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STABLE ISOTOPIC INDICATORS OF NUTRIENT SOURCES IN A TEMPERATE NORTH PACIFIC ESTUARY, OREGON, USA.

Sigleo\*, A.C., Visual Plumes Consulting, 1541 NW Spring St, Newport, Oregon 97365

ABSTRACT

The distributions of δ13C and δ15N in suspended particles were examined monthly over a two year period at ten stations along a 60 km transect of the Yaquina River and Estuary, Oregon. The objective of this work was to define annual dissolved nutrient budgets for an estuary in the northwestern part of the U.S. under various scenarios for watershed rainfall/runoff conditions. Organic material in estuaries is a mixture of land-derived and oceanic carbon and nitrogen. In addition, *in situ* biological processes both produce and consume organic components. In the Yaquina estuary both δ13C and δ15N in planktonic material increased from the freshwater terrestrial region of the river downstream to the Pacific Ocean. Isotopic carbon increased from -27.7 ± 1.4 to -22.1 ± 1.5 per mil δ13C between the freshwater terrestrial region of the river to the Pacific Ocean. Particulate nitrogen increased from 2.6 ± 1.0 per mil δ15N in the freshwater region to 7.2 ± 1.4 per mil δ15N at the ocean. Relative to salinity, the isotopic increases were linear during winter and early spring indicating that simple mixing of the two end members was occurring. During summer, the isotopic increases were increasingly non-linear, indicating that processes in addition to simple mixing of the two end members were occurring. Isotopic data suggest that river outflow provided a source of nutrients in the freshwater portion of the estuary, whereas heterotrophic remineralization and nutrient recycling were important in the tidal regions of the estuary in the summer.

INTRODUCTION

Both the seasonal and spatial patterns of the del15N of microalgae from plankton tows suggested that there was a range of sources of nitrate for primary production in the Yaquina estuary. During periods of high rainfall and river runoff, the surrounding watershed was the most likely source of dissolved carbon and nitrogen. During the summer, upwelling of nutrients along the Pacific Coast can provide nitrate that was tidally introduced to the lower estuary. Even in summer, river nitrate continued to provide nitrogen in the upper reaches of the river and a steady drawdown is observed throughout he summer and early Fall. A “hump” in the forest to sea isotope graph suggested that the algae were increasing consuming the dregs of nitrate that contained higher 15N.

The Yaquina watershed is classified as forested, although in fact it consists predominantly of single species, douglas fir, silviculture (Noble and Dirzo, 1997; Ohmann and Gregory, 2002; Wimberely and Ohmann, 2004). Logged areas frequently are colonized by pioneer broad-leaved trees, primarily red alder. Red alder (*Alnus* spp.) converts atmospheric nitrogen to bioavailable nitrogen in alder roots via the symbiotic relationship with the actinomycete *Frankia* spp (Vogal and Gower, 1998). As a result, in heavily logged areas of the Pacific Northwest, leaching from decayed alder litter now is a major source of nitrate to coastal rivers, including the Yaquina (Compton et al., 2003; Sigleo et al., 2010).

Previously nitrogen in coastal Oregon rivers came from the decay of anadromous salmon carcasses (Bilby et al., 1996; Koyama et al., 2005; Scheuerell et al., 2005). Annual fish returns, however, have decreased to 8% or less of historical numbers (Gresh et al., 2000; Meengs and Lackey, 2005). The combination of decreased fish returns and increased timber harvesting altered the primary source of watershed nitrogen from anadromous fish decay to alder litter decay (Gresh et al., 2000; Compton et al., 2003; Tiegs et al., 2008). Domestic sewage discharge and agricultural runoff presently are minor sources of nitrogen in ssolved carbon and nitrogen. During his system due to low population density and the dominance of silviculture (Wimberely and Ohmann, 2004; Brown and Ozretich, 2009; Sigleo et al., 2010). Yaquina Bay has a major commercial fishery, and the intertidal areas provide primary habitat for shellfish, oyster aquaculture, and migratory birds (Lamberson et al., 2011). Commercial fisheries, shellfish aquaculture, and tourism all require high standards of water quality. The USEPA lists high nutrient concentrations, particularly that of nitrogen, as a major cause of impairment in rivers and streams in the United States (USEPA, 2006). For these reasons, understanding nitrogen sources and sinks is essential to the management of nitrogen in estuaries and coastal waters.

The goal of the following study was to determine the spatial and temporal variability of water column nitrate, and organic carbon and nitrogen concentrations in suspended sediments. The stable isotopic composition of carbon and nitrogen in suspended sediments were measured to provide information on the marine and watershed contributions of carbon and nitrogen, and on the trophic level of nitrogen (Fry et al., 2003; Carmichael and Valiela, 2005). Isotopes also integrate nitrogen dynamics at longer scales than nutrient concentrations alone and may provide a historical perspective on sediment nitrogen sources (Fry et al., 2003).

**Methods**

Study Area

The Yaquina Bay empties into the Pacific Ocean at Newport, Oregon (44.6oN, 124.0oW, Fig. 1). The estuary has a semi-diurnal tidal regime with diurnal inequalities, and a mean tidal range of 2.4 m (NOAA Station 9435380)**.** Seagrasses, macroalgae and benthic diatoms form dense patches in the intertidalzones and provide net sinks for nitrate, particularly during the summer growing season (Larned, 2003; Kentula and DeWitt, 2003; Sin et al., 2007; Weilhoefer et al., 2015).

TheOregon Coast has a maritime climate with wet winters and cool dry summers. Yaquina River discharge averages 6.9 m3 sec-1, although flows can vary from 0.062 m3 sec-1 during late summer low flow conditions to 186 m3 sec-1 during storm events (http://apps.wrd.state.or.us/apps/sw/hydro\_near\_real\_time/display\_hydro\_graph.aspx?station\_nbr=14306030). River discharge is high in late fall, winter and early spring (November to April) and low the remainder of the year. Nitrate export from the river to the estuary also is strongly seasonal with up to 94% of river nitrate export occurring during the winter season when biological productivity is minimal (Sigleo and Frick, 2007). The Yaquina River discharges between 266 and 1210 metric tonnes of dissolved nitrate annually into the Yaquina estuary near the head of tide at Elk City (Sigleo and Frick, 2007). The annual load varies relative to rainfall with greater nitrate being exported in wetter years and less nitrate exported during drought years (Sigleo and Frick, 2007). The amount of both dissolved and particulate carbon exported from Oregon streams also varies relative to rainfall and stream flow (Argerich et al., 2016).

Another source of nitrate in Pacific Northwest estuaries comes from ocean upwelling during spring and summer. Coastal upwelling is a seasonal occurrence in response to northerly winds that bring cold, nutrient-rich water to the surface along the Oregon coast (Barth et al., 2000; Colbert and McManus, 2003; Du and Peterson, 2014). Summer upwelling events provide twice daily pulses of nutrient-rich water that supplement nutrient depleted waters in coastal bays and estuaries (Small and Menzies, 1981; Sigleo et al., 2005; Brown and Ozretich, 2009).

Sample collection

Surface water samples were collected approximately monthly from September 1999 through December 2001 at ten stations beginning at the mouth of the Yaquina estuary near the OSU dock, six stations approximately 10 km apart along the estuary, the Elk City floating public dock, located nesr the confluence of the Yaquina River and Elk Creek; at the USGS stream gage 14306030 (presently operated by Oregon Water Resources Department near Chitwood, OR (Lat 44 39 29 N Long 123 50 15 W); and at the Eddyville bridge (Fig. 1). During the summer of 2001 samples also were collected in the Pacific Ocean surf zone north of the north jetty.

Water samples for nutrients and suspended sediments were collected by submersion of 10 liter Nalgene carboys. Water samples collected for dissolved nutrients (nitrite, nitrate + nitrite, ammonium, phosphate and silicate) were filtered (Cole Parmer 142mm nylon filter membranes), and frozen for later analysis by the Marine Science Institute (MSI), University of California, Santa Barbara, CA using a Lachat QwickChem 8000 Autoanalyzer for simultaneous determination of nitrite, nitrate + nitrite, ammonium, phosphate and silicate (Strickland and Parsons, 1977). Analytical information, including blank procedures, sample replicate results and other quality assurance details are available at [www.msi.ucsb.edu/Analab](http://www.msi.ucsb.edu/Analab).

Suspended sediments for organic carbon and nitrogen concentrations and carbon and nitrogen isotopic analyses were collected by filtration on glass fiber filters, freeze dried and stored in a desiccator until analysis. Suspended sediment samples were analyzed for δ 15N and δ 13C on an isotope ratio mass spectrometer (Delta plus, Finnigan, Bremen, Germany) interfaced with an elemental analyzer (ECS 4010, Costech, Valencia, CA), located at the Integrated Stable Isotope Research Facility at the Western Ecology Division of the EPA, Corvallis, Oregon. Measurement precision and accuracy were 0.04 ‰ and 0.23 for δ 13C, and 0.12 ‰ and 0.20 for δ 15N as determined by standards run with the study samples (J. Compton, pers. communication).

Dissolved oxygen, salinity and temperature were measured in the field with a Yellow Springs Instruments (YSI, Yellow Springs, Ohio) Model 85 O2, conductivity, temperature meter at the same time the sediment samples were collected. Statistical analyses and graphics were performed with Microsoft Excel and Sigma Plot 10.

**Results**

Water Column Characteristics

Dissolved nitrate values varied seasonally with concentrations increasing rapidly with the first major Fall storm and continuing to increase with increasing river discharge through the winter (Fig. ). Dissolved nitrate varied from 1 in late Fall to 125 µmol l-1 with largest values coinciding with high river discharge during the winter storms. The lowest nitrate values occurred in early fall prior to the winter rains (Fig. ).

Dissolved silica varied from 15 µmol l-1 in the summer at the ocean area to over 200µmol l-1 in the river during the winter (Fig. ). Silica concentrations, greater than those of nitrate, were sufficient to promote healthy diatom growth. Ammonium and phosphate mean concentrations varied from 0.34 to over7 µmol l-1 and 0.21 to 1.7 µmol l-1 respectively (Fig. ). Water column temperature varied from 8 to10o C during the winter, and increased to 22o C in July and August. Salinity ranged from 0.07 in the freshwater river to over 34at the ocean. Salinity ranges in theestuarine mixing zone were in the intermediate range of 16 to 20.

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## Sediment Characteristics

The sediments at Stable carbon isotope values for δ13C were -26.0 ± 0.77 in suspended sediments and -25.9 ± 0.37 in benthic sediments (Fig. 4). The similar values for δ13C between suspended and benthic sediments suggest resuspension and mixing occurred during tidal inflow. The carbon isotopic data showed an increase from -27 δ13C in the freshwater river to -21.5 δ13C at the seawater site (Fig. ). The nitrogen stable isotope values were 3.72 ± 0.31 δ15N in suspended sediments (Fig. ). The nitrogen isotopic values from the freshwater to the ocean influenced intertidal area increased from 3.8 to 5.4 δ15N in suspended sediments.

Discussion

Benthic nitrogen sources

In Yaquina Bay benthic nitrate fluxes ranged from –122 to -4 mol N m-2 hr-1, whereas ammonia fluxes ranged from –52 to 101 mol N m-2 hr-1 (Sin et al., 2007). The sediments were always a net sink for nitrate and nitrate uptake rates were highest during the warmest month (August) and lowest during the coolest months (November and January). Ammonium was generally released from sediments into the water column in the dark, whereas in the light it was utilized by benthic microalgae at the sediment-water interface (Sin et al., 2007). Because benthic microalgae at the sediment–water interface utilized ammonia, orthophosphate and silicate in the light, the results suggest the benthic N contribution was minimal, although additional studies are needed to support the result (Sin et al., 2007)

Middleburg and Herman (2007) noted that the processing of organic matter in tidal estuaries occurs under dynamic conditions. The tidally induced repetitive cycles of resuspension and deposition of estuarine particles transform and degrade riverine organic matter, and sustain the heterotrophic status of estuaries (Middleburg and Herman, 2007). This was reflected in the stable carbon isotope values between suspended (-26.0 ± 0.77 δ13C) and benthic (-25.99 ± 0.37 δ13C) sediments, suggesting resuspension and mixing during tidal inflow. The carbon isotopic data increased from -27 δ13C in the freshwater river at Elk City to -21.5 δ13C at the seawater site. This is a typical increase indicating a greater proportion of upland C-3 plants (-31 to -27.5 δ13C) in the freshwater region relative to a greater amount of plankton (-22.5 to -20 δ13C) in seawater particles (Coffin et al., 1989).

The stable isotope values for nitrogen in suspended sediments averaged 3.72 ± 0.31 δ15N. The nitrogen isotopic values increased from 3.8 to 5.4 δ15N in the suspended sediment from the freshwater to ocean influenced intertidal area. Biological processes, including denitrification, discriminate for molecules containing the lighter isotope 14N relative to the heavier isotope 15N (Mariotti et al., 1981). For that reason, the isotopic composition of the remaining nitrate becomes enriched in 15N. Owens (1985) noted that the 15N content of suspended particles in estuaries reflects the effects of both hydrodynamic mixing of freshwater and ocean sources as well as biological transformations within the estuary. Increased residence time increases microbial degradation leading to higher 15N values in the refractory nitrogen (Carmichael and Valiela, 2005).

Residence time effects

The extent to which organic material and nutrients are modified in an estuary depends on residence time.The Pacific seaboard is typified by steep mountain slopes, cliff-dominated shorelines, and streams and small rivers that flow rapidly to the sea and are likely to be relatively short and tidally mixed (Uncles and Smith 2005). The Yaquina has an average tidal range of 2.4 m over a length of 37 km (Uncles and Smith 2005). During late summer low flow conditions, the total water exchange time in the Yaquina estuary from Elk City to the mouth of the estuary was calculated at 18 tidal cycles, or a water residence time of 9 days (Choi, 1975). During winter storms when fresh water overrides the saline tidal wedge, the residence time decreases to between less than a day to five tidal cycles (Choi, 1975; Lemagie and Lerczak, 2015). Maximum nitrate concentrations also occur during this time, although due to low light there is minimal biological productivity. The stable isotope data indicate a mixing of suspended and benthic sediments from a very strong tidal prism with a rapid, forceful flooding tide causing twice daily sediment resuspension.

Secondary sewage treatment utilizes alternating nitrification-denitrification to remove nitrogen from sewage effluent worldwide (David et al., 2006). For this reason sewage effluent typically is enriched in 15N from the secondary treatment that utilizes alternating nitrification-denitrification to remove nitrogen species (Hadwen and Arthington, 2007). This effect may be seen in the slight increase in suspended sediment 15N at station TD where samples were collected below the Toledo City outfall (Fig. ).

State of the Estuary

Weilhoefer et al., (2015) found high nitrogen adapted diatom species present in coastal Oregon estuaries and side creeks, and concluded that the area was eutrophic. In fact historically, decaying salmon carcasses provided high levels of estuarine nitrogen that would have acclimated the diatoms to a relatively high nitrogen diet (Bilby et al., 1996; Koyama et al.,2005; Scheuerell et al., 2005). At the present time, returning salmon are 8% of historical returns and dissolved N is supplemented by alder litter (Gresh et al., 2000; Compton et al., 2003; Meengs and Lackey, 2005; Tiegs et al., 2008).

Previously Sin et al., (2007) concluded that despite considerable N loading from river and oceanic sources, there was sufficient biological activity, including the microalgal community, to consume nitogen and prevent eutrophication. Chemical measures for eutrophication using nutrient concentrations and isotopic values in West Coast estuarine sediments found δ15N values of 9-11‰ in eutrophic estuaries, considerably greater than values of 3.7 to 4‰ δ15N for Yaquina Bay sediments (Fry et al., 2003). Fry et al. (2003) concluded that regional factors for estuaries of the U. S. West Coast include strong tidal exchanges that decrease the impacts of watershed N.

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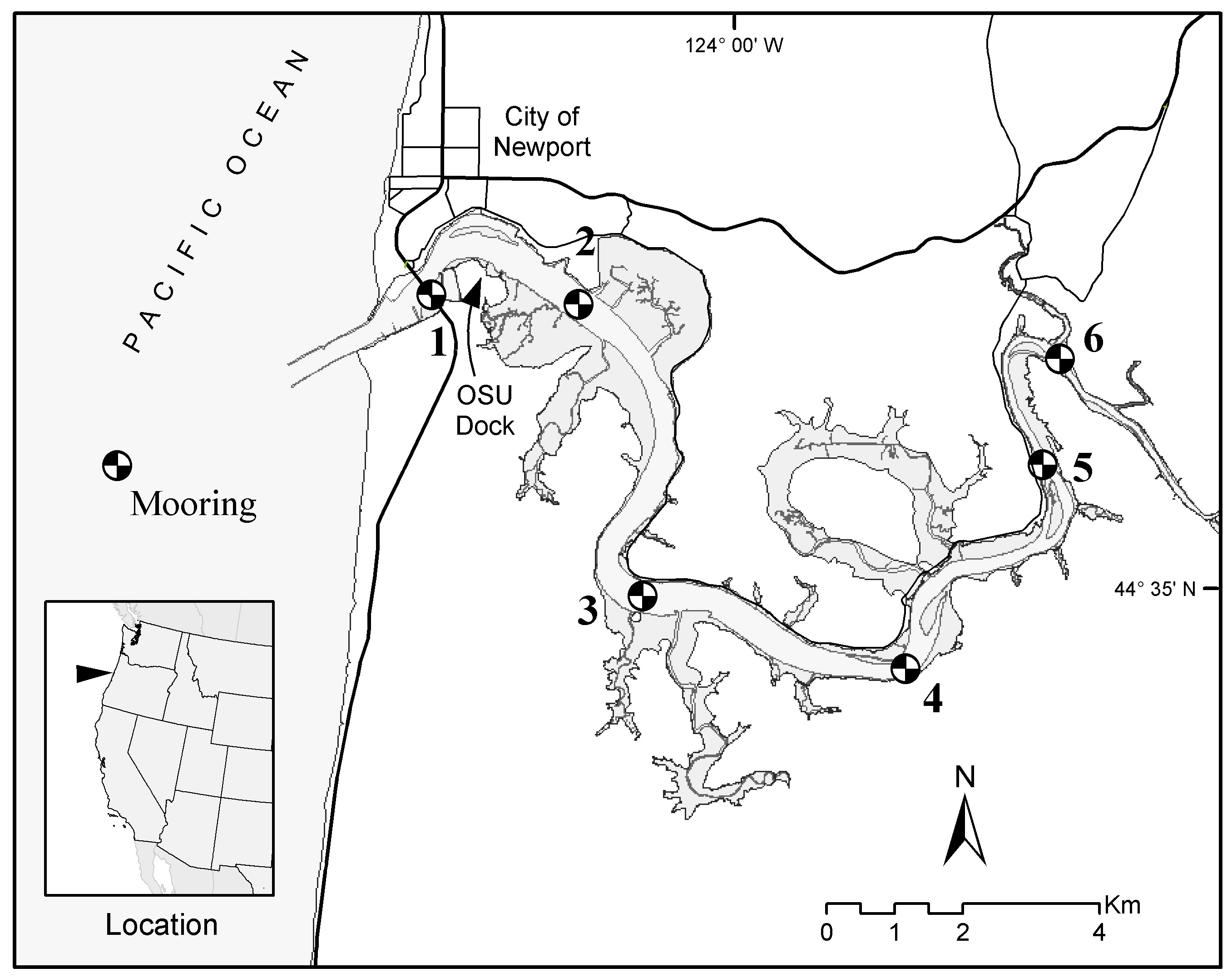
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Yaquina River nitrate-N load in kg-day-1 at Elk City.

