MARINE ENVIRONMENTAL RESEARCH

ELSEVIER

Marine Environmental Research 48 (1999) 353–375

www.elsevier.com/locate/marenvrev

Using stable isotopes to trace sewage-derived material through Boston Harbor and Massachusetts Bay

J. Tucker[a,*], N. Sheats[b], A.E. Giblin[a], C.S. Hopkinson[a], J.P. Montoya[b]

[a]*The Ecosystems Center, Marine Biological Laboratory, Woods Hole, MA 02543, USA*
[b]*Harvard University, Cambridge, MA 02138, USA*

Received 1 February 1998; received in revised form 1 November 1998; accepted 1 June 1999

Abstract

Using stable isotopes, we assessed the effects of long-term sewage inputs within Boston Harbor and extending into adjacent Massachusetts Bay. We used nitrogen and sulfur stable isotopes ($\delta^{15}N$ and $\delta^{34}S$) to distinguish between sources of these elements to sediments, particulate organic matter, algae, and animals. The isotope data revealed the widespread presence of sewage-derived particulate and dissolved materials. Incorporation of sewage-derived effluent particulates into sediments of the harbor and into Massachusetts Bay was apparent in the $\delta^{15}N$ values of surface sediments and in sediment profiles. Changes towards more typical marine values over time indicated a lessening of sewage inputs. The incorporation of sewage particulates into blue mussels as revealed by the combination of $\delta^{15}N$ and $\delta^{34}S$ values in their tissues was also evident and suggested the importance of sewage-derived nutrients to the local food web.

Keywords: Stable nitrogen isotope; Stable sulfur isotope; Sewage; Sediments; Particulate organic matter; Mussels; Macroalgae

1. Introduction

Stable isotopes have been used effectively to trace sewage as it physically and biologically moves through ecosystems. Several investigators have documented

* Corresponding author. Tel.: +1-508-548-3705; fax: +1-508-457-1548.

0141-1136/99/$ - see front matter
PII: S0141-1136(99)00069-0

isotopic differences between sewage particles and naturally occurring particulates (Gearing, Gearing, Maughan & Oviatt, 1991; Sweeney & Kaplan, 1980a; Sweeney, Kalil & Kaplan, 1980). Benthic infauna and benthic-feeding animals from sewage-impacted areas have shown isotopic signatures distinct from those collected at reference sites. Rau, Sweeney, Kaplan, Mearns and Young (1981) reported that both ridgeback prawn (*Sicyonia ingentis*) and dover sole (*Microstomus pacificus*) from a sewage-polluted site on the southern California coast had lighter $\delta^{13}C$ and $\delta^{15}N$ signatures than did those collected from a non-polluted site. A later study from the same area also found distinct but smaller differences in the $\delta^{15}N$ isotope signal of Dover sole, a change which the authors attributed to the improvement of sewage treatment practices in the intervening years (Spies, Kruger, Ireland & Rice, 1989).

Similar studies have been conducted in the Atlantic. At Deep-Water Dumpsite 106 off the coast of New Jersey, where municipal sewage sludge had been dumped for over 6 years, the $\delta^{15}N$ and $\delta^{34}S$ isotopic signatures from surface deposit-feeding urchins (*Echinus affinus*) and sea cucumbers (*Benthodytes sanguinolenta*) were lighter than those from an upcurrent reference site (Van Dover, Grassle, Fry, Garritt & Starczak, 1992). Moore, Shea, Hillman and Stegeman (1996) used $\delta^{15}N$ and $\delta^{34}S$ isotopic analyses of winter flounder (*Pleuronectes americanus*) from Boston Harbor and Massachusetts Bay to demonstrate the influence of sludge dumping near Deer Island. From these and other studies (Gearing et al., 1991) it is evident that sewage particulates do become incorporated into marine food webs.

Similarly, the fate of dissolved nutrients of sewage origin has also been traced using stable isotopes. $\delta^{15}N$ values in the macroalgae *Fucus* changed from typical marine values to much heavier values along a transect from offshore to a sewage outfall site in Sweden (Hansson et al., 1997). In Waquoit Bay, MA, nitrate originating from septic systems was traced into phytoplankton and macroalgae by using stable isotopes (McClelland, Valiela & Michener, 1997).

The stable nitrogen isotope is useful both as an organic matter (OM) source indicator and as a trophic level indicator. It may be used to distinguish between sources of sewage or marine-derived material (Van Dover et al., 1992) because sewage-derived OM, terrestrial in origin, is usually isotopically light ($\delta^{15}N$ averaging around 3‰) compared to marine values (averaging around 7‰; Table 1). Stable nitrogen isotopes are also useful in tracing OM through food webs because, in general, values in consumers reflect those of their food, after accounting for a 2–4‰ enrichment due to trophic fractionation (Peterson & Fry, 1987).

The stable isotope of sulfur, ^{34}S, is arguably a better source indicator because the isotopic separation between terrestrial and marine OM is much larger for sulfur than it is for nitrogen. The $\delta^{34}S$ values for terrestrial vegetation range from +2 to +6‰, whereas marine plant material ranges from +17 to +21‰ (Peterson & Fry, 1987). An exception occurs in sediments, where sulfate reduction results in a large range of values (−40 to +15‰; Kaplan, 1963). Sulfur is not useful as a trophic level indicator because there is very little fractionation of sulfur during trophic transfer (Peterson, Howarth & Garritt, 1985).

Table 1
$\delta^{15}N$ and $\delta^{35}S$ values from components of sewage-related and marine systems, including NO_3^-, NH_4^+, effluent and water column POM (particulate organic matter), and sediment POM

Sample type	Site	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)	Reference
Sewage				
Effluent NH_4^+	Deer Island, MA	7.2		This report
Effluent NH_4^+	Falmouth, MA	8–30		Jordan, Nadelhoffer & Fry, 1997
Effluent NO_3^-	Falmouth, MA	(−1)–40		Jordan et al., 1997
Effluent POM	Deer Island, MA	3	2–3	This report
Effluent POM	Deer Island, MA	1.1	5.8	Hunt et al., 1995
Effluent POM	South CA coast	2.5	(−0.1)	Sweeney et al., 1980
Effluent floc	South CA coast	3	(−12.9)	Sweeney & Kaplan, 1980a
Effluent POM	Whites Pt., CA	1.8		Spies et al., 1989
Floc total OM	Whites Pt. Outfall, CA	5.8–5.9		Peters et al., 1978
Total OM	Whites Pt. Outfall, CA	3.2		Peters et al., 1978
Sludge	Deer Island, MA	3.3	7.9	This report
Sludge	DS 106, NY	3.2	4.0	Hunt, Dragos, Peven, Uhler & Steinhauer, 1993; Hunt et al., 1996
Sludge	Providence, RI		3.0	Van Dover et al., 1992
Sludge	Middlesex, NJ	−1.1	2.3	Van Dover et al., 1992
Sludge	Bergen, NJ	6.1	2.3	Van Dover et al., 1992
Sludge	Yonkers, NY	7.2	3.5	Van Dover et al., 1992
Sludge	South CA coast		(−0.2)–0.1	Sweeney & Kaplan, 1980a
Sediment POM	Whites Pt. Outfall, CA	1.8–3.6	(−12.3)–(−10.6)	Sweeney et al., 1980
Sediment POM	Whites Pt. Outfall, CA	3.2		Sweeney et al., 1980
Marine				
NH_4^+	Subsurface western N. Pacific	6.5–7.5		Miyake & Wada, 1967
NH_4^+	Woods Hole Great Harbor, MA	7.1		Holmes et al., 1998
NO_3^-	Deep oceans	4.8–6.9		Liu & Kaplan, 1989
NO_3^-	Subsurface N. Atlantic	5.2		Liu & Kaplan, 1989
NO_3^-	N. Pacific	5.6		Wada et al., 1975
NO_3^-	N. Pacific	6.3–7.2		Miyake & Wada, 1967
NO_3^-	Subsurface E. Tropical Pacific	4.8–6.8		Cline & Kaplan, 1975
Water column POM (macroalgae)	Massachusetts Bay		19.0	This study

(Table continued on next page)

Table 1 (*continued*)

Sample type	Site	$\delta^{15}N$ (‰)	$\delta^{34}S$ (‰)	Reference
Water column POM	Massachusetts Bay	5.0		This study
Water column POM	Plum Island Sd., MA	5.8–7		Deegan & Garritt, 1997
Water column POM	Woods Hole, MA	7.5–12		Wainwright & Fry, 1994
Water column POM	Georges Bank	5.1		Fry, 1988
Water column POM	Atlantic Shelf/Slope	10		Altabet & McCarthy, 1985
Water column POM	Sargasso Sea	5–7		Altabet, 1988
Water column POM	North Sea	4.1–11.5		Mariotti, Lancelot & Billen, 1984
Water column POM	S. California Bight	6.5–12.1		Sweeney & Kaplan, 1980b
Water column POM	N. Pacific plankton	4.9		Wada, Kadonaga & Matsuo, 1975
Sediment POM	Massachusetts Bay	6.0		This study
Sediment POM	Plum Island Sd., MA	8.9		Deegan & Garritt, 1997
Sediment POM	Gulf of Maine	6–6.8		Mayer, Macko & Cammen, 1988
Sediment POM	N. Atlantic	6.1		Van Dover et al., 1992
Sediment POM	Mid-Atlantic coastal bays	6.2		Macko, 1983
Sediment POM	N. Mid-Atlantic Bight	5.7		Hopkinson, unpublished, 4/93
Sediment POM	Eastern Bering Sea	6.9–8.9		Peters, Sweeney & Kaplan, 1978
Sediment POM	Gulf of Alaska	4.1–7		Peters et al., 1978
Sediment POM	Tanner Basin, CA	7.8		Peters et al., 1978
Sediment POM	Santa Barbara Basin, CA	7.5		Sweeney & Kaplan, 1980b

2. Study site

Domestic and industrial wastes have been discharged into Boston Harbor as untreated or primary treated effluent since colonial times but especially since the late 1800s. Effluent, comprised of liquid and suspended particulates, has been delivered through several outfall pipes off Deer Island in the northern part of the harbor and Nut Island in the southern harbor. In addition, sewage sludge, comprised of solids that settle out of the wastewater stream, was dumped into the northern harbor at sites off Deer Island and Long Island (Dolin, 1990). The practice of dumping sludge ceased in December 1991. Additional inputs have been delivered through numerous combined sewer overflows (CSOs) along the perimeter of the harbor. When CSOs are activated, raw sewage and storm runoff are dumped directly into the harbor.

The Massachusetts Water Resources Authority (MWRA) has been working to renovate the entire sewage system of the Boston metropolitan area with the goal of improving water quality in Boston Harbor. In addition to the cessation of sludge dumping, CSO activations have become less frequent (Lavery, Coughlin, Steinhauer

& Connor, 1994) and there is a new sewage treatment facility on Deer Island that has upgraded treatment to secondary level. A new outfall tunnel will divert all effluent nine miles offshore into the deep waters of Massachusetts Bay. Sewage diversion is expected to further improve water quality in the harbor.

Currently, nutrient loading rates to Boston Harbor are among the highest of those reported for coastal systems (Kelly, 1997; Nixon & Pilson, 1983). Nitrogen loading is reported to be about 13 000 metric tons per year, about 90% of which is from sewage effluent (Alber & Chan, 1994; Hunt, West & Peven, 1995). Most of the discharge, almost 70%, is into the more northern part of the harbor. About 60% of the nitrogen in the sewage effluent is in the dissolved inorganic form (DIN = ammonia + nitrate + nitrite), primarily ammonia. Particulates make up 17% and the balance is dissolved organic nitrogen (DON; Hunt et al., 1995). Prior to December 1991, when sludge was actively being dumped within the northern harbor, it represented about 8% of total N. The sludge deposits that remain continue to be a source of sewage-derived particulates.

Although Boston Harbor ranks as one of the most heavily nutrient-loaded estuaries, water column concentrations of nutrients are not correspondingly high. Annual mean concentrations of nitrogen in the harbor are only about 10 μM for DIN and 23 μM for total nitrogen (TN) compared to loadings of 1122 mmol m^{-3} $year^{-1}$ (307 μM day^{-1}) and 1728 mmol m^{-3} $year^{-1}$ (473 μM day^{-1}), respectively (Kelly, 1997). Other estuaries, such as New York Bay, Delaware Bay, Chesapeake Bay, Patuxent River Estuary, Potomac River Estuary, and San Francisco Bay have double or more the DIN concentrations of Boston Harbor, even though their loading rates are lower (Kelly, 1997; Nixon & Pilson, 1997). Studies indicate that most of the nutrients are removed from Boston Harbor by physical rather than biological processes (Giblin, Hopkinson & Tucker, 1997; Kelly, 1997; Signell & Butman, 1992). Water residence time is only 2–10 days (Signell & Butman, 1992) resulting in strong gradients of nutrients, particulates, and chlorophyll *a* radiating from the harbor into western Massachusetts Bay.

In this study we examined the pervasiveness and persistence of sewage-derived OM within Boston Harbor and the adjacent waters of Massachusetts Bay. We used stable isotopes of nitrogen and sulfur as sewage tracers to distinguish between three types of OM sources: (1) particulates of sewage origin; (2) primary producers that utilized sewage-derived DIN; and (3) particulates of marine origin. In sediments, stable isotopes provided an historical record of sewage inputs, including recent changes. Animal and plant samples revealed the importance of sewage-derived nutrients to the local food web.

3. Methods

We collected sediment, algal, and animal samples at various times from 1990 to 1994, both during and following sludge dumping. Sediments were sampled again in Boston Harbor in 1998. Samples were collected contemporaneously with benthic nutrient cycling studies being conducted within the MWRA monitoring program

(Giblin et al., 1997; Tucker, Giblin & Hopkinson, 1999). Sediment samples were taken twice while sludge was still being dumped within Boston Harbor; once in September 1990 and once in September 1991. All other samples were obtained after the cessation of sludge dumping. Depending on the site, sediments were sampled three to five times per year from 1992 through 1994, and four times in 1998. Sediments were collected in small (2.5-cm-diameter) core tubes by diver or from a box core. Cores were sectioned in 1-cm intervals to 10 cm and then by 2-cm intervals to the bottom of the core ($\leqslant$15 cm). Sections were dried at 105°C, then homogenized with a mortar and pestle.

When present, macrofauna were also collected from the sediment cores. Animals were maintained in clean seawater for 24 h for depuration. Specimens were either dried whole (small polychaetes), or if large enough (clams, lobsters, sea cucumbers), dissected to obtain clean muscle tissue and then dried. Samples that could not be handled immediately were frozen. After drying at 55°C, samples were homogenized in a Wig-L-Bug dental grinder (Crescent Dental, Lyons, IL).

In October 1994, we collected macroalgae and *Mytilus edulis* (blue mussels) from buoys and pilings within northern Boston Harbor, and from navigation buoys along the shipping channel through Broad Sound and into Massachusetts Bay. In the harbor, samples were taken from six sites: (1) an old dock at Station BH03 (where sludge had been dumped); (2) pilings at the end of an airport runway at the entrance to the Charles River; (3) the University of Massachusetts dock in Dorchester Bay; (4) a buoy in outer Dorchester Bay; (5) pylons of the Long Island Bridge between the northern part of the harbor and the southern part; and (6) a navigation buoy in the center of the northern harbor. Outside the harbor, samples were taken from four navigation buoys along the shipping channel: Buoy 4, closest to the harbor entrance; the NC (North Channel) Buoy; the BG Buoy; and the B (Boston) Buoy which is located just east of the new outfall site (Fig. 1).

We collected blue mussels at eight of the nine sites in the harbor and bay. We were not able to find the same algal species at all sites; however, we did collect either *Ulva* or *Enteromorpha* at all sites and assumed they would have similar stable isotopic ratios because they are so closely related taxonomically. Within the harbor, we collected *Ulva* at six sites and in Broad Sound and Massachusetts Bay, we collected *Enteromorpha* at four sites. Upon return to the laboratory, all samples were thoroughly rinsed with deionized water and frozen. Mussels were later dissected for muscle and mantle tissue, and dried. Algae were dried. Dry samples were pooled and homogenized in the Wig-L-Bug grinder.

In all cases, sediment, animal, and algal samples analyzed for $\delta^{15}N$ received no further treatment beyond drying and homogenizing. For $\delta^{34}S$ analysis, subsamples were rinsed five times with deionized water to remove seawater sulfate, then redried before analysis. All samples run for $\delta^{34}S$ were free of sediments and seawater sulfate. Sediments were not analyzed for $\delta^{34}S$ because sulfate reduction in sediments produces a very large range of values (−40 to +15‰; Kaplan et al., 1963).

Stable isotope analyses of sewage sludge, sediments, animal tissue, and algae were conducted at the Marine Biological Laboratory's Stable Isotope Laboratory. $\delta^{15}N$ analyses were made using an automated elemental analyzer with a cryogenic

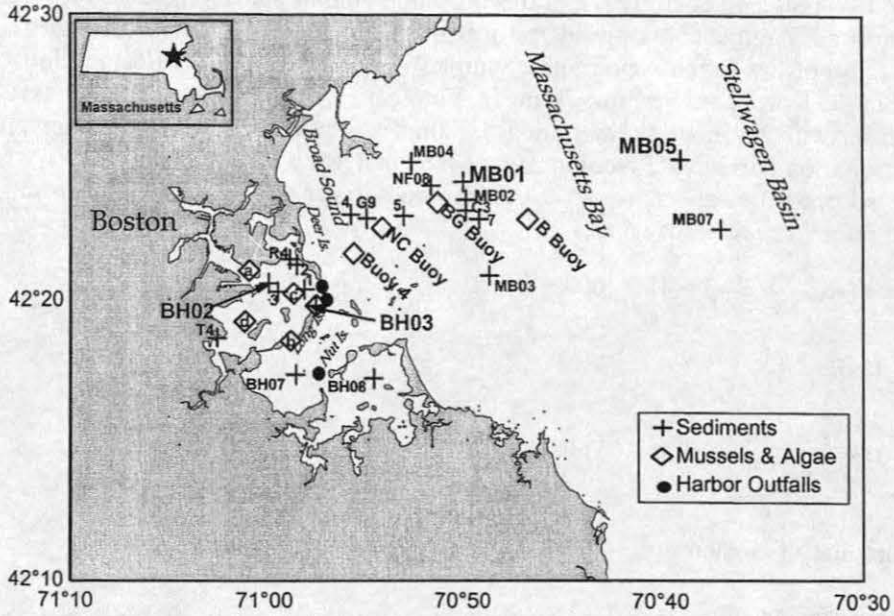

Fig. 1. Map of Boston Harbor and Massachusetts Bay, showing outfalls (●), sediment stations (+), and mussel and algae stations (◇). To avoid more clutter on the map, the mussel and algae stations in the harbor are coded as follows: (a) airport runway pilings; (b) Long Island bridge pylons; (c) central harbor buoy; (d) Dorchester Bay buoy. The star on the inset shows the location of Boston in the state of Massachusetts.

purification system coupled to a Finnigan Delta S isotope ratio mass spectrometer (Fry, Brand, Mersch, Tholke & Garritt, 1992). $\delta^{34}S$ analyses were made as SO_2 on a Finnigan MAT 251 using a sealed tube combustion, $BaSO_4$ precipitation and decomposition to SO_2 technique (Dornblaser, Giblin, Fry & Peterson, 1994). Standards were N_2 in air for nitrogen and Canyon Diablo troilite for sulfur. Working standards were pure tank gases (> 99.9%) calibrated against the primary standards. Replicate analyses generally agreed to within 0.2‰ for nitrogen and 0.4‰ for sulfur.

For analysis of $\delta^{15}N$ in water column particulate organic matter (POM) samples, water samples were collected on 17 one-day cruises between November 1993 and February 1996. Particulates were collected on precombusted GF/F filters by gentle vacuum filtration. Filters were dried at 60°C and stored over desiccant for later mass spectrometer analysis. Isotope analyses of water column POM were carried out at Harvard University. Analyses were made by continuous flow isotope mass spectrometry using a Carlo Erba NA1500 elemental analyzer interfaced to a VG Prism II isotope ratio mass spectrometer with N_2 in air as the standard. Precision of replicate analyses was ±0.15‰.

The $\delta^{15}N$ for effluent ammonium was obtained from sewage effluent that was collected from the Deer Island treatment facility on nine dates, approximately monthly, between November 1994 and December 1995. $\delta^{15}N$–NH^{4+} was measured using the 'ammonia diffusion' method (Holmes, McClelland, Sigman, Fry &

Peterson, 1998; Sigman et al., 1997). In this procedure, ammonia gas is diffused from a concentrated sample and trapped onto acidified glass fiber filters sandwiched between two porous Teflon membranes. Samples were analyzed in the Boston University Stable Isotope Laboratory using a Finnigan Delta-S isotope ratio mass spectrometer with N_2 in air as the standard. Samples were blank, percent recovery, and fractionation corrected. Precision of replicate analyses was $\pm 0.2‰$.

Stable isotope ratios are expressed as del (δ) values in per mil (‰) deviations from standard reference materials where:

$$\delta X = [(R_{\text{sample}}/R_{\text{std}}) - 1] \times 1000;$$

$$X = {}^{15}\text{N or } {}^{34}\text{S};$$

$$R = {}^{15}\text{N} : {}^{14}\text{N or } {}^{34}\text{S} : {}^{32}\text{S}.$$

4. Results and discussion

4.1. Source signals

For the purpose of this study, we considered endmember sources for isotopes to be either sewage derived or marine in origin. Other terrestrial sources were not considered because they are overwhelmed by the sewage input of nutrients to Boston Harbor. We present values for: (1) the sewage endmembers: sludge, effluent particulates, and effluent NH_4^+ (primary component of sewage DIN); and (2) the marine endmembers: particulates, sediments, and NO_3^+ (primary component of marine DIN). The values were either measured in this study or taken from the literature as detailed later.

4.1.1. Sewage endmembers

A sludge sample taken from the Deer Island Treatment Facility in April 1990 and analyzed in this study had a $\delta^{15}N$ value of 3.3‰ and a $\delta^{34}S$ value of 7.9‰. Effluent particulates sampled monthly by the MWRA from December 1993, to November 1994, had a reported average $\delta^{15}N$ value of 1.1‰ (range 0–1.9‰) and an average $\delta^{34}S$ value of 5.8‰ (range 4.5–8.4‰; Hunt et al., 1995). These $\delta^{15}N$ values fell within the range of sewage particulates measured from other sewage-impacted sites (Table 1). The sulfur values were heavier than most terrestrial sources, and may have indicated some seawater infiltration into the sewage system. NH_4^+ in the effluent, analyzed in this study, was heavier than the particulates at 7.2‰ (standard error SE = 0.24, $n = 9$, range = 6.1–8.3‰).

4.1.2. Marine endmembers

Literature values for $\delta^{15}N$ of water column POM in the Atlantic range from 4 to 12‰ (Table 1). In this study, POM from samples taken away from sewage inputs in

Massachusetts Bay averaged 5.0‰. Further offshore on Georges Bank, $\delta^{15}N$ of POM had previously been measured at about 5.1‰ (Fry, 1988). We have used 5‰ as the marine water column endmember representing particles not affected by sewage. $\delta^{34}S$ measured in macroalgae (both *Ulva* and *Enteromorpha*) in this study averaged 19.1‰ (SE = 0.14, $n = 9$), a value within the 17–21‰ range normally reported for marine primary producers (Peterson & Fry, 1987). We have used a value of 19‰ for the offshore endmember for $\delta^{34}S$.

Literature $\delta^{15}N$ values of POM in surface marine sediments range from 4 to 9‰ (Table 1). We have used a background $\delta^{15}N$ value of 6‰ that we measured in sediment profiles from Stellwagen Basin for the marine sediment $\delta^{15}N$ endmember (see discussion later). This value was 1‰ heavier than water column POM which is consistent with findings that sedimenting POM is typically heavier than suspended POM (Altabet, 1988; Altabet & Francois, 1994).

4.2. Sediments

The $\delta^{15}N$ signatures of POM in surface sediments (0–1 cm) were lower in harbor areas in closest proximity to either the Deer or Nut Island Outfall than they were from the eastern boundary of Broad Sound and seaward (Table 2, Fig. 2). Regional averages for the years 1990–94 were 4.6‰ (SE = 0.13, $n = 16$), 5.3‰ (SE = 0.29, $n = 6$), and 5.6‰ (SE = 0.64, $n = 3$) in the northern harbor, southern harbor and Broad Sound, respectively. The means of surface values from Massachusetts Bay and Stellwagen Basin were each 6.3‰ (SE = 0.12, $n = 15$ and SE = 0.10, $n = 2$, respectively). We attribute these differences in $\delta^{15}N$ values to isotopically light sewage inputs into the harbor.

Surface samples from the northern harbor indicated that $\delta^{15}N$ values increased with time from cessation of sludge dumping (after December 1991, indicated by an arrow off the x-axis of Fig. 3; Table 2, Fig. 3). Samples from all northern harbor stations in 1990 and 1991 averaged 4.1‰ (SE = 0.20, $n = 3$) and 4.3‰ (SE = 0.50, $n = 2$), respectively. In 1992, the harborwide average was somewhat higher, 4.7‰ (SE = 0.15, $n = 8$); by 1994, values had increased to an average of 4.9‰ (SE = 0.60, $n = 2$). In 1998, that average was 5.5‰ (SE = 0.14, $n = 8$). These data indicated that the northern harbor area was losing its sewage signal over time ($p = 0.013$; Fig. 3).

We used these values to quantify the change in sewage input in the northern harbor by calculating sewage contribution to total sediment N before and after cessation of sludge dumping at two sites. One site was Station BH03, which was located off Long Island within the area that had been used for sludge disposal. Sediments at this site were characterized by a thick (3–5-cm) surface flocculent layer. The second site was Station BH02, located in the center of the northern harbor near both the old Long Island and Deer Island disposal sites, but not within either site. The thick flocculent layer was not present at this site. Estimates were calculated using the following simple mixing model:

$$\delta_Y = \delta_S(X) + \delta_M(1 - X),$$

Table 2
Station names, location, sampling dates and $\delta^{15}N$ values for surface (0–1 cm) sediments

Location	Station	1990	1991	1992						1993		1994			1998			
		Sept	Sept	Apr	May	Jun	Aug	Oct	Nov	Feb	Jul	Jul	Aug	Oct	May	Jul	Aug	Oct
	1	3.7																
	2	4.3																
Northern	3	4.3																
Harbor	BH03		4.8	4.6	4.6	4.8	5		5.5	5.2				5.5	5.2	5.7	5.5	6.2
	BH02		3.8				4.5							4.3	5	5.2	5.9	5.2
	R4						4											
	T4						4.5											
Southern	BH07		5.8				5.7					5.9						
Harbor	BH08		5.2				4					5.5						
	4	4.4																
Broad	5	5.8																
Sound	G9								6.6									
	MB04	6.7						6.7			6.2							
	NF08												5.8					
Massachusetts	MB01							7	5.9	5.8				6.1				
Bay	MB02	6.4						6.8						6.1				
	C3							6.1										
	7	7.3																
	MB03							5.8						6.3				
Stellwagen	MB05													6.4				
Basin	MB07												6.2					

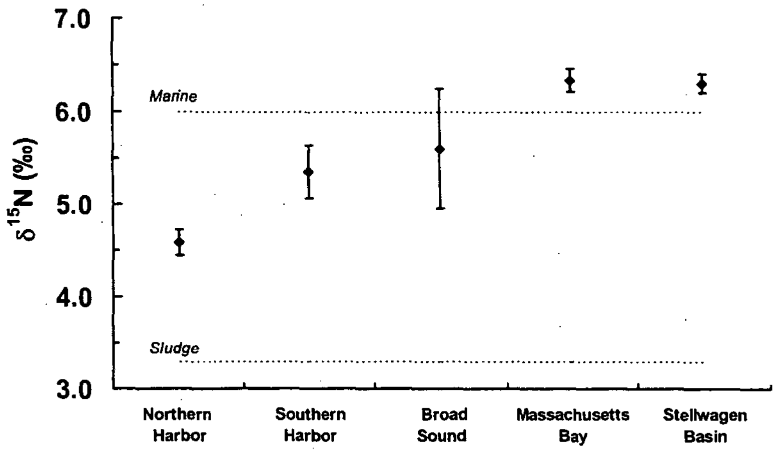

Fig. 2. The average $\delta^{15}N$ values for surface sediments for various regions of Boston Harbor and Massachusetts Bay, including all samples from 1990 to 1994. Error bars represent the standard error of the mean. The dotted lines in this figure and in Figs. 3 and 4 provide reference points between the marine endmember value determined from subsurface sediments in Stellwagen Basin and a sewage endmember (sludge) value. The other endmember for sewage-derived material relevant to sediments would be that for effluent particulates, or 1.1‰. Station locations may differ from year to year.

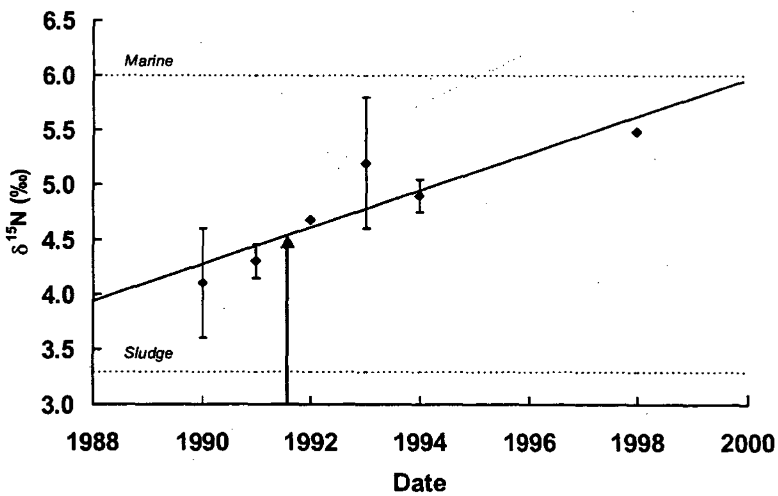

Fig. 3. Change in annual average in the $\delta^{15}N$ values over time for the northern harbor stations. Error bars represent the standard error of the mean. Annual averages were used to remove the variation due to seasonal differences. (Equation for regression line: $y = 0.17x - 331.9$; $r^2 = 0.8187$; $p = 0.013$.) Dotted lines are as described in legend for Fig. 2.

where δ_Y, δ_S, and δ_M are the $\delta^{15}N$ values of the sediment, the sewage sludge endmember (3.3‰), and the marine endmember (6‰), respectively, and X is the fraction of the sediment N derived from sewage.

According to this model, in 1991 the sludge contribution to surface sediment at Station BH03 was 44%. By 1994, that contribution had decreased to about 19% and in 1998 was 11%. We attributed this decrease to the incorporation of non-sewage derived particulates into the sediment and to remineralization of nitrogen from sediment OM. The shift back towards normal marine sediments at this heavily impacted site demonstrated the potential for rapid recovery of the system after inputs changed.

Sediments from Station BH02 in the central part of northern harbor area, which did not receive sludge directly, but continue to receive inputs through effluent particulates, showed less change in their stable isotopic signature over the 1991–94 timeframe. Using the effluent POM value (1.1‰) as the sewage endmember instead of the sludge value, we found that for this area, sewage-derived N decreased from 45% in 1991 to 35% in 1994. The smaller change reflected continued inputs from sewage discharge into the harbor, and episodic CSO activations along the perimeter of the harbor. By 1998, average $\delta^{15}N$ values of surface sediments at Station BH02 (5.3‰) had increased, resulting in the calculated sewage contribution decreasing to 14%. This decrease between 1994 and 1998 corresponded well with reductions in particulate loading to the harbor from the Deer Island Treatment Facility effluent that have occurred as treatment improvements have come on line (M. Hall, pers. comm.).

Broad Sound, particularly near the harbor entrance, is directly affected by the outfall plume (Figs. 1 and 2), but is also an area of active sediment reworking (Knebel, Rendigs & Bothner, 1991). Sediment values in Broad Sound were quite variable, and no trend with time could be discerned (Table 2, Fig. 2). In 1990, sediments from Station 4 near the harbor entrance and Station 5 in eastern Broad Sound had $\delta^{15}N$ values of 4.4 and 5.8‰, respectively. Sediment values at Station 4 were very similar to harbor values. In 1992, sediment $\delta^{15}N$ from another site in eastern Broad Sound, Station G9, was heavier, 6.6‰.

Surface sediments from Massachusetts Bay became lighter between 1990 and 1994, in contrast to the pattern observed in the harbor (Table 2). In 1990, $\delta^{15}N$ averaged 6.8‰ (range 6.4–7.3‰), in 1992, 6.4‰ (range 5.8–7.0‰), and in 1993 and 1994, 6.0 and 6.1‰, respectively (range 5.8–6.3‰). Our offshore stations in Stellwagen Basin were similar to Massachusetts Bay stations with an average $\delta^{15}N$ value for surface sediments of 6.3‰ (Fig. 2).

We also measured $\delta^{15}N$ values of subsurface sediments (from 0–15 cm depth) from sediment cores taken at the Harbor and Bay sites. These values reflected the same trends in $\delta^{15}N$ values as the surface sediments, being lightest at the inshore harbor areas and heaviest offshore (Fig. 4). Changes in profiles were also consistent with recent changes in sewage disposal practices, especially at the old sludge disposal site, BH03.

In 1991, the sediment $\delta^{15}N$ signature at BH03 was 4.8‰ at the surface and decreased with depth to a lighter, more sludge-like value of 3.8‰ (Fig. 4a). In 1992 the range in surface values was 4.5–5.5‰, with an average of 4.9‰. A profile from April of that year, just 4 months after dumping ceased, was heavier at all depths except the surface. In 1993 the surface had increased to 5.2‰, and by 1994 to 5.5‰.

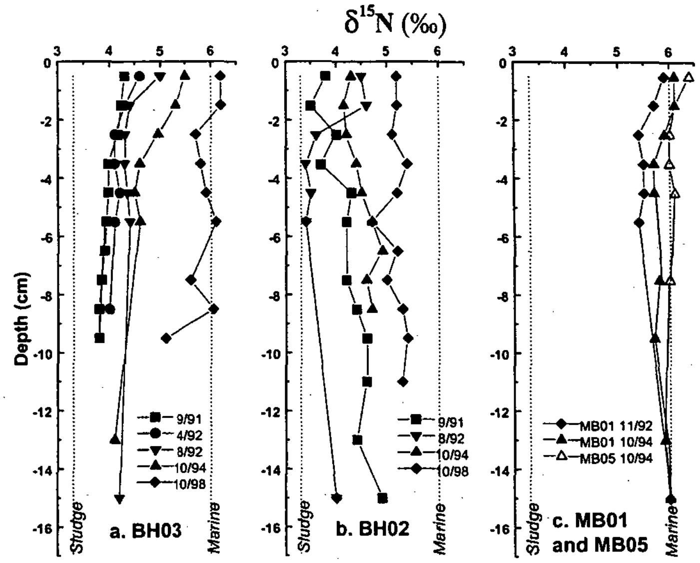

Fig. 4. Changes over time in $\delta^{15}N$ values in sediment profiles for Boston Harbor and Massachusetts Bay, and compared to one profile from Stellwagen Basin: (a) Station BH03 in 9/91 (■), 4/92 (●), 8/92 (▼), 10/94 (▲) and 10/98 (◆); (b) Station BH02 in 9/91 (■), 8/92 (▼), 10/94 (▲) and 10/98 (◆); (c) Massachusetts Bay in 11/92 (◆) and 10/94 (▲), and Stellwagen Basin in10/94 (ρ). Dotted lines are as described in the legend for Fig. 2.

Profiles from August 1992, and October 1994, also showed the trend towards heavier values over time. By October 1998, the sediment profile was very similar to those that had been measured from Massachusetts Bay; i.e., sediments from what had been the sludge disposal site had begun to resemble, isotopically, typical marine sediments. We attribute these changes largely to the reduction of sewage particulates being delivered to the harbor and the concomitant relative increase in marine particulates being incorporated into these sediments.

Of particular interest was the change in the top 4 cm of sediment observed in the October 1994 profile, which was 5.5‰ at the surface, and decreased with depth more gradually than the other profiles to a value of 4.6‰ at 3.5 cm. Porewater profiles of Eh and sulfide concentrations for this same time showed oxidized sediments up to 10 cm deep (Giblin et al., 1997), indicating deep irrigation of the sediments. This depth roughly coincided with the thickness of an amphipod (*Ampelisca* sp.) mat complex that has progressively carpeted the sediments at this site since the cessation of sludge dumping (Kropp & Diaz, 1995). The rapid appearance of heavier, more marine-like isotope values deeper in the profiles since 1994 may be related to the burrowing and irrigation activities of the amphipods which have accelerated the exchange of sewage and marine particulates. The amphipod mat complex has spread throughout the harbor and is thought to play a major role in governing rates of sediment processes (Howes, 1998; Tucker et al, 1999).

At Station BH02 in the central northern harbor, depth profiles of $\delta^{15}N$ from 1991–94 (Station BH02; Fig. 4b) were more irregular than observed at the sludge disposal site (BH03). This may have been due to differences in bioturbation or even nearby channel-dredging activities, as well as continued inputs from the Deer Island Outfall. Stable isotope values from these sediments obtained through 1994 indicated that this area of the harbor had responded slowly to harbor clean-up activities. Our benthic studies supported this observation. Sediments from this area were characterized by a very thin oxidized layer (at times sediments were anoxic to the surface) and high concentrations of reduced porewater constituents such as sulfides and ammonium (Giblin et al., 1997).

In 1998, porewater profiles from Station BH02 suggested that sediments at this station had become more oxidized than in previous years (Tucker et al., 1999). A $\delta^{15}N$ profile from October 1998, revealed higher, less 'sewage'-like values than for previous years (Fig. 4b). These higher values were present throughout the profile to a depth of 10 cm. Combined with knowledge that effluent particulate loading from the Deer Island Outfall has decreased (M. Hall, pers. comm.), these data suggested that sediments in the central northern harbor area have begun to show signs of recovery from long-term sewage inputs.

Although biogeochemical processes are important in determining stable isotope values in sediments (Cifuentes, Sharp & Fogel, 1988), we believe that in Boston Harbor the mixing of sewage particulates into and out of the sediments has been the dominant factor. Remineralization would tend to leave the residual sediment OM heavier, as has been reported for soils (Nadelhoffer & Fry, 1988); however, we typically measured lighter values with depth in harbor profiles. Isotopic changes in DIN that may occur as a result of denitrification would also have an effect on the isotopic value of sediment OM, but only after the isotopically changed DIN had been first incorporated into phytoplankton and then redeposited on the sediments. Giblin et al. (1997) calculated that remineralized N from sediments could support as much as 40% of primary productivity in Boston Harbor; however, the sewage inputs were an order of magnitude greater than the contribution from sediments and far exceeded the demands of primary productivity. For these reasons, we believe that to date geochemical processes have played a relatively minor role in determining sediment isotopic values in Boston Harbor.

The $\delta^{15}N$ profiles in Massachusetts Bay (Fig. 4c) had heavier values than those from the harbor stations, yet they were lighter than expected for uncontaminated sediments, suggesting a sewage influence even at this distance (~15 km) from the Deer Island Outfall. Evidence of sewage inputs to Massachusetts Bay sediments has also been seen in profiles of other contaminants. Elevated levels of *Clostridium perfringens*, silver, and other sewage indicators were measured in core profiles taken in 1990 and 1992 from Massachusetts Bay near our station MB01 (Bothner, Buchholtz ten Brink, Paramenter, d'Angelo & Doughten, 1993; Butman et al., 1992). However, a positive shift in our isotope profiles from 1992 to 1994 suggested a reduction in the delivery of sewage particulates to this area.

Sediment profiles of $\delta^{15}N$ from Stellwagen Basin indicated that sediments in this area have been unaffected by Boston Harbor sewage discharge (Fig. 4c). Profile values decreased from 6.4‰ at the surface to a nearly constant 6‰ from just below the surface to 15 cm (Fig. 3c). The flatness of the isotope profile from this site and the fact that the two Massachusetts Bay cores converged at depth to the same value of 6‰ suggested that the Stellwagen profile represented background values for marine sediments. In addition, the value of 6‰ was similar to that observed in offshore marine sediments in the Atlantic (Table 1). Corroborating evidence supporting the absence of sewage particulates at this site included silver profiles that were much lower than those in the depositional areas of Massachusetts Bay, and nearly as low as those from a reference site east of Stellwagen Bank (Bothner et al., 1993). These stable nitrogen isotope values also supported nutrient and chlorophyll concentration data that indicate Stellwagen Basin has been generally outside of the range of nutrients from the effluent plume (Kelly & Turner, 1995; Libby et al., 1995).

4.3. Mussels, macroalgae, and particulate organic nitrogen

There was a tendency for stable isotope values in both the mussel and algae samples to get heavier with distance away from the Deer Island Outfall (Fig. 5); however, we found large variability in samples taken from within the harbor. Values for *Ulva* in the harbor averaged 7.5‰ (SE=0.59, $n = 6$, range 6.1–9.5‰), with the samples from BH03 at 6.1‰ and the center of the harbor at 6.8‰ (marker 'c' on Fig. 1). *Enteromorpha* from Broad Sound at the NC Buoy was 7.3‰; it increased to 8.1‰ at the BG Buoy, and to 14.4‰ at the most seaward site, the B Buoy.

Blue mussel $\delta^{15}N$ values increased from about 4.2‰ near the harbor mouth at Buoy 4 to 6.9‰ at the B Buoy (Fig. 5; Table 3). Within the harbor, the range was 5.4 to 6.9‰, with the lightest values from mussels from Dorchester Bay (marker 'd' on Fig. 1) and the heaviest from Long Island Bridge (marker 'b' on Fig. 1). Mussels were not collected from the central northern harbor. Mussels from Station BH03 had a $\delta^{15}N$ value of 5.9‰.

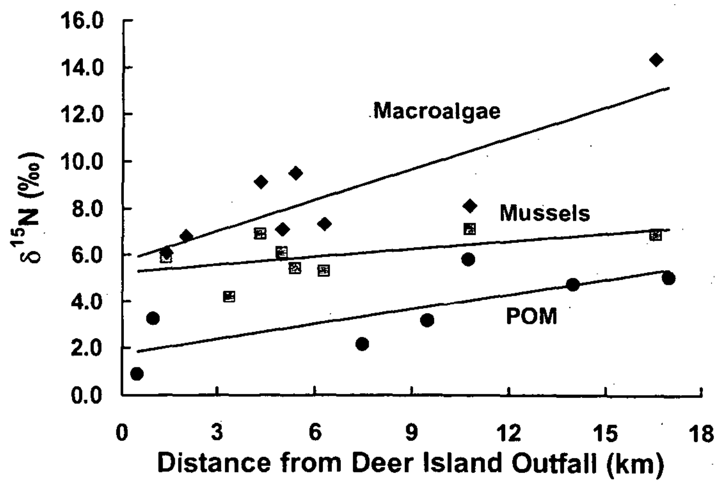

Fig. 5. Del ^{15}N values in macroalgae (◆), blue mussels (▩), and water column particulate organic matter (POM) (●) with distance from the Deer Island Outfall. For macroalgae, $y = 0.44x + 5.69$, $r^2 = 0.71$; for mussels, $y = 0.11x + 5.22$, $r^2 = 0.30$; for PON, $y = 0.21 + 1.73$, $r^2 = 0.58$.

Table 3
$\delta^{15}N$ values of POM, primary producers, and benthic animals from Boston Harbor, Massachusetts Bay, and Stellwagen Basin, and feeding modes of animals

Animal	Feeding mode	Boston Harbor		Massachusetts Bay			Stellwagen Bay	
		BH02	BH03	MB01	MB02	MB03	MB05	MB07
Polychaete (Goniadidae)	Carnivore		10.7	12.3				
Polychaete (*Nephtys*)	Carnivore			13.1				
Burrowing anemone (*Ceriantheopsis*)	Carnivore					10.1		
Ribbon worm (Nemertea)	Carnivore			11.3			12.7	
Winter flounder (*Pleuronectes americanus*)	Carnivore							
1991		8.1			12.4			
1992		10.6			13.0			
1993		11.8			11.9			
Lobster (*Homarus americanus*)	Omnivore					12.0		
Mud star (*Ctenodiscus*)	Omnivore						8.9	9.7
Polychaete (Phyllodicidae)	Omnivore		10.2					
Polychaete (Ampharetidae)	Deposit feeder		5.2					
Polychaete (Maldanidae)	Deposit feeder				10.9			
Polychaete (Arabellidae)	Deposit feeder				12.1			
Sea cucumber (unidentified)	Deposit feeder					8.8		
Sea cucumber (*Caudina*)	Deposit feeder						14.0	
Amphipod (*Leptocheirus*)	Deposit feeder		3.6					
Clam (*Thracia conradi*)	Deposit feeder			8.4	8.4			
Black clam (*Artica islandes*)	Suspension feeder						17.0	
Amphipod (*Ampelisca*)	Suspension feeder		6.4					
Mussel (*Mytilus edulis*)	Suspension feeder	5.8[a]	5.9		7.1[a]	6.9[a]		
Ulva	Primary producer	6.8[a]	6.1					
Enteromorpha	Primary producer				8.1[a]	14.4[a]		
POM (surface sediments)		4.2	5.0	6.2	6.4	6.1	6.4	6.2

[a] Mussels and macroalgae samples were taken from buoys close to Stations BH02, MB02, and MB03.

Our assumption when we collected *M. edulis* together with *Ulva* or *Enteromorpha* from the same pilings or buoys was that we would be sampling primary consumers adjacent to primary producers representative of their food source. Our results, however, showed this to be a faulty assumption. Site by site, the $\delta^{15}N$ values of the algae were higher than those from mussels (Fig. 5). The overall average $\delta^{15}N$ for all mussel samples was 6.0 (SE = 0.35, $n = 8$) whereas that for the algae was 8.5 (SE = 0.92, $n = 8$). Trophic level considerations, in contrast, would predict a food source 2–3‰ lighter than the consumer. Clearly the macroalgae were not a suitable proxy for particulates ingested by the mussels.

These results hinted at a non-algal and isotopically light component in the mussel diet. Effluent particulates were a likely source. Effluent particulates taken from the Deer Island Treatment Facility averaged 1.1‰ (Hunt et al., 1995), and water column POM in the effluent plume, comprising a mixture of effluent particulates and phytoplankton, averaged 0.9‰. With distance from the outfall, POM values increased, presumably as the ratio of effluent particulates to phytoplankton decreased, and was 5.2‰ 20 km away. Mussel values tracked the $\delta^{15}N$ of POM with an offset of +2–3‰, the amount expected from a trophic shift. This pattern suggested a partial dependence on sewage effluent by the mussels that decreased in the offshore direction in parallel with effluent dilution.

More compelling evidence of mussel incorporation of sewage particulates came from the stable sulfur isotope values. In Fig. 6, we have plotted the stable nitrogen isotope values against the sulfur isotope values for the mussels and the endmember signals. As the sewage endmember we plotted the average values reported for effluent particulates: 1.1‰ for nitrogen and 5.8‰ for sulfur (Hunt et al., 1995). For the marine endmember we have used our values of 5‰ for nitrogen in offshore POM and 19‰ for sulfur in offshore macroalge.

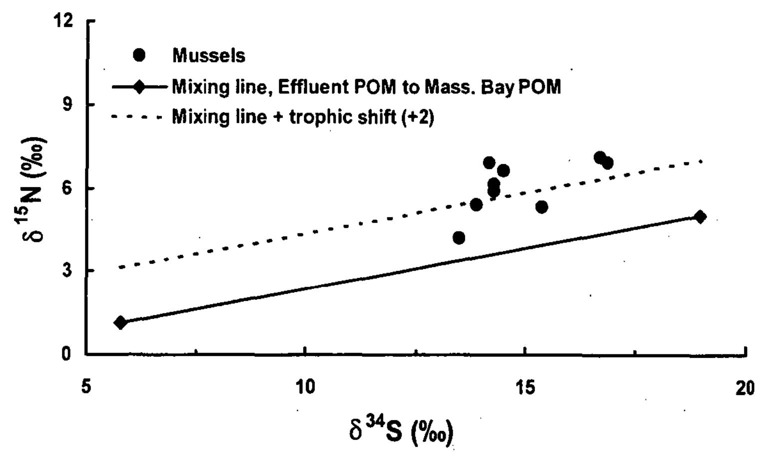

Fig. 6. Dual isotope plot of $\delta^{34}S$ versus $\delta^{15}N$ values for blue mussels (●) plotted with a simple mixing line drawn through the endmember values for effluent POM and uncontaminated Massachusetts Bay particulate organic matter (POM). The dashed line represents a +2‰ trophic shift expected from animals ingesting POM.

The graph shows that the mussels varied in both their N and S isotopes. Mussel values plot on the graph just above the mixing line between the effluent particulates and the offshore POM. If we adjust the mixing line for a trophic shift in N of +2‰, the line then passes through most of the mussel values. Two values, from Buoy 4 and the NC Buoy, still fall well below the line suggesting a disproportionate contribution of material light in ^{15}N (i.e., sewage-derived) to the diet of mussels at these sites.

It was possible to quantify the contribution of sewage particulates in the mussel diet from the $\delta^{34}S$ analysis. Of the various components of POM, only effluent particulates had $\delta^{34}S$ values different from seawater. Effluent particulate $\delta^{34}S$ values averaged 5.8‰ in 1994, whereas $\delta^{34}S$ of macroalgae was about 19‰. Stable sulfur isotopes values from *Ulva* and *Enteromorpha* all fell in a narrow range between +18.4 and +19.9‰, typical of marine algae (Peterson & Fry, 1987). Using the mixing equation with endmember $\delta^{34}S$ values of 5.8 and 19‰, we calculated that in the effluent plume at Buoy 4, the contribution of sewage particulates to mussel diet was nearly 42%. The average for mussels in the harbor was 36% (range 34–39%), whereas the sewage contribution to mussel diet at the outermost (B) buoy was 16%.

4.4. Other animals

Previous studies from other areas (Rau et al., 1981; Spies et al., 1989; Van Dover et al., 1992) and in the Boston Harbor/Massachusetts Bay system (Moore et al., 1996) have successfully used stable isotopes measured in benthic animals as sewage indicators. We collected a variety of benthic animals from Boston Harbor and Massachusetts Bay and grouped them according to feeding mode or trophic level, and included Moore et al.'s (1996) winter flounder data (Table 3). On average, $\delta^{15}N$ values increased according to trophic level, with filter feeders or deposit feeders having the lowest $\delta^{15}N$ values and carnivores having the highest. This increase reflects the isotopic fractionation associated with food assimilation and trophic transfer. (Notable exceptions are the high values for a sea cucumber [14‰] and the black clam [17‰] from Station MB05 in Stellwagen Basin. We cannot explain these values at this time.)

At every trophic level up to the carnivores, isotopic values were higher in organisms collected from Massachusetts Bay than from Boston Harbor (Fig. 7). The difference between locations was presumably driven by inputs of sewage material at the base of the harbor food web. The overlap in the carnivores was due to the changing isotopic signal in winter flounder that were collected off Deer Island from 1991 to 1993 (Moore et al., 1996). Flounder $\delta^{15}N$ changed to more marine-like values after 1991, the year that sludge dumping stopped. This change provided a good indication that less sewage-derived material was entering the lower levels of the food web.

Interestingly, two different Gammarid amphipods collected from the mats at station BH03 at the same time (24 February 1993) had quite different $\delta^{15}N$ signatures. The difference illustrates how stable isotopes can be used to tease apart two different feeding modes in such similar species living in close association. *Ampelisca* sp. is the mat builder, is tube dwelling and feeds primarily by suspension feeding, whereas *Leptocheirus pinguis* lives in the mat but is a deposit feeder (Whitlatch,

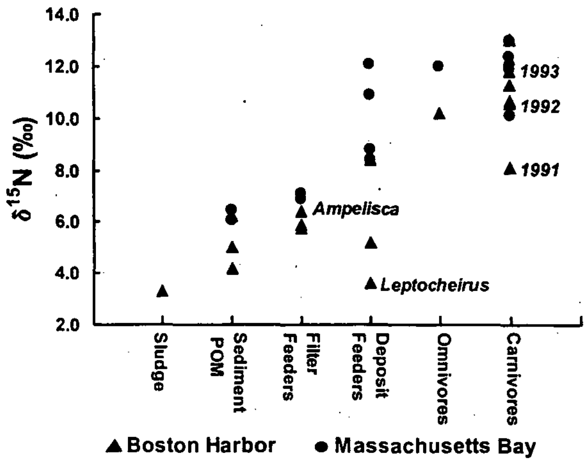

Fig. 7. $\delta^{15}N$ values for animals collected in Boston Harbor (▲) and Massachusetts Bay (●), separated by feeding strategy. The dates in the carnivores column identify data for winter flounder collected in successive years after sludge disposal ceased (Moore et al., 1996). Different feeding strategies for two coexisting amphipods (*Ampelisca* sp. and *Leptocheirus* sp.) are identifiable through N stable isotopes.

1982; Kropp, pers. comm.). In accordance with these two life history strategies and isotopically speaking, *L. pinguis* ($\delta^{15}N = 3.6$) looked much more like sludge than did *Ampelisca* ($\delta^{15}N = 6.4$).

5. Conclusions

Nitrogen and sulfur stable isotopes revealed widespread evidence of sewage-derived particulate and dissolved materials in Boston Harbor and Massachusetts Bay. It was clear from differences in $\delta^{15}N$ values that a large portion of the sediment OM in Boston Harbor has historically comprised sewage sludge and effluent particulates. This was in contrast to sediments of Massachusetts Bay which showed only small indications of sewage influence. Increases in $\delta^{15}N$ values in northern Boston Harbor sediment towards more 'marine' values over time from 1991 to 1998 reflected the cessation of sludge disposal and successive improvements in sewage treatment. These changes also demonstrated the potential of the system to recover after disposal practices are changed.

Nitrogen stable isotopes also enabled us to identify a sewage signal in organisms, and suggested a higher contribution of sewage-derived materials to the harbor food web than to that of Massachusetts Bay. In combination with the sulfur stable isotope, which provided an unambiguous sewage signal, we were able to identify that blue mussels were consuming a food source with a significant sewage component.

From this and other studies it is clear that sewage materials enter marine food webs. This occurs either when sewage-derived inorganic nutrients are taken up by primary producers, or when effluent particulates or sludge are directly ingested by consumers. The stable isotope of sulfur was particularly useful in this regard, as values lighter than typical marine values were clear indicators of effluent particulates. Nitrogen signals were dominated by the mixing of sewage effluent and sludge into both the water column and sediments. Now that measurements of the stable nitrogen isotope in waters with low concentrations of DIN are becoming more routine, we may be able to distinguish the effects of biogeochemical processes from the mixing effects in Boston Harbor and Massachusetts Bay. A sampling program is currently underway that will provide data on concentrations and isotopic ratios of the dissolved and particulate nitrogen pools. Data such as these will greatly improve our understanding of the fates of various sources of nitrogen as land use change increases in the coastal zone.

Acknowledgements

We would like to thank Dave Giehtbrock and Dave Vasiliou for help in diving to collect samples and processing many of the sediment samples. Dave Olmstead provided expert help as master of the R/V *Asterias*. Sediment, mussel, and algae samples were run by the Stable Isotope Laboratory at the Marine Biological Laboratory, under the direction of K. Tholke. The $\delta^{15}N$ of effluent NH_4^+ was analyzed at the Boston University Stable Isotope Laboratory, under the direction of R.H. Michener. Hap Garritt provided helpful advice on animal and algal sample preparation, and Jane Tucker benefited from many conversations with Jack Kelly and Carlton Hunt about nutrient loading and concentrations in Boston Harbor and Massachusetts Bay. Research conducted at The Ecosystems Center of the Marine Biological Laboratory was sponsored by NOAA National Sea Grant College Program Office, Department of Commerce, under Grant No. NA46RG04700, Woods Hole Oceanographic Institution Sea Grant Project No. R/P-56. Matching funds were provided by the Massachusetts Water Resources Authority. Research conducted at Harvard University was supported by MIT Sea Grant Award No. 5700000270. The views expressed herein are those of the authors and do not necessarily reflect the views of NOAA or MWRA or any of their subagencies

References

Alber, M., & Chan, A. B. (1994). *Sources of contaminants to Boston Harbor: revised loading estimates.* Massachusetts Water Resources Authority Technical Report No. 94-1.

Altabet, M. A. (1988). Variations in nitrogen isotopic composition between sinking and suspended particles: implications for nitrogen cycling and particle transformation in the open ocean. *Deep-Sea Research, 35*, 535–554.

Altabet, M. A., & McCarthy, J. J. (1985). Temporal and spatial variations in the natural abundance of ^{15}N in PON from a warm-core ring. *Deep-Sea Research, 32*, 755–772.

Altabet, M. A., & Francois, R. (1994). Sedimentary nitrogen isotopic ratio as a recorder for surface ocean nitrate utilization. Global Biogeochem. *Cycles, 8*, 103–116.

Bothner, M. H., Buchholtz ten Brink, M., Parmenter, C. M., d'Angelo, W. M., & Doughten, M. W. (1993). *The distribution of silver and other metals in sediments from Massachusetts and Cape Cod bays—an interim compilation.* US Geological Survey Open File Report No. 93-725.

Butman, B., Bothner, M. H., Hathaway, J. C., Jenter, H. L., Knevel, H. J., Manheim, F. T., & Signell, R. P. (1992). *Contaminant transport and accumulation in Massachusetts Bay and Boston Harbor: a summary of U.S. Geological Survey studies*. US Geological Survey Open-File Report No. 92-202.

Cifuentes, L. A., Sharp, J. H., & Fogel, M. L. (1988). Stable carbon and nitrogen isotope biogeochemistry in the Delaware estuary. *Limnol. Oceanogr., 33*, 1102–1115.

Cline, J. D., & Kaplan, I. R. (1975). Isotopic fractionation of dissolved nitrate during denitrification in the eastern tropical North Pacific Ocean. *Mar. Chem., 3*, 271–299.

Deegan, L. A., & Garritt, R. H. (1997). Evidence for spatial variability in estuarine foodwebs. *Mar. Ecol. Prog. Ser., 147*, 31–47.

Dolin, E. J. (1990). *Dirty water clean water*. MIT Sea Grant Report No. MITSG 90-21.

Dornblaser, M. M., Giblin, A. E., Fry, B., & Peterson, B. J. (1994). Effects of sulfate concentration in the overlying water on sulfate reduction and sulfur storage in lake sediments. *Biogeochemistry, 24*, 129–144.

Fry, B. (1988). Food web structure on Georges Bank from stable C, N, and S isotopic compositions. *Limnol. Oceanogr., 33*, 1182–1190.

Fry, B., Brand, W., Mersch, F. J., Tholke, K., & Garritt, R. (1992). Automated analysis system for coupled $\delta^{13}C$ and $\delta^{15}N$ measurements. *Analytical Chemistry, 64*, 288–291.

Gearing, P. J., Gearing, J. N., Maughan, J. T., & Oviatt, C. A. (1991). Isotopic distribution of carbon from sewage sludge and eutrophication in the sediments and food web of estuarine ecosystems. *Environ. Sci. Technol., 25*, 295–301.

Giblin, A. E., Hopkinson, C. S., & Tucker, J. (1997). Benthic metabolism and nutrient cycling in Boston Harbor, Massachusetts. *Estuaries, 20*, 346–364.

Hansson, S., Hobbie, J. E., Elmgren, R., Larsson, U., Fry, B., & Johansson, S. (1997). The stable nitrogen isotope ratio as a marker for food web interactions and fish migration. *Ecology, 78*, 2249–2257.

Holmes, R. M., McClelland, J. W., Sigman, D. M., Fry, B., & Peterson, B. J. (1998). Measuring ^{15}N–NH_4^+ in marine, estuarine and fresh waters: an adaptation of the ammonia diffusion method for samples with low ammonium concentrations. *Marine Chemistry, 60*, 235–243.

Howes, B. L. (1998). *Sediment metabolism within Massachusetts Bay and Boston Harbor relating to rates and controls of sediment–water column exchanges of nutrients and oxygen in 1997*. Boston: Massachusetts Water Resources Authority. Report No. ENQUAD 98-20.

Hunt, C. D., Dragos, P., Peven, C., Uhler, A., & Steinhauer, W. (1993). *Synthesis of 106-Mile Site sediment trap chemistry, physical oceanographic measurements, and modeling results*. Final Report to the Environmental Protection Agency Oceans and Coastal Protection Division, Washington, DC.

Hunt, C. D., West, D. E., & Peven, C. S. (1995). *Deer Island effluent characterization and pilot treatment plant studies: June 1993–November 1994*. MWRA Technical Report No. 95-7.

Hunt, C. D., Dragos, P., King, K., Albro, C., West, D., Uhler, A., Ginsburg, L., Pabst, D., & Redford, D. (1996). The fate of sewage sludge dumped at the 106-Mile Site–sediment trap study results. *J. Mar. Environ. Eng., 2*, 285–323.

Jordan, M. J., Nadelhoffer, K. J., & Fry, B. (1997). Nitrogen cycling in forest and grass ecosystems irrigated with ^{15}N-enriched wastewater. *Ecological Applications, 7*, 864–881.

Kaplan, I. R., Emery, K. O., & Rittenberg, S. C. (1963). The distribution and isotopic abundance of sulphur in recent marine sediments off southern California. *Geochim. Cosmochim. Acta, 27*, 297–331.

Kelly, J. R. (1997). Nitrogen flow and the interaction of Boston Harbor with Massachusetts Bay. *Estuaries, 20*, 365–380.

Kelly, J. R., & Turner, J. (1995). *Water column monitoring in Massachusetts and Cape Cod bays: annual report for 1994*. MWRA Environmental Quality Department Technical Report No. 95-17.

Knebel, H. J., Rendigs, R. R., & Bothner, M. H. (1991). Modern sedimentary environments in Boston Harbor, Massachusetts. *J. Sed. Petr., 61*, 791–804.

Kropp, R. K., & Diaz, R. J. (1995). *Infaunal community changes in Boston Harbor 1991–1994*. MWRA Technical Report No. 95-21.

Lavery, P., Coughlin, K., Steinhauer, M., & Connor, M. (1994). *State of Boston Harbor: 1993*. MWRA Technical Report No. 94-6.

Libby, P. S., Kelly, J. R., Albro, C. S., Hennessy, J. T., Turner, J., Borkman, D., Reed, L., Vaillancourt, R., & Heil, C. (1995). *Water quality monitoring in Massachusetts and Cape Cod Bays: October–December 1994*. MWRA Environmental Quality Department Technical Report No. 95-10.

Liu, K.-K., & Kaplan, I. R. (1989). The eastern tropical Pacific as a source of ^{15}N-enriched nitrate in seawater off southern California. *Limnol. Oceanogr., 34*, 820–830.

Macko S. A. (1983). Sources of organic nitrogen in mid-Atlantic coastal bays and continental shelf sediments of the United States: isotopic evidence. *Carnegie Institution Washington Year Book, 83*, 390–394.

Mariotti, A., Lancelot, C., & Billen, G. (1994). Natural isotopic composition of nitrogen as a tracer of origin for suspended organic matter in the Scheldt estuary. *Geochim. Cosmochim. Acta, 48*, 549–555.

Mayer, L. M., Macko, S. A., & Cammen, L. (1988). Provenance, concentrations and nature of sedimentary organic nitrogen in the Gulf of Maine. *Mar. Chem., 25*, 291–304.

McClelland, J. W., Valiela, I., & Michener, R. H. (1997). Nitrogen stable isotope signatures in estuarine food webs: a record of increasing urbanization in coastal watersheds. *Limnol. Oceanogr., 42*, 930–937.

Miyake, Y., & Wada, E. (1967). The abundance ration of $^{15}N/^{14}N$ in marine environments. *Rec. Oceanog. Works Japan, 9*, 37–53.

Moore, M. J, Shea, D., Hillman, R., & Stegeman, J. J. (1996). Trends in hepatic tumours and hydropic vacuolation, fin erosion, organic chemicals and stable isotope ratios in winter flounder from Massachusetts, USA. *Mar. Pollut. Bull., 32*, 458–470.

Nadelhoffer, K. J., & Fry, B. (1988). Controls on natural nitrogen-15 and carbon-13 abundances in forest soil organic matter. *Soil Sci. Soc. Am. J., 52*, 1633–1640.

Nixon, S. W., & Pilson, M. E. Q. (1983). Nitrogen in estuarine and coastal ecosystems. In E.J. Carpenter, & D. B. Capone, *Nitrogen in the marine environment* (pp. 565–648). New York: Academic Press.

Peters, K. E., Sweeney, R. E., & Kaplan, I. R. (1978). Correlation of carbon and nitrogen stable isotope ratios in sedimentary organic matter. *Limnol. Oceanogr., 23*, 598–604.

Peterson, B. J., & Fry, B. (1987). Stable isotopes in ecosystem studies. *Ann. Rev. Ecol. Syst., 18*, 293–320.

Peterson, B. J., Howarth, R. W., & Garritt, R. H. (1985). Multiple stable isotopes used to trace the flow of organic matter in estuarine food webs. *Science, 227*, 1361–1363.

Rau, G. H., Sweeney, R. E., Kaplan, I. R., Mearns, A. J., & Young, D. R. (1981). Differences in animal ^{13}C, ^{15}N, and D abundance between a polluted and an unpolluted coastal site: likely indicators of sewage uptake by a marine food web. *Estuarine, Coastal and Shelf Science, 13*, 701–707.

Sigman, D. M., Altabet, M. A., Michener, R., McCorkle, D. C., Fry, B., & Holmes, R. M. (1997). Natural abundance-level measurement of the nitrogen isotopic composition of oceanic nitrate: an adaptation of the ammonia diffusion method. *Mar. Chem., 57*, 227–242.

Signell, R. P., & Butman, B. (1992). Modeling tidal exchange and dispersion in Boston Harbor. *Journal of Geophysical Research, 97*, 15 591–15 606.

Spies, R. B., Kruger, H., Ireland, R., & Rice Jr., D. W. (1989). Stable isotope ratios and contaminant concentrations in a sewage-distorted food web. *Mar. Ecol. Prog. Ser., 54*, 157–170.

Sweeney, R. E., & Kaplan, I. R. (1980a). Tracing flocculent industrial and domestic sewage transport on San Pedro Shelf, southern California, by nitrogen and sulfur isotope ratios. *Marine Environ. Res. 3*, 215–224.

Sweeney, R. E., & Kaplan, I. R. (1980b). Natural abundances of ^{15}N as a source indicator for near-shore marine sedimentary and dissolved nitrogen. *Mar. Chem., 9*, 81–94.

Sweeney, R. E., Kalil, E. K., & Kaplan, I. R. (1980). Characterisation of domestic and industrial sewage in southern California coastal sediments using nitrogen, carbon, sulphur and uranium tracers. *Marine Environ. Res., 3*, 225–243.

Tucker, J., Giblin, A. E., & Hopkinson, C. S. (1999). *Metabolism, nutrient cycling and denitrification in Boston Harbor sediments in 1998*. MWRA Environmental Quality Department Technical Report No. 99-08.

Van Dover, C. L., Grassle, J. R., Fry, B., Garritt, R. H., & Starczak, V. R. (1992). Stable isotope evidence for entry of sewage-derived organic material into a deep-sea food web. *Nature, 360*, 153–155.

Wada, E., Kadonaga, T., & Matsuo, S. (1975). ^{15}N in nitrogen of naturally occurring substances and global assessment of denitrification from isotopic viewpoint. *Geochem. J., 9*, 139–148.

Wainright, S. C., & Fry, B. (1994). Seasonal variation of the stable isotopic compositions of coastal marine plankton from Woods Hole, Massachusetts and Georges Bank. *Estuaries, 17*, 552–560.

Whitlatch, R. B. (1982). The ecology of New England tidal flats: a community profile. US Fish and Wildlife Service, Biological Services Program, Washington, D.C. FWS/OBS-81/01.