:55	TB601-4	0.74	0.85	131	15.6	0.29	7260	13	10.1	501	7.8	0.07	0.61	192
7/20/99 1:00	TB601-5	0.69	4.11	202	21.8	0.40	1372	2.48	1.85	264	7.7	0.51	0.71	78
7/20/99 4:02	TB601-6	0.65	4.81	215	22.5	0.33	755	1.36	0.85	215	7.3	0.99	0.71	46
7/20/99 6:25	TB601-7	0.80	3.36	176	20.2	0.34	3096	5.59	4.19	530	7.4	0.42	0.65	113
7/20/99 8:37	TB601-8	0.81	2.54	157	18.2	0.32	4683	8.46	6.27	230	7.5	0.11	0.53	143
7/20/99 11:25	TB601-9	0.67	3.07	201	22.5	0.38	1252	2.26	1.70	202	7.4	0.67	0.65	68

Sample Date & Time	Sample ID	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
7/20/99 13:40	TB601-10	0.64	5.80	214	23.0	0.42	806	1.46	1.04	256	7.2	0.89	1.07	52
7/19/99 13:12	TB606-1	1.11	5.80	98	11.3	0.26	10321	18.6	14.4	313	7.7	0.09	1.03	141
7/19/99 16:05	TB606-2	0.95	0.99	62	8.4	0.19	13277	24.0	18.4	179	7.8	0.03	0.41	134
7/19/99 18:40	TB606-3	1.17	1.04	53	10.7	0.19	15178	27.4	21.5	219	7.9	0.03	0.30	105
7/19/99 23:50	TB606-5	0.86	0.59	74	8.4	0.19	12616	22.8	17.7	287	8.1	0.03	0.36	122
7/20/99 2:50	TB606-6	0.84	1.52	109	11.9	0.20	8930	16.1	12.2	329	7.6	0.05	0.36	146
7/19/99 12:45	TB609-1	1.13	1.41	71	10.4	0.28	13112	23.7	18.4	197	7.7	0.03	0.41	145
7/19/99 15:30	TB609-2	1.21	2.84	39	8.4	0.22	15971	28.9	22.5	161	7.8	0.03	0.34	98
7/19/99 18:15	TB609-3	2.19	1.50	41	24.1	0.27	18381	33.2	26.2	186	7.7	0.02	0.04	65
7/19/99 20:40	TB609-4	1.70	1.49	41	18.0	0.22	17846	32.2	25.4	172	8.0	0.03	0.12	66
7/19/99 23:15	TB609-5	1.27	1.98	46	12.3	0.18	16065	29.0	22.8	413	8.0	0.05	0.24	91
7/20/99 2:15	TB609-6	1.10	1.14	64	9.3	0.21	13927	25.2	19.6	394	7.8	0.05	0.30	131
7/20/99 5:10	TB609-7	1.53	3.02	41	13.9	0.24	17003	30.7	24.3	122	7.9	0.06	0.29	89
7/20/99 7:02	TB609-8	2.00	2.25	39	22.0	0.23	18091	32.7	25.9	270	7.8	0.03	0.14	71
7/20/99 10:05	TB609-9	0.84	1.66	66	10.7	0.15	13643	24.6	19.4	185	7.7	0.08	0.41	93
7/20/99 12:20	TB609-10	1.12	2.64	62	11.1	0.19	14187	25.6	20.1	242	7.9	0.04	0.38	122
7/19/99 12:37	TB609D-1	0.98	1.74	55	8.4	0.18	14554	26.3	20.4	177	7.8	0.07	0.37	123
7/19/99 15:25	TB609D-2	1.66	1.40	38	17.0	0.18	17472	31.6	24.9	334	7.8	0.03	0.11	74
7/19/99 18:10	TB609D-3	2.20	0.93	41	25.4	0.23	18616	33.6	26.5	282	7.7	0.01	0.00	56
7/19/99 20:35	TB609D-4	2.04	1.07	39	22.8	0.26	18719	33.8	26.7	160	8.0	0.05	0.05	57
7/19/99 23:10	TB609D-5	1.47	1.40	43	14.7	0.20	16872	30.5	24.0	169	7.9	0.04	0.21	82
7/20/99 2:10	TB609D-6	1.28	2.05	44	11.3	0.20	16331	29.5	23.1	244	7.8	0.04	0.32	101
7/20/99 5:05	TB609D-7	1.93	1.95	39	22.0	0.24	18277	33.0	26.1	240	7.8	0.02	0.07	67
7/20/99 7:05	TB609D-8	2.19	1.29	38	25.9	0.25	18848	34.1	26.9	149	7.7	0.02	0.00	54
7/20/99 10:00	TB609D-9	1.77	1.98	42	19.5	0.24	17767	32.1	25.3	148	7.8	0.02	0.57	147
7/20/99 12:20	TB609D-10	1.19	2.37	56	11.5	0.20	15167	27.4	21.4	169	7.9	0.04	0.39	113
12/3/99 15:50	MR104-1	0.19	0.30	199	67.5	0.05	32.5	0.06	0.01	---	6.8	0.22	0.04	7
12/3/99 18:35	MR104-2	0.20	0.37	201	67.9	0.04	7.67	0.01	0.02	---	6.8	0.28	0.04	8
12/3/99 21:28	MR104-3	0.19	0.81	202	68.6	0.04	22.6	0.04	0.01	---	6.7	0.19	0.08	9
12/4/99 0:15	MR104-4	0.20	0.53	202	68.4	0.04	16.9	0.03	0.02	---	6.8	0.36	0.13	12
12/4/99 3:00	MR104-5	0.19	0.65	202	68.6	0.04	84.7	0.15	0.02	---	6.8	0.28	0.08	11
12/4/99 5:30	MR104-6	0.18	0.38	203	69.0	0.03	28.3	0.05	0.02	---	6.9	0.18	0.05	10

Sample Date & Time	Sample ID	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
12/4/99 8:15	MR104-7	0.19	0.59	203	68.8	0.04	37.1	0.07	0.03	---	6.9	0.24	0.07	11
12/4/99 10:30	MR104-8	0.21	0.56	204	69.0	0.04	345	0.62	0.02	---	6.9	0.20	0.04	9
12/4/99 13:10	MR104-9	0.20	0.45	205	69.4	0.04	35.7	0.06	0.01	---	6.8	0.15	0.04	10
12/4/99 15:55	MR104-10	0.19	0.53	204	69.1	0.04	42.9	0.08	0.02	---	6.9	0.15	0.04	10
12/3/99 16:20	KR203.7-1	0.66	0.45	198	51.7	0.23	9.64	0.02	0.01	---	6.9	---	0.19	11
12/3/99 19:00	KR203.7-2	0.32	0.22	198	51.7	0.02	20.2	0.04	0.01	---	6.8	0.15	0.02	3
12/3/99 21:50	KR203.7-3	0.33	0.43	198	52.0	0.03	2.64	0.00	0.01	---	6.9	0.15	0.02	3
12/4/99 0:40	KR203.7-4	0.32	0.06	199	52.1	0.03	534	0.96	0.01	---	7.2	0.22	0.02	3
12/4/99 3:20	KR203.7-5	0.32	0.36	200	52.8	0.03	13.9	0.03	0.02	---	6.9	0.21	0.02	3
12/4/99 5:45	KR203.7-6	0.34	0.64	202	53.3	0.03	301	0.54	0.01	---	7.2	0.31	0.03	3
12/4/99 8:45	KR203.7-7	0.33	0.28	202	53.4	0.04	13.2	0.02	0.01	---	6.9	0.20	0.02	3
12/4/99 11:00	KR203.7-8	0.32	0.19	202	53.8	0.03	14.6	0.03	0.01	---	7.2	0.21	0.02	3
12/4/99 13:40	KR203.7-9	0.33	0.22	202	53.6	0.03	33.2	0.06	0.01	---	7.0	0.23	0.03	4
12/4/99 16:25	KR203.7-10	0.32	0.23	203	54.2	0.04	29.5	0.05	0.01	---	6.9	0.18	0.02	3
12/3/99 16:30	WR303-1	0.36	0.63	212	34.4	0.03	0.47	0.00	0.02	---	7.1	0.16	0.05	4
12/3/99 19:15	WR303-2	0.36	0.13	213	35.0	0.03	13.7	0.02	0.02	---	7.2	0.16	0.05	4
12/3/99 22:05	WR303-3	0.36	0.44	215	35.4	0.03	8.94	0.02	0.02	---	7.1	0.21	0.06	4
12/4/99 0:45	WR303-4	0.39	0.31	216	36.1	0.04	18.9	0.03	0.02	---	7.1	0.36	0.06	4
12/4/99 3:35	WR303-5	0.36	0.49	218	36.4	0.03	12.9	0.02	0.02	---	7.1	0.24	0.06	4
12/4/99 6:00	WR303-6	0.35	0.35	218	36.9	0.04	4.22	0.01	0.02	---	7.1	0.14	0.06	4
12/4/99 8:55	WR303-7	0.35	0.35	218	37.4	0.03	22.2	0.04	0.02	---	7.1	0.15	0.07	6
12/4/99 11:15	WR303-8	0.36	0.25	220	37.8	0.04	21.6	0.04	0.02	---	7.1	0.18	0.07	4
12/4/99 13:50	WR303-9	0.35	0.09	219	37.9	0.04	40.6	0.07	0.02	---	7.2	0.19	0.06	4
12/4/99 16:40	WR303-10	0.38	0.58	220	37.9	0.04	16.9	0.03	0.02	---	7.2	0.28	0.07	4
12/3/99 16:45	TR405-1	1.59	1.53	231	55.4	1.31	5.44	0.01	0.02	---	7.0	---	---	---
12/3/99 19:35	TR405-2	0.57	1.85	231	55.8	0.17	15.7	0.03	0.02	---	7.0	---	---	---
12/3/99 22:20	TR405-3	0.53	1.68	232	55.4	0.18	11.1	0.02	0.02	---	7.3	0.21	0.11	8
12/4/99 1:05	TR405-4	0.55	1.70	234	55.8	0.14	357	0.65	0.02	---	7.1	0.65	0.14	8
12/4/99 3:50	TR405-5	0.55	1.52	233	56.2	0.15	13.7	0.02	0.02	---	7.0	0.26	0.12	8
12/4/99 6:15	TR405-6	0.55	1.77	235	56.5	0.14	1.52	0.00	0.02	---	7.1	0.23	0.12	7
12/4/99 9:05	TR405-7	0.54	1.25	237	56.3	0.13	3.05	0.01	0.02	---	7.1	0.20	0.13	8
12/4/99 11:30	TR405-8	0.52	1.37	236	54.6	0.11	4.70	0.01	0.02	---	7.1	0.21	0.11	7

Sample Date & Time	Sample ID	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
12/4/99 14:10	TR405-9	0.54	1.51	235	55.6	0.16	44.5	0.08	0.02	---	7.2	0.21	0.13	8
12/4/99 16:50	TR405-10	0.54	1.45	238	56.6	0.14	15.5	0.03	0.02	---	7.0	0.22	0.14	8
12/3/99 16:55	TI504-1	0.32	1.60	157	61.3	0.15	49.7	0.09	0.09	---	6.3	0.96	0.32	48
12/3/99 19:45	TI504-2	0.48	3.79	152	65.0	0.19	384	0.69	0.04	---	6.3	1.35	0.49	46
12/3/99 22:30	TI504-3	0.50	1.47	226	54.8	0.21	30.2	0.05	0.03	---	7.0	0.17	0.18	9
12/4/99 1:16	TI504-4	0.40	3.42	155	65.6	0.19	28.8	0.05	0.04	---	6.4	0.97	0.38	36
12/4/99 4:00	TI504-5	0.29	1.99	159	62.4	0.12	24.0	0.04	0.04	---	6.4	0.92	0.33	50
12/4/99 6:25	TI504-6	0.39	3.30	164	61.8	0.14	16.7	0.03	0.04	---	6.4	1.14	0.66	47
12/4/99 9:15	TI504-7	0.42	3.25	191	61.5	0.28	42.3	0.08	0.05	---	6.6	0.70	0.39	26
12/4/99 11:40	TI504-8	0.45	2.76	204	60.1	0.29	10.2	0.02	0.04	---	6.8	0.42	0.33	20
12/4/99 14:25	TI504-9	0.30	2.27	176	64.2	0.26	29.8	0.05	0.04	---	6.5	0.71	0.36	38
12/4/99 17:05	TI504-10	0.23	1.62	169	61.8	0.10	56.1	0.10	0.04	---	6.5	0.84	0.39	44
12/3/99 17:10	TB601-1	0.77	7.30	172	59.6	0.29	47.8	0.09	0.05	---	6.6	1.18	0.31	25
12/3/99 20:05	TB601-2	0.74	6.19	176	59.8	0.29	46.2	0.08	0.05	---	6.5	0.87	0.34	25
12/3/99 22:45	TB601-3	0.61	3.03	212	58.3	0.25	10.6	0.02	0.03	---	---	0.26	0.22	12
12/4/99 1:25	TB601-4	0.57	3.88	203	59.6	0.29	19.7	0.04	0.04	---	6.7	0.53	0.29	14
12/4/99 4:20	TB601-5	0.53	4.84	178	64.3	0.30	20.8	0.04	0.05	---	6.7	0.82	0.33	26
12/4/99 6:40	TB601-6	0.56	4.51	183	61.7	0.27	19.1	0.03	0.05	---	6.6	0.64	0.33	25
12/4/99 9:25	TB601-7	0.63	3.60	201	56.5	0.26	10.5	0.02	0.04	---	6.9	0.45	0.28	15
12/4/99 11:35	TB601-8	1.00	2.99	209	56.4	0.56	13.2	0.02	0.04	---	6.9	---	0.49	29
12/4/99 14:25	TB601-9	0.51	2.96	203	59.9	0.34	20.2	0.04	0.05	---	6.7	0.59	0.33	19
12/4/99 17:05	TB601-10	0.43	3.22	181	63.2	0.23	80.1	0.14	0.06	---	6.5	0.95	0.34	29
12/3/99 16:04	TB606-1	0.71	1.66	117	30.2	0.23	7027	13	9.9	---	7.4	0.06	0.17	65
12/4/99 8:25	TB606-7	0.76	1.85	130	33.4	0.21	6029	11	8.4	---	7.7	0.05	0.16	54
12/4/99 10:40	TB606-8	0.75	2.17	121	31.6	0.23	6850	12	9.6	---	7.8	0.06	0.11	56
12/4/99 13:20	TB606-9	0.82	1.83	99	27.0	0.27	9178	17	13	---	7.9	0.10	0.12	52
12/4/99 16:10	TB606-10	0.70	2.25	146	38.5	0.20	4276	7.7	6.0	---	7.5	0.10	0.10	52
12/3/99 15:20	TB609-1	0.37	1.38	170	51.4	0.11	1831	3.3	2.8	---	7.2	0.07	0.14	48
12/3/99 17:50	TB609-2	0.59	1.61	146	39.1	0.13	3998	7.2	5.5	---	7.6	0.08	0.13	55
12/3/99 21:00	TB609-3	0.81	2.13	100	27.1	0.28	8672	16	12	---	7.8	0.09	0.15	61
12/3/99 23:50	TB609-4	0.52	2.35	164	43.5	0.16	1190	2.2	1.7	---	7.6	0.44	0.15	62
12/4/99 2:20	TB609-5	0.57	1.75	179	47.6	0.10	1566	2.8	2.2	---	7.2	0.09	0.11	36

Sample Date & Time	Sample ID	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	Cl ⁻ (ppm)	Salinity (psu)	SO ₄ (mM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
12/4/99 5:10	TB609-6	0.56	1.43	165	44.0	0.14	2734	4.94	3.9	---	7.3	0.07	0.12	43
12/4/99 7:45	TB609-7	0.91	2.36	68	20.4	0.34	12001	22	17	---	7.9	0.02	0.13	54
12/4/99 10:10	TB609-8	0.91	1.44	46	16.6	0.35	14196	26	20	---	8.0	0.01	0.02	50
12/4/99 12:45	TB609-9	0.61	1.68	149	42.2	0.17	4294	7.8	6.0	---	7.5	0.05	0.12	47
12/4/99 15:40	TB609-10	0.64	1.69	129	36.6	0.20	6359	11	8.9	---	7.8	0.08	0.15	48
12/3/99 15:30	TB609D-1	0.67	2.23	103	32.3	0.25	8134	15	12	---	7.8	0.05	0.29	69
12/3/99 18:10	TB609D-2	0.64	1.75	137	36.7	0.19	5248	9.5	7.4	---	7.7	0.13	0.16	39
12/3/99 21:02	TB609D-3	0.94	1.33	27	10.9	0.41	16122	29	23	---	8.0	0.12	0.00	51
12/3/99 23:55	TB609D-4	0.97	1.42	33	12.0	0.37	15906	29	23	---	7.9	0.08	0.00	53
12/4/99 2:35	TB609D-5	0.84	2.37	79	23.1	0.33	10766	19	15	---	7.9	0.07	0.33	63
12/4/99 5:20	TB609D-6	0.88	2.20	65	19.0	0.34	12114	22	17	---	7.9	0.03	0.22	58
12/4/99 7:55	TB609D-7	0.94	1.25	23	10.1	0.41	16324	29	23	---	8.0	0.01	0.02	64
12/4/99 10:15	TB609D-8	0.96	1.18	15	8.2	0.44	17262	31	24	---	8.0	0.01	0.00	48
12/4/99 12:55	TB609D-9	0.88	1.85	47	15.3	0.36	13941	25	19	---	8.0	0.01	0.15	62
12/4/99 15:35	TB609D-10	0.69	1.89	120	33.27	0.22	7120	13	10	---	7.7	0.04	0.18	47

APPENDIX E: PARTICULATE CHEMISTRY OF SAMPLES FROM 24 HOUR EXPERIMENTS

Sample Date & Time	Sample ID	SPM (mg-l-1)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)
7/19/99 14:45	TB601-1	16.9	8.1	1.3	8.2	1967	295	0.41	4.6
7/19/99 17:10	TB601-2	24.5	8.0	1.3	7.7	1622	267	0.42	4.2
7/19/99 19:40	TB601-3	16.6	7.0	1.1	6.6	1422	253	0.44	3.9
7/19/99 21:55	TB601-4	12.0	7.6	1.2	7.6	1914	275	0.41	3.6
7/20/99 1:00	TB601-5	9.7	---	---	---	---	---	0.57	5.2
7/19/99 12:45	TB609-1	5.1	5.3	0.8	5.2	1025	176	0.63	4.9
7/19/99 15:30	TB609-2	5.1	5.9	1.0	6.2	1449	209	0.57	5.0
7/19/99 18:15	TB609-3	3.4	---	---	---	---	---	0.77	5.6
7/19/99 20:40	TB609-4	6.8	4.2	0.9	4.8	1052	202	0.64	3.7
7/19/99 23:15	TB609-5	8.0	3.1	0.5	3.1	965	104	0.30	2.8
7/20/99 2:15	TB609-6	4.4	6.2	1.0	6.4	1544	242	0.94	7.5
7/20/99 5:10	TB609-7	4.2	5.4	0.9	5.5	1743	207	0.50	4.6
7/19/99 12:37	TB609D-1	7.4	6.9	1.1	6.9	1602	247	0.42	3.8
7/19/99 15:25	TB609D-2	9.3	6.8	1.2	6.7	1325	260	0.42	3.9
7/19/99 18:10	TB609D-3	4.4	5.1	0.9	4.9	1028	290	0.64	5.0
7/19/99 20:35	TB609D-4	5.8	5.1	0.8	5.0	1143	237	0.45	3.6
7/19/99 23:10	TB609D-5	5.4	5.6	1.0	5.6	1661	209	0.37	3.8
7/20/99 2:10	TB609D-6	8.5	5.1	0.9	5.1	1269	187	0.33	3.1
7/20/99 5:05	TB609D-7	6.1	4.9	0.8	4.8	1158	234	0.56	4.3
12/3/99 17:10	TB601-1	21.9	8.3	1.1	8.7	1122	322	0.33	3.5
12/3/99 20:05	TB601-2	30.1	8.3	1.2	9.1	1194	367	0.18	2.6
12/3/99 22:45	TB601-3	66.2	8.9	1.3	9.4	1125	401	0.06	0.9
12/4/99 1:25	TB601-4	49.0	8.8	1.3	9.4	1167	412	0.09	1.5
12/4/99 4:20	TB601-5	30.5	8.8	1.5	9.6	1226	228	0.19	2.6
12/4/99 6:40	TB601-6	25.0	8.2	1.1	9.1	1137	304	0.06	1.3
12/4/99 9:25	TB601-7	28.9	8.0	1.2	8.8	1026	335	0.13	1.9
12/4/99 11:35	TB601-8	38.4	8.7	1.2	9.3	1096	353	0.07	1.5

Sample Date & Time	Sample ID	SPM (mg/l-1)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)
12/4/99 14:25	TB601-9	36.3	12.8	1.7	12.7	1473	537	0.11	1.7
12/3/99 15:20	TB609-1	17.2	8.6	1.2	9.4	1135	365	0.32	4.1
12/3/99 17:50	TB609-2	38.8	8.5	1.5	9.2	1233	256	0.07	1.3
12/3/99 21:00	TB609-3	16.0	7.6	1.2	8.0	1129	245	0.17	2.4
12/3/99 23:50	TB609-4	12.7	7.9	1.2	8.3	1042	251	0.12	1.4
12/4/99 2:20	TB609-5	23.5	8.8	1.3	9.1	1135	258	0.26	2.4
12/4/99 5:10	TB609-6	20.5	8.8	1.5	9.6	1242	269	0.10	1.6
12/4/99 7:45	TB609-7	21.7	8.2	1.3	8.2	1164	292	0.13	1.6
12/4/99 10:10	TB609-8	16.1	8.1	1.2	7.9	1130	284	0.19	2.2
12/4/99 12:45	TB609-9	11.9	7.7	1.1	7.8	967	270	0.10	1.3
12/3/99 15:30	TB609D-1	56.8	8.1	1.4	8.4	1262	238	0.14	2.4
12/3/99 18:10	TB609D-2	35.6	8.3	1.4	8.7	1218	258	0.10	1.8
12/3/99 21:02	TB609D-3	56.1	8.2	1.2	8.0	1154	282	0.17	2.4
12/3/99 23:55	TB609D-4	16.3	7.5	1.1	7.4	1067	251	0.14	2.1
12/4/99 2:35	TB609D-5	29.2	8.1	1.3	8.3	1238	253	0.15	2.2
12/4/99 5:20	TB609D-6	23.8	7.4	1.2	7.8	1122	251	0.15	2.0
12/4/99 7:55	TB609D-7	48.3	7.2	1.1	6.8	1015	269	0.18	2.7
12/4/99 10:15	TB609D-8	22.7	6.9	1.0	6.5	983	257	0.18	2.5

APPENDIX F: AVERAGE DISSOLVED RIVER END-MEMBERS

Sampling Date	River Average*	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
10/11/97	Miami	0.16	0.30	212	76.6	---	---	---	---	---	---
	Kilchis	0.38	0.25	214	63.8	---	---	---	---	---	---
	Wilson	0.38	0.28	215	55.6	---	---	---	---	---	---
	Trask	0.67	1.33	225	71.1	---	---	---	---	---	---
	Tillamook	0.51	1.20	157	60.8	---	---	---	---	---	---
	AVERAGE	0.50	0.74	213	62.9	---	---	---	---	---	---
11/29/97	Miami	0.19	0.49	194	69.8	---	---	6.8	---	---	---
	Kilchis	0.30	0.19	191	54.2	---	---	7.1	---	---	---
	Wilson	0.69	0.43	221	47.3	---	---	7.2	---	---	---
	Trask	0.48	1.12	244	59.4	---	---	7.2	---	---	---
	Tillamook	0.51	1.52	226	67.3	---	---	6.8	---	---	---
	AVERAGE	0.52	0.67	221	54.3	---	---	---	---	---	---
1/10/98	Miami	0.19	0.11	210	76.8	---	---	7.0	---	---	---
	Kilchis	0.37	0.16	215	68.1	---	---	7.0	---	---	---
	Wilson	0.44	0.25	231	58.7	---	---	7.3	---	---	---
	Trask	0.46	0.81	250	64.4	---	---	7.2	---	---	---
	Tillamook	0.19	0.85	175	67.2	---	---	6.4	---	---	---
	AVERAGE	0.42	0.48	230	63.2	---	---	---	---	---	---
2/7/98	Miami	0.21	0.24	208	69.4	---	---	7.0	---	---	---
	Kilchis	0.41	0.19	201	54.4	---	---	7.1	---	---	---
	Wilson	0.93	0.18	223	44.8	---	---	7.2	---	---	---
	Trask	0.33	1.08	249	47.7	---	---	7.3	---	---	---
	Tillamook	0.16	1.19	165	56.4	---	---	6.9	---	---	---
	AVERAGE	0.53	0.51	220	49.6	---	---	---	---	---	---

Sampling Date	River Average*	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
3/22/98	Miami	0.17	0.28	200	60.2	---	---	6.9	---	---	---
	Kilchis	0.29	0.29	188	48.7	---	---	7.0	---	---	---
	Wilson	0.48	0.56	212	44.7	---	---	7.2	---	---	---
	Trask	0.55	1.97	234	66.6	---	---	7.0	---	---	---
	Tillamook	0.19	2.09	164	46.7	---	---	6.5	---	---	---
	AVERAGE	0.43	1.07	208	52.6	---	---	---	---	---	---
4/11/98	Miami	0.17	0.44	214	61.0	---	---	7.1	---	---	---
	Kilchis	0.23	0.53	203	51.4	---	---	7.2	---	---	---
	Wilson	1.19	0.46	222	41.8	---	---	7.1	---	---	---
	Trask	0.54	3.34	235	46.5	---	---	7.3	---	---	---
	Tillamook	0.24	1.09	186	44.9	---	---	6.9	---	---	---
	AVERAGE	0.75	1.76	223	45.0	---	---	---	---	---	---
5/23/98	Miami	0.05	0.62	211	57.1	---	---	6.8	---	---	---
	Kilchis	0.14	0.88	199	49.8	---	---	7.1	---	---	---
	Wilson	0.63	0.78	217	38.8	---	---	7.0	---	---	---
	Trask	0.33	1.52	244	42.4	---	---	7.1	---	---	---
	Tillamook	0.06	1.41	176	47.5	---	---	6.4	---	---	---
	AVERAGE	0.37	1.14	218	42.9	---	---	---	---	---	---
6/24/98	Miami	0.07	0.89	204	49.4	---	---	6.9	---	---	---
	Kilchis	0.21	0.60	193	37.5	---	---	7.3	---	---	---
	Wilson	0.12	0.74	219	34.4	---	---	7.1	---	---	---
	Trask	0.15	1.17	220	26.1	---	76	7.1	---	---	---
	Tillamook	0.26	0.39	180	34.9	---	---	7.7	---	---	---
	AVERAGE	0.15	0.88	213	30.9	---	---	---	---	---	---

Sampling Date	River Average*	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
7/12/98	Miami	---	---	---	---	---	---	---	---	---	---
	Kilchis	0.17	0.50	218	47.9	---	---	7.0	---	---	---
	Wilson	0.05	0.68	222	30.7	---	---	7.4	---	---	---
	Trask	1.07	2.66	275	29.8	---	---	7.2	---	---	---
	Tillamook	---	---	---	---	---	---	---	---	---	---
	AVERAGE	0.46	1.35	240	36.0	---	---	---	---	---	---
8/26/98	Miami	0.16	0.40	240	53.5	---	---	7.1	---	---	---
	Kilchis	0.14	0.35	241	49.0	---	---	6.9	---	---	---
	Wilson	0.08	0.76	237	31.3	---	---	7.0	---	---	---
	Trask	0.12	0.84	250	20.3	---	---	7.4	---	---	---
	Tillamook	0.37	0.77	200	32.3	---	---	7.3	---	---	---
	AVERAGE	0.13	0.68	241	32.1	---	---	---	---	---	---
10/17/98	Miami	0.12	0.21	215	94.7	0.04	---	6.9	0.20	0.03	15.1
	Kilchis	0.25	0.27	210	80.5	0.04	113	7.2	0.06	0.01	3.91
	Wilson	1.81	0.95	226	70.1	0.17	147	7.1	0.37	0.16	7.77
	Trask	0.46	3.66	241	81.2	0.33	---	7.1	0.94	0.50	17.6
	Tillamook	0.21	2.13	191	82.6	0.27	---	6.5	0.09	0.26	49.2
	AVERAGE	1.01	1.69	225	76.2	0.20	---	---	0.46	0.24	12.9
11/29/98	Miami	0.12	1.16	211	83.5	0.02	56	6.7	---	---	---
	Kilchis	0.26	0.34	221	71.8	0.02	60	---	---	---	---
	Wilson	0.52	0.63	233	62.9	0.04	85	7.0	---	---	---
	Trask	0.64	2.42	245	84.9	0.39	192	6.9	---	---	---
	Tillamook	0.42	3.03	178	79.5	0.31	---	6.4	---	---	---
	AVERAGE	0.51	1.41	230	73.3	0.18	---	---	---	---	---

Sampling Date	River Average*	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
1/2/99	Miami	0.24	0.33	218	79.1	0.03	51	7.0	0.32	0.17	18.7
	Kilchis	0.39	0.18	218	69.0	0.02	98	6.9	0.14	0.03	3.25
	Wilson	0.51	0.64	237	57.6	0.04	52	---	0.16	0.08	4.02
	Trask	0.62	4.78	252	74.3	0.39	122	7.0	0.15	0.29	8.41
	Tillamook	0.57	7.36	172	65.6	0.43	93	6.5	1.21	0.64	35.0
	AVERAGE	0.53	2.57	232	66.4	0.19	92	---	0.25	0.19	8.26
2/27/99	Miami	0.24	0.80	157	42.7	---	---	6.0	---	---	---
	Kilchis	0.23	0.27	138	20.6	---	---	6.0	---	---	---
	Wilson	0.44	0.40	181	28.2	---	87	7.2	---	---	---
	Trask	0.55	0.75	209	41.1	---	71	7.2	---	---	---
	Tillamook	0.58	2.78	189	44.7	---	94	7.0	---	---	---
	AVERAGE	0.48	0.75	189	33.8	---	---	---	---	---	---
4/2/99	Miami	0.18	0.13	207	54.1	0.04	33	7.0	0.11	0.03	10.6
	Kilchis	0.30	0.05	193	35.3	0.03	40	7.2	0.04	0.00	1.86
	Wilson	0.31	0.09	218	33.8	0.03	42	7.2	0.16	0.03	4.06
	Trask	0.37	1.25	232	37.7	0.08	53	7.2	0.23	0.09	7.68
	Tillamook	0.33	1.28	198	44.6	0.13	120	6.9	0.50	0.36	21.9
	AVERAGE	0.33	0.60	217	36.3	0.05	51	---	0.19	0.07	6.22
5/26/99	Miami	0.21	0.52	220	51.9	0.05	---	---	---	---	---
	Kilchis	0.36	0.37	214	44.0	0.06	---	---	---	---	---
	Wilson	1.10	0.73	215	24.8	0.23	---	---	---	---	---
	Trask	0.43	1.81	239	30.1	0.23	---	---	---	---	---
	Tillamook	0.40	1.13	208	30.4	0.20	---	---	---	---	---
	AVERAGE	0.68	1.22	224	28.9	0.22	---	---	---	---	---

Sampling Date	River Average*	PO ₄ (μM)	NH ₄ (μM)	H ₄ SiO ₄ (μM)	NO ₃ +NO ₂ (μM)	NO ₂ (μM)	DOC (μM)	pH	Fe (μM)	Mn (μM)	Ba (nM)
7/19/99	Miami	0.18	0.87	227	45.4	0.09	170	7.0	0.50	0.10	14.4
	Kilchis	0.27	0.81	217	39.3	0.10	185	7.0	0.07	0.02	4.20
	Wilson	0.20	1.12	234	28.6	0.20	190	7.2	0.30	0.09	6.49
	Trask	0.64	8.49	246	21.7	0.35	283	7.2	0.66	0.21	8.97
	Tillamook	0.32	2.66	193	22.7	0.29	368	7.0	2.94	1.47	53.0
	AVERAGE	0.51	6.37	241	23.8	0.31	259	---	0.60	0.20	9.06
10/17/99	Miami	0.27	0.70	243	48.8	0.07	---	6.8	0.40	0.23	12.7
	Kilchis	0.25	0.14	241	43.9	0.07	---	6.7	0.05	0.02	3.96
	Wilson	0.01	0.60	233	33.3	0.10	---	6.9	0.15	0.13	6.73
	Trask	0.17	0.70	251	20.6	0.10	---	7.0	0.11	0.06	6.66
	Tillamook	0.34	0.96	200	30.8	0.09	---	6.9	2.16	0.20	27.3
	AVERAGE	0.15	0.65	245	24.9	0.10	---	---	0.20	0.07	7.35
12/3/99	Miami	0.19	0.50	202	68.6	0.04	---	6.8	0.22	0.06	9.30
	Kilchis	0.37	0.30	200	52.9	0.06	---	6.9	0.19	0.04	4.04
	Wilson	0.36	0.36	217	36.5	0.03	---	7.1	0.21	0.06	4.17
	Trask	0.66	1.55	234	55.8	0.28	---	7.1	0.22	0.12	7.44
	Tillamook	0.38	2.51	179	61.5	0.20	---	6.6	0.83	0.39	33.8
	AVERAGE	0.45	0.85	214	48.0	0.12	---	---	0.26	0.10	7.48

* River end member concentrations reported as the concentration at the farthest down stream station with salinity less than 0.09 psu. Average river end member concentrations were calculated as the flow weighted concentration using concentrations of all rivers except the Miami River.

APPENDIX G: AVERAGE PARTICULATE RIVER END-MEMBERS

Sampling Date	River Average*	SPM (mg ^l ⁻¹)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)
1/10/98	Miami	---	---	---	---	---	---	---	---
	Kilchis	0.5	---	---	---	---	---	---	---
	Wilson	3.6	---	---	---	---	---	---	---
	Trask	5.1	---	---	---	---	---	---	---
	Tillamook	---	---	---	---	---	---	---	---
	AVERAGE	3.5	---	---	---	---	---	---	---
4/11/98	Miami	1.5	---	---	---	---	---	---	---
	Kilchis	3.1	---	---	---	---	---	---	---
	Wilson	1.5	---	---	---	---	---	---	---
	Trask	3.3	---	---	---	---	---	---	---
	Tillamook	---	---	---	---	---	---	---	---
	AVERAGE	2.5	---	---	---	---	---	---	---
10/17/98	Miami	1.5	5.3	0.9	5.8	1135	1534	---	---
	Kilchis	1.7	2.2	0.4	2.7	607	570	---	---
	Wilson	5.5	6.2	1.1	6.9	2628	730	---	---
	Trask	8.8	6.3	1.0	6.9	2646	1738	---	---
	Tillamook	4.0	6.9	0.8	8.7	4431	1680	---	---
	AVERAGE	5.6	5.5	0.9	6.3	2384	1062	---	---
1/2/99	Miami	9.9	7.8	1.3	8.0	1229	379	0.27	4.1
	Kilchis	6.8	6.9	1.5	8.6	1441	267	0.26	4.9
	Wilson	59	8.3	1.3	8.4	1246	364	0.07	1.3
	Trask	57	8.5	1.3	8.7	1275	433	0.15	1.8
	Tillamook	14	8.1	1.0	8.9	2223	612	0.48	5.5
	AVERAGE	43	8.0	1.3	8.6	1390	389	0.18	2.6

Sampling Date	River Average*	SPM (mg l ⁻¹)	Al (%wt)	Ti (%wt)	Fe (%wt)	Mn (ppm)	Ba (ppm)	N (%wt)	C (%wt)
4/2/99	Miami	1.7	7.2	1.2	8.8	1342	475	0.65	6.6
	Kilchis	---	7.2	1.1	7.9	977	255	---	---
	Wilson	3.6	6.9	1.3	7.9	1072	349	0.27	3.2
	Trask	2.8	6.9	1.0	7.6	1660	416	0.74	7.1
	Tillamook	---	6.7	1.0	8.2	2323	375	---	---
	AVERAGE	3.2	6.9	1.1	7.8	1360	357	0.51	5.2
7/19/99	Miami	---	---	---	---	---	---	---	---
	Kilchis	---	---	---	---	---	---	---	---
	Wilson	---	---	---	---	---	---	---	---
	Trask	---	---	---	---	---	---	---	---
	Tillamook	---	---	---	---	---	---	---	---
	AVERAGE	17	8.1	1.3	8.2	1967	295	---	---
10/17/99	Miami	2.3	4.6	0.8	5.1	958	190	0.63	6.4
	Kilchis	---	---	---	---	---	---	---	---
	Wilson	1.2	4.2	0.7	4.5	1349	221	3.02	18.3
	Trask	8.0	7.3	1.1	7.7	2346	278	0.73	5.4
	Tillamook	3.6	4.0	0.5	6.5	3736	321	2.40	20.4
	AVERAGE	6.6	6.1	0.9	6.5	2063	250	1.23	8.4
12/3/99	Miami	---	---	---	---	---	---	---	---
	Kilchis	---	---	---	---	---	---	---	---
	Wilson	---	---	---	---	---	---	---	---
	Trask	---	---	---	---	---	---	---	---
	Tillamook	---	---	---	---	---	---	---	---
	AVERAGE	36	9.0	1.3	9.6	1174	362	---	---

*River end member concentrations reported as the concentration at the farthest down stream station with salinity less than 0.09 psu. Average river end member concentrations were calculated as the flow weighted concentration using concentrations of all rivers except the Miami River. Average particulate river end-members for July and December 1999 are concentrations at the upper estuary with lowest salinity (1.05 and 0.04, respectively, for July and December).

APPENDIX H: BOX MODEL CALCULATIONS

Appendix H provides a detailed description of the mass balance calculations used in other chapters of this dissertation. The modeling approach for each chapter was selected 1) to match data available from this research to the data requirements of each model and 2) to provide consistency with modeling approaches reported in the literature. In Chapters 3 and 4, the estuary mass balances for Mn, Ba, and Fe were modeled after the approach described by Klinkhammer and Bender (1981) and Yang and Sanudo-Wilhelmy (1998). In Chapter 2, nutrient fluxes were estimated using a steady state box-model approach described by Gordon et al. (1996). Both models assumed conservation of salts within the estuary. Both models assumed that input from groundwater and precipitation and evaporative losses were negligible relative to river and ocean input. Notation varied between the two models so the notation used in previous chapters was continued in this appendix.

Estuarine Flushing Time

Estuarine flushing times were used in modeling calculations throughout this dissertation. Estuarine flushing times were calculated using the freshwater fraction method (Dyer 1997). The freshwater fraction method was described by equation (1) where T was flushing time, V_E was estuarine volume for that sampling date, Q was river discharge, S_s was salinity of coastal seawater (NE Pacific surface waters

44°49.1' N 126°03.0' W: 32.64 psu, Wheeler, unpublished data), and S_n was the mean salinity observed in the estuary.

$$T = (V_E Q^{-1}) (S_s - S_n S_s^{-1}) \quad (1)$$

Estimates of estuary volume for each sampling date were calculated using the tidal prism reported by Johnson (1972) and corrected for daily tidal height change. River discharge data on each sampling date was first used to estimate flushing time (single date Q). This “single Q” estimate of flushing time was then used to calculate a mean river discharge over that time period, and a flushing time was calculated from this mean discharge (Mean Q). These estimates of flushing time assumed that the estuary was well mixed throughout the year. The circulation patterns of Tillamook Bay have not been extensively studied. Burt and McAllister (1959) described Tillamook Bay as stratified during the high discharge of winter shifting to a well-mixed estuary during the spring, summer, and fall months. Therefore, winter estimates of flushing time may be underestimated. Spring and summer estimates of flushing times would also be expected to be smaller than calculated here because of upwelling decreased flushing time (Duxbury 1979)

Estuarine Box Model (Mn, Ba, Fe)

Estuary mass balances for Mn, Ba, and Fe were modeled after the approach described by Klinkhammer and Bender (1981) and Yang and Sanudo-Wilhelmy (1998). The mass balance for this system was described by a box model dividing the study area into four components: the southern rivers (Kilchis, Wilson, Trask, and Tillamook Rivers), the northern river (Miami), the estuary, and the ocean (Figure H.1). Q_O represented water exchange from the ocean while Q_E was the flow

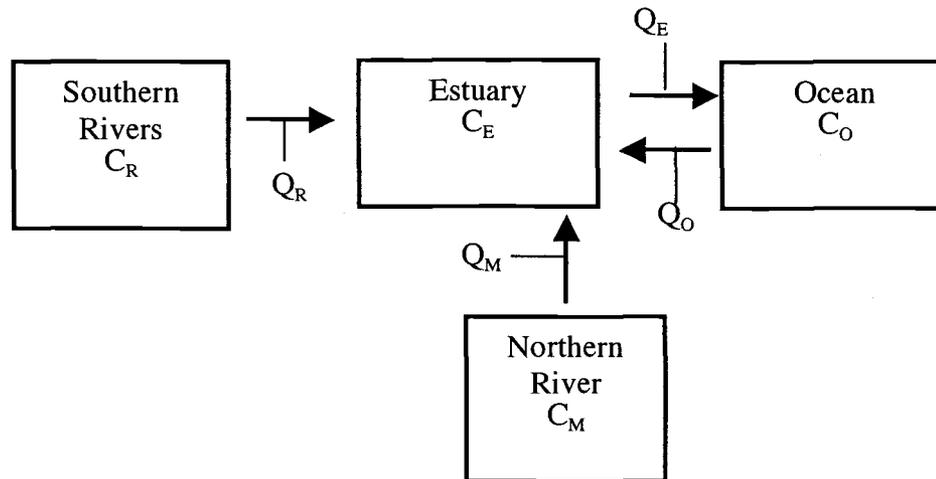


Figure H.1. Box model of the Tillamook Bay estuary where Q_R was the total discharge from the southern rivers (Kilchis, Wilson, Trask, and Tillamook Rivers), Q_M was the discharge from the Miami River, Q_E was the flow from the estuary, and Q_O was the exchange from the ocean. Average flow-weighted concentration of an element in the southern rivers was C_R , concentration of the element in the northern river C_M , average estuary C_E , and ocean end-member C_O (measured at the station at the mouth of the estuary).

from the estuary. Q_R was the river discharge from the southern rivers. Q_M was the river discharge from the northern river. S_O was the salinity measured at the ocean end-member. S_E was the average salinity within the estuary. Salinity for the northern and southern rivers was less than 0.09 psu and assumed to be effectively zero. The average estuarine salinity was calculated from the volume-weighted concentrations measured at estuary stations, not including the ocean end-member station.

Assuming conservation of salts within the estuary, the water budget for the estuary was described by equations (2) and (3).

$$Q_E S_E = Q_O S_O \quad (2)$$

$$Q_E = Q_O (S_O / S_E) \quad (3)$$

Since there are only three sources of water to the estuary, the water balance could be written as equation (4).

$$Q_E = Q_R + Q_M + Q_O \quad (4)$$

Combining equations (3) and (4), ocean exchange (Q_O) was described by equation (5).

$$Q_O = \frac{(Q_R + Q_M)}{S_O S_E^{-1} - 1} \quad (5)$$

For each sampling event, the water budget was based on reported river discharges into the estuary and a calculated rate of exchange (Q_O) from the ocean to the estuarine box. River discharge for the Wilson and Trask Rivers were provided by the USGS (<http://water.usgs.gov>). River flow data for the Miami, Kilchis, and Tillamook Rivers between October 1997 and October 1998 was provided by the Oregon Department of Environmental Quality (ODEQ, unpublished data). Daily streamflow data for the Miami, Kilchis, and Tillamook Rivers was not available for 1999 and was calculated from mean daily flow in 1997 and 1998 records, normalized to flow measured in the Wilson River.

Estimates of Q_O along with values for Q_R , Q_M and the average river end-member concentration of total Mn, Ba, and Fe in the southern rivers (C_R), the northern river (C_M), and ocean (C_O) were used to calculate the total input of each element into the estuarine box using equation (6). Average river end-member

concentrations for each sampling date were a flow weighted average using the concentration at the farthest down stream station on each river with salinity less than 0.09 psu. The concentration of each element measured at the station located at the estuary mouth was designated as the ocean end-member concentration (C_O).

$$\text{Total } F_{\text{in}} = Q_R C_R + Q_M C_M + Q_O C_O \quad (6)$$

All fluxes were reported in g s^{-1} with losses from the estuary indicated as a negative flux. The flux of each element from the southern rivers (F_R) was equal to the average river end-member concentration of the southern rivers (C_R) times the total river discharge (Q_R) from those rivers. Flux from the northern river (F_M) was equal to the Miami River concentration (C_M) times Miami River flow (Q_M). Flux of each element from the ocean to the estuary (F_O) was calculated as the concentration at the ocean end-member (C_O) times the calculated ocean exchange (Q_O). The flux from the estuary (F_E) to the ocean was equal to the total input from the rivers and the ocean in equation (4) times the average concentration of each element within the estuary as described by equation (7).

$$F_E = \text{Flux out} = C_E (Q_R + Q_M + Q_O) \quad (7)$$

Errors associated with model inputs (F_R , F_M , F_O , Total F_{in}) and outputs (F_E) were propagated using the methods described by Taylor (1982) and included uncertainties in SPM concentrations, salinity, streamflow, particulate and dissolved concentrations, and estuarine volume. Generally, error terms were less than 30% of the calculated flux values. However, during winter (January 1999), the error associated with the calculated flux from the estuary (F_E) was as much as 500% of the calculated flux values. During other months, the flux “imbalance” exceeded the

flux error, indicating that an additional source or sink was required to balance the model.

Additional terms were calculated to account for missing sources or sinks of an element for the box model, including loss of material from the estuary via sedimentation (R_s) and burial (F_b) and input of materials from resuspension (F_{re}) and benthic flux (F_D). Equation (8) described the sedimentation rate (R_s) calculation. A sedimentation rate was calculated for sampling events where there was a net loss or removal (L) of suspended particulate material (SPM) within the estuary compared to conservative mixing predictions. To calculate SPM loss within the estuary, SPM concentrations measured in samples were plotted against salinity concentrations of samples. This relationship of SPM versus salinity was fitted with a best-fit high order polynomial using KaleidaGraph™ (Synergy Software©) to estimate departures from conservative mixing. Estuarine loss of SPM (L) was calculated by difference between the conservative end-member mixing line and the line fitted to the observations as depicted in Figure H.2. Estuary volume for each sampling date (V_E) was calculated using the tidal prism reported by Johnson (1972) and corrected for daily tidal height change. As described above, estuarine flushing time for each sampling (T) data was calculated using the freshwater fraction method (Dyer 1997). A dry sediment density (ρ) of 2.65 g cm^{-3} was assumed (as referenced in Yang and Sanudo-Wilhelmy 1998).

$$R_s = (L V_E) (T A_E \rho)^{-1} \quad (8)$$

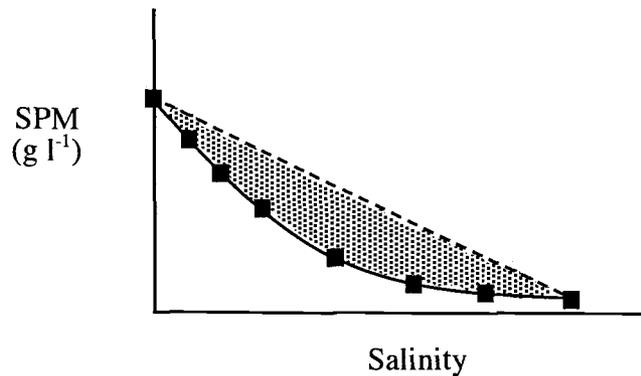


Figure H.2. Depiction of method used to calculate loss of SPM within the estuary. Squares represent measurements of SPM concentrations and salinity for a sampling event. Solid line depicts polynomial fitted to sample observations, and dashed line depicts the conservative mixing line between the river and ocean end-members. Loss of SPM (L) within the estuary is represented by the filled area and calculated as the difference (in grams per liter) between the conservative mixing line and the line fitted to the observations.

Assuming a porosity of 0.9 (ϕ), sediment burial (F_S) was then described by equation (9). C_p was the average estuarine concentration of Mn, Ba, or Fe in suspended particulate material collected during a sampling event.

$$F_S = R_S A_E [(1-\phi) \rho C_p] \quad (9)$$

A resuspension rate (F_{Re}) for each element was calculated if there was an observed SPM excess over conservative mixing predictions during a sampling event. The resuspension rate (F_{Re}) calculated for each element was described by equation (10) and was based on the excess SPM within the estuary (E) over conservative mixing, the average surface sediment Mn, Ba, or Fe concentrations

measured within the estuary (C_p), the estuarine volume (V_E), and the flushing time (T) during each sampling event. In a method similar to that depicted in Figure H.2, excess SPM within the estuary was calculated for a given sampling event by plotting SPM concentrations measured in samples against salinity. This relationship of SPM versus salinity was fitted with a best-fit high order polynomial using KaleidaGraph™ (Synergy Software©) to estimate departures from conservative mixing. Excess SPM within the estuary (E) was calculated by difference between the conservative end-member mixing line and the line fitted to the observations.

$$F_{Re} = T^{-1} (E C_p V_E) \quad (10)$$

Input of an element from benthic flux (F_D) was calculated using the excess concentration of dissolved Mn, Ba, or Fe above conservative mixing predictions (D), estuary volume (V_E), and flushing time of the estuary (T) for each sampling event, as described in equation (11). Dissolved Mn, Ba, or Fe in excess of conservative mixing was calculated for each sampling event by plotting dissolved element concentrations versus salinity and fitting that the data to a high order polynomial using KaleidaGraph™ (Synergy Software©). Excess dissolved Mn, Ba, or Fe (D) was then calculated by difference between the conservative end-member mixing line and the line fitted to the observations.

$$F_D = T^{-1} (D V_E) \quad (11)$$

Estuarine Box Model (PO_4^{-3} , $N+N$, H_4SiO_4 , NH_4^+)

Nutrient fluxes were estimated using a box model approach described by Gordon and others (1996) for the Land Ocean Interactions in the Coastal Zone

(LOICZ) project. Using the LOICZ approach, the estuary was modeled as a single box with input from the five rivers combined as a single input and exchange with the coastal ocean as shown in Figure H.3.

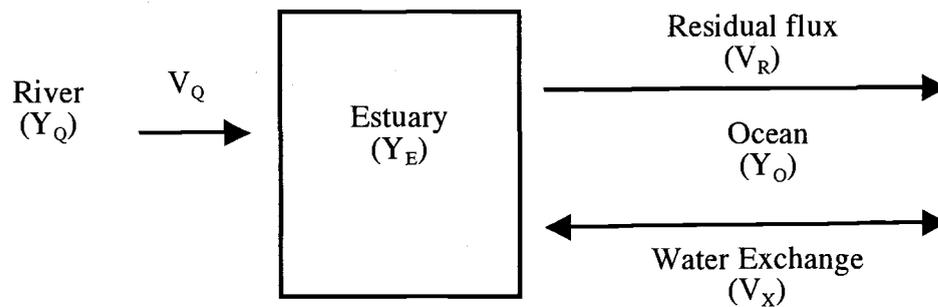


Figure H.3. Box model of the Tillamook Bay estuary where V_Q was the total river discharge (Miami, Kilchis, Wilson, Trask, and Tillamook Rivers), V_R was the residual flux from estuary to the ocean, and V_X was water exchange between the estuary and ocean. Average flow-weighted concentration of an element in the rivers was Y_Q , average estuary concentration Y_E , and ocean end-member concentration Y_O (measured at 44.65° N 124.18° W, unpublished data).

In the box model, the estuary had a freshwater inflow of V_Q from the five rivers feeding into the estuary. As mentioned previously, river discharge data used in the model was provided by the USGS and ODEQ or was calculated when the river discharge record was incomplete. The model assumed that input from groundwater and precipitation and evaporative losses were effectively zero. Given these assumptions, the freshwater inflow equaled the net water exchange with the

ocean so the residual flow to the ocean (V_R) was $-V_Q$. Mixing exchange between the ocean and the estuary was characterized by the exchange flow, V_X .

The flux of an element from the rivers (F_Q) to the estuary was equal to the average river end-member concentration (Y_Q) times the total river discharge (V_Q). The flux from the estuary to the ocean (F_E) was calculated from the average of the concentration in the estuary (Y_E) and in the ocean (Y_O) times the residual flow to the ocean (V_R). This assumed that the concentration in the outflow at the seaward end of the estuary was the average of Y_O and Y_E . Substituting V_R for $-V_Q$, flux of an element from the estuary to the ocean was described by equation (12).

$$F_E = -\frac{(Y_E + Y_O)}{2} V_Q \quad (12)$$

The flux of an element from the ocean to the estuary (F_O) was the net exchange between the ocean and estuary and described by equation (13).

$$F_O = Y_O V_X - Y_E V_X = (Y_O - Y_E) V_X \quad (13)$$

Based on equations (12) and (13), the equation for mass conservation of a dissolved nutrient the estuary could be described by equation (14) where Y_E was the average nutrient concentration in estuarine samples for a sampling event, Y_O was ocean nutrient concentration at 44.65° N 124.18° W (Wheeler, unpublished data), and Y_Q was the average nutrient concentration of the flow-weighted river end-member. Nutrient fluxes were reported in moles per second. Fluxes into the estuary were positive values; fluxes out of the estuary were negative.

$$Y_Q V_Q + (Y_O - Y_E) V_X - \frac{(Y_O + Y_E)}{2} V_Q = 0 \quad (14)$$

Equation (15) was used to describe the mass conservation of salt with the estuary, where S_O , S_E , and S_Q were ocean (44.65° N 124.18°W), average estuary, and flow-weighted river end-member salinities, respectively.

$$S_Q V_Q + (S_O - S_E) V_X - \frac{(S_O + S_E)}{2} V_Q = 0 \quad (15)$$

Solving for V_X , the water exchange between the ocean and the estuary was described by equation (16).

$$V_X = V_Q \frac{(S_O + S_E - 2S_Q)}{2(S_O - S_E)} \quad (16)$$

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