

Distribution and retention of effluent nitrogen in surface sediments of a coastal bay

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Abstract

Anthropogenic nitrogen (N) often causes coastal eutrophication, yet little is known about the fate and retention of effluent N in coastal waters and, hence, about the system's ability to assimilate excess N loads. We used the spatial distribution of stable N isotope ratios and algal pigments in sedimentary organic matter from a Baltic bay receiving tertiary-treated effluent to evaluate the extent of effects and the role of nearshore marine environments as sinks of anthropogenic N. Surface sediments (0–2 cm and 2–4 cm) exhibited a pronounced spatial gradient of $\delta^{15}\text{N}$, with the most elevated values ($\sim 8\%$) near the outfall; values decreased linearly to values of $\sim 4\%$ outside the bay. Sedimentary pigment concentrations were consistent with water-column data and showed that phytoplankton biomass was elevated in the inner reaches of the bay. In particular, diatoms were heavily labeled ($\delta^{15}\text{N} \sim 10\%$), reached maximum abundance near the effluent outfall, and were likely the main mechanism delivering effluent N to the sediments. Sediments within the bay removed $\sim 5\text{--}11\%$ of wastewater N inputs, with 50% of the sequestered effluent N buried in the basin nearest to the outfall. Magnitudes of N removal by sediments ($23\text{--}26 \times 10^4 \text{ kg N yr}^{-1}$) were less than those estimated for denitrification ($30\text{--}60 \times 10^4 \text{ kg N yr}^{-1}$), but they were substantially greater than biological uptake by macroalgae ($\sim 2 \times 10^4 \text{ kg N yr}^{-1}$). Taken together, these patterns demonstrate the idea that coastal sediments can be effective sinks of wastewater N, even after 30 yr of effluent input.

Anthropogenic wastewater inputs are important point-sources of nitrogen (N) that can contribute to coastal eutrophication and that are likely to be exacerbated as populations expand along coastal watersheds. Understanding the dispersal and retention of wastewater N is essential for water quality management in urban coastal areas, yet the role of coastal sediments in sequestering anthropogenic N is largely unknown (Tappin 2002).

Coastal ecosystems can remove N by biological uptake, denitrification, or permanent burial in sediments. In general, estuaries with a long water residence time (0.5–12 months) remove 30–65% of their total N inputs (Nixon et al. 1996), but the relative importance of the different N sinks and spatial variability in removal processes are poorly understood. Sedimentary denitrification is generally thought to be quantitatively the most important sink for N (Seitzinger 1988; Nixon et al. 1996) and commonly removes 20–50% of the

total N input to estuaries (Seitzinger 1988), depending on water residence time (Nixon et al. 1996) and N loading (Seitzinger 1988). In contrast, long-term storage of N within biota is considered insignificant in temperate estuaries (Boynton et al. 1995; Nixon et al. 1996; Savage and Elmgren 2004). Less is known about N burial in sediments. Models estimate that burial of particulate N can eliminate 28–53% of total N inputs (Boynton et al. 1995), and isotopic tracer studies demonstrate that $\sim 75\%$ of NO_3^- can be assimilated by diatoms and deposited in sediments during low-flow conditions (Holmes et al. 2000). These patterns indicate that coastal sediments may be important sinks for anthropogenic N in coastal areas, particularly those with long water residence times.

Stable isotopes have been used to trace effluent N in macroalgae (e.g., McClelland et al. 1997; Savage and Elmgren 2004), phytoplankton, and higher trophic levels (Hansson et al. 1997; Tucker et al. 1999) in coastal ecosystems. The approach is particularly effective when tertiary sewage treatment elevates the effluent $\delta^{15}\text{N}$ value above background values, thus distinguishing it from other N sources (Heaton 1986). Similarly, analysis of sedimentary pigments can be used to reconstruct the abundance and composition of primary producers and, therefore, ecosystem responses to nutrient inputs (e.g., Leavitt and Hodgson 2001; Bianchi et al. 2002).

This study combines sedimentary $\delta^{15}\text{N}$ and pigment analyses to model the distribution and process of large-scale burial of effluent-derived dissolved inorganic N (DIN) in coastal sediments. Estimates of N burial in sediments are compared to N removal estimates for denitrification (Elm-

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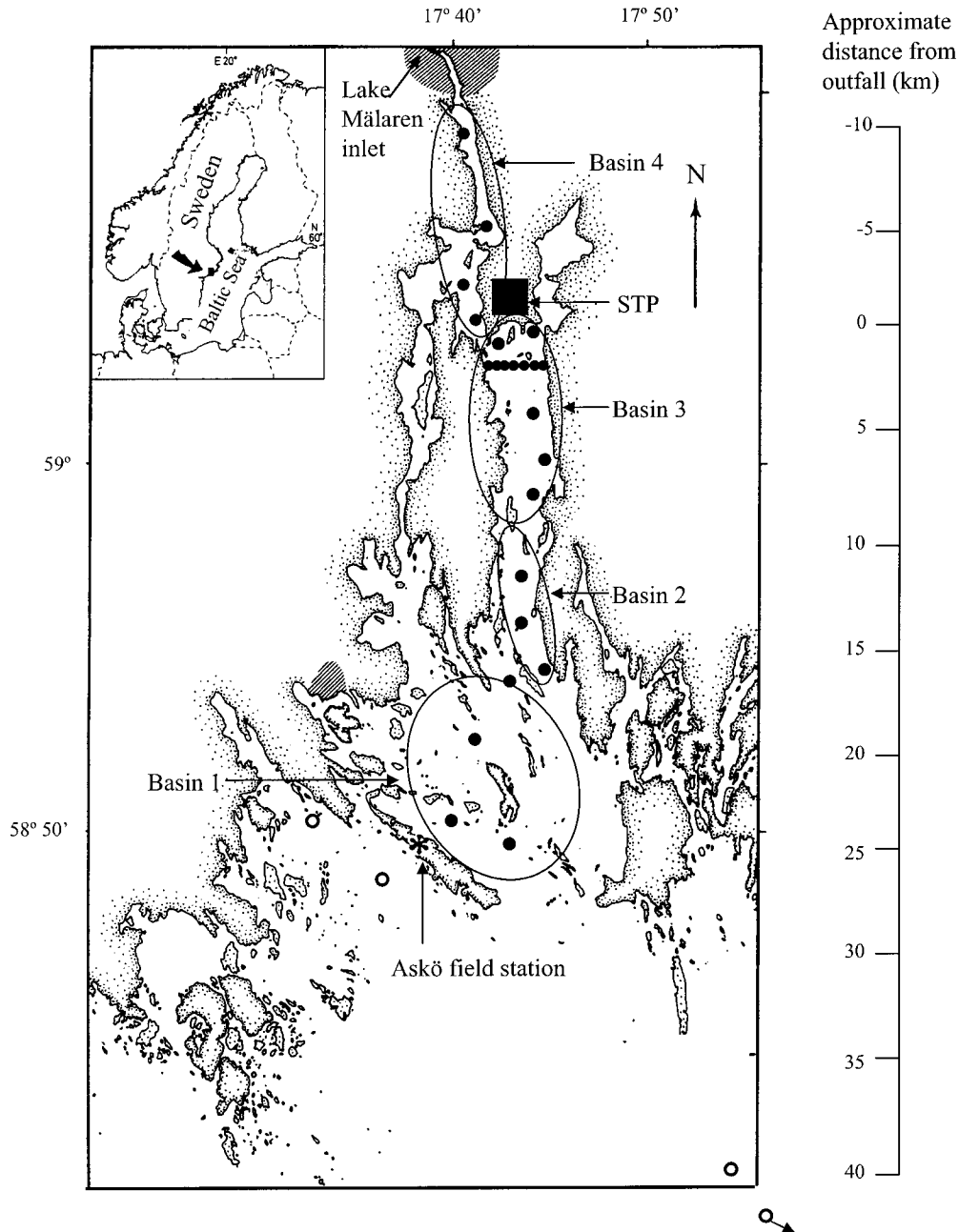


Fig. 1. Map of Himmerfjärden showing the 23 sampling sites in the bay (solid circles) and the four open Baltic sites (open circles) where surface sediments were collected and sliced at 0–2-cm and 2–4-cm intervals. One open Baltic site located southwest of the map is indicated in the lower right-hand corner. The four basins used in the N sinks calculations according to Engqvist (1996) are illustrated on the map. The approximate distance (km) from the outfall is presented alongside. Stations north of the treatment plant are presented as negative distances. STP = sewage treatment plant; * = Askö field station.

gren and Larsson 1997) and macroalgal storage (Savage and Elmgren 2004) to evaluate the relative importance of different N sinks.

Materials and methods

Site description—Himmerfjärden (59°00'N, 17°45'E) is a 232-km² coastal inlet of the Baltic Sea located ~60 km south

of Stockholm, Sweden (Fig. 1). The embayment is connected to the open Baltic in the south and to Lake Mälaren via locks in the north. The bay has a mean depth of 17 m, with a maximum depth of 52 m. It is thermally stratified in summer and commonly exhibits bottom-water hypoxia and reduced sediments in deeper areas, especially in the inner basins. The water is brackish (6‰), but unlike most estuaries, it experiences only minor salinity fluctuations ($\pm 2\%$) and lacks

tidal forcing. The bay receives tertiary-treated effluent from ~250,000 people; this effluent is discharged at approximately 25-m depth into basin 3. The bay has undergone changes in effluent N loads since the start-up of the Himmerfjärden sewage treatment plant (STP) in 1974 and has been monitored intensively since 1976 (Elmgren and Larson 1997, 2001). Progressively more people were connected to the STP during the late-1970s and 1980s, and effluent loads increased to about 8×10^5 kg total N (TN) between 1985 and 1990. Improved N reduction measures were initiated during the period extending from 1988 to 1993, and this period was followed by further denitrification (~85% N removal) in 1997, so that annual total effluent N loads in 2001 were about 3×10^5 kg TN. Effluent N is predominantly (~90%) discharged as dissolved inorganic nitrogen (DIN), which comprises ~50% ammonia and 50% nitrite or nitrate.

Sampling—Sediments were sampled with a Kajak-type gravity corer (Blomqvist and Abrahamsson 1985) at 27 sites at increasing distances from the effluent outfall. Seven cores were taken along a 3-km east–west transect (1 km from the outfall) to study local spatial variability. However, because there was little difference in sedimentary isotopes or pigments among transect sites (e.g., coefficients of variation were 5% of mean values for $\delta^{15}\text{N}$ values in 2–4 cm), only the mean values are presented in the figures, but all samples were used in regression analyses. Sediments were sectioned at 2-cm intervals and the 0–2 cm and 2–4 cm samples retained for analyses. All cores were collected in the first 2 weeks of May 2002, following the spring bloom. In three cores in which the uppermost layer consisted entirely of flocculent algal material, the top 2 cm were designated “flocculent layer,” and the more consolidated material below was termed 0–2 cm and 2–4 cm. Samples were frozen and stored at -20°C in the dark until processed (within a month).

Analyses—Subsamples (~5 mg) of bulk sediments were freeze-dried and homogenized for analysis of stable nitrogen isotope ratios ($\delta^{15}\text{N}$) and elemental content using a Thermoquest (Finnigan-MAT) Delta Plus^{XL} mass spectrometer interfaced with a Carlo Erba NC2500 elemental analyzer. Nitrogen stable isotope ratios are reported in the conventional δ notation with respect to atmospheric N (Mariotti 1983) and were standardized with the use of calibrated organic standards (e.g., wheat, lake sediment). Reproducibility of N isotope analyses was better than $\pm 0.25\%$.

Most of the remaining bulk sediment samples were lyophilized and extracted for pigments using a mixture of acetone:methanol:water (80:15:5 by volume) following the extraction protocol of Leavitt and Findlay (1994). Extracts were filtered and dried and concentrations determined in each sediment interval using a Hewlett Packard 1050 high-performance liquid chromatography (HPLC) system calibrated with authentic standards from the U.S. Environmental Protection Agency, using procedures detailed in Leavitt and Hodgson (2001). Pigments identified included those characteristic of total algae (β -carotene, chlorophyll *a* (Chl *a*), pheophytin *a*), siliceous algae and some dinoflagellates (fucoxanthin), diatoms (diatoxanthin), cryptophytes (alloxanthin), and colonial cyanobacteria (canthaxanthin). Ratios of

Chl *a* to pheophytin *a* were calculated to assess the degree of preservation of labile pigments (Leavitt and Hodgson 2001). Pigment concentrations are expressed as nmoles pigment g^{-1} organic matter (OM). Organic matter (OM) content, determined as mass loss-on-ignition (LOI) at 500°C , was highly correlated (0–2 cm: $r^2 = 0.90$; 2–4 cm: $r^2 = 0.93$) to C content, determined on a Carlo Erba NC2500 elemental analyzer, reflecting low carbonate content and relatively stable mineral composition within the bay.

Effluent N burial in sediments—To estimate effluent N burial in sediments, we calculated the amount of effluent N (kg N yr^{-1}) retained in the sediments of each of the four basins of the bay (Fig. 1; Engqvist 1996) as follows: First, we assumed that the mean %N and $\delta^{15}\text{N}$ values of the cores within each basin were representative of the depositional zone for that basin, consistent with the transect in basin 3. Second, we assumed that permanent sediment accumulation occurred at depths with recorded seasonal anoxia (Elmgren and Larsson 1997) or laminated sediments (observed during sampling), corresponding to depths below 10 m in basin 4, below 20 m in basin 3, and below 35 m in basins 1 and 2. These zones are known to have low densities of benthic macrofauna (Savage and Elmgren 2004) and, hence, little bioturbation or mineralization by metazoans. Third, mass accumulation rates in depositional areas were assumed to be $0.2 \text{ g cm}^{-2} \text{ yr}^{-1}$ for basins 3 and 4 and $0.1 \text{ g cm}^{-2} \text{ yr}^{-1}$ for basins 2 and 1, based on annual laminae and radiometric (^{210}Pb , ^{137}Cs) analyses (Bianchi et al. 2002; Savage unpubl. data). Thus, we calculated the mass accumulation of total N (TN) in 0–2 cm and 2–4 cm in each basin (kg TN yr^{-1}) as:

$$\% \text{N} \times \text{mass accumulation rate} \times \text{accumulation area} \quad (1)$$

The fraction of TN derived from effluent inputs (*X*) was estimated for the 0–2-cm and 2–4-cm intervals of each basin using the average sedimentary $\delta^{15}\text{N}$ values for each basin and a two-source isotopic mixing model (Tucker et al. 1999):

$$\delta^{15}\text{N}_x = X(\delta^{15}\text{N}_{\text{effluent}}) + (1 - X)(\delta^{15}\text{N}_y) \quad (2)$$

where $\delta^{15}\text{N}_x$ is the mean sedimentary $\delta^{15}\text{N}$ value for each basin, $\delta^{15}\text{N}_{\text{effluent}}$ is the isotopic value of effluent DIN from the Himmerfjärden treatment plant ($\delta^{15}\text{N}_{\text{effluent}} = 38\%$), and $\delta^{15}\text{N}_y$ is the isotopic value of Baltic proper marine DIN ($\delta^{15}\text{N}_y = 4\%$) (Savage and Elmgren 2004). We assumed that postdepositional alteration of the primary $\delta^{15}\text{N}$ signal was minimal, in accordance with incubation experiments that showed OM $\delta^{15}\text{N}$ was unaltered during oxic degradation (Lehmann et al. 2002) and with the relative absence of benthic macrofauna in anoxic regions. However, because anoxic decay can deplete $\delta^{15}\text{N}$ values by ~3‰ (Lehmann et al. 2002), our analyses may underestimate the amount of effluent N burial in the anoxic inner basins. Sedimentary burial of effluent N ($\text{kg effluent N yr}^{-1}$) was calculated for each basin by multiplying the percent effluent N (Eq. 2) by the total N mass accumulation (Eq. 1). In this way, we could compare N burial rates with known N loads to estimate spatial variability of effluent N burial.

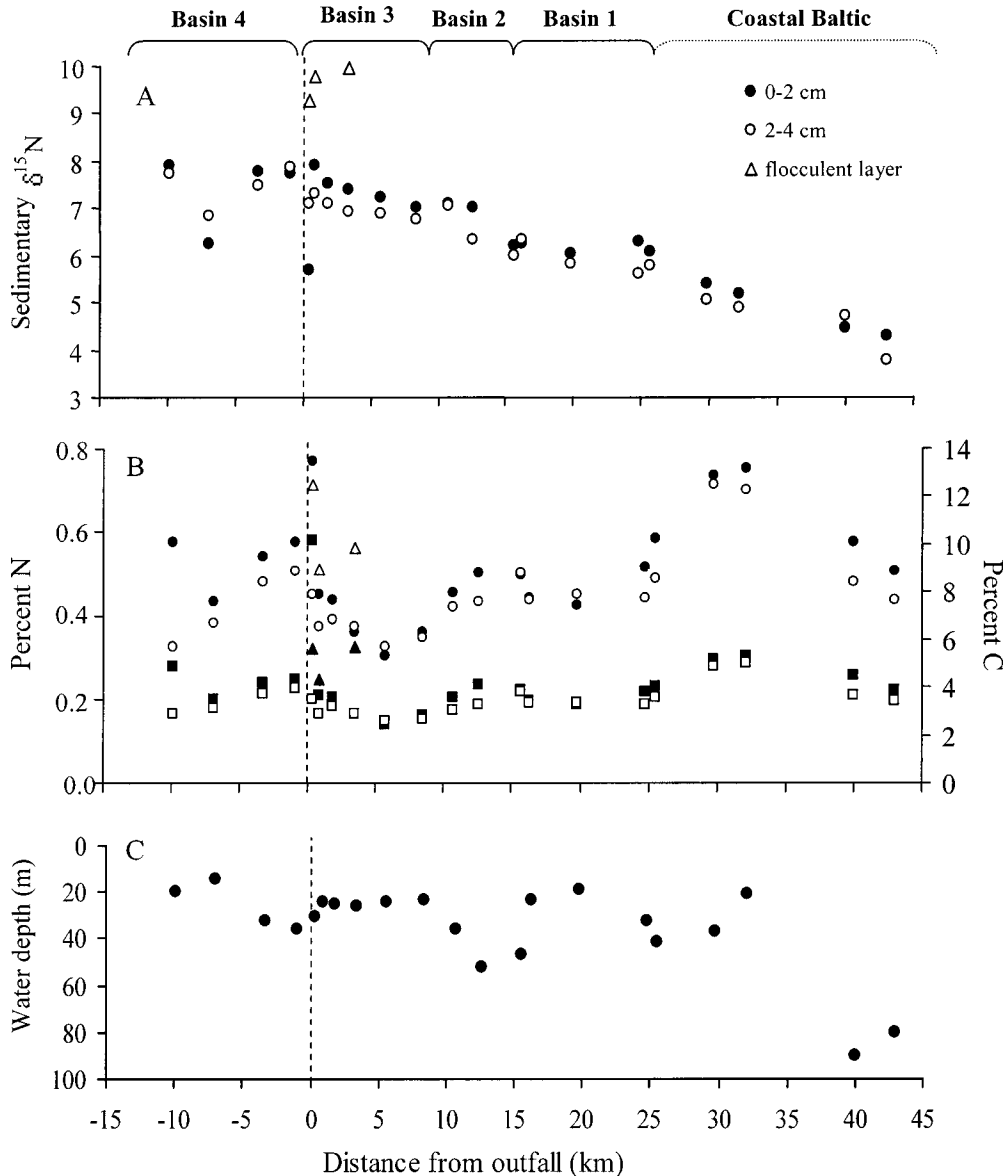


Fig. 2. (A) Spatial patterns in nitrogen stable isotope ratios ($\delta^{15}\text{N}$) in surface sediments as a function of distance (km) from the sewage outfall. Stations north of the outfall are denoted as negative distances. The position of the sewage treatment plant is indicated by a dashed line and the four basins are superimposed. Stable isotope ratios for the 0–2-cm, 2–4-cm, and flocculent layer samples are presented individually. (B) Percent N and percent C in surface sediments as a function of distance (km) from the outfall. Percent N values presented as circles on the primary y-axis and percent C values presented as squares on the secondary y-axis. Solid markers refer to 0–2-cm samples and open markers refer to 2–4-cm samples. (C) Water depth (m) at the sampling stations.

Results

General description—Sediments had high OM content ($9.6 \pm 0.4\%$ on average), and flocculent layer samples had even higher OM content ($26 \pm 6\%$). Molar C:N ratios were 9.0 ± 0.1 on average and were consistent throughout the bay, except at the station nearest the outfall (C:N = 15). Both C and N contents were elevated within 0.5 km of the outfall, in the coastal Baltic and in cores from stations deeper than 40 m (Fig. 2). The presence of laminations at most

stations within 10 km of the sewage outfall attests to persistent anoxia of the surface sediment. Cores from deeper stations (>40 m) in basin 2 had laminations downcore, indicating previous anoxia. At outer stations in Himmerfjärden, laminations were absent, and the presence of macrofauna attested to better bottom-water oxygen conditions.

Stable isotopes—Sedimentary $\delta^{15}\text{N}$ values exhibited a pronounced spatial gradient from $\sim 8\%$ near the outfall to $\sim 4\%$ at the mouth of the bay (Fig. 2A). Sediment $\delta^{15}\text{N}$ was

generally elevated ($>7\text{‰}$) up to 12 km from the outfall, with the most-enriched samples found in the vicinity of the outfall. Beyond 15 km seaward, $\delta^{15}\text{N}$ values continued to decrease to values of $\sim 4\text{‰}$ outside the bay. Where present, flocculent samples were $\sim 2.5\text{‰}$ more enriched in $\delta^{15}\text{N}$ than in deeper layers. Similarly, 0–2-cm intervals were more enriched than the 2–4-cm layers at comparable sites (sign test, $p < 0.05$). Apparently, modern spatial gradients of N isotopes did not arise from natural processes, as analysis of sediments from ca. 1970 (pre-STP) revealed that $\delta^{15}\text{N}$ values varied little among sites located at -5 km ($\sim 5.2\text{‰}$), -2 km ($\sim 6.0\text{‰}$), and 7.5 km (5.7‰) (Savage unpubl. data), despite signals of $\sim 8\text{‰}$ in inflowing water from Lake Mälaren (Renberg et al. 2001).

There was a significant negative relationship between sedimentary $\delta^{15}\text{N}$ and distance from the outfall (0–2 cm: $r^2 = 0.58$, $p < 0.05$; 2–4 cm: $r^2 = 0.56$, $p < 0.05$). There was no correlation between water depth and $\delta^{15}\text{N}$ in surface layers or deeper intervals, but there was a significant positive relationship between %N in deeper layers (2–4 cm) and water-column depth ($r^2 = 0.22$, $p < 0.05$), possibly because of sediment focusing. Otherwise, neither N nor C content was related to distance from the outfall or water-column depth.

Sedimentary pigments—Concentrations of sedimentary pigments indicative of total algal biomass decreased from north to south along the bay. Sedimentary β -carotene concentrations were greatest (>200 nmol g^{-1} OM) near the Lake Mälaren outlet, declined to ~ 150 nmol g^{-1} OM near the outfall, and declined to <100 nmol g^{-1} OM beyond 5 km seaward (Fig. 3). Concentrations of Chl *a*, its degradation products, and pheophytin *b* were also elevated in basin 4. However Chl *a* preservation (Chl *a*: pheophytin *a*) was poor, except at deep stations.

Concentrations of biomarker pigments indicated that diatoms were the predominant algal group, with fucoxanthin being 200–300% more abundant than most other carotenoids (Fig. 4), despite its higher chemical lability (Leavitt and Hodgson 2001). Fucoxanthin concentrations in more-consolidated sediments were greatest near the outfall (up to 700 nmol g^{-1} OM) and at deep (>35 m) stations in basin 2 (~ 500 nmol g^{-1} OM). Concentrations of this pigment were greater in the surface (0–2 cm) than in the deep layers (2–4 cm), indicating some postdepositional degradation (c.f., Bianchi and Findlay 1991). Elevated concentrations of fucoxanthin (up to 400 nmol g^{-1} OM) and trace amounts of diatom-specific diatoxanthin were the only carotenoids isolated from the flocculent material. Diatoxanthin was abundant in basin 4 (up to 200 nmol g^{-1} OM) and was present at moderate levels in sediments from the open Baltic (100–150 nmol g^{-1} OM).

Pigments from cryptophytes (alloxanthin) and from green algae and cyanobacteria (lutein–zeaxanthin) were low throughout the bay, but exhibited their greatest concentrations in sediments from basin 4 (>60 nmol g^{-1} OM). Although we could not separate lutein (green algae) from zeaxanthin (cyanobacteria) on our HPLC system, the low concentrations of the other cyanobacterial pigment (canthaxanthin) and elevated concentrations of pheophytin *b* (Fig. 3) in basin 4 indicate that high concentrations of lutein–

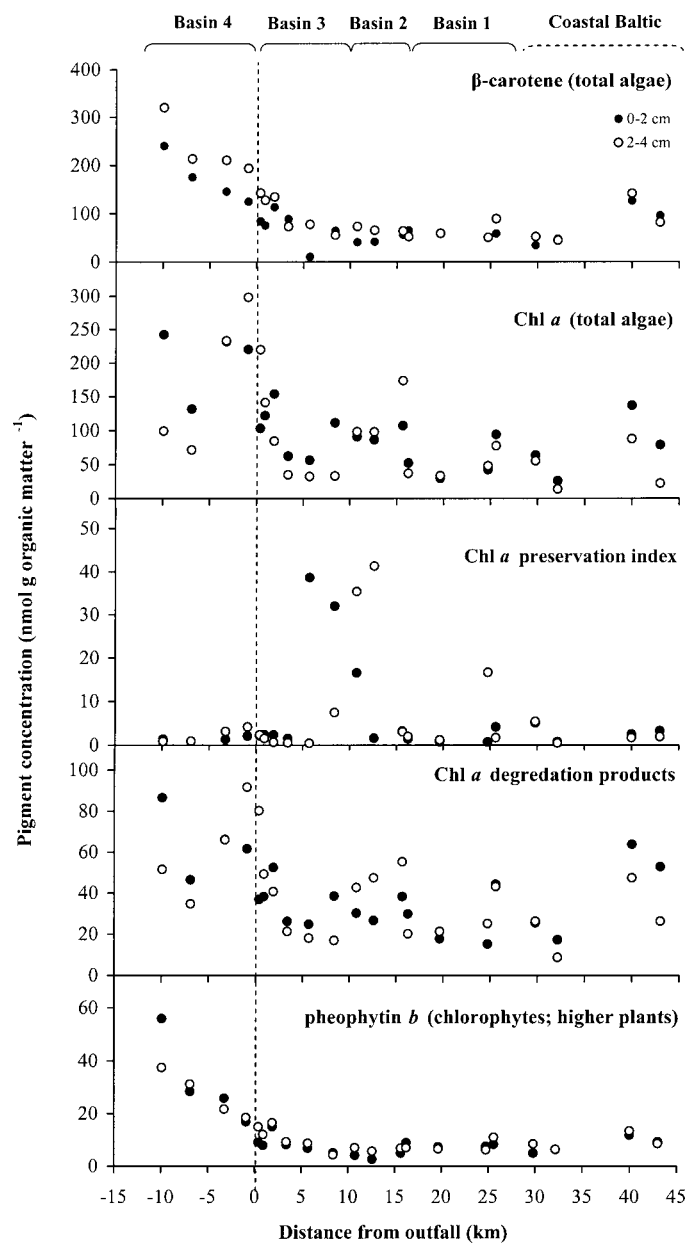


Fig. 3. Sedimentary pigment concentrations for total algal abundance (β -carotene, chlorophyll *a*), Chl *a* degradation products, and chlorophylls and higher plants (pheophytin *b*), normalized to percent organic matter (nmol pigment g OM^{-1}) as a function of distance (km) from the sewage outfall. The Chl *a* preservation index (Chl *a*: pheophytin *a* ratio) is also presented. Concentrations for the 0–2-cm and 2–4-cm intervals indicated separately. Note the different scales for pigment concentrations along the y-axis.

zeaxanthin near the L. Mälaren inlet were derived mainly from chlorophyte algae. Unlike most the other studied pigments, levels of canthaxanthin (cyanobacteria) were not particularly elevated in basin 4.

N sequestration in sediments—Mass balance calculations estimated that $23\text{--}26 \times 10^4$ kg of total N was retained in the sediments throughout the bay (Table 1). This value is equivalent to $\sim 25\%$ of the total N inputs in 2001, estimated

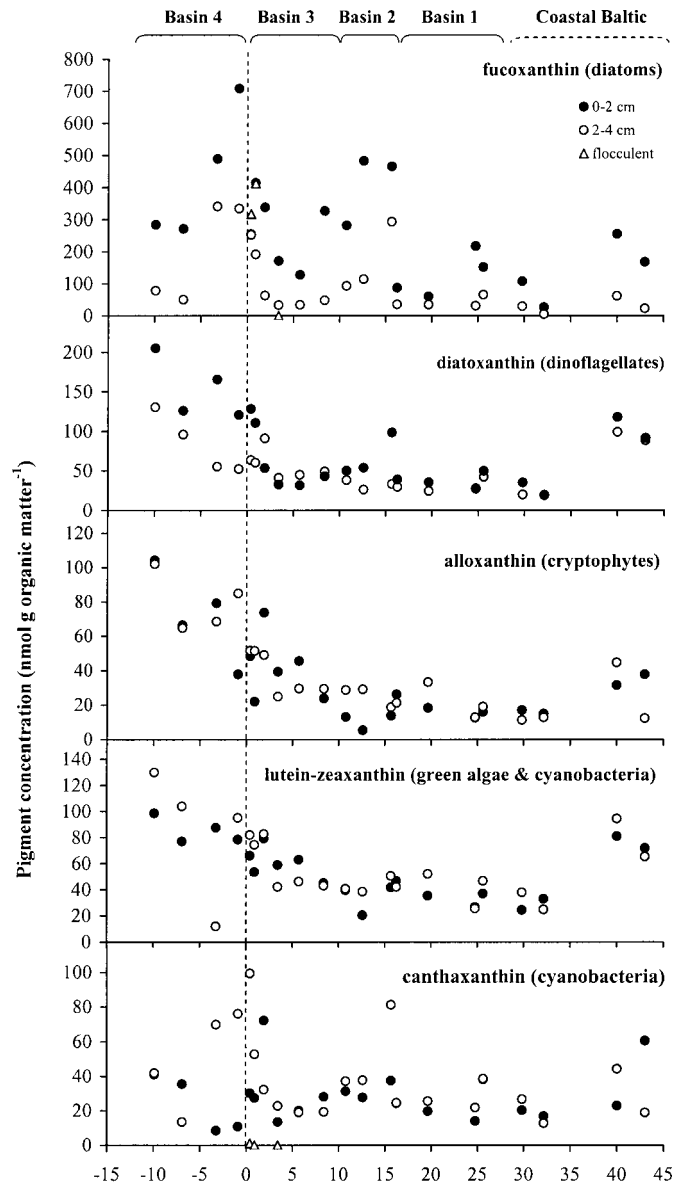


Fig. 4. Sedimentary carotenoid pigment concentrations for different algal classes normalized to percent organic matter ($\text{nmol pigment g OM}^{-1}$) as a function of distance (km) from the sewage outfall. Pigments identified include fucoxanthin (siliceous algae, mostly diatoms), diatoxanthin (diatoms), alloxanthin (cryptophytes), lutein-zeaxanthin (greens and cyanobacteria), and canthaxanthin (colonial cyanobacteria). Note the different scales for pigment concentrations along the y-axis.

as $\sim 100 \times 10^4$ kg N from all sources (STP, catchment runoff, L. Mälaren inflow, atmospheric sources). Based on isotopic-mixing models (see Materials and methods), burial of effluent N was estimated as $\sim 1.7\text{--}2.2 \times 10^4$ kg N for the whole bay, which is 5–11% of the total effluent N inputs ($15\text{--}32 \times 10^4$ kg effluent N yr^{-1}). Overall, the basin nearest the outfall (basin 3) was responsible for half of all effluent N burial ($\sim 1.0\text{--}1.3 \times 10^4$ kg), whereas basin 4 assimilated $0.4\text{--}0.5 \times 10^4$ kg of effluent N. In contrast, basins 1 and 2 retained only about $0.1\text{--}0.2 \times 10^4$ kg of annual effluent loads.

Discussion

Delineating effluent influence—Surface sediment $\delta^{15}\text{N}$ values reflected a gradient of decreasing influence of anthropogenic N with distance from the outfall. This pattern is consistent with water-column monitoring in Himmerfjärden (Larsson and Hagström 1982) and surveys of coastal sediments in the southern Baltic Sea (Struck et al. 2000; Voss et al. 2000). The influence of effluent N was most pronounced in the innermost basins, with sedimentary $\delta^{15}\text{N}$ values generally above 7‰ within 12 km of the outfall (Fig. 2A), in agreement with macroalgal $\delta^{15}\text{N}$ values in Himmerfjärden (Savage and Elmgren 2004). The station nearest the L. Mälaren inlet also exhibited heavy sedimentary $\delta^{15}\text{N}$, indicating a possible additional input of enriched N from L. Mälaren, where recent sediments have $\delta^{15}\text{N}$ values of $\sim 8\text{‰}$ (Renberg et al. 2001). Thus, we cannot rule out the possibility that some transfer of N from L. Mälaren has contributed to the enriched N in sediments near the inlet, although the overall trend indicates that this is only a localized effect. Moreover, although the volume of freshwater discharged into Himmerfjärden from L. Mälaren ($\sim 187 \times 10^6$ m^3 yr^{-1}) is, on average, five times greater than the volume discharged by the treatment plant ($\sim 37 \times 10^6$ m^3 yr^{-1}), TN load in the wastewater (738×10^3 kg TN yr^{-1} ; 1980–1992) was about nine times higher than that from L. Mälaren (87×10^3 kg TN yr^{-1} ; 1980–1992) (Elmgren and Larsson 1997). Further, the absence of a defined gradient in sediments deposited prior to ca. 1970, despite elevated $\delta^{15}\text{N}$ in L. Mälaren at that time (Renberg et al. 2001), indicates that present-day gradients in N isotopes arise from effluent inputs since the initiation of the STP. Thus, we assume that the isotopic gradient in Himmerfjärden primarily reflected a decreasing contribution of effluent N seaward.

We surmise that the isotopic gradient recorded in Himmerfjärden surface sediments mainly reflected a decreasing fraction of effluent N with distance from the outfall rather than differences in isotopic discrimination due to biogeochemical processes. The isotopic composition of DIN can be modified by nitrification, denitrification, algal uptake, and remineralization, with seasonal variations in the relative processes (Cifuentes et al. 1989). Thus, separating the effects of biogeochemical processes from eutrophication signals is not a straightforward process (Cornwell et al. 1996). However, rather than causing a decline in sedimentary $\delta^{15}\text{N}$ with distance from the sewage outfall, denitrification in the water column (Cifuentes et al. 1989; Bratton et al. 2003) and in sediments (Lehmann et al. 2003) could be expected to substantially increase (up to 40‰; Montoya 1994) the $\delta^{15}\text{N}$ in the residual DIN pool. Denitrification is a strongly discriminatory process that releases $^{14}\text{N}_2$ or $^{14}\text{N}_2\text{O}$ as gas in preference to $^{15}\text{N}_2$ (Heaton 1986). Any remaining residual N will be heavily enriched in ^{15}N and could, through uptake, become incorporated into the biological material and, ultimately, the sedimentary deposits (Middelburg and Nieuwenhuize 1998; Velinsky and Fogel 1999). Thus, incomplete in situ denitrification would be expected to increase the ^{15}N -enriched wastewater signal ($\delta^{15}\text{N} = 38\text{‰}$) further with distance from the outfall, rather than the observed decrease re-

Table 1. The mass accumulation rate, mean nitrogen content, and stable isotopic ratios for each interval in each basin and depositional area used to estimate retention of A) total nitrogen (TN) and B) effluent N. All accumulation estimates given in kg.

| A) Retention of total nitrogen | | | | | | |
|-----------------------------------|---|---|--|------------------------|---|---|
| Basin | M.A.R.* (g cm ⁻² yr ⁻¹) | Depositional area (km ²) | Mean % N (0–2 cm) | Mean ± N (2–4 cm) | TN burial (0–2 cm) (kg N in basin per yr) | TN burial (2–4 cm) (kg N in basin per yr) |
| B4 | 0.2 | 5.5 | 0.53 | 0.42 | 58,404 | 46,592 |
| B3 | 0.2 | 16.6 | 0.42 | 0.37 | 138,782 | 122,046 |
| B2 | 0.1 | 5.2 | 0.49 | 0.45 | 25,229 | 23,441 |
| B1 | 0.1 | 10.4 | 0.38 | 0.33 | 39,280 | 34,277 |
| Total for bay | | | | | 261,696 | 226,356 |
| B) Retention of effluent nitrogen | | | | | | |
| Basin | Mean δ ¹⁵ N value (0–2 cm) | % effluent‡ (0–2 cm) | Mean δ ¹⁵ N value (2–4 cm) | % effluent (2–4 cm) | Effluent N burial (0–2 cm) (kg N in basin per yr) | Effluent N burial (2–4 cm) (kg N in basin per yr) |
| B4 | 7.4 | 9.0 | 7.5 | 9.2 | 5,241 | 4,276 |
| B3 | 7.5 | 9.3 | 7.2 | 8.3 | 12,887 | 10,143 |
| B2 | 6.8 | 7.3 | 6.5 | 6.5 | 1,840 | 1,524 |
| B1 | 6.0 | 5.2 | 5.3 | 3.3 | 2,060 | 1,134 |
| Total for bay | | | | | 22,028 | 17,078 |

* M.A.R., mass accumulation rate.

† Assuming depositional area is equivalent to depths below 10 m in B4, 20 m in B3, and 35 m in B2 and B1.

‡ Based on two-source isotopic mixing model using effluent DIN (δ¹⁵N = 38‰) and marine DIN (δ¹⁵N = 4‰).

recorded in the surface sediments with distance from the outfall (Fig. 2A). In contrast, fractionation during algal uptake results in ¹⁵N-depleted OM (ca. –9‰; Cifuentes et al. 1989) and may be expected to result in the observed spatial gradient of δ¹⁵N, as dissolved N becomes isotopically lighter with distance from the effluent outfall. Moreover, because mean sediment accumulation rates are ~1 cm yr⁻¹ (Bianchi et al. 2002), our analysis of integrated 2-cm intervals will eliminate seasonal variability in δ¹⁵N arising from short-term biological or geochemical processes.

Process of effluent sequestration—Sedimentation of diatoms was apparently an important mechanism that sequestered effluent N in estuary sediments. Regular water-column sampling during the past 20 yr shows that diatoms dominate (>50%) the phytoplankton community during spring months (Elmgren and Larsson 1997) and that diatom biomass near the outfall during high effluent discharge years was double that in outer coastal areas (Larsson and Hagström 1982). Elevated concentrations of fucoxanthin (Fig. 4), enriched δ¹⁵N values, and OM content (>19%) in flocculent material and consolidated sediments near the outfall (Fig. 2) all indicated that effluent-derived nutrients were assimilated in diatoms and deposited in the sediments. Although we did not directly evaluate mechanisms of deposition, previous research shows that eutrophic conditions can result in an increase in diatom biomass (Turner and Rabalais 1994; Elmgren and Larsson 1997; Philippart et al. 2000) and that 30–60% of daily diatom biomass produced in spring in a Baltic coastal area escapes heterotrophic grazing and settles to the seabed (Heiskanen and Kononen 1994). Altogether, these patterns indicate that diatoms that peaked in abundance in spring were the main mechanism delivering effluent N to the sediments.

Analysis of sedimentary pigments supported data from

water-column monitoring (Elmgren and Larsson 2001) and showed that total phytoplankton biomass (β-carotene; Chl *a*) was greatest in the inner basins and decreased seaward, except for some deeper (>35-m) stations (Fig. 3), where, presumably, sediment focusing enhances the depositional environment and pigment preservation (Cuddington and Leavitt 1999). Concentrations of sedimentary pigments characteristic of cryptophytes (alloxanthin) and green algae (lutein–zeaxanthin, pheophytin *b*) were relatively higher near the inlet of L. Mälaren (Fig. 4). These algal groups are characteristic of freshwaters and may have partly entered basin 4 from L. Mälaren through flushing following above-average rainfall in 2001 (SMHI pers. comm.) or may be stimulated by the slightly lower salinity in basin 4. Cyanobacteria (as canthaxanthin) were recorded in high concentrations in the outer coastal sites and near the outfall, where they are probably stimulated in summer by water-column stratification, low N availability following enhanced sewage treatment (Elmgren and Larsson 2001), and high P release from sediments in Himmerfjärden (Elmgren and Larsson 1997). Cyanobacterial blooms are a natural phenomenon in the Baltic Sea (Bianchi et al. 2000) and are regularly recorded in offshore waters during summer seasons (Elmgren and Larsson 2001).

Comparison of N sinks—Estimates of N burial in Himmerfjärden indicated that about 23–26 × 10⁴ kg N was buried in sediments per annum, representing ~25% of recent inputs from all sources (Table 1). This value is similar to the lower estimates for particulate N burial in Chesapeake Bay, where sediments removed 28–53% (13–1,300 × 10⁴ kg N yr⁻¹) of total N inputs (Boynton et al. 1995). When analyzed in combination with stable isotopes, we further estimated that up to 11%, or 1.7–2.2 × 10⁴ kg of the 15–32 × 10⁴ kg of effluent N, was deposited in the whole bay. Sequestration

of effluent N was greatest in basins 3 ($\sim 1.0\text{--}1.3 \times 10^4$ kg yr^{-1}) and 4 ($\sim 0.4\text{--}0.5 \times 10^4$ kg N), sites adjacent to the effluent outfall. In contrast, basins 1 and 2 removed only $0.1\text{--}0.2 \times 10^4$ kg effluent N, reflecting the relatively small areas of permanent sediment accumulation or smaller quantities reaching these outer basins. Thus, although algal uptake and sedimentation removed up to 11% of wastewater DIN in this coastal environment, burial of effluent N in sediments exhibited wide spatial variability. Differences in burial of total N ($\sim 25\%$) and of effluent N ($\sim 11\%$) may reflect the addition of N from relict deposits (Jonsson et al. 1990) or postdepositional transformations of N from various sources (Lehmann et al. 2002) with material from the STP more easily decomposed and lost from the sediment. Further research is required to evaluate these competing hypotheses.

Comparison among potential N sinks indicated that sediment burial is less effective than denitrification at removing excess N, but that both processes are substantially more important than biotic uptake and in vivo storage in this coastal ecosystem. Previous N budget calculations have demonstrated that the macroalga *Fucus vesiculosus* can only assimilate $\sim 3\%$ of total N loads in the bay, and because there is no long-term biomass accumulation, macroalgae do not represent a permanent N sink (Savage and Elmgren 2004). In contrast, N losses via benthic denitrification may remove half of total N inputs in estuaries (Seitzinger 1988), depending largely on water residence time (Nixon et al. 1996). Himmerfjärden experiences limited water exchange, particularly in the bottom waters in the inner basins (Engqvist and Omstedt 1992). Consequently, sediment denitrification is considered to be a significant loss mechanism in the bay. Preliminary studies in basin 3 estimate that denitrification can remove at least $20 \text{ mg N m}^{-2} \text{ d}^{-1}$, equivalent to $\sim 500 \text{ kg N d}^{-1}$ (Elmgren and Larsson 1997). Further, because these estimates are based on the acetylene block method, they likely underestimate true rates of N loss (Seitzinger et al. 1993). The N burial estimates presented here are mean rates over annual or longer timescales and are not intended to provide absolute values for effluent N removal, but rather to explore its relative importance as a sink of anthropogenic N relative to other processes. Overall, comparison of potential basin-wide N removal by denitrification ($30\text{--}60 \times 10^4$ kg N yr^{-1}), sedimentation ($23\text{--}26 \times 10^4$ kg N yr^{-1}), and macroalgal uptake ($\sim 2 \times 10^4$ kg N yr^{-1}) clearly indicates that sediment accumulation can be an important mechanism moderating coastal eutrophication.

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