

# Determination of the relative contribution of various sources of nitrogen to primary production in Martha's Vineyard ponds

Javier Lloret, Anne Giblin, Rich McHorney

The Ecosystems Center, Marine Biological Laboratory

## Background

Wastewater, fertilizer and atmospheric deposition are the three major external sources of nitrogen to our estuaries and coastal ponds. Nitrogen from these three sources enters estuaries and promotes primary producer growth. Excessive amounts of nitrogen can cause algal overgrowth and eutrophication, resulting in an overall degradation of the natural environment. Quantifying the relative contribution of the various sources of external nitrogen to excessive primary producer growth is key for understanding which of those sources (or combinations of them) are likely causes of eutrophication, and as a first step for developing effective management strategies to remediate its negative effects.

The nitrogen present in wastewater, fertilizers and atmospheric deposition differ greatly in its isotopic composition. Examining the stable isotopic signatures of nitrogen in environmental samples allows us to determine the origin of that nitrogen and the relative importance of its various sources.

Estuarine suspended materials, mostly composed of phytoplankton cells, rapidly incorporate the nitrogen available in estuaries. The captured nitrogen is used by phytoplankton to grow. Due to the rapid and efficient incorporation of nitrogen by plankton, the isotopic signature of the particulate nitrogen (PON) usually reflects the isotopic signature of the mix of the various available nitrogen sources, and it can therefore provide us with information about the relative importance of nitrogen sources in an estuary.

## Methodology

The data and conclusions presented in this brief report resulted from the analysis of stable isotopic signatures of PON present in estuarine waters. Water samples were collected in various ponds in Martha's Vineyard during the period between June and October 2021. A total of 101 particulate samples were analyzed.

To obtain approximate estimates of the relative contributions from the most likely and distinguishable sources (wastewater, fertilizers or atmospheric deposition) we used IsoSource (Phillips et al., 2005), a stable isotope mixing model developed by the U.S. EPA.

Stable isotope mixing models are often used to quantify source contributions to a mixture. Examples include

pollution source identification, trophic web studies, analysis of water sources for soils, plants or water

**Table 1.** Ranges and midpoints of  $\delta^{15}\text{N}$  values in wastewater, fertilizers, and atmospheric deposition. Values averaged from compilations in the literature (Aravena et al., 1993; Bateman and Kelly, 2007; Chen et al., 2011; Heaton, 1986; Jia and Chen, 2010; Kaushal et al., 2011; Kendall, 1998; Kim et al., 2017; Kreitler, 1979; Li et al., 2016; Su et al., 2005; Xue et al., 2009)

Nitrogen sources	$\delta^{15}\text{N}$ range (‰)	$\delta^{15}\text{N}$ midpoint (‰)
Wastewater	7.3 to 21.0	14.2
Inorganic fertilizers	-3.9 to 3.1	-0.4
Atmospheric deposition	-8.1 to -2.9	-5.5

bodies, and many others. In our case, the mixing models are used to quantify relative contributions of wastewater, fertilizer and atmospheric nitrogen to PON samples. To perform our calculations, we entered the mid-point in the range of  $\delta^{15}\text{N}$  for each of the three nitrogen sources (Table 1) and calculated the % contribution of the various sources to the nitrogen present in our samples of particulates collected in the various ponds.

## Results and discussion

The results of the analysis of the relative contributions of wastewater, fertilizer and atmospheric nitrogen in PON are summarized in Table 2:

**Table 2.** Averages and ranges for relative contributions of wastewater, fertilizer and atmospheric nitrogen in PON samples collected in various ponds.

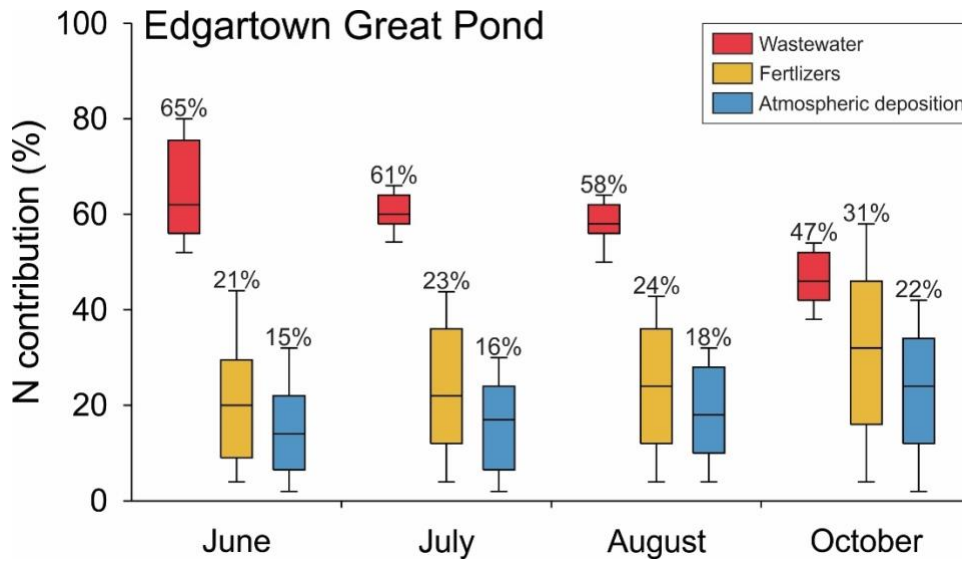
Estuary/Pond	N source	% Contribution (mean $\pm$ s.d.)	Range (%)
Edgartown Great Pond	Wastewater	55 $\pm$ 9	34-82
	Fertilizer	26 $\pm$ 16	0-66
	Atmospheric	19 $\pm$ 12	0-46
Crackatuxet Cove	Wastewater	51 $\pm$ 8	32-68
	Fertilizer	28 $\pm$ 17	0-66
	Atmospheric	21 $\pm$ 13	0-50
Chilmark Pond	Wastewater	58 $\pm$ 8	34-76
	Fertilizer	24 $\pm$ 15	0-66
	Atmospheric	17 $\pm$ 11	0-46
Tisbury Great Pond	Wastewater	53 $\pm$ 9	30-74
	Fertilizer	27 $\pm$ 17	0-66
	Atmospheric	20 $\pm$ 12	0-50

Overall, our data confirmed that wastewater was the largest contributor of nitrogen to PON in the selected estuaries. In average, wastewater contributed between 51-58% of the nitrogen found in the particulates. The rest of the nitrogen could be linked to fertilizers (21-27%) and atmospheric sources (17-21%). A more detailed description of source contributions in each pond is presented below.

### ***Contributions of various sources of nitrogen to Edgartown Great Pond and Crackatuxet Cove***

Wastewater contributed around 55% of the nitrogen present in samples of PON collected in Edgartown Great Pond (Table 2). Values were, however, quite variable across samples and along the season. Wastewater contributions were larger during June and July, high in August, but decreased substantially in October (Fig. 1). This decrease could potentially be linked to the opening of the inlet in August 7, and the re-establishment of the connection with the open sea that could have helped flush away some of the excess nitrogen in the pond. Our samples from August 10, only three days after the re-opening of the inlet, did not seem to reflect much of an effect of the inlet opening, indicating that the flushing of nutrients and subsequent measurable response of PON could take several days or even weeks.

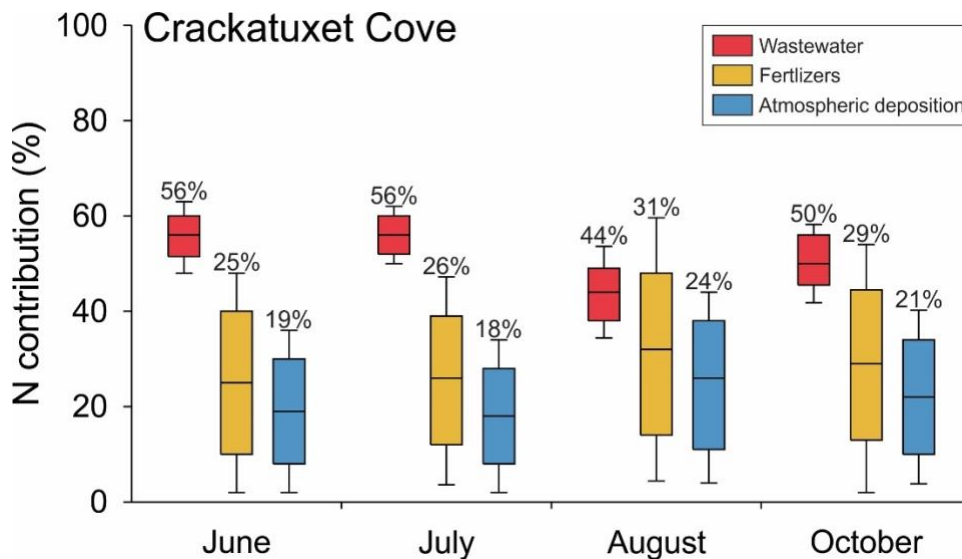
The estimated contributions of fertilizers and atmospheric nitrogen were quite variable, but combined represented less than half of the nitrogen available for PON. The slight increase observed in October for fertilizer and atmospheric contributions were attributable to the parallel decrease in wastewater nitrogen, rather than an increase in the total amount of nitrogen from those two sources (Fig. 1).



**Figure 1.** Relative contributions of various sources of nitrogen to PON in Edgartown Great Pond during the summer and early fall. Boxes represent the range between the first and third quartiles of the distribution. Horizontal lines indicate the median. Whiskers are the 5 and 95 percentiles. Averages are shown as numbers on top of each box.

The contributions of wastewater nitrogen to PON in the adjacent Crackatuxet Cove averaged 51%, slightly lower than those observed in Great Pond (Table 2). The lower wastewater contributions are likely a result of the lower urban development in the Crackatuxet watershed compared to that of Great Pond. Despite being located immediately adjacent to the Great Pond inlet, Crackatuxet Cove did not show a marked decrease in wastewater contributions after the re-opening. Crackatuxet cove is virtually isolated from the main pond, and operations in the pond's inlet did not seem to affect it (Fig. 2).

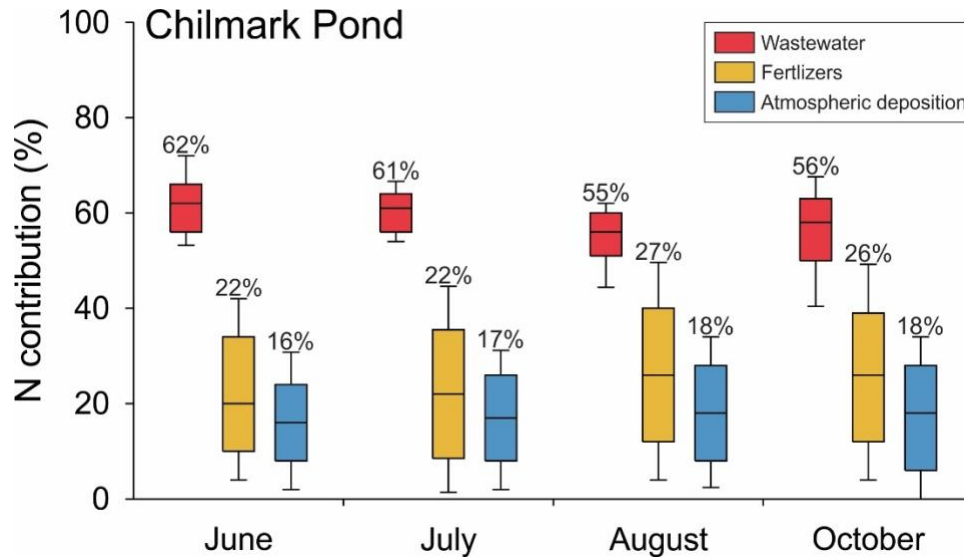
The estimated contributions of fertilizers and atmospheric nitrogen to Crackatuxet Pond were quite variable, and combined represented about half of the nitrogen available for PON (Fig. 2).



**Figure 2.** Relative contributions of various sources of nitrogen to PON in Crackatuxet Cove during the summer and early fall. Boxes represent the range between the first and third quartiles of the distribution. Horizontal lines indicate the median. Whiskers are the 5 and 95 percentiles. Averages are shown as numbers on top of each box.

### ***Contributions of various sources of nitrogen to Chilmark Pond***

Wastewater contributed around 58% of the nitrogen present in samples of PON collected in Chilmark Pond (Table 2). Despite certain variability, wastewater contributions were consistently high across all samples and along the season (Fig. 3). The estimated contributions of fertilizers and atmospheric nitrogen were quite variable, but combined represented less than half of the nitrogen available for PON (Fig. 3).

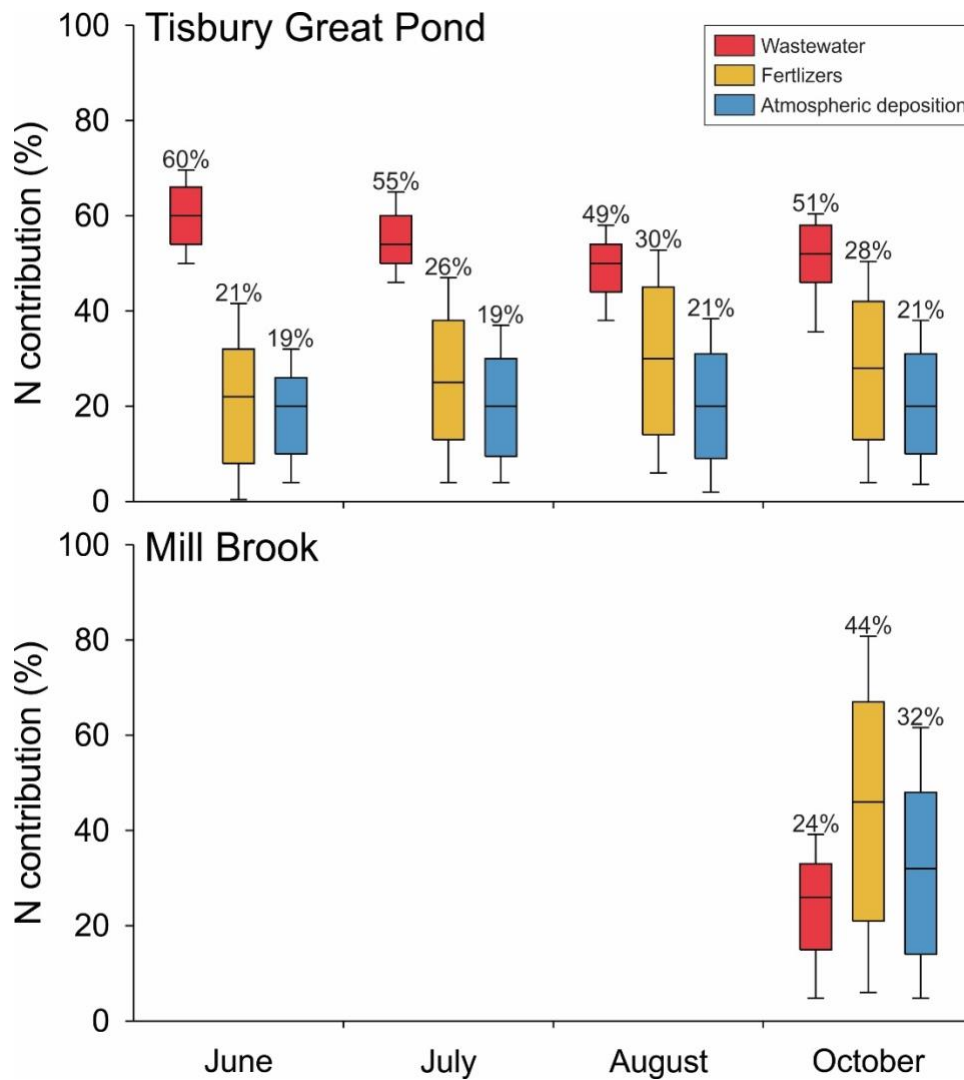


**Figure 3.** Relative contributions of various sources of nitrogen to PON in Chilmark Pond during the summer and early fall. Boxes represent the range between the first and third quartiles of the distribution. Horizontal lines indicate the median. Whiskers are the 5 and 95 percentiles. Averages are shown as numbers on top of each box.

### ***Contributions of various sources of nitrogen to Tisbury Great Pond***

Wastewater contributed around 53% of the nitrogen present in samples of PON collected in Tisbury Great Pond (Table 2). Despite certain variability, wastewater contributions were relatively consistent across samples and along the season (Fig. 4 top panel). The estimated contributions of fertilizers and atmospheric nitrogen were quite variable, but combined represented less than half of the nitrogen available for PON (Fig. 4 top panel).

We also had the opportunity to analyze samples from the Mill Brook area, a freshwater stream that flows into Tisbury Great Pond at its northern end. Even though our samples are limited to October, we clearly observed that wastewater was not the largest contributor of nitrogen to PON in the Mill Brook (Fig. 4 bottom panel). Fertilizers and, to a certain extent atmospheric deposition, seemed to be the largest contributors of nitrogen in this particular area (Fig. 4 bottom panel). This fact probably confirms that this stream is not a major source of wastewater nitrogen to the Tisbury Great Pond. The low wastewater and relatively higher fertilizer contributions is consistent with the relatively undeveloped land and presence of small farms in the northern area of Tisbury Great Pond drained by the Mill Brook stream.



**Figure 4.** Relative contributions of various sources of nitrogen to PON in Tisbury Great Pond (top panel) and Mill Brook (bottom panel) during the summer and early fall. Boxes represent the range between the first and third quartiles of the distribution. Horizontal lines indicate the median. Whiskers are the 5 and 95 percentiles. Averages are shown as numbers on top of each box.

## References

- Aravena, R., Evans, M.L., Cherry, J.A., 1993. Stable isotopes of oxygen and nitrogen in source identification of nitrate from septic systems. *Groundwater* 31, 180–186. <https://doi.org/10.1111/J.1745-6584.1993.TB01809.X>
- Bateman, A.S., Kelly, S.D., 2007. Fertilizer nitrogen isotope signatures. <http://dx.doi.org/10.1080/10256010701550732> 43, 237–247. <https://doi.org/10.1080/10256010701550732>
- Chen, N., Hong, H., Huang, Q., Wu, J., 2011. Atmospheric nitrogen deposition and its long-term dynamics in a southeast China coastal area. *J. Environ. Manage.* 92, 1663–1667. <https://doi.org/10.1016/J.JENVMAN.2011.01.026>

- Heaton, T.H.E., 1986. Isotopic studies of nitrogen pollution in the hydrosphere and atmosphere: A review. *Chem. Geol. Isot. Geosci. Sect.* 59, 87–102. [https://doi.org/10.1016/0168-9622\(86\)90059-X](https://doi.org/10.1016/0168-9622(86)90059-X)
- Jia, G., Chen, F., 2010. Monthly variations in nitrogen isotopes of ammonium and nitrate in wet deposition at Guangzhou, south China. *Atmos. Environ.* 44, 2309–2315. <https://doi.org/10.1016/J.ATMOSENV.2010.03.041>
- Kaushal, S.S., Groffman, P.M., Band, L.E., Elliott, E.M., Shields, C.A., Kendall, C., 2011. Tracking nonpoint source nitrogen pollution in human-impacted watersheds. *Environ. Sci. Technol.* 45, 8225–8232. <https://doi.org/10.1021/es200779e>
- Kendall, C., 1998. Tracing Nitrogen Sources and Cycling in Catchments, in: Kendall, C., McDonnell, J.J. (Eds.), *Isotope Tracers in Catchment Hydrology*. Elsevier, pp. 519–576. <https://doi.org/10.1016/b978-0-444-81546-0.50023-9>
- Kim, H., Lee, K., Lim, D. II, Nam, S. II, Kim, T.W., Yang, J.Y.T., Ko, Y.H., Shin, K.H., Lee, E., 2017. Widespread anthropogenic nitrogen in Northwestern Pacific ocean sediment. *Environ. Sci. Technol.* 51, 6044–6052. [https://doi.org/10.1021/ACS.EST.6B05316/ASSET/IMAGES/LARGE/ES-2016-05316G\\_0004.JPEG](https://doi.org/10.1021/ACS.EST.6B05316/ASSET/IMAGES/LARGE/ES-2016-05316G_0004.JPEG)
- Kreitler, C.W., 1979. Nitrogen-isotope ratio studies of soils and groundwater nitrate from alluvial fan aquifers in Texas. *J. Hydrol.* 42, 147–170. [https://doi.org/10.1016/0022-1694\(79\)90011-8](https://doi.org/10.1016/0022-1694(79)90011-8)
- Li, Y., Zhang, H., Tu, C., Fu, C., Xue, Y., Luo, Y., 2016. Sources and fate of organic carbon and nitrogen from land to ocean: Identified by coupling stable isotopes with C/N ratio. *Estuar. Coast. Shelf Sci.* 181, 114–122. <https://doi.org/10.1016/J.ECSS.2016.08.024>
- Phillips, D.L., Newsome, S.D., Gregg, J.W., 2005. Combining sources in stable isotope mixing models: Alternative methods. *Oecologia* 144, 520–527. <https://doi.org/10.1007/S00442-004-1816-8/FIGURES/4>
- Su, M.L., Zhang, J., Hong, T.C., Guo, S.Z., 2005. Factors influencing nutrient dynamics in the eutrophic Jiaozhou Bay, North China. *Prog. Oceanogr.* 66, 66–85. <https://doi.org/10.1016/J.POCEAN.2005.03.009>
- Xue, D., Botte, J., De Baets, B., Accoe, F., Nestler, A., Taylor, P., Van Cleemput, O., Berglund, M., Boeckx, P., 2009. Present limitations and future prospects of stable isotope methods for nitrate source identification in surface- and groundwater. *Water Res.* 43, 1159–1170. <https://doi.org/10.1016/J.WATRES.2008.12.048>