

Oxygen and Nutrient Exchanges at the Sediment-Water Interface: a Global Synthesis and Critique of Estuarine and Coastal Data

W. R. Boynton¹ · M. A. C. Ceballos¹ · E. M. Bailey¹ · C. L. S. Hodgkins¹ · J. L. Humphrey¹ · J. M. Testa¹

Received: 20 December 2016 / Revised: 18 May 2017 / Accepted: 8 June 2017 / Published online: 9 August 2017
© Coastal and Estuarine Research Federation 2017

Abstract Estuarine and coastal marine sediment-water fluxes are considered to be important ecological features, but a global-scale assessment has yet to be developed. Goals of this work were to assemble a global-scale database of net sediment-water flux measurements, examine measurement techniques, characterize the geographic distribution and magnitude of sediment fluxes, explore the data for controls on sediment flux magnitude, and assess the importance of sediment fluxes in ecosystem-level metabolism and primary production. We examined 480 peer-reviewed sources and found sediment flux data for 167 estuarine and coastal systems. Most measurements were made in North America, Europe, and Australia. Fluxes varied widely among systems, some by several orders of magnitude. Inter-annual variability within sites was less than an order of magnitude but time series flux data to evaluate this were rare. However, limited time series data exhibited large and rapid responses to decreased external nutrient loading rates, climate change effects (possible temperature effects), and variability in trophic conditions. Comparative analyses indicated organic matter supply to sediments set the upper limits of flux magnitude, with other factors playing secondary roles. Two metrics were developed to assess ecosystem-level importance of sediment-water fluxes. Sediments represented 30% or more of depth-integrated rates of aerobic system respiration at depths of <10 m. An annual phytoplankton production data set was used to estimate N and

P demand; sediments supplied an average of 15–32% of N and 17–100% of P demand and, in some cases, was as large or larger than external nutrient inputs. The percent of demand supplied by sediments was highest in temperate latitudes and lower in high and tropical latitudes.

Keywords Sediment-water nutrient exchanges · Sediment oxygen consumption · Estuarine nutrient dynamics

Introduction

Exceptionally high rates of primary production are associated with coastal and estuarine waters throughout the world (Boynton et al. 1982; Cloern et al. 2014) and this production of organic matter is further reflected in high levels of secondary production when compared to lake, shelf, and open ocean rates (Nixon 1988; Houde and Rutherford 1993). Multiple factors contribute to this production but perhaps the primary factor in many of these systems is a nutrient supply coming not only from adjacent landscapes but also, in some cases, from topographic upwelling of deeper, nutrient-rich ocean water and from direct atmospheric deposition of nitrogen to estuarine and coastal surface waters. However, nutrient supply rate from external sources is not a sufficient explanation. Additional factors such as water clarity, tidal energy subsidy, stratification regime, water residence time, and others come into play in many instances (e.g., Nixon 1988; Wulff et al. 1990).

A characterizing feature of these productive systems is that they are relatively shallow. For example, a large survey of estuaries revealed an average depth of less than 10 m (Bricker et al. 2007). As a consequence, zones of primary production in near-surface euphotic layers are in close proximity to deeper waters and sediments where decomposition

Communicated by Iris C. Anderson

✉ W. R. Boynton
boynton@umces.edu

¹ Chesapeake Biological Laboratory, University of Maryland Center for Environmental Science, 146 Williams Street, Solomons, MD 20688, USA

and nutrient recycling processes occur. These coupled processes are often referred to as benthic-pelagic (B/P) coupling (Nixon 1981; Jensen et al. 1990; Kemp et al. 1999). An important consequence of this tight coupling in shallow waters is that essential, and often limiting, nutrients (nitrogen, N; phosphorus, P; dissolved silica, DSi) are recycled from sediments and aphotic waters and returned to surface waters via mixing processes (e.g., Webb and D'Elia 1980; Miller et al. 2006). For example, in the relatively shallow Patuxent River estuary, Boynton et al. (2008) found that recycled N and P from sediments were a much larger source than new external inputs during warm seasons and of similar magnitude even during cold seasons. This situation is in sharp contrast to deeper systems where once euphotic zone nutrients are used, often associated with a spring plankton bloom, those nutrients are deposited in particulate organic forms and are lost for the season, the year, or longer until they are returned to euphotic waters via mixing or advection. Of course, in some of these shallow systems, light does reach the bottom and hence complicates B/P coupling because autotrophic as well as heterotrophic processes are active.

During the past half century, many coastal ecosystems have become overly enriched with nutrients leading to serious eutrophication problems (Kemp et al. 2005; Diaz and Rosenberg 2008). In efforts to understand eutrophication, an impressive diversity of research and monitoring activities have yielded overwhelming amounts of data, but relatively few cross-system syntheses have been performed (Carpenter et al. 2009; Kemp and Boynton 2012). However, a few recent syntheses have either included or focused on coastal and estuarine systems. For example, Cloern et al. (2014) produced an analysis of primary production based on data from 131 shallow coastal and estuarine systems and found production varied 10-fold among these systems, 5-fold from year to year, and argued that long-term sites be established using a standard measurement method to further understanding of global-scale shallow water production. Sediment denitrification rates have also received considerable review and synthesis despite the fact that measurements of this process have a shorter history than those of other sediment processes. For example, Cornwell et al. (1999) reviewed and critiqued denitrification measurement methods and summarized knowledge concerning factors controlling this process. Seitzinger et al. (2006) developed a comparative analysis of rates across a spectrum of aquatic systems and found denitrification rates were strongly influenced by N load and water residence times. Piña-Ochoa and Álvarez-Cobelas (2006) reported on a cross-system analysis (136 data sets) and found denitrification rates increased from oceans to lakes, peaked during warm periods of the year, and exhibited a strong relationship to water column NO_3 concentration.

Despite the fact that the technically simpler measurements of sediment-water oxygen and nutrient exchanges have been

made for many decades and such flux estimates have been incorporated into water quality models for more than three decades (Di Toro 1980), we are not aware of any global-scale assessment of available data. Several authors have synthesized sediment flux data for comparative purposes but the scale was at a regional (Twilley et al. 1999) or even less comprehensive scale. We are overdue for a global-scale assessment of this process.

We had several goals in developing this sediment-water flux synthesis, using a comparative analysis approach, and these included (1) to assemble a global-scale database of sediment-water flux measurements (O_2 as sediment oxygen consumption or SOC, NH_4 , NO_2 , NO_3 , PO_4 , and DSi) and associated water column and sediment variables and make the database available to all interested researchers; (2) to examine the techniques used to make these measurements; (3) to characterize the geographic distribution, magnitude, and seasonality of sediment-water fluxes; (4) to examine the database for relationships between sediment-water flux and a selection of environmental conditions influencing sediment-water flux seasonality and magnitude; and (5) to use a “broad brush” approach in which the relative importance of sediment-water fluxes in system-level metabolism and primary production is evaluated. Finally, we hope the assembled database will become a “living document” with additions as new data become available and corrections of whatever omissions or mistakes we may have made in assembling this database.

Literature Search Approach and Search Results

Several approaches were used to identify peer-reviewed papers concerning sediment-water oxygen and nutrient exchanges and associated environmental data. We first gathered papers we used in past work and then reviewed the literature cited sections of these papers to identify additional relevant papers. We then used the University of Maryland's Research Port to access large numbers of journals dealing with aquatic sciences (e.g., *Aquatic Ecology*, *Biogeochemistry*, *Estuaries and Coasts*, *Limnology and Oceanography*, *Marine Ecology Progress Series*). We also used tools such as the Google Scholar, JSTOR, Springer, Mendeley, Science Direct, Web of Science, and Scopus plus the University of Maryland Libraries' primary catalog and its discovery tools. In using all these tools, we applied the following keyword searches: sediment oxygen and nutrient fluxes, sediment-water nutrient fluxes, sediment-water interface, in situ sediment core incubation, bell jars, benthic chambers, benthic fluxes, oxygen uptake, sediment oxygen demand/consumption (SOD/SOC), and sediment respiration. We also examined papers identified via the above searches by authors to find additional papers they may have published as well as papers published by co-authors. We examined the literature cited sections of all papers

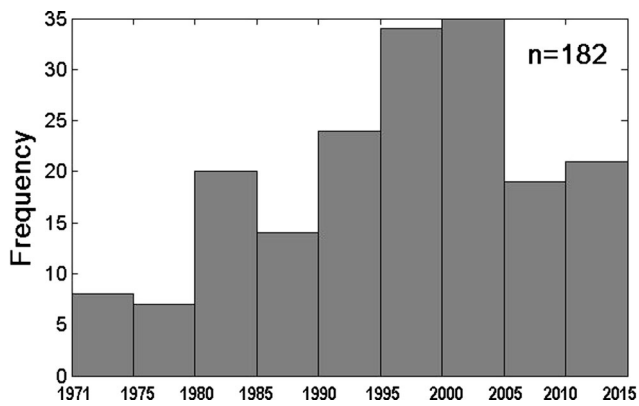


Fig. 1 Histogram indicating the number of peer-reviewed papers used in this analysis arranged by half-decade of publication date. The n of 182 refers to the number of peer-reviewed papers used in this analysis

for additional relevant papers. Although our literature search was exhaustive, we surely overlooked some publications.

We examined papers from 80 different journals. We included data from several technical reports and dissertations but our focus was on the peer-reviewed literature. We examined a total of 480 documents and were able to extract net sediment flux and associated environmental data for 167 different ecosystems and distinctly different parts of large ecosystems (e.g., low, mid, and high salinity zones of Chesapeake Bay were counted as three sites). Slightly over half of the papers yielding information useful for this work were published during a 15-year period between 1991 and 2005 (Fig. 1). We did not find any papers meeting our criteria prior to 1970. Earlier, Nixon et al. (1976) reached the same conclusion and attributed this early lack of interest in sediment processes in marine waters to the fact that in deeper oceanic systems the role of sediment oxygen consumption and nutrient recycling processes is relatively small. During the 1970s, the role of sediments in much shallower coastal and estuarine systems was recognized as being important and measurement programs were subsequently initiated. However, we have a considerably shorter historical record to work with compared to the study of these processes in lakes

(e.g., Mortimer 1941). The publication of papers during the most recent decade has been at a rate about half that of the previous decade despite increased awareness of accelerating eutrophication trends in these systems, broad use of water quality models including sediment processes, and intensified efforts to reverse eutrophication trends.

Data describing these sediment-water fluxes are not evenly distributed along global coastlines (Figs. 2 and 3, Table 1). About 70% of all sites were located in North America, Europe, and Australia, a finding similar to that of Cloern et al. (2014) regarding global distribution of annual-scale phytoplankton primary production measurements. Data from shallow zones of the Arctic and Antarctica were sparse and this was of concern because these regions are experiencing severe influences of climate change. Likewise, there were few measurements from anywhere along the coasts of Africa and from the complex coastlines of Asia where land use change and human activities are intensifying.

Criteria for Inclusion and Description of the Flux Database

After initial inspection of sediment-water flux data from peer-reviewed publications, we made a number of decisions regarding criteria for inclusion in the database and subsequent analyses. First, our data set was limited to sites with water depths less than 100 m to focus on estuarine and coastal systems. We did include data from a few deeper sites for comparative purposes, and because a few of these were also of historical and pioneering interest (e.g., Smith and Teal 1973). Second, we only included flux measurements made using intact sediment cores or in situ chambers with incubations taking place either in situ, on shipboard or in a laboratory setting; flux estimates derived from diagenetic models based on pore water nutrient concentration gradients or those based on the relatively new eddy covariance methods (e.g., Berg et al. 2003) were not

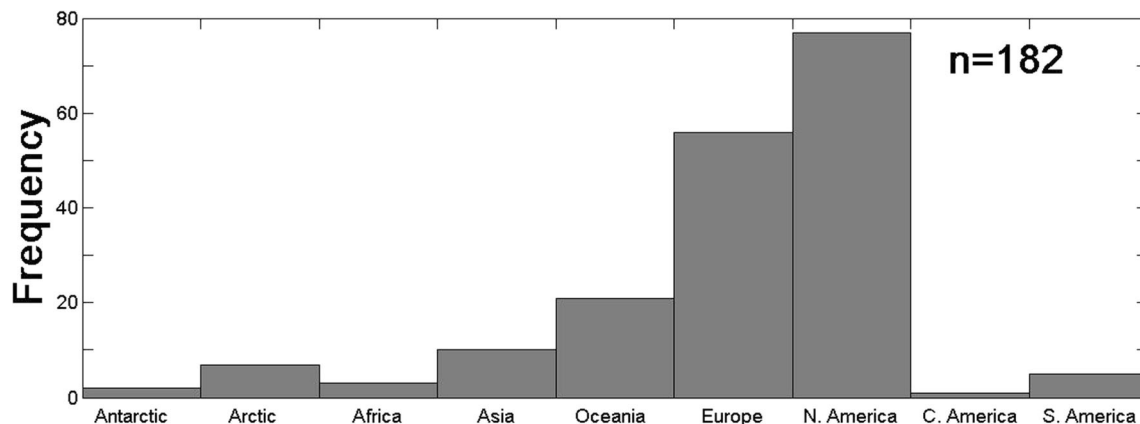


Fig. 2 Histogram indicating the number of studies available by continent or area

included. Third, only flux measurements made in the dark were included and we did not include flux data if macrophytic plants (e.g., seagrasses or macroalgae) were contained in the incubation chamber. A few of the net sediment-water fluxes were exposed to light for a portion of the day but all fluxes reported here were conducted in the dark. More detailed analyses regarding the seemingly more complex sediment-water flux dynamics of shallow photic environments have been reported by Anderson et al. (2003), McGlathery (2008), Anderson et al. (2010) and in a series of papers by Sundbäck and colleagues (Sundbäck and Graneli 1988; Sundbäck et al. 2000 and Sundbäck et al. 2004). Finally, there is a literature concerning the use of large field-based flumes (e.g., Wolaver et al. 1985; Dame et al. 1991) and tunnels (Dame et al. 1984; Prins and Smaal 1994) used primarily in intertidal locations and focusing on dense macrobenthic (oyster or mussel reefs) or tidal marsh communities. Nutrient fluxes associated with these very metabolically active systems were often one to two orders of magnitude greater than those found in non-reef sub-tidal communities. These data, which are limited in spatial and temporal coverage, have been summarized by Asmus et al. (1998) and were not included in this analysis.

The flux database contains a total of 49 variables (14 categorical and 35 numeric) including net sediment-water fluxes of oxygen (O_2 ; synonymous with sediment oxygen consumption, SOC), ammonium (NH_4), nitrite (NO_2), nitrate (NO_3), nitrite plus nitrate ($NO_2 + NO_3$), dissolved inorganic phosphorus (PO_4 or DIP), and dissolved silica (DSi) as well as sample location, date of measurement, measurement techniques, and a variety of water column and sediment characteristics (Table 2). We did not include dissolved inorganic carbon

(DIC) or dissolved organic nitrogen (DON) fluxes because such measurements remain relatively rare. There were very few studies that contained data for all of these variables; most had 30 to 70% of all variables available. In addition to the general criteria indicated above, we only included data sets in our analysis that reported sampling location, literature source, date of measurement, light conditions at the sediment surface, description of the measurement technique (i.e., intact cores or in situ chambers), stirring method, core or chamber area, and at least one sediment-water flux measurement for one of the analytes of interest. Most studies reported fluxes of several analytes for multiple time periods during a year and additional values for water column and sediment conditions. Studies reporting multi-year time series of sediment flux data were rare. In a limited number of cases, the minimum data needed for inclusion in the data set were not reported in the paper containing the sediment flux data. In these cases, we were able to obtain the required data by contacting authors or we were able to find other papers containing the needed data. The current database contains 2879 lines of data and is available on the web (www.gonzo.cbl.umces.edu) and at Mendeley Data (<http://dx.doi.org/10.17632/8gc3ys3jx6.2>).

Sediment-Water Flux Measurement Methods

Computing Sediment-Water Flux Estimates

There was substantial uniformity in the approaches used for estimating sediment-water fluxes. In the majority of cases,

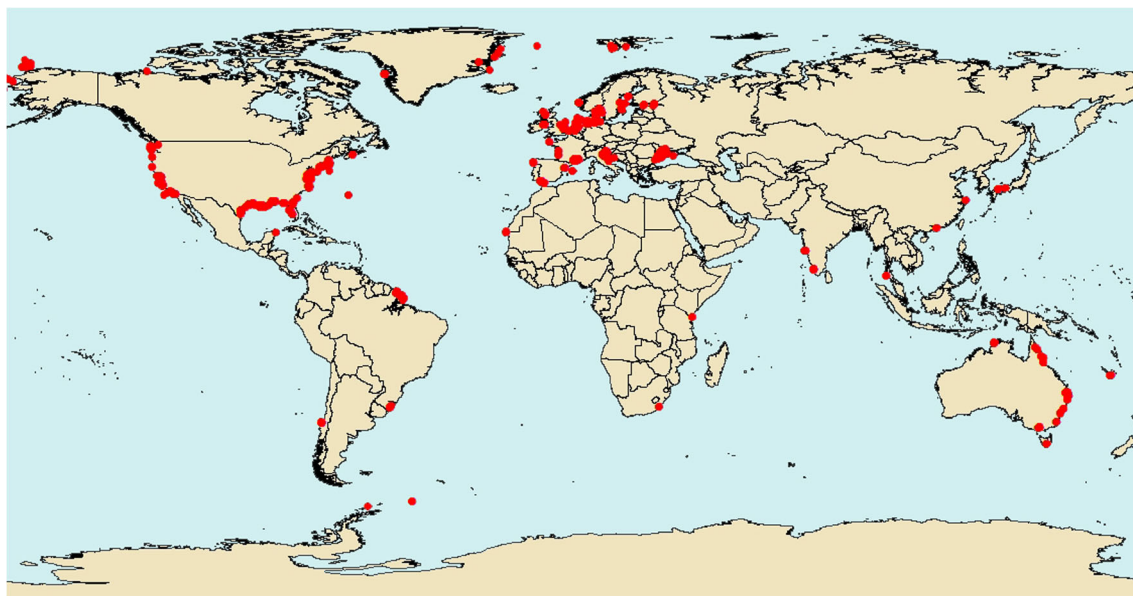


Fig. 3 Map indicating the general location of all sediment-water oxygen and nutrient flux sampling sites. More detailed sampling site location data are provided in the net sediment-water flux database

Table 1 Listing by region or continent of sites where sediment-water oxygen and nutrient flux data were found in the peer-reviewed literature and included in this analysis ($n = 227$). Estuary/coastal area names, data sources, and state/area and country where data were collected are indicated. In several instances, a site is listed more than once because

data were collected by different investigators during different years and at different sites (e.g., Potomac River data from Callender and Hammond 1982 and from Bailey et al. 2003), or because data from larger systems (e.g., Baltic Sea, Chesapeake Bay) were separated into geographic regions. Complete citations can be found in Boynton and Ceballos (2017)

Region	Estuary name	Reference	State/area	Country
Arctic	Western Arctic	Clough et al. 2005	Alaska	USA
Arctic	Svalbard Fjords	Glud et al. 1998	Arctic fjords	Norway
Arctic	N Bering-Chukchi Shelf	Henriksen et al. 1993	Alaska/Siberia	USA/Russia
Arctic	Franklin Bay	Link et al. 2011	SE Beaufort Sea Bay	Canada
Arctic	Young Sound	Rysgaard et al. 1996a	NE Greenland	Greenland
Arctic	Young Sound	Rysgaard et al. 1998	NE Greenland	Greenland
Arctic	Disko Bay	Rysgaard et al. 2004	E and W coasts	Greenland
Arctic	Scoresby Sound	Rysgaard et al. 2004	E and W coasts	Greenland
Arctic	Greenland Sea	Rysgaard et al. 2004	E and W coasts	Greenland
Arctic	Young Sound	Rysgaard et al. 2004	E and W coasts	Greenland
Arctic	Greenland Sea	Rysgaard et al. 2004	E and W coasts	Greenland
N. America	Long Island Sound	Aller and Benninger 1981	New York	USA
N. America	Laguna Madre	An and Gardner 2000	Texas	USA
N. America	Baffin Bay	An and Gardner 2000	Texas	USA
N. America	Baffin Bay	An and Gardner 2002	Texas	USA
N. America	Laguna Madre	An and Gardner 2002	Texas	USA
N. America	Galveston Bay	An and Joye 2001	Texas	USA
N. America	Potomac River	Bailey et al. 2003	Maryland	USA
N. America	Buzzards Bay	Banta et al. 1995	Massachusetts	USA
N. America	California Coast-Central	Berelson et al. 1996	California	USA
N. America	California Coast-Southern	Berelson et al. 1996	California	USA
N. America	Monterey Bay Shelf	Berelson et al. 2003	California	USA
N. America	California Coast-North	Berelson et al. 2013	California	USA
N. America	Oregon Coast-Central	Berelson et al. 2013	Oregon	USA
N. America	Caloosahatchee River	Buzzelli et al. 2013	Florida	USA
N. America	St Lucie Estuary	Buzzelli et al. 2013	Florida	USA
N. America	Elkhorn Slough	Caffrey et al. 2002	California	USA
N. America	Elkhorn Slough	Caffrey et al. 2010	California	USA
N. America	Potomac River	Callender and Hammond 1982	Virginia-Maryland	USA
N. America	Tampa Bay	Carlson and Yarbro 2006	Florida	USA
N. America	James River	Cerco 1985	Virginia	USA
N. America	Gunston Cove, Potomac	Cerco 1989	Virginia	USA
N. America	San Francisco Bay Delta	Cornwell et al. 2014	California	USA
N. America	San Francisco Bay North	Cornwell et al. 2014	California	USA
N. America	Chesapeake Bay-North	Cowan and Boynton 1996	Maryland	USA
N. America	Chesapeake Bay-Mid	Cowan and Boynton 1996	Maryland	USA
N. America	Chesapeake Bay-South	Cowan and Boynton 1996	Virginia	USA
N. America	Mobile Bay	Cowan et al. 1996	Alabama	USA
N. America	Washington State Shelf	Devol and Christensen 1993	Washington State	USA
N. America	Gulf of Mexico-Louisiana	Dortch et al. 1994	Louisiana	USA
N. America	Narragansett Bay, Upper (Providence River)	Elderfield et al. 1981	Rhode Island	USA
N. America	Narragansett Bay, Middle	Elderfield et al. 1981	Rhode Island	USA
N. America	Narragansett Bay, Lower	Elderfield et al. 1981	Rhode Island	USA
N. America	Pamlico Sound Complex	Fisher et al. 1982	North Carolina	USA
N. America	Gulf of Mexico-Texas	Flint and Kamykowski 1984	Texas	USA
N. America	Chesapeake Bay-North	Fluxzilla-Mainstem ^a	Maryland	USA
N. America	Chesapeake Bay-Mid	Fluxzilla-Mainstem ^a	Maryland	USA
N. America	Chesapeake Bay-South	Fluxzilla-Mainstem ^a	Virginia	USA
N. America	Patuxent River	Fluxzilla-PAX ^a	Maryland	USA
N. America	Narragansett Bay, Upper (Providence River)	Fulweiler 2015 figures	Rhode Island	USA
N. America	Narragansett Bay, Middle	Fulweiler 2015 figures	Rhode Island	USA
N. America	Sassafras River estuary	Gao et al. 2012	Maryland	USA
N. America	Gulf of Mexico-Louisiana	Gardner et al. 1993	Louisiana	USA
N. America	Laguna Madre	Gardner et al. 2006	Texas	USA

Table 1 (continued)

Region	Estuary name	Reference	State/area	Country
N. America	Baffin Bay	Gardner et al. 2006	Texas	USA
N. America	Sabine Lake	Gardner et al. 2006	Texas	USA
N. America	East Matagorda Bay	Gardner et al. 2006	Texas	USA
N. America	Nueces Estuary	Gardner et al. 2006	Texas	USA
N. America	Plum Isl Sound-Parker River	Giblin et al. 2010	Massachusetts	USA
N. America	San Francisco Bay South	Grenz et al. 2000	California	USA
N. America	San Francisco Bay South	Hammond et al. 1985	California	USA
N. America	Halifax Harbor	Hargrave and Phillips 1981	Nova Scotia	Canada
N. America	La Jolla Bight-Pacific Ocean	Hartwig 1975	California	USA
N. America	Georgia Bight-Sapelo Island	Hopkinson 1985 and 1987	Georgia	USA
N. America	Georgia Bight-Sapelo Island	Hopkinson and Wetzel 1982	Georgia	USA
N. America	Plum Isl Sound-Parker River	Hopkinson et al. 1999	Massachusetts	USA
N. America	Chesapeake Bay-Mid	Kemp and Boynton 1981	Maryland	USA
N. America	Chesapeake Bay-Mid	Kemp et al. 1990	Maryland	USA
N. America	Childs river estuary	LaMontagne et al. 2002	Massachusetts	USA
N. America	Mid Atlantic Bight-Little Egg Inlet	Laursen and Seitzinger 2002	New Jersey	USA
N. America	Gulf of Mexico-Louisiana	Lehrter et al. 2012	Louisiana	USA
N. America	Gulf of Mexico-Louisiana	Lin et al. 2011	Louisiana	USA
N. America	Great Bay	Lyons et al. 1982	New Hampshire	USA
N. America	Long Island Sound-Flax Pond	Mackin and Swider 1989	New York	USA
N. America	Lower St Johns River estuary	Malecki et al. 2004	Florida	USA
N. America	South Atlantic Bight-GA, USA	Marinelli et al. 1998	Georgia	USA
N. America	Narragansett Bay, Middle	McCaffrey et al. 1980	Rhode Island	USA
N. America	Gulf of Mexico-Louisiana	Morse and Rowe 1999	Louisiana	USA
N. America	Weeks Bay	Mortazavi et al. 2012	Alabama	USA
N. America	Gulf of Mexico-Louisiana	Murrell and Lehrter 2011	Louisiana	USA
N. America	Pensacola Bay	Murrell et al. 2009	Florida	USA
N. America	Narragansett Bay, Middle	Nixon et al. 1976	Rhode Island	USA
N. America	Narragansett Bay, Lower	Nixon et al. 1976	Rhode Island	USA
N. America	Potter Pond	Nowicki and Nixon 1985	Rhode Island	USA
N. America	Gulf of Mexico-Louisiana	Nunnally et al. 2013	Louisiana	USA
N. America	Choptank River estuary	Owens 2009	Maryland	USA
N. America	Tampa Bay	Owens and Cornwell 2012	Florida	USA
N. America	Port Madison, Puget Sound	Pamatmat 1971	Washington State	USA
N. America	Cherrystone Inlet	Reay et al. 1995	Virginia	USA
N. America	York River	Rizzo 1990	Virginia	USA
N. America	Neuse River Estuary	Rizzo and Christian 1996	North Carolina	USA
N. America	Buzzards Bay	Rowe et al. 1975	Massachusetts	USA
N. America	Gulf of Mexico-Louisiana	Rowe et al. 2002	Louisiana	USA
N. America	Ochlockonee Bay	Seitzinger 1987	Florida	USA
N. America	Gay Head	Smith 1978	Massachusetts	USA
N. America	Escambia Bay	Smith and Caffrey 2009	Florida	USA
N. America	Deep-Sea-MA, USA	Smith and Teal 1973	Massachusetts	USA
N. America	Castle Harbor	Smith et al. 1972	Bermuda	Bermuda
N. America	Woods Hole-Great Harbor	Smith et al. 1973	Massachusetts	USA
N. America	Buzzards Bay	Smith et al. 1973	Massachusetts	USA
N. America	Fourleague Bay	Teague et al. 1988	Louisiana	USA
N. America	Boston Harbor	Giblin et al. 1997	Massachusetts	USA
N. America	Massachusetts Bay	Hopkinson et al. 2001	Massachusetts	USA
N. America	Boston Harbor	Tucker et al. 2014	Massachusetts	USA
N. America	Massachusetts Bay	Tucker et al. 2014	Massachusetts	USA
N. America	Cape Code Bay	Tucker et al. 2014	Massachusetts	USA
N. America	Galveston Bay	Warnken et al. 2000	Texas	USA
N. America	Galveston Bay	Zimmerman and Benner 1994	Texas	USA
C. America	Nichupté Lagoon	Valdes-Lozano et al. 2006	Quintana Roo	Mexico
S. America	Amazon Shelf	Aller et al. 1996	Amazon River	Brazil
S. America	Concepcion Bay	Farias et al. 1996	Central Chile	Chile
S. America	Chile Shelf-Concepcion	Farias et al. 2004	Central Chile	Chile
S. America	Concepcion Bay	Munoz et al. 2004	Central Chile	Chile
S. America	Patos Lagoon	Niencheski and Jahnke 2002	Southern Brazil	Brazil

Table 1 (continued)

Region	Estuary name	Reference	State/area	Country
Europe	Texel coast-North Sea	Andersen and Helder 1987	North Sea	Netherlands
Europe	Texel coast-Mokbaai	Andersen and Helder 1987	Wadden Sea	Netherlands
Europe	Texel coast-Wadden Sea	Andersen and Helder 1987	Wadden Sea	Netherlands
Europe	Kiel Bight	Balzar et al. 1983	Baltic Sea	Germany
Europe	Kiel Bight	Balzar et al. 1984	Baltic Sea	Germany
Europe	Po River Delta	Bartoli et al. 1996	Northern Adriatic	Italy
Europe	Tjarno Pond	Bartoli et al. 2003	West coast Sweden	Sweden
Europe	Bay of Pempoul	Boucher and Boucher-Rodoni 1988	Brittany	France
Europe	Gulf of Trieste-Deep	Cermelj et al. 2001	Northern Adriatic	Italy
Europe	Palmones estuary	Clavero et al. 2000	Strait of Gibraltar	Spain
Europe	Gulf of Finland	Conley et al. 1997	Baltic Sea	Finland
Europe	Lindaspollene	Dale 1978	West coast	Norway
Europe	Pontevedra Ria	Dale and Prego 2002	NW Spain	Spain
Europe	Loch Thurnaig (Ewe)	Davies 1975	Scottish highlands	Scotland
Europe	Marano Lagoon	De Vittor et al. 2012	Northern Adriatic	Italy
Europe	Grado Lagoon	De Vittor et al. 2012	Northern Adriatic	Italy
Europe	Gulf of Lions	Denis and Grenz 2003	NW Mediterranean	France
Europe	Baltic Sea-Askö	Edberg and Hofsten 1973	Baltic Sea	Sweden
Europe	Sea of Åland	Edberg and Hofsten 1973	Baltic Sea	Sweden
Europe	Bothnian Sea	Edberg and Hofsten 1973	Baltic Sea	Sweden
Europe	Gullmar Fjord	Enoksson and Samuelsson 1987	Skagerrak	Sweden
Europe	Gulf of Trieste-Deep	Faganeli and Ogrinc 2009	Northern Adriatic	Italy/Slovenia
Europe	Grado Lagoon	Faganeli and Ogrinc 2009	Northern Adriatic, Gulf of Trieste	Italy/Slovenia
Europe	Strunjan Lagoon	Faganeli and Ogrinc 2009	Northern Adriatic, Gulf of Trieste	Italy/Slovenia
Europe	Dragonja River	Faganeli and Ogrinc 2009	Northern Adriatic, Gulf of Trieste	Italy/Slovenia
Europe	Bay of Cadiz	Ferron et al. 2009	Iberian Peninsula	Spain
Europe	Gulf of Cadiz	Ferron et al. 2009	Iberian Peninsula	Spain
Europe	Marennes-Oleron Bay	Feuillet-Girard et al. 1997	Eastern French Atlantic coast	France
Europe	Bay of Cadiz	Forja et al. 1994	Southwest Spain	Spain
Europe	Black Sea-W	Friedl et al. 1998	Danube/Dniester	Bulgaria
Europe	Black Sea-NW	Friedl et al. 1998	Danube/Dniester	Romania
Europe	Black Sea-NW	Friedrich et al. 2002	NW shelf	Romania
Europe	Bay of Cadiz	Gomez-Parra and Forja 1993	Atlantic Spanish coast	Spain
Europe	Skagerrak	Hall et al. 1996	NE North Sea	Norway/Denmark
Europe	Adriatic Sea-NW	Hammond et al. 1999	Northern Italian coast	Italy
Europe	Aarhus Bay	Hansen and Blackburn 1992	Aarhus Bight	Denmark
Europe	Aarhus Bay	Jensen et al. 1990	SW Kattegat	Denmark
Europe	Aarhus Bay	Jensen et al. 1995	SW Kattegat	Denmark
Europe	Norsminde Fjord	Jorgensen and Sorensen 1985	Jutland	Denmark
Europe	Baltic Sea-Mid	Koop et al. 1990	Baltic Sea	Sweden
Europe	Faellesstrand lagoon	Kristensen 1993	Fyn Island	Denmark
Europe	Rhone River mouth	Lansard et al. 2008	Gulf of Lions	France
Europe	Skagerrak	Lohse et al. 1995	Eastern North Sea	Denmark
Europe	North Sea-South	Lohse et al. 1995	North Sea	England/Germany/Netherlands
Europe	German Bight	Lohse et al. 1995	North Sea	Germany/Denmark
Europe	North Sea-Central	Lohse et al. 1995	North Sea	Germany/Netherlands
Europe	Albufera of Majorca	Lopez et al. 1995	Balearic Islands	Spain
Europe	Humber estuary	Mortimer et al. 1998	English Channel coast	England
Europe	Great Ouse-DEEP	Nedwell and Trimmer 1996	North Sea	UK
Europe	Gulf of Bothnia	Nedwell et al. 1983	Umea	Sweden
Europe	Loch Linnhe	Overmell et al. 1995	West coast	Scotland
Europe	Aarhus Bay	Rasmussen and Jørgensen 1992	East of Jutland peninsula	Denmark
Europe	Bassin d'Arcachon	Rysgaard et al. 1996	Southern France	France
Europe	Lagoon Etang du Prevost	Rysgaard et al. 1996	Southern France	France
Europe	Randers Fjord	Sørensen et al. 1979	E Jutland	Denmark
Europe	Kysing Fjord	Sørensen et al. 1979	E Jutland	Denmark
Europe	Vallda	Sundbäck et al. 2000	W Sweden, between Kattegatt and Skagerak	Sweden
Europe	Rortangen	Sundbäck et al. 2000	W Sweden, between Kattegatt and Skagerak	Sweden
Europe	Ragardsvik	Sundbäck et al. 2003	West coast	Sweden
Europe	Bassholmen	Sundbäck et al. 2003	West coast	Sweden

Table 1 (continued)

Region	Estuary name	Reference	State/area	Country
Europe	Gullmar Fjord	Sundbäck et al. 2004	Skagerrak	Sweden
Europe	Adriatic Sea-NW	Tahey et al. 1996	NW Italian coast	Italy
Europe	Thau Lagoon	Thouzeau et al. 2007	SE French coast	France
Europe	Great Ouse-Shallow	Trimmer et al. 1998	East coast UK	England
Europe	W Irish Sea	Trimmer et al. 1999	Irish coast	Ireland
Europe	W Irish Sea	Trimmer et al. 2003	Central Irish Sea	Ireland
Europe	North Sea-South	Van Raaphorst et al. 1992	Dutch coast	Netherlands
Europe	Ebro River delta	Vidal et al. 1989	E Spanish coast	Spain
Europe	Alfacs Bay	Vidal et al. 1997	Ebro Delta, NW Mediterranean	Spain
Europe	Humber Estuary	Watson and Frickers 1995	North Sea	UK
Europe	North Sea-South	Watson and Frickers 1995	North Sea/Humber	UK
Europe	Black Sea-W	Wijsman et al. 1999	Black Sea	Romania
Europe	Black Sea-NW	Wijsman et al. 1999	Black Sea	Ukraine
Asia	Cochin Backwater System	Abhilash et al. 2012	SW coast	India
Asia	East China Sea	Aller et al. 1985	Shanghai	China
Asia	Ao Nam Bor	Kristensen et al. 1991	Phuket Island	Thailand
Asia	Ao Nam Bor	Kristensen et al. 1998	Phuket Island	Thailand
Asia	Makirina Bay	Lojen et al. 2004	Central Dalmatia	Croatia
Asia	Harima-Nada	Nakamura 2003	Seto Inland Sea	Japan
Asia	Mandovi River	Pratihary et al. 2009	Goa	India
Asia	Central West Coast India	Pratihary et al. 2013	Goa-Arabian Sea	India
Asia	Hiroshima Bay	Seiki et al. 1989	Seto Inland Sea	Japan
Asia	Pearl River Estuary	Zhang et al. 2014	Macau	China
Africa	Umngazana Estuary	Dye 1983	Mngazana system	South Africa
Africa	Gazi bay	Mwashote and Jumba 2002	Gazi, Kwale County	Kenya
Africa	Cap Blanc, Northwest Africa	Rowe et al. 1977	Spanish Sahara	Morocco
Oceania	Great Barrier Reef Continental Shelf	Alongi et al. 2007	Queensland coast	Australia
Oceania	Port Phillip Bay	Berelson et al. 1998	Melbourne	Australia
Oceania	Lagoon of New Caledonia	Boucher et al. 1994	Southwest Lagoon	New Caledonia
Oceania	Port Hacking Estuary	Bulleid 1984	Sydney	Australia
Oceania	Commercial Shrimp Farm	Burford and Longmore 2001	SE Queensland	Australia
Oceania	Bremer River	Cook et al. 2004	Queensland	Australia
Oceania	Huon-Castle Forbes Bay	Cook et al. 2004a	Tasmania	Australia
Oceania	Huon-Port Cygnet	Cook et al. 2004a	Tasmania	Australia
Oceania	Manly Lagoon	Eyre and Ferguson 2002	Sydney region	Australia
Oceania	Curly Curly and Dee Why lagoons	Eyre and Ferguson 2002	Sydney region	Australia
Oceania	Brunswick	Eyre and Ferguson 2005	New South Wales	Australia
Oceania	Broadwater	Eyre et al. 2011	Southern Moreton Bay	Australia
Oceania	Brunswick	Ferguson et al. 2004	New South Wales	Australia
Oceania	Simpsons	Ferguson et al. 2004	New South Wales	Australia
Oceania	Sandon	Ferguson et al. 2004	New South Wales	Australia
Oceania	Deception Bay	Ferguson and Eyre 2010	Queensland	Australia
Oceania	Deception Bay	Ferguson and Eyre 2012	Queensland	Australia
Oceania	W. Moreton Bay	Ferguson et al. 2007	Brisbane, Queensland	Australia
Oceania	Noumea Lagoon	Grenz et al. 2003	South Pacific island	New Caledonia
Oceania	Noumea Lagoon	Grenz et al. 2010	South Pacific island	New Caledonia
Oceania	Bombah Broadwater	Heggie et al. 2008	Adjacent to Tasman Sea	Australia
Oceania	Port Phillip Bay	Nicholson and Longmore 1999	SE Australia	Australia
Oceania	Creeks of Darwin Harbor	Smith et al. 2012	Northern Australia	Australia
Oceania	Corunna Lagoon	Spooner and Maher 2009	SE New South Wales	Australia
Oceania	Port Douglas	Trott et al. 2004	Northern Queensland	Australia
Antarctica	Signy Island	Nedwell et al. 1993	South Orkney Islands	Antarctica
Antarctica	Marian Cove	Shim et al. 2011	King George Island	Antarctica

^a Chesapeake Bay data available from a web site (www.gonzo.cbl.umces.edu)

water overlying sediments (contained in either intact sediment cores or in situ chambers) was repeatedly sampled during an incubation period during which the core or chamber was

sealed from the atmosphere and external water (i.e., batch mode operation). Dissolved nutrient or oxygen concentration data were then plotted as a function of time and a

Table 2 List of variables included in the net sediment-water flux database. Brief explanations of variables are provided in the table as are units for numeric variables

	Variable	Description/units	
General	Estuary/coastal area	Common name	
	General characteristics	Estuarine or coastal system type	
	Literature source	Reference	
	State/region		
	Country		
	World region	Continents, Arctic, C. America	
	Weather conditions	Dry, wet, normal river flow conditions	
	Photic/aphotic incubation	Incubation conditions	
	Photic/aphotic sediments	Photic = >1% light to sediments	
	Temperature range	Annual range where available; °C	
	Measurement methods	Measurement technique	In situ chambers or Intact cores
		Measurement frequency	Number of measurements during incubation
		Incubation duration	Length of incubation period; hrs
Stirring technique		Magnetic stir bar/probe stirring/paddle	
Flow-through or batch incubation			
Core or chamber diameter		cm	
Core length		cm	
Sediment height in core		cm	
Core or chamber volume		cm ³	
Core or chamber area		cm ²	
Site specifics	Latitude	Decimal degrees (DD)	
	Longitude	Decimal degrees (DD)	
	Day	Not used	
	Month	Numeric	
	Year	Numeric	
	Water depth	Meters	
	Bottom water temperature	°C	
	Bottom water salinity	Unitless	
	Bottom water pH	Unitless	
	Bottom water NH ₄	μM	
	Bottom water PO ₄	μM	
	Bottom water NO ₃	μM	
	Bottom water NO ₂₊₃	μM	
	Bottom water DSi	μM	
	Bottom water O ₂	μM	
	Sediment fluxes	O ₂ or SOC	μmol O ₂ m ⁻² h ⁻¹
		NH ₄	μmol N m ⁻² h ⁻¹
PO ₄		μmol P m ⁻² h ⁻¹	
NO ₂		μmol N m ⁻² h ⁻¹	
NO ₃		μmol N m ⁻² h ⁻¹	
NO ₂₊₃		μmol N m ⁻² h ⁻¹	
DSi		μmol DSi m ⁻² h ⁻¹	
Sediment characteristics		POC	Usually top 1 cm; % DW
	PON	Usually top 1 cm; % DW	
	PP	Usually top 1 cm; % DW	
Other variables	Sediment chlorophyll- <i>a</i>	Usually top 1 cm; mg Chlorophyll- <i>a</i> m ⁻²	
	Water column respiration	g O ₂ m ⁻² day ⁻¹	
	Data averaged by site	Indicates data averaging by authors or us	
	Data averaged by time	Indicates data averaging by authors or us	

Other variables are defined in the text. Note that in many cases, the units provided in the original publications were not the same as those indicated in this table; we converted all reported values to the units indicated

POC particulate organic carbon, *PON* particulate organic nitrogen, *PP* particulate phosphorus

volumetric rate of change (e.g., μmol l⁻¹ h⁻¹) estimated, usually using a linear regression model. In most cases, three or more samples were collected during the incubation period but in some of the earlier studies water samples from chambers or cores were collected only at the start and termination of the incubation period. The volumetric rate of change was converted to an areal flux

estimate using the area and volume dimensions of the core or chamber. In many, but not all, cases a “blank” core or chamber containing bottom water but no sediment was also incubated and results used to remove water column effects from the sediment flux estimate. In most cases authors indicated “blank” corrections were small and that has been our experience as well. Data from “blank” incubations were

rarely presented. A generalized formula for computing net sediment-water flux in batch mode is provided below:

(Formula 1)

$$\text{Net sediment-water flux } (\mu\text{moles O}_2, \text{N, P, or DSi m}^{-2}\text{h}^{-1}) \\ = (dC_s/dt - dC_b/dt) \times (V/A) \times U$$

where

- dC_s/dt rate of change in concentration in the sediment core or in situ chamber (usually as $\mu\text{mol O}_2, \text{N, P, or DSi L}^{-1} \text{time}^{-1}$)
- dC_b/dt rate of change in concentration in the blank core or in situ chamber (usually as $\mu\text{mol O}_2, \text{N, P, or DSi L}^{-1} \text{time}^{-1}$)
- V volume of water in the sediment core or in situ chamber (usually liters or cubic meters)
- A surface area of sediments in the sediment core or in situ chamber (usually square centimeters or square meters)
- U constant for unit conversions of time, volume, and area

A second approach to estimating net sediment-water flux involved the use of intact sediment cores connected to a flow-through system of water supply. In this case, water in the core was replaced at a constant rate with bottom water, usually filtered bottom water from the sampling site. The flux was estimated by determining the difference in analyte concentration between water entering and leaving the core. These data, coupled with the rate of water entering or leaving the core, and the core area, and volume were used to produce a flux estimate. Blank core results are also used as a correction for water column processes. A generalized formula for computing net sediment-water flux in flow-through mode is provided below:

(Formula 2)

$$\text{Net sediment-water flux } (\mu\text{moles O}_2, \text{N, P, or DSi m}^{-2}\text{h}^{-1}) \\ = \{[(C_o - C_i) - (C_{OB} - C_{IB})] \times Q\} / A_C \times U$$

where

- C_o concentration of analyte leaving sediment core (usually $\mu\text{mol O}_2, \text{N, P, or DSi L}^{-1}$)
- C_i concentration of analyte entering sediment core (usually $\mu\text{mol O}_2, \text{N, P, or DSi L}^{-1}$)
- C_{OB} concentration of analyte leaving blank sediment core (usually $\mu\text{mol O}_2, \text{N, P, or DSi L}^{-1}$)
- C_{IB} concentration of analyte leaving blank sediment core (usually $\mu\text{mol O}_2, \text{N, P, or DSi L}^{-1}$)
- Q flow rate of water entering the core (usually L h^{-1})
- A_C surface area of sediment core (usually cm^2)
- U constant for unit conversions of time, volume, and area

Measurement Techniques

Key features of sediment-water flux methods are shown in a series of histograms (Fig. 4) including core or in situ chamber area, method of mixing water contained in cores or chambers, measurement approach (batch versus flow-through system), incubation duration, shipboard or lab incubation versus in situ incubation, and frequency of sampling during an incubation period.

Core or Chamber Surface Area The surface area of incubation devices ranged over three orders of magnitude from 10.2 to 31,400 cm^2 . The median surface area was 139 cm^2 (Fig. 4a). In general, devices with larger surface areas were used in situ while incubation systems with smaller surface areas were generally retrieved using a coring device and incubated under shipboard or laboratory conditions. There are advantages and disadvantages associated with sediment samples of differing surface areas. For example, Boynton et al. (1981) argued that larger sediment surface areas led to better integration of small-scale patchiness. More recently, Asmus et al. (1998) and Macreadie et al. (2006) also suggested larger sediment surface area smoothed out small-scale variability, stood a better chance of including larger benthic infauna which can be important contributors to sediment-water flux magnitude and composition (e.g., Kemp and Boynton 1981; Piepenburg et al. 1995), and avoided sediment disturbances related to core transport to laboratory facilities. While there are important advantages, larger surface area devices also have some significant disadvantages including (1) larger in situ devices are often expensive to build and operate; (2) many require use of a diver to ensure the chamber has properly settled on the bottom and to determine the height of the chamber above the sediment surface; (3) in many cases, the deploying vessel must stay at the site during the incubation period thus limiting the number of sites that can be sampled during a fixed period of time; in early years, we used in situ chambers (e.g., Boynton and Kemp 1985) and were able to take measurements at a maximum of three sites per day while in later years, using intact cores incubated on shipboard, we were able to sample 6 to 10 sites per day (Cowan et al. 1996); and (4) the possibility of conducting experiments by modifying conditions is more readily accomplished in cores rather than in situ devices, and this is especially true of cores using flow-through incubation conditions (An and Gardner 2002). However, the literature indicates there are no hard and fast rules concerning chamber surface area requirements.

Mixing Chambers or Cores The vast majority of investigators elected to mix the water contained in sediment flux incubation chambers (Fig. 4b). For those working in estuarine and

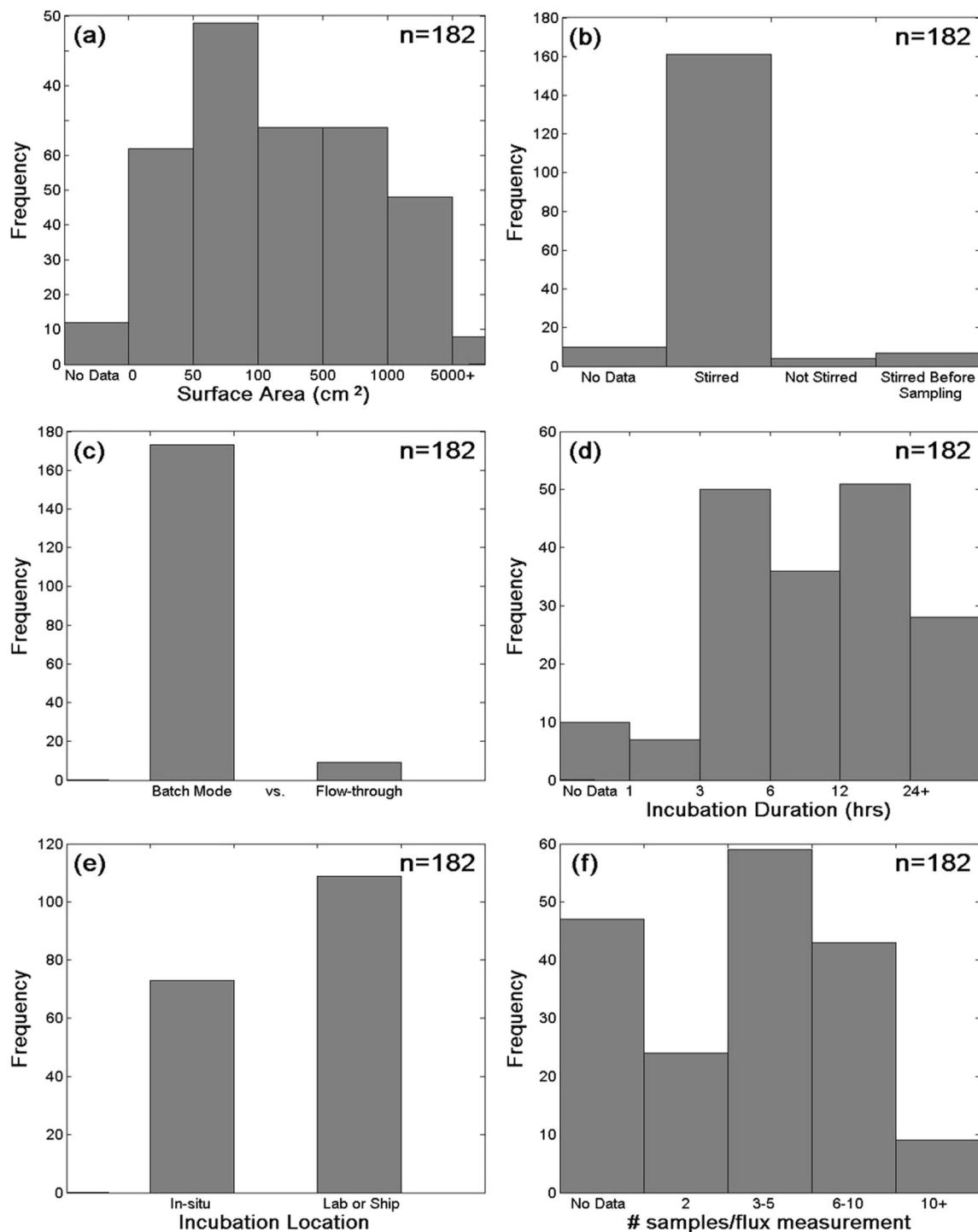


Fig. 4 Histograms showing characteristics of techniques used to make sediment-water flux measurements including: **(a)** core or chamber area, **(b)** mixing of water in cores or chambers, **(c)** batch versus flow-through

incubation approach, **(d)** incubation duration, **(e)** incubation location, and **(f)** sampling frequency

coastal systems, it appears intuitively obvious that mixing, induced by tidal or wave action, is needed to capture at least some aspect of in situ conditions. Of the studies examined here, 92% included stirring the water overlying the sediments contained in cores or chambers in some fashion, but did not

report quantitative mixing rates. Many used a spinning magnet suspended in the core above the sediment surface, a wand-like device attached to an oxygen probe, a recirculating pumping system, or a paddle-like device mounted inside the chamber. In flow-through systems the momentum of inflowing water

was used to mix chamber water in some cases and supplementary stirring was used in other cases. Several early studies indicated stirring was accomplished only just before and after a sample was extracted from a chamber or core (e.g., Nixon et al. 1976). Only 2% of studies did not use any stirring and several authors (e.g., Rizzo et al. 1992; Bartoli et al. 1996) argued against mixing to avoid resuspending the nepheloid layer and compromising the accuracy of measurements. About 6% of studies did not mention mixing of water in chambers.

Batch and Flow-Through Incubation Systems The vast majority of sediment-water flux measurements have been made using a batch mode approach (Fig. 4c). It is likely most investigators selected this approach because it is simpler to operate in both in situ and lab or shipboard situations. However, the flow-through approach offers some advantages including being able to compute a flux with fewer concentration measurements, maintaining conditions in the incubation chamber closer to in situ conditions by adjusting chamber flushing rates, and being able to conduct flux experiments by adjusting conditions in the water entering the incubation core.

Incubation Duration The duration of core or chamber incubations varied from less than 3 to greater than 24 h; most lasted between 3 and 12 h (Fig. 4d). Selection of appropriate incubation times is both a function of sediment metabolic activity and chamber or core volume. If the volume is relatively small or the metabolic activity high, then concentration changes can be detected in a shorter period of time and vice versa (Boynton et al. 1981). Selecting incubation duration is thus a balancing act between obtaining detectable changes in concentration while maintaining conditions in the core or chamber close to in situ conditions. Many investigators used dissolved oxygen concentration in the core or chamber as a guide to selecting incubation duration and indicated they did not allow dissolved oxygen concentration to decrease by more than about 20–25% of the initial value during the incubation period (e.g., Rasmussen and Barker Jørgensen 1992).

Incubation Approach Both in situ and lab or shipboard approaches for incubating sediments have been widely used for making net sediment flux measurements (Fig. 4e). In general, in situ incubations have been used at shallow sites more frequently than at deeper depth sites while lab or shipboard incubations have been used at intermediate or deeper sites where intact sediments are collected with a coring device, brought to the surface, and then incubated. However, there is limited information concerning which approach yields more accurate estimates. Several investigators have made simultaneous sediment-water flux estimates using both in situ and intact core approaches. Pamatmat (1971), Kemp et al. (1992), Watson et al. (1993), Watson and Frickers (1995), Miller-

Way et al. (1994), Mortimer et al. (1998), Grenz et al. (2003), and Lansard et al. (2008) all reported reasonably close agreement between in situ chamber and intact core flux measurements of O₂ and several nutrients. However, Hammond et al. (1985) favored in situ approaches in situations where macrofauna were important. Macreadie et al. (2006) reported larger fluxes of O₂, NO₂, and NO₃ from in situ chambers than from cores. They suggested sediment compression during coring would collapse macrofaunal burrows and disrupt microbial activity, leading to the observed differences in flux magnitude. Huettel et al. (2014) made a strong case for efficient sediment decomposition of organic matter in permeable sediments via pressure gradient effects in inner shelf zones. The bulk of the information available suggests that either approach can yield realistic results if care is taken to maintain in situ conditions in cores and if the sampling strategy recognizes the need for larger cores or chambers if macrofauna are important players in sediment-water flux dynamics.

Measurement Frequency The number of nutrient or dissolved oxygen samples collected during a sediment-water flux measurement also varied widely (Fig. 4f). Some earlier studies (e.g., Nixon et al. 1976) obtained just a time zero and final concentration measurement but the majority of studies obtained between 3 and 10 samples during an incubation period. In many cases, a dissolved oxygen probe was inserted into the core or in situ chamber and much more frequent measurements were obtained for DO concentration. A surprising number of investigators failed to indicate how many samples were collected during a sediment-water flux measurement.

We have three final technique observations. First, virtually all authors explicitly stated that sediment cores or in situ chambers were well flushed with ambient bottom water before starting the incubation period to ensure starting conditions were close to ambient levels. There was broad recognition that insertion of in situ chambers or extraction of sediment cores strongly affected conditions in water overlying sediments and these conditions needed to be adjusted back to ambient conditions by flushing with bottom water. Second, while there was broad agreement that some level of mixing of water contained in cores or chambers was important, there was also emphasis on avoiding sediment resuspension during sediment flux measurements. It seems that most investigators assumed that resuspension would substantially effect flux measurements although there are few data available to evaluate this idea (Boynton et al. 1981; Boynton 1985; Porter et al. 2006). Finally, in most studies, emphasis was placed on starting the incubation period as soon as possible after either inserting in situ chambers or extracting sediment cores. Time delays between sampling and initiation of incubation were on the order of 1 to 3 h and were somewhat longer if cores needed to be transported to a laboratory setting.

Results and Discussion

Water Column and Sediment Characteristics

This analysis begins by examining physical and chemical characteristics of the water column and sediments at sites where sediment-water oxygen and nutrient flux measurements were conducted (Figs. 5 and 6).

This analysis focused on coastal and estuarine sites with maximum water depths of less than 100 m but did include a few sites with greater or much greater water depths for comparative purposes. Most of the sediment-water flux work has been done in waters less than 10 m in depth (50%) and about 67% of all flux measurements occurred in waters less than 20 m deep (Fig. 5a). Measurements at depths between 50 and 100 m were poorly represented in the data set. In previous sediment-water flux, work conducted in both relatively shallow (Kemp et al. 1992) and deep systems (Hargrave 1973) water depth was shown to influence the magnitude of sediment processes.

Sediment-water flux measurements were conducted over a wide temperature range (-1.7 to >30 °C; Fig. 5b). However, the majority of measurements (90%) were made at bottom water temperatures between 5 and 28 °C. Measurements made at less than 5 °C or greater than 28 °C were less well represented in the data set and reflect the paucity of data from high latitudes and shallow tropical systems.

Sediment-water flux measurements also encompassed a large salinity range and, with the exception of one salinity category (salinity 30 to 35), were about equally represented in the data set (Fig. 5c). The spike in the frequency of measurements made at salinities between 30 and 35 reflects the large number of sediment-water flux measurements made in Boston Harbor and inshore portions of Massachusetts Bay (Giblin et al. 1997; Hopkinson et al. 2001; Tucker et al. 2014).

Dissolved oxygen conditions in bottom waters at sediment-water flux sites varied from near-anoxic to over 300 μM (Fig. 5d). The majority of measurements were made with bottom water dissolved oxygen concentrations ranging from about 150 to 300 μM , which are concentrations unlikely to inhibit net sediment-water O_2 rates or other aerobic biogeochemical processes (Balzer et al. 1983; Nunnally et al. 2013). However, about 15% of net sediment-water fluxes were made under hypoxic conditions ($\text{O}_2 < 100$ μM) and about 10% under severe hypoxia. Under such conditions net sediment-water exchanges of N and P would very likely be affected (e.g., Cowan and Boynton 1996) and anaerobic pathways of carbon metabolism become dominant (e.g., Fenchel and Blackburn 1979; Marvin-DiPasquale et al. 2003).

Concentrations of dissolved nutrients in bottom waters at sites where sediment-water flux measurements were conducted are of particular interest because they can act to modify flux magnitude and also serve as an indicator of B/P coupling

(Fig. 5e–h). Ammonium concentrations ranged from below levels of detection to 91 μM but 70% were less than 5 μM and 84% were less than 10 μM . Dissolved inorganic phosphorus concentrations ranged from below levels of detection to 33 μM but the majority of concentrations were less than 5 μM (95%). The distribution of nitrate concentrations was very similar to those of ammonium with the majority of concentrations less than 5 μM (55%) and 45% between 5 and 25 μM . There were a few extreme nitrate values (>500 μM) but these were rare and were from severely enriched locations (e.g., Great Ouse estuary; Nedwell and Trimmer 1996). Dissolved silica concentrations exhibited a distribution different from other dissolved nutrients with both relatively low and high concentrations frequently reported. About 40% of all reported measurements were less than 10 μM while about 27% were greater than 50 μM . Overall, dissolved silica concentrations ranged from below detection to 399 μM . We had expected to find greatly enhanced dissolved nutrient concentrations at these sites because of close proximity to sediment nutrient sources but, with a few exceptions, this was not the case. It is likely in these mainly shallow systems physical mixing/transport was sufficient to prevent the accumulation of nutrients in bottom waters. However, in most cases, bottom water nutrient concentrations were well above estuarine phytoplankton half-saturation values (e.g., K_s ; Sarthou et al. 2005).

Similar to bottom water nutrient concentrations, sediment particulate organic matter concentrations and sediment organic matter elemental ratios are of interest because they represent the fuel driving sediment-water fluxes (Fig. 6). The majority of these measurements (all reported as percent dry weight, % DW) were from samples collected from the top 1 cm of the sediment column although a few included materials from the top 5–10 cm of sediments. Sediment particulate organic carbon (POC) concentrations ranged from 0.1–13.7% and averaged $2.01 \pm 1.36\%$. About 77% of POC measurements had concentrations less than 3%; sediment POC concentrations above 5% were rare. Although poorly represented in the data set sediment POC concentrations at high latitudes tended to be lower than those from tropical and temperate zones. Sediment POC and sediment chlorophyll-a values were significantly correlated ($\rho = 0.02$; $n = 832$), suggesting that phytoplankton were an important component of sediment POC values. Sediment particulate organic nitrogen (PON) values ranged from 0.1–1.25% and averaged $0.31 \pm 0.21\%$. About 90% of values were less than 0.6%. Higher values were rare but did occur at higher northern latitudes. Sediment particulate phosphorus (PP) concentrations ranged from 0.1–0.94% and averaged $0.11 \pm 0.06\%$. Most (73%) values were between 0.1 and 0.2%. Values in excess of 0.3% were rare. The number of sediment PP values in the data set was much lower than for either POC or PON. Sediment chlorophyll-a values ranged from 1.1 to 418 mg m^{-2} and averaged 42.4 ± 48.1 mg m^{-2} . Relatively high values were recorded from both north and

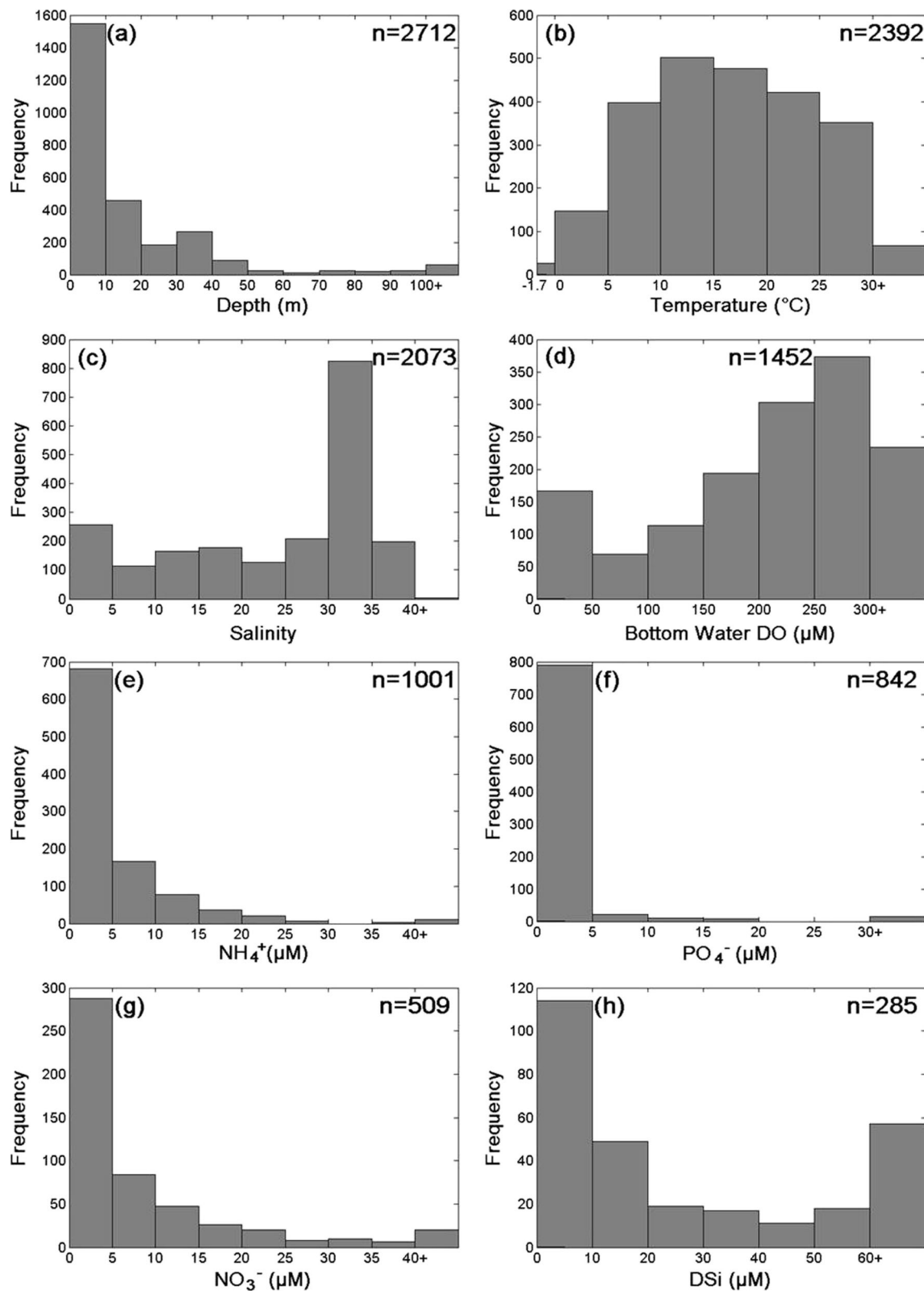


Fig. 5 Histograms describing conditions at locations where sediment-water flux measurements were made, including: (a) water depth, (b) water temperature, (c) salinity, (d) dissolved oxygen

concentration, (e) NH₄ concentration, (f) PO₄ concentration, (g) NO₃ concentration, and (h) DSi concentration. All concentration data were from bottom waters

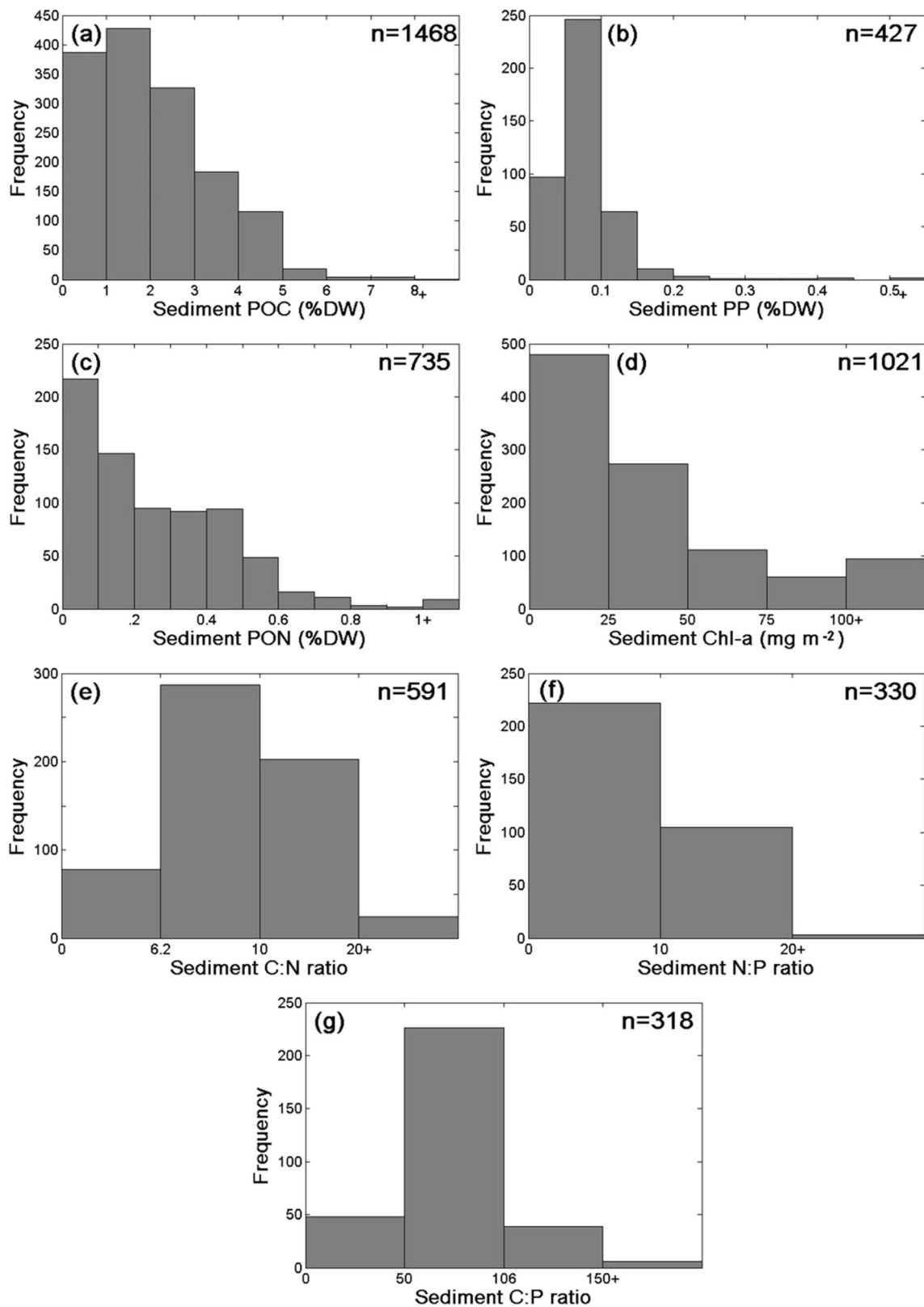


Fig. 6 Histograms summarizing sediment particulate carbon, nutrient, and chlorophyll-a concentrations and elemental ratios measured at sediment-water flux measurement sites, including: (a) particulate organic carbon, (b)

particulate phosphate, (c) particulate organic nitrogen, (d) sediment chlorophyll-a, (e) sediment C/N ratio, (f) sediment N/P ratio, and (g) sediment C/P ratio. All are mole-based ratios and DW indicates dry weight of sediments

south temperate zones. The few available values from the tropics were relatively low possibly because chlorophyll-*a* degradation rates are rapid at elevated temperatures (Sun et al. 1993).

Surficial sediment particulate carbon and nutrient composition ratios suggested phytoplankton to be the primary source of organic matter based on Redfield ratios of phytoplankton composition (POC/PON/PP = 106:16:1; Redfield 1934). Sediment POC/PON ratios (atomic basis) averaged 10.3 ± 4.7 and were thus somewhat elevated beyond the Redfield value of 6.6 for phytoplankton. About 13% of all values were less than 6.6, most were between 6.6 and 20 (83%) and values greater than 20 were rare (4%). This distribution suggests a preferential loss of N to denitrification or anammox assuming that phytoplankton debris was the primary source material. The majority of sediment POC/PP ratios (86%; average = 78.4 ± 29.9) were equal to or less than the POC/PP Redfield ratio of 106 suggesting PP was preferentially retained in sediments relative to POC, possibly as P sorbed to iron-rich sediments. Finally, PON/PP ratios were relatively low (average = 8.5 ± 3.8); 67% of observations were less than 10 and 99% less than 20, suggesting either preferential loss of N or retention of P in sediments.

Net Sediment-Water Oxygen and Nutrient Flux Magnitude and Geographic Distribution

Despite almost five decades of effort, the geographic distribution of sediment-water flux measurements from these shallow estuarine and coastal systems remains limited. Most of the measurements were collected at sites in North America between Southern New England and the Chesapeake Bay and from the Baltic Sea and adjacent areas. There were far fewer measurements available from the southern hemisphere and most of these were from 20° to 40° south latitude. The tropical region from 20° north to 20° south latitude was especially lacking in measurements. In addition, there were few measurements in either the northern or southern hemispheres at latitudes greater than 60° (Figs. 7 and 8). There was considerable variability in the magnitude of sediment-water fluxes for all analytes, often by three to four orders of magnitude in the most extreme cases. Some of the extreme variability was associated with, for example, net sediment-water O₂ flux measurements reported from sites with extremely low O₂ concentrations in bottom waters or NH₄ fluxes from oligotrophic and very cold waters. It is likely the season in which measurements were made also played a role in flux variability.

Net sediment-water O₂ fluxes ($n = 2365$) ranged from about 0.0014 to 18 mmol O₂ m⁻² h⁻¹ with most values between 0.2–7 mmol O₂ m⁻² h⁻¹. In general, O₂ fluxes measured in cold waters (<5 °C) were lower than those measured at higher temperatures but there were a few exceptions to this pattern such as those from Signy Island (Nedwell et al. 1993)

and Marian Cove, King George Island (Shim et al. 2011), both off the Antarctic peninsula. However, there were also a substantial number of smaller fluxes recorded at intermediate or higher temperatures (15–30 °C) indicating factors in addition to temperature were influencing O₂ fluxes. Sediment-water fluxes of NH₄ ($n = 2313$) ranged from -613 to 2700 μmol N m⁻² h⁻¹, but most were between 20 and 300 μmol N m⁻² h⁻¹. In latitudinal zones where data were abundant (30–40° N latitude) larger NH₄ fluxes were often observed at higher temperatures. High ammonium fluxes (>100 μmol N m⁻² h⁻¹) were rarely reported at temperatures less than 10 °C. Finally, NH₄ uptake by sediments was rare and, with few exceptions, also small. Sediment-water NO₃ fluxes ($n = 1296$) were directed both into and out of sediments with somewhat higher fluxes being directed into sediments. Nitrate fluxes ranged from -1990 to 830 μmol N m⁻² h⁻¹ but most were between -200 and 100 μmol N m⁻² h⁻¹. In latitudinal zones where data were more abundant (30–40° N) larger NO₃ fluxes were often observed at intermediate water temperatures (10–15 °C), again indicating that factors other than temperature were influencing flux magnitude. Sediment-water PO₄ fluxes ($n = 1823$) were also directed both into and out of sediments with releases of PO₄ from sediments to water being far more common. PO₄ fluxes exhibited a large range (-230 to 900 μmol P m⁻² h⁻¹) but most were between -25 to 100 μmol P m⁻² h⁻¹. PO₄ fluxes were consistently low (<10 μmol m⁻² h⁻¹) at temperatures below 10 °C. Sediment fluxes of DSi ($n = 1135$) were mainly directed out of sediments (97%) but there were instances of DSi uptake by sediments but generally at smaller rates. DSi fluxes exhibited a smaller range than other sediment-water fluxes (-560 to 2250 μmol DSi m⁻² h⁻¹) but the majority were in the range of 10 to 400 μmol DSi m⁻² h⁻¹. Temperature influence on DSi flux was not clear. There were data groups where relatively high DSi fluxes were reported from cold waters and lower DSi fluxes from warmer waters.

We also explored net sediment-water fluxes as a function of temperature and color coded each observation relative to sediment organic carbon content (Fig. 9). As expected, there was a general increase in flux magnitude with increasing temperature for three of the four fluxes (NH₄, O₂, and PO₄) but DSi fluxes were highest at intermediate temperatures. There were very few large fluxes associated with low sediment organic carbon content (<1%) but large fluxes were not consistently associated with organic-rich sediments.

Sediment Flux Ratios

Examination of sediment flux ratios (O/N and N/P) can provide qualitative insights into other processes involved in the decomposition of deposited organic matter. This approach is based on the idea that the aerobic decomposition of phytoplankton-

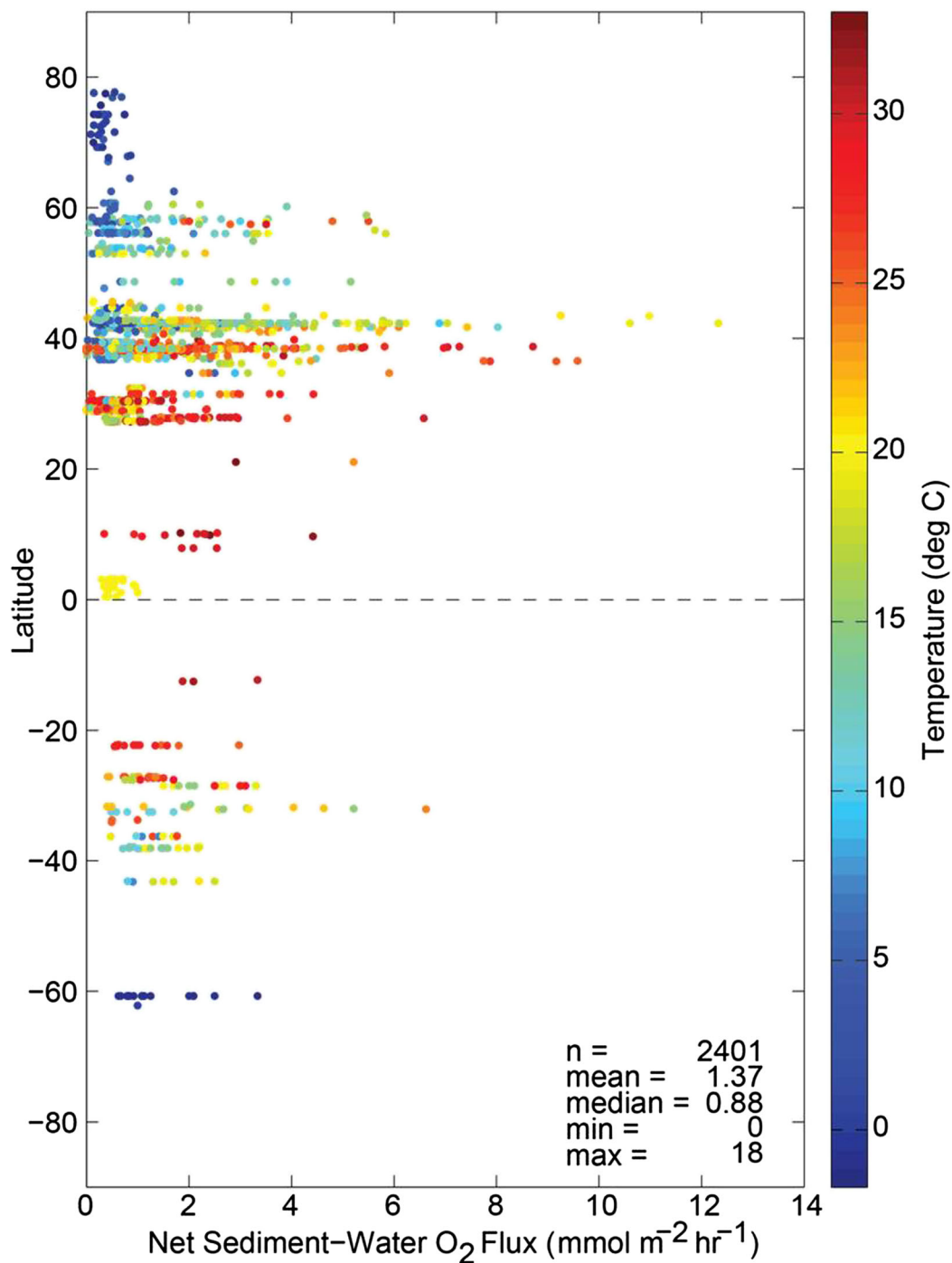


Fig. 7 Net sediment-water O₂ fluxes plotted as a function of latitude. Each *dot* represents a sediment-water flux measurement contained in the database. *Dots* are color coded for bottom water temperature at the time of

measurement. One extreme value (18 mmol m⁻² h⁻¹; Parker River, USA) is not shown on the figure. Net sediment-water O₂ fluxes were plotted as positive values but represent O₂ consumption by sediments

derived organic matter results in the production of 1 atom of N for every 13.25 atoms of O consumed (Redfield 1934). For example, Nixon (1981) reported O/N flux ratios for Narragansett Bay that were generally above those expected for simple aerobic decomposition of organic matter and argued that low sediment releases of NH₄ relative to oxygen consumption rates were due to active sediment nitrification

coupled to sediment denitrification. Subsequent work by Seitzinger et al. (1984) confirmed high rates of denitrification in Narragansett Bay. In Chesapeake Bay, Boynton and Kemp (1985) and Cowan and Boynton (1996) found similar departures of O/N flux ratios but with a seasonal switch wherein ratios were high during winter-spring, indicating nitrification-denitrification activity, but closer to Redfield proportions

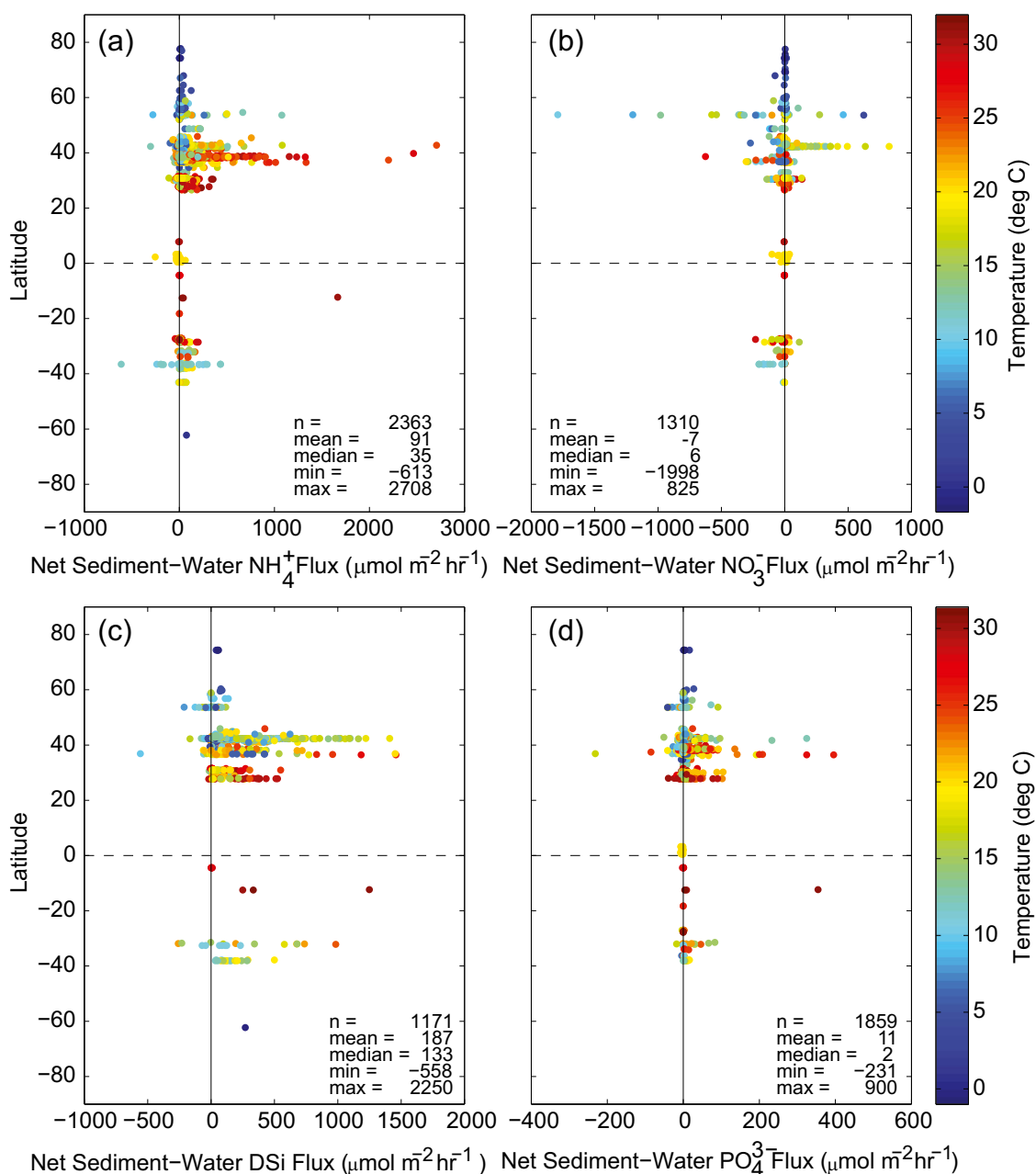


Fig. 8 Sediment-water nutrient fluxes plotted as a function of latitude, including: (a) NH_4 flux, (b) NO_3 flux, (c) DSi flux, and (d) PO_4 flux. Each dot represents a sediment-water flux measurement contained in the database. Dots are color coded for bottom water temperature at the time of

measurement. The maximum flux value for DSi ($2250 \mu\text{mol m}^{-2}\text{h}^{-1}$) and PO_4 ($900 \mu\text{mol m}^{-2}\text{h}^{-1}$) are not shown because bottom water temperature values were not available for those measurements. Note that *negative values* indicate net sediment-water flux into sediments

during summer-fall when sediment nitrification was likely inhibited by low dissolved oxygen conditions and remineralized NH_4 was simply shunted back to the water column.

Sediment flux O/N (as NH_4) and N/P (as NH_4 and PO_4) ratios were calculated for all locations where data were available (Fig. 10). Given the diverse locations where sediment flux measurements were conducted, a large range in both ratios emerged (0.03 – 992 for O/N and 0.06 – 974 for N/P) and averaged 89 ± 140 and 18 ± 24 , respectively. Two strong

patterns emerged. First, 72% of O/N flux ratios were greater, often by a large margin, than expected based on Redfield proportions (~ 13 expected) and only 11% were lower than Redfield proportions. Second, about 76% of N/P flux ratios were less than expected Redfield proportions (~ 16). Only 16% of N/P flux ratios exceeded 30. The O/N flux ratio results are consistent with coupled sediment nitrification-denitrification (and anammox) driving higher than expected flux ratios, due to loss of N as N_2 gas. Indeed, there is a growing literature reporting enhanced denitrification rates in these shallow and

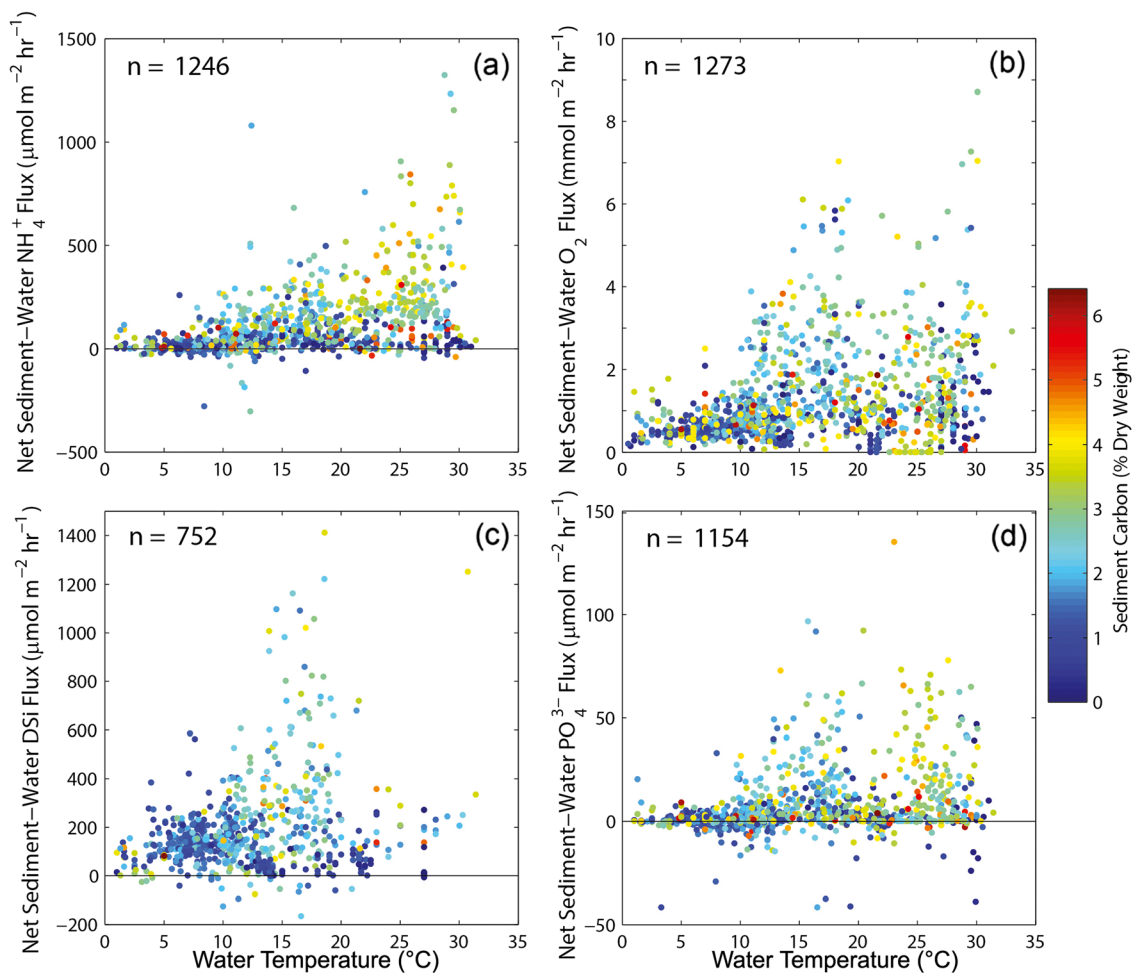


Fig. 9 Relationship between net sediment-water fluxes of (a) NH_4^+ , (b) O_2 , (c) dissolved silica, and (d) PO_4^{3-} and water temperature for all stations in the global data set. Coloring of observations is scaled to % sediment organic carbon (DW). Data collected at sites with depths greater than

300 m or with sediment %C content greater than 6.5 were omitted. Note that net sediment-water O_2 flux was plotted as a positive flux but represents O_2 consumption by sediments

often nutrient enriched systems (e.g., Cornwell et al. 2016). In addition, O/N flux ratios were positively correlated with bottom water DO concentrations, an expected result if coupled nitrification-denitrification (i.e., NH_4 removal) was enhanced by elevated O_2 concentrations ($r = 0.43$, $n = 1008$, $p < 0.001$). An alternative explanation might be that N is preferentially buried in some way but sediment composition ratios (Fig. 6) do not support this idea and we have no direct measurements of POC, PON, or PP burial rates in the data set. The generally low N/P flux ratios suggest either a preferential loss of N from deposited organic matter, enhanced retention of P in sediments, or both. Both sediment POC/PP and PON/PP ratios were lower than expected based on Redfield proportions and are thus consistent with both denitrification and sediment retention of P. The above analyses and conclusions are based on a “broad brush” approach so we expect that these results do not apply to all situations. For example, we did not consider shallow sediments exposed to sufficient light to stimulate autotrophic/heterotrophic activity that might lead to different

flux ratios given sediment O_2 release and competition between algae and bacteria for nutrients. We have also assumed that phytoplankton-derived organic matter is the dominant organic matter source to sediments, which may be true for deep and/or eutrophic systems but not for systems with high terrestrial inputs or those dominated by seagrasses or mangroves with higher C/N, C/P, and N/P sediment composition ratios or for situations where microalgae are dominant organic matter sources typically having lower C/N ratios (~7 to 13; Sundbäck et al. 2004, 2006).

Net Sediment-Water Flux Time Series

Eutrophication of estuaries and coastal waters has become a global-scale issue often generating algal blooms, both deep and shallow water hypoxia and anoxia, loss of aquatic macrophytes, and other negative water quality and habitat effects (Diaz and Rosenberg 2008). In response to eutrophication impacts on these productive ecosystems, numerous

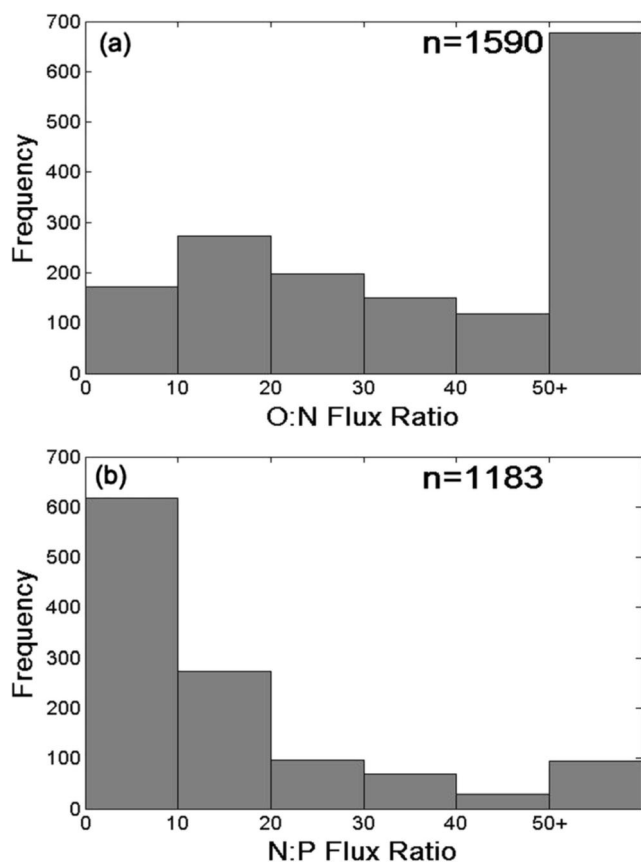


Fig. 10 Frequency histograms of (a) net sediment-water O/N flux ratios and (b) N/P flux ratios based on all available data in the net sediment-water flux data set

monitoring programs were initiated or intensified (e.g., Baltic Sea, Chesapeake Bay, San Francisco Bay, Danish coastal waters, Tampa Bay) and for many of these sites, there are now a time series of data spanning three or more decades. Such data are essential for evaluating estuarine status and trends in response to management actions, supporting statistical analyses aimed at discovering, understanding and clarifying cause-effect relationships, and finally for calibration and verification of water quality and ecosystem-scale models. While these monitoring programs are invaluable, they generally focus on collection of simple concentration measurements (e.g., dissolved oxygen, nutrient concentration). Concentrations reveal the status of an estuary and provide a consistent measurement to generate time series, but they provide only a snapshot in time. Few monitoring programs measure water column respiration, water column nutrient recycling, or even phytoplankton primary production, which is often the primary source of organic matter driving hypoxia in estuaries and coastal systems experiencing eutrophication (Cloern et al. 2014). These rate measurements are more difficult, expensive, and time-consuming to measure, but they provide estimates of the turnover of nutrients and organic material which fundamentally drive the eutrophication process. Not surprisingly, a similar

situation exists regarding monitoring of sediment-water fluxes in estuarine and coastal systems, which is a serious oversight considering that a substantial percentage of system-level metabolism and nutrient biogeochemical processing can occur in sediments in shallow systems. We found that 83% of the sites included in the database were monitored for just one or 2 years, and 93% of all sites were monitored for 3 years or less. Just 3% of sites were monitored for 6 or more years (Fig. 11).

The utility of longer-term monitoring of sediment processes is evident in the few examples that do exist to address large nutrient load reductions, climate change, and strong inter-annual variability in river flow effects. Between 1991 and 2000, Boston Harbor experienced decreased loads of total nitrogen (TN), total phosphorus (TP), and POC by between 80 and 90% associated with upgrades at waste water treatment facilities and eventual offshore disposal of waste waters (Taylor et al. 2011). Water column concentrations of TN and TP decreased in linear proportion to loads, while chlorophyll-a, POC, and dissolved oxygen concentrations also decreased but in a non-linear fashion and with a 2–3-year lag in response. Phytoplankton production responded to load changes, where production peaks of 5–8 $\text{g C m}^{-2} \text{day}^{-1}$ decreased to 1–1.5 $\text{g C m}^{-2} \text{day}^{-1}$. Tucker et al. (2014) synthesized data from a long-term program of sediment-water flux measurements conducted for 9 years during initial waste water treatment modifications and for 10 years after offshore disposal was operational. Prior to offshore disposal, rates of O_2 and DIN flux were very large (annual mean O_2 and DIN fluxes ranged from 1.70 to 4.60 $\text{mmol O}_2 \text{m}^{-2} \text{h}^{-1}$ and 0.200 to 0.46 $\text{mmol N m}^{-2} \text{h}^{-1}$, respectively) and inter-annual variability was also large (factor of 2–3). As load reductions were achieved, annual average O_2 and nutrient fluxes decreased by about a factor of two and were less variable in recent years. Tucker et al. (2014) noted that sediment processes did not exhibit long-term legacy effects in Boston Harbor, as strong management actions effectively reduced nutrient

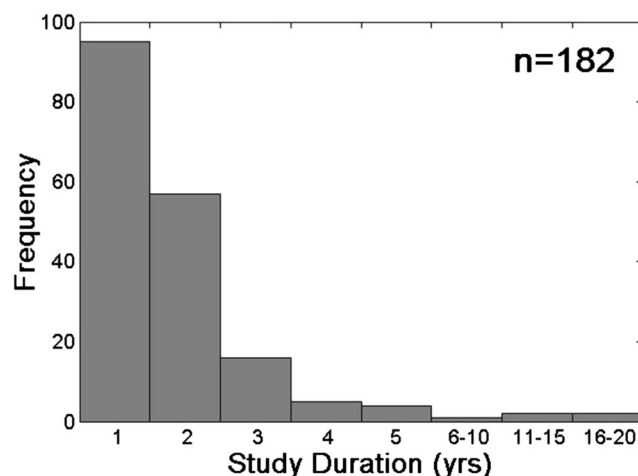


Fig. 11 Histogram showing the frequency of duration (years) of net sediment-water flux studies

loads and sediment processes responded quickly. In this case, Tucker et al. (2014) argued the rapid response was due, in part, to the lack of hypoxia or anoxia in this vertically well-mixed system even when nutrient loads were very large. The availability of oxygen prevented the development of strong sediment-based N and P feedback loops that can sustain or intensify eutrophication (Kemp et al. 2005).

Studies in Narragansett Bay have revealed the effect of climate on sediment-water fluxes. Fulweiler and Nixon (2009) organized an oxygen and nutrient sediment-water flux time series for one location in Narragansett Bay, which was not continuous, but spanned a three decade period (1976–2006). During this period, there was a large decrease in the spring phytoplankton bloom, perhaps caused by warmer waters. This presumably led to reduced organic matter deposition to sediments and large decreases in O_2 , NH_4 , and PO_4 sediment-water fluxes in the mid-Bay region. As a result, the percentage of N and P supplied by sediments to support phytoplankton nutrient demand was sharply reduced, nudging the Bay towards oligotrophication. In subsequent work, Fulweiler et al. (2010) reported that the clear sediment-water flux signal observed in the mid-Bay in response to changes in temperature and plankton dynamics was not uniform along the salinity gradient of the Bay suggesting other factors were involved including some management actions related to waste water disposal.

The Patuxent River estuary, a tributary of Chesapeake Bay, has a 60-year history of eutrophication and associated legal battles concerning water quality management approaches. These legal battles have led to management actions designed to reduce nutrient loads that, to date, have had only small impacts on water and habitat quality (D'Elia et al. 2003; Testa et al. 2008). This coastal plain estuary has experienced loss of submerged macrophytes, declines in water clarity, and seasonal and diel-scale hypoxia in deep and shallow waters, respectively. As part of the USEPA Chesapeake Bay Program, a comprehensive monitoring program was established in the mid-1980s and for a 16-year period included measurements of sediment-water oxygen and nutrient fluxes at a few sites. One of the important characteristics of this system is the strong influence of river flow and associated inputs of nutrients and sediments (Boynton and Kemp 2000). The conceptual model linking net sediment-water O_2 fluxes to these variables is similar to that used by Fulweiler and Nixon (2009) wherein nutrients were supplied via river and point sources and supported production of algal biomass which then settled to the bottom and provided fuel for sediment processes, including O_2 flux. The time series for O_2 flux at a site in the mesohaline region of the Patuxent was examined for relationships to both a local (e.g., mesohaline water column chlorophyll-a concentration) and a more distant feature (river flow at the basin fall line; Fig. 12). O_2 flux at the Patuxent mesohaline site responded to both distant forcing associated with river flows and local conditions (chlorophyll-a concentrations). During the period of record, Patuxent river flow, water column

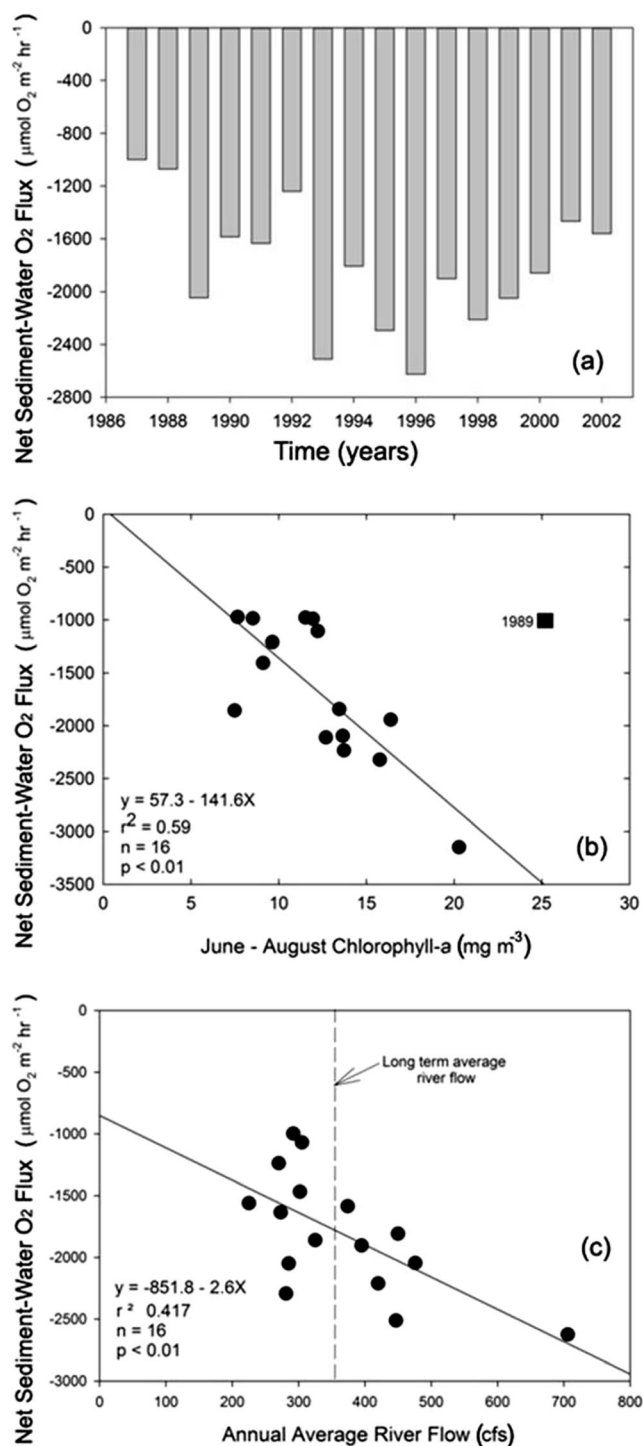


Fig. 12 A time series plot (16 years) of (a) summer (June–August) net sediment-water O_2 fluxes from the mesohaline Patuxent River estuary and scatter plots of (b) summer (July–August) net sediment-water O_2 fluxes versus water column chlorophyll-a concentration, and (c) summer (June–August) net sediment-water O_2 fluxes versus average river flow at the head of the estuary. The 1989 data in (b) were not included in the regression model. The abbreviation *cfs* in (c) indicates cubic feet per second of river flow. Note that net sediment-water O_2 fluxes in all panels were plotted as *negative values* indicating O_2 uptake by sediments

chlorophyll-a, and O₂ flux varied by factors of 3.3, 3.0, and 3.0, respectively, confirming substantial inter-annual variability at this site in both water column and sediment processes. The fact that responses were on an inter-annual time scale, rather than longer time scales, also supports the conclusion by Tucker et al. (2014) that there is little memory in estuarine sediment processes. Using shorter time series of sediment-water flux data Boynton and Kemp (2000) and Bailey and Boynton (2008) also reported similar responses to riverine forcing and with local water column and sediment conditions.

Time series data are useful for understanding ecosystem changes over time. The need for more and longer time series of sediment-water nutrient and oxygen flux measurements continues to be an important issue. Long-term data also serve to constrain and calibrate the growing number of numerical models applied in the coastal zone (e.g., Testa et al. 2014, Fennel et al. 2009, Katsev et al. 2007, Sohma et al. 2008). Models applied in

shallow estuaries have increasingly included sediment biogeochemical modules, which require validation data, especially given the substantial contribution of sediments to the nutrient and oxygen cycling processes within the models. Where numerical models are a central tool in the development of eutrophication remediation strategies (e.g., Cerco and Noel 2013) and the analysis of long-term changes in ecosystems (e.g., Li et al. 2016), net sediment-water flux time series serve to play an essential role.

Factors Influencing Net Sediment-Water Flux Magnitude and Characteristics

The literature describes a diverse array of factors that influence either the magnitude and/or the characteristics of sediment-water oxygen and nutrient fluxes. We have summarized the major processes influencing sediment-water exchanges and listed a representative sampling of published

Table 3 A listing of major factors influencing sediment-water oxygen and nutrient fluxes, a brief description of mechanisms, and representative papers in which these influencing factors were examined

Factor	Influence on sediment-water flux	Representative studies
Hypoxia/anoxia	Depressed SOC rates; increased N and P fluxes; inhibition of coupled nitrification-denitrification; enhanced methane flux	Krom and Berner 1980; Nedwell et al. 1983; Balzer et al. 1983; Cerco 1989; Koop et al. 1990; Sundby et al. 1992; Jensen et al. 1995; Cowan and Boynton 1996; Faganeli and Ogrinc 2009; Murrell and Lehrter 2011; Nunnally et al. 2013; Berelson et al. 2013; Gelesh et al. 2016
Macrofauna and meiofauna effects	Excretion and O ₂ consumption; porewater nutrient advection; microbial gardening; stimulating nitrification-denitrification via O ₂ penetration into deeper sediments; sediment particulate C and nutrient mixing	Kemp and Boynton 1981; Lyons et al. 1982; Andersen and Helder 1987; Hopkinson 1987 Henriksen et al. 1993; Aller 1994; Piepenburg et al. 1995; Clough et al. 2005; Welsh 2003; Bosch et al. 2015
Sediment organic matter input	Supply rate and quality of organic matter reaching sediments sets upper limits on diagenesis and sediment-water fluxes	Kemp and Boynton 1981; Hopkinson 1985; Hammond et al. 1985; Seitzinger 1991; Fisher et al. 1992; Jensen et al. 1990; Hansen and Blackburn 1992; Middelburg et al. 1993; Nedwell et al. 1993; Zimmerman and Benner 1994; Banta et al. 1995; Berelson et al. 1996; Rizzo and Christian 1996; Cowan and Boynton 1996; Vidal et al. 1997; Rysgaard et al. 1998; Wijsman et al. 1999; Grenz et al. 2000 Warnken et al. 2000; Clavero et al. 2000; Hopkinson et al. 2001; Caffrey et al. 2002; Trimmer et al. 2003; Denis and Grenz 2003; Eyre and Ferguson 2005; Clough et al. 2005; Spooner and Maher 2009; Link et al. 2011; Shim et al. 2011; Smith et al. 2012; Provoost et al. 2013; Tucker et al. 2014; Huettel et al. 2014
Bottom water temperature	General influence on most biogeochemical rate processes; temperature interactions with organic matter supply rate to sediments	Cerco 1989; Jensen et al. 1990; Kristensen 1993; Banta et al. 1995; Vidal et al. 1997; Rysgaard et al. 1998; Clavero et al. 2000; Hopkinson et al. 2001; Eyre and Ferguson 2005; Faganeli and Ogrinc 2009; Giblin et al. 2010
pH	Elevated pH increases sediment NH ₄ and PO ₄ fluxes	Seitzinger 1991; Bailey et al. 2006; Gao et al. 2012
Salinity variability	Induces sorption or desorption of sediment NH ₄ ; influences relative rate of sulfate reduction and FeS formation and P retention in sediments	Cornwell and Sampou 1995; Marvin-DiPasquale and Capone 1998; Pratihary et al. 2009; Giblin et al. 2010 Jordan et al. 2008
Bottom water NO ₃ concentration	Sediment NO ₃ flux proportional to bottom water NO ₃ concentration	Koop et al. 1990; Cowan and Boynton 1996; Cornwell et al. 2016
Sediment resuspension; permeable sediments	Nutrient and O ₂ fluxes elevated via pore water advection or exposure of deeper sediment porewater and organics	Dade 1993; Sanford 1997; Porter et al. 2004, 2006, 2010; Lin et al. 2011; Huettel et al. 2014

papers examining these processes (Table 3). The literature is remarkably consistent regarding four of these factors: (1) low O_2 conditions (hypoxia with bottom water $O_2 < 63$ to $100 \mu M$) increase sediment-water flux of NH_4 and PO_4 , especially under elevated temperature conditions, and inhibit coupled sediment nitrification-denitrification; (2) macrofauna/meiofauna modify sediment-water fluxes in a variety of ways, including direct animal excretion of dissolved nutrients and consumption of O_2 , pumping of sediment porewater nutrients to overlying waters, enhancing remineralization of organic matter (microbial gardening), stimulating coupled nitrification-denitrification by introducing O_2 into deeper sediments, and vertical mixing of particulate carbon and nutrients; (3) the

supply of organic matter to sediments, especially labile organic matter, is often reported to be the “master variable” regulating the upper limits of sediment-water flux magnitude; and (4) elevated bottom water temperatures tend to enhance biogeochemical rate processes. Other factors influencing sediment-water fluxes apparently have been less studied or their importance is restricted to special environments. For example, pH effects on sediment-water fluxes seem to be limited to less buffered tidal freshwater systems experiencing severe eutrophication.

Several of our analyses emphasized the role of key drivers (indicated above) in this diverse, global sediment-

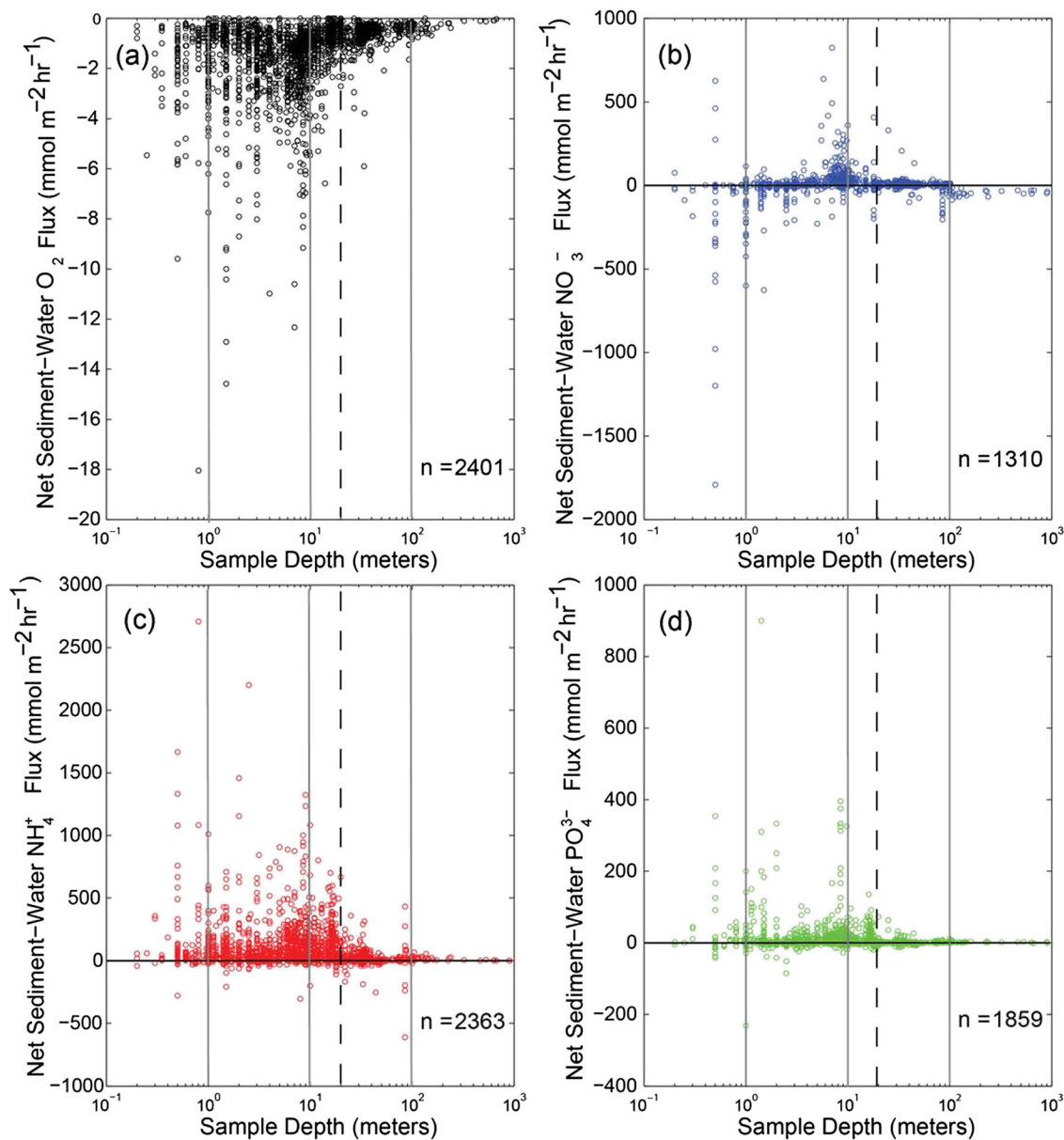


Fig. 13 Sediment-water fluxes plotted as a function of water depth at the sampling sites where measurements were conducted. Fluxes include: (a) O_2 , (b) NO_3^- , (c) NH_4^+ , and (d) PO_4^{3-} . The vertical dashed line in each panel simply indicates a water depth of 20 m

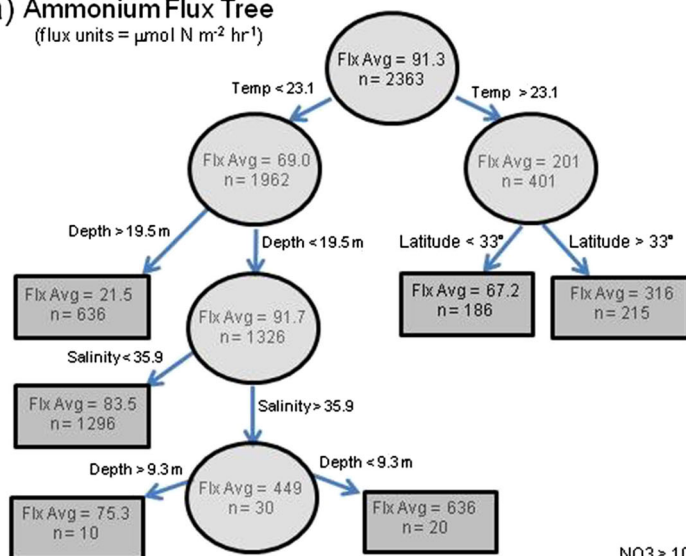
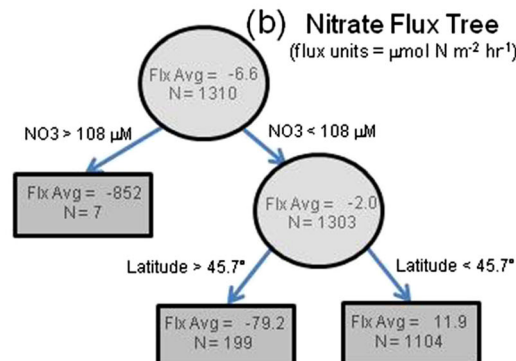
(a) Ammonium Flux Tree(flux units = $\mu\text{mol N m}^{-2} \text{hr}^{-1}$)**(b) Nitrate Flux Tree**(flux units = $\mu\text{mol N m}^{-2} \text{hr}^{-1}$)

Fig. 14 Two example plots (NH_4 and NO_3 sediment-water fluxes) of results from a multivariate, non-parametric statistical procedure referred to as RPART in the R package. The program produces a binary classification or regression tree by finding the independent variable (environmental conditions at a sediment-water flux site) that best “splits” a

response variable (a specific sediment-water flux) into groups and then repeats the splitting procedure with sub-groups until a small average cross-validated predicted value is reached where further splitting overfits the data. The *darker gray rectangles* represent terminal splits of the flux data

water flux data set (Figs. 13 and 14, Table 4). For all flux variables (O_2 , NH_4 , NO_3 , and PO_4) flux magnitude decreased sharply below depths between 10 and 20 m, while virtually no elevated fluxes were reported at depths greater than 30–40 m. Using smaller data sets, others (e.g., Hargrave 1973; Kemp et al. 1992) reported similar results. It appears that as the water column deepens microbial respiration uses more of the available OM and less reaches the bottom to fuel sediment-water fluxes. Indirectly, this result supports the notion that OM supply is a primary factor controlling the magnitude of sediment processes. We also found that sediment-water fluxes tended to be smaller at very shallow depths (e.g., Fig. 13a). This may result both from (1) wave induced resuspension of less dense, labile OM particles and transport of these particles to adjacent deeper areas, (2) a greater dominance of autotrophic processes retaining N, P, and Si in sediments, and (3) more active nitrification in well oxygenated sediments shunting NH_4 to NO_3 and eventually to N_2 via denitrification.

A summary of a statistical analysis is provided in Table 4 in which all sediment-water fluxes were examined for correlations with variables in the data set believed to influence flux magnitude. This analysis produced many significant

correlations, in part because the number of observations was so large. Correlation coefficients were generally small (<0.4) indicating a modest portion of a particular flux variance was explained by a single variable. However, results were consistent with our current understanding of controls on sediment-water flux, as (1) one or more sediment characteristics (e.g., POC, PON concentration in surficial sediments) were significantly correlated with fluxes supporting the idea that OM supply is very important, (2) bottom water DO was negatively correlated with both NH_4 and PO_4 fluxes, as expected, because at low DO conditions nitrification is suppressed or turned off and phosphorus is released from iron oxy-hydroxides back into solution, (3) NO_3 fluxes were inversely correlated with bottom water NO_3 concentrations, as have been previously reported, and (4) both depth and temperature were well correlated with three of the four sediment fluxes.

The second statistical analysis involved the use of a multivariate, non-parametric procedure now commonly referred to as RPART in the R package (Therneau and Atkinson 2015). This program produces a binary classification or regression tree by finding the independent variable (environmental conditions at a sediment-water flux site) that best “splits” a

Table 4 A summary of Spearman correlation analysis of net sediment-water fluxes versus a selection of physical, chemical, and biological variables measured at sites where net sediment-water flux measurements were conducted

Sediment flux	Statistics	Physical variables				Bottom water concentrations						Sediment concentrations			
		Depth	Temp	Salinity	Latitude	pH	NH ₄	PO ₄	NO ₃	DSi	O ₂	POC	PON	PP	Sed CHL- <i>a</i>
O ₂	Spearman correlation	<i>0.369</i>	<i>-0.388</i>	0.093	0.070	ns	ns	ns	ns	ns	ns	<i>-0.222</i>	<i>-0.143</i>	<i>-0.149</i>	<i>-0.134</i>
	<i>n</i>	2316	1999	1807	2401							1294	587	398	1005
	Sig.(2-tailed)	<0.001	<0.001	<0.001	<0.001							<0.001	<0.001	0.003	<0.001
NH ₄	Spearman correlation	<i>-0.218</i>	<i>0.396</i>	<i>-0.169</i>	<i>-0.074</i>	ns	<i>0.319</i>	0.117	ns	<i>0.152</i>	<i>-0.326</i>	<i>0.421</i>	<i>0.463</i>	<i>0.261</i>	0.190
	<i>n</i>	2180	1902	1699	2363		949	779		259	1321	1281	665	406	933
	Sig.(2-tailed)	<0.001	<0.001	<0.001	<0.001		<0.001	<0.001		0.014	<0.001	<0.001	<0.001	<0.001	<0.001
PO ₄	Spearman correlation	<i>-0.122</i>	<i>0.266</i>	<i>-0.067</i>	<i>-0.054</i>	ns	0.125	<i>0.267</i>	<i>-0.172</i>	0.162	<i>-0.217</i>	<i>0.258</i>	<i>0.358</i>	<i>0.257</i>	0.104
	<i>n</i>	1731	1493	1428	1859		702	726	268	198	1162	1168	572	412	848
	Sig.(2-tailed)	<0.001	<0.001	<0.001	<0.001		<0.001	<0.001	0.005	0.023	<0.001	<0.001	<0.001	<0.001	0.002
NO ₃	Spearman correlation	0.104	ns	ns	ns	ns	<i>-0.129</i>	ns	<i>-0.320</i>	ns	<i>0.290</i>	0.177	<i>-0.251</i>	ns	ns
	<i>n</i>	1240					375		380		797	825	209		
	Sig.(2-tailed)	<0.001					0.012		<0.001		<0.001	<0.001	<0.001		
DSi	Spearman correlation	ns	0.176	ns	ns	ns	0.141	<i>0.258</i>	ns	0.171	<i>-0.154</i>	<i>0.348</i>	<i>0.273</i>	<i>0.477</i>	ns
	<i>n</i>		981				257	262		227	775	787	221	53	
	Sig.(2-tailed)		<0.001				0.024	<0.001		0.01	<0.001	<0.001	<0.001	<0.001	

The analysis was conducted using Hmisc::rcorr in R (Harrell et al. 2016). Table entries having correlation coefficients greater than 0.2 were arbitrarily shown in italic simply to indicate relatively higher correlations. Note that O₂ flux values were negative and thus the positive and negative correlations with depth and temperature, respectively, indicated O₂ flux was lower and higher at greater depths and higher temperatures, respectively. The notation “ns” indicates a non-significant correlation

response variable (a specific sediment-water flux) into groups and then repeats the splitting procedure with sub-groups until a small average cross-validated predicted value is reached where further splitting over-fits the data (Venables and Ripley 2002). This approach is particularly useful when there are many possible influences on a process and assists in identification of the most important influences (Fig. 14). RPART analyses for all sediment-water fluxes revealed that available environmental variables such as temperature, depth, location, and bottom water conditions (O₂ and nutrient concentrations) frequently appear in the resultant trees, similar to results from the correlation analyses. For example, temperature was the strongest variable in the NH₄ flux tree and bottom water NO₃ concentration in the NO₃ flux tree. However, there was not a consistent and small group of environmental variables associated with all sediment fluxes suggesting that a relatively simple statistical model of global-scale sediment-water flux was not likely to emerge.

Ecosystem-Scale Importance of Net Sediment-Water Flux

Thus far we have focused on the measurement, magnitude, composition, geographic distribution, and factors controlling

net sediment-water fluxes in estuarine and coastal marine systems. However, sediment-water processes are tightly linked to water column processes, where benthic-pelagic (B/P) coupling indicates there are pathways of influence going in both directions (e.g., Kemp and Boynton 1992). In this section, we consider two influences of sediment-water fluxes on water column and whole systems dynamics.

First, we examined the fraction of total water column aerobic respiration (i.e., O₂ utilization) associated with sediments. In a limited number of studies, both sediment respiration and water column respiration were concurrently measured. We organized these data and computed the percent of total system O₂ utilization (water column plus sediments) represented by net sediment-water O₂ fluxes. Overall, the percent of system respiration represented by sediments ranged from about 5 to almost 90%. We then plotted these values as a function of total system depth because several authors have previously argued that % O₂ flux decreased as a function of depth (Hargrave 1973; Kemp et al. 1992) because, in deeper systems, the utilization of particulate organic matter by plankton reduces that amount of material reaching the bottom to fuel processes such as O₂ flux (Fig. 15). Three conclusions emerged from this diagram. First, our analysis of the

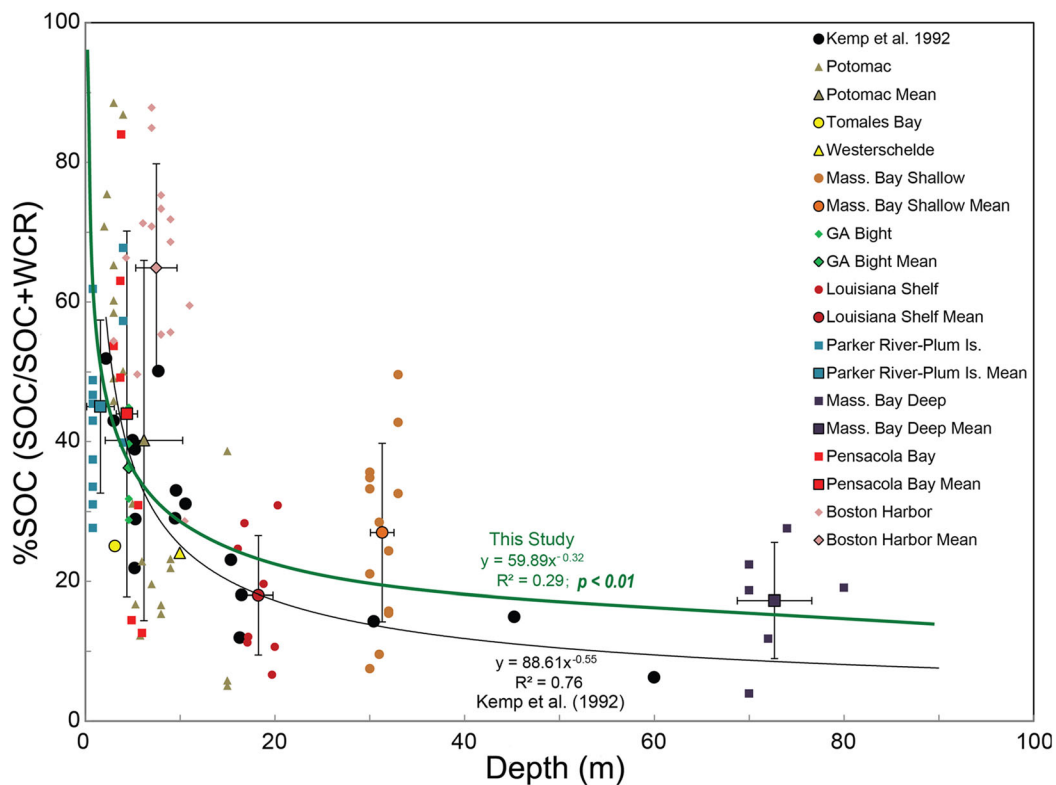


Fig. 15 A scatter plot of the percent net sediment-water O₂ flux (labeled as SOC) of total system aerobic respiration (SOC plus water column respiration, WCR) as a function of water depth at the measurement site. Data from a more limited analysis from Kemp et al. (1992) are also shown

importance of O₂ flux in aerobic system respiration from the new global data set largely followed the pattern reported earlier by Kemp et al. (1992) for shallow systems. It appears that at depths greater than 10 m O₂ flux rarely accounts for more than 30% of system respiration. Second, in shallow systems (<5 m depth), there is a very substantial range in the percent of respiration attributable to O₂ flux (12–87%). The lower values may result because we, and others, have found O₂ flux to be lower in very shallow systems where autotrophic rather than respiratory processes are more important and because these sites are more prone to sediment resuspension by wave action leading to transport of less dense particulate organic material to adjacent and deeper waters. Third, there were four sites where the percent of system respiration associated with sediments was often higher than expected based on system depth (Potomac River estuary, inner and outer Boston Harbor, and Massachusetts Bay). All of these systems were heavily impacted by high nutrient loading rates, high plankton production, and deposition of planktonic debris to sediments when measurements were conducted. It appears that under these conditions, sediments become relatively more important as a sink for dissolved oxygen across a considerable range of depths (3–70 m).

We used another approach to examine a second aspect of B/P coupling in these systems. In this effort, we estimated the amount of N (as NH₄) and P (as PO₄) released from sediments relative to the N and P demand of phytoplankton communities. We used a

data set for annual phytoplankton primary production developed by Cloern et al. (2014) for 131 estuaries and coastal systems and converted these carbon-based estimates into N and P demand assuming a Redfield C/N/P ratio of 106:16:1. We then binned the primary production data by latitude and compared phytoplankton demand with sediment nutrient releases from the same

Table 5 Summary of the percent of estimated phytoplankton N and P demand potentially supplied by sediment-water fluxes of NH₄ and PO₄

Latitudinal zone	Percent sediment nutrient supply, %					
	Nitrogen			Phosphorus		
	Average	Median	Max	Average	Median	Max
>60 N	15	16	15	48	57	24
30–59 N	32	21	30	69	31	137
0–29 N	11	12	12	17	7	42
0–29 S	32	4	189	99	2	641
30–59 S	15	23	17	39	31	39
>60 S	nd	nd	nd	nd	nd	nd

Primary production data were from Cloern et al. (2014) and were averaged by site in cases where more than 1 year of data were available. The same averaging procedure was followed for sediment-water fluxes although few sites had more than several years of data. The estimated N and P demand of phytoplankton and the percent of N and P supplied by sediments were calculated for average, median, and maximum values. Carbon-based estimates of production were converted to N and P demand using a C/N/P Redfield ratio of 106:16:1 (Redfield 1934)

latitudinal bins (Table 5). Several interesting points emerged from this “broad brush” approach. First, sediments supplied about a third of phytoplankton demand in both north and south temperate zones and about half that or somewhat less in the tropics and high northern latitudes. Second, at all latitudinal bins sediments supplied a greater proportion of P than N demand and this is consistent with earlier reports and with the suggestion that preferential P release from sediments plays a role in inducing N-limitation often observed in estuarine and coastal systems (e.g., Nixon et al. 1976; Howarth 1988; Fisher et al. 1999). Third, and somewhat surprisingly, when maximum sediment N and P releases from latitudinal zones were compared to maximum phytoplankton demand from the same zones the percent N and P supplied by sediments increased. In other words, in more eutrophic conditions the sediments became relatively more important as a source of N and P. Finally, we also matched sediment flux estimates from the same sites where annual primary production rates were reported by Cloern et al. (2014). While this might appear to be a more accurate analysis, it was difficult to accurately locate sites for both water column and sediment measurements and there were a limited number of sites (26) where both measurements were obtained. However, results were similar to those from the latitudinal analysis. Sediments supplied an average of 28% of N and 72% of P demand by phytoplankton, sediments provided more P than N relative to phytoplankton demand and sediments provided larger percentages of demand when demand was largest. While these analyses do not provide conclusive evidence that phytoplankton nutrient demand is met by sediment-water fluxes, they indicate that sediments play a key role across latitudes and habitats.

Physics in Cores and Chambers: Unresolved Issues

We return to the issue of stirring and resuspension of sediments in water overlying sediments contained in cores or in situ chambers because these appear to be important issues that have not received adequate attention. Quantitative guidance on these issues is in short supply and what is known is seldom built into measurement systems.

The current consensus seems to be that stirring is important but should be at levels that, on the one hand, do not induce sediment resuspension and, on the other hand, avoid stagnation of water in the core or chamber. In other words, physics should be muted and constant during the incubation period. However, there is ample evidence that (1) sediment resuspension does occur on a regular basis in many estuarine systems (e.g., Chesapeake Bay, Sanford et al. 1991; Hudson River estuary, Traykovski et al. 2004; San Francisco Bay, Barnard et al. 2013), (2) near-bottom current speeds vary widely in

these systems, (3) sediment composition (i.e., sediment grain size) influences resuspension thresholds, and (4) sediment resuspension events due to storm-induced mixing can substantially elevate bottom water nutrient concentrations (e.g., Fanning et al. 1982). Therefore, core or chamber incubations with low or modest mixing might provide a conservative measure of sediment-water flux.

A sparse literature indicates that stirring plays a role in influencing flux magnitude. For example, Sørensen et al. (1979) reported that net sediment-water O_2 flux measurements conducted in Danish fjords increased by 70% in stirred versus non-stirred sediment cores and further noted that stirring levels were adjusted to avoid sediment resuspension. Rasmussen and Barker Jørgensen (1992) reported that O_2 flux was impeded by 3–5 and 12–16% in winter and summer, respectively, due to O_2 transport resistance through the diffusive boundary layer and concluded stirring was essential. Many others have indicated the importance of stirring and in some cases indicated that stirring was adjusted such that water movement was in the range of 5 to 10 $cm\ s^{-1}$, a speed that did not induce sediment resuspension (e.g., Boucher and Boucher-Rodoni 1988; Farías et al. 1996; Burford and Longmore 2001; Cook et al. 2004). Detailed examinations of current speed versus O_2 flux and sediment-water nutrient flux are rare but a few examples are available. Boynton et al. (1981) conducted in situ chamber measurements (0.30 m^2 chamber surface area) at different current speeds measuring summer season O_2 flux in three sediment types (sand, muddy-sand, and mud) in a Chesapeake Bay tributary. O_2 flux responded to current speeds in a near-linear fashion increasing by 55, 72, and 96% in sand, muddy-sand, and mud sites, respectively, over a range of current speeds between 5 and 20 $cm\ s^{-1}$. O_2 flux also increased beyond the linear pattern when sediment resuspension occurred at the muddy-sand site. Boynton (1985) extended the previous work to examine the effects of current speed on sediment-water nutrient fluxes and reported increases in NH_4 flux in all sediment types but a large increase in NH_4 flux was associated with sediment resuspension (at 35 $cm\ s^{-1}$ in muddy-sand and at 21 $cm\ s^{-1}$ in mud sediments). In contrast, PO_4 fluxes were highest at intermediate speeds in sand sediments and mainly decreased with increasing current speed in muddy-sand and mud sediments, possibly due to sorption of dissolved phosphorus to iron-rich sediment particles. Vidal et al. (1989) also found strong influence of stirring on in situ chamber measurements of NH_4 and NO_3 fluxes but all measurements were apparently made at sub-resuspension stirring rates and actual stirring rates were not reported. In intertidal reef systems, Asmus et al. (1998) used large field-based flumes equipped with current meters to measure nutrient fluxes and reported

advective flushing of nutrients from pore waters by wave action and tidal water flows (flows ranged from 1 to 13 cm s⁻¹) played an important role in stimulating large nutrient fluxes. Finally, Dale and Prego (2002) reported that upwelling events along the NW coast of Spain led to sediment resuspension and associated large sediment NH₄ fluxes.

There are some important shortcomings associated with these approaches including (1) the measurement periods were relatively short (multiple hours) so it is unclear if these enhanced rates are sustainable or transient and (2) in all cases, stirring regimes were primitive using just measures of current speed in the chamber or flume. Sanford (1997) and others (e.g., Nowell and Jumars 1984; Sanford and Crawford 2000) argued for measurements of mixing time and turbulence dissipation rate as critical for matching physical conditions in microcosms, mesocosms, or flumes with physical conditions in estuaries. Sanford (1997) also concluded that this serious issue is “ignored, inadequately characterized or unreported” in many, if not most, sediment-water flux studies. The issue of mixing or stirring in sediment flux cores and chambers remains simplistic with the qualitative goals of mixing being to prevent stagnation but avoid sediment resuspension.

There are a few examples where more quantitative evaluations of the physical environments were considered and effects evaluated. In a series of papers, Porter et al. (2004, 2006, 2010) used 1 m³ mesocosms to evaluate flow effects on both sediment and water column processes and via mixing devices estimated turbulence intensities, energy dissipation rates, and bottom shear velocities typical of shallow estuarine environments. They reported (1) increased bottom shear increased sediment nutrient regeneration, (2) massive sediment disturbances increased fluxes for 2–3-week periods after which fluxes returned to pre-disturbance levels, (3) simulated tidal resuspension events did not increase dissolved inorganic nitrogen fluxes under either light or dark conditions or O₂ flux under dark conditions, and (4) exposure of mesocosm sediments to repeated resuspension events tended to shift ecological processes from the benthos to the water column.

We suggest sediment-water flux practitioners spend more time and effort designing measurement systems that better mimic the physics of the environment being investigated. At this point, the general approach to physical mixing issues includes thoroughly flushing cores or chambers before beginning a flux measurement to ensure bottom water conditions are closely approximated, stirring with some device to avoid stagnation but not stirring enough to induce resuspension and keeping the incubation period as short as possible to retain realistic conditions in cores or chambers. One relatively simple improvement in sediment-water flux technique would be to use a dye to establish mixing time in cores or chambers which is far more useful than indicating the number of rotations of a stir bar or simply claiming the system was well

mixed (Sanford pers. comm.). However, this relatively simple modification does not address pore water pumping in permeable, sandy sediments induced by pressure gradients created by bottom currents, waves, and benthic animals (Huettel et al. 2014).

Concluding Comments

This synthesis was focused on building a community accessible sediment-water flux data set, evaluating sediment-water flux techniques, examining the global-scale spatial coverage and magnitude of sediment-water fluxes, examining the few available sediment-water flux time series for hints of response times to changes in environmental forcing, and estimating the role sediment-water fluxes play in community respiration and supplying phytoplankton nutrient demand.

Our analyses indicated sediments played an important and sometimes dominant role in estuarine and coastal metabolism and nutrient supply for phytoplankton production. The global distribution of measurements was very uneven, with most being from northern temperate systems; data from high latitudes and from the coasts of South America, Africa, and Asia were very sparse or missing altogether. In addition, time series measurements of sediment-water fluxes were also rare, preventing a rigorous evaluation of seasonal, inter-annual, and decadal scales of variability. However, the few long time series available indicate sediment fluxes were responsive to changing conditions (e.g., nutrient loading rates) and responses were fast rather than slow (seasonal to annual time scales). For these reasons, a global-scale mass balance assessment of sediment-water fluxes was not possible. To achieve improved global coverage and make possible quantitative mass balance type assessments of these processes, longer-term (decadal) sites should be established, particularly in areas mentioned above and more attention should be devoted to measuring water column (e.g., temperature, salinity, O₂, chlorophyll-a, nutrient concentrations, and water column production and respiration) and sediment properties (e.g., POC, PON, PP, chlorophyll-a concentrations, Eh, grain size). The data template used in this analysis might be used to guide future measurement efforts. Current measurement techniques, using either in situ or shipboard incubation of relatively small sediment chambers (<1000 cm²), seem adequate but additional fluxes should be added when possible (i.e., denitrification, CO₂ flux, measures of anaerobic respiration). Better quantification of mixing in cores or chambers should also become standard and use of much larger chambers or even flumes should be adopted at sites where large macrobenthic communities are present. Finally, we hope the database developed for this analysis will be useful to others working in these shallow and dynamic systems, and as new information comes

available, added to the current data set and used for additional analyses.

Acknowledgements Review and synthesis work is not possible without the assistance and encouragement of many colleagues. We acknowledge the long-term support of staff at the Maryland Department of Environment, the Maryland Department of Natural Resources, and the EPA Chesapeake Bay Program. We are especially grateful to Jane Tucker and colleagues at the Ecosystem Center for sharing their large sediment-water flux data set with us, to James Cloern and colleagues at the Menlo Park USGS Laboratory for the use of their global primary production data set, and to the many researchers who responded to our questions concerning data in published papers, dissertations, and reports. Larry Sanford and Dong Liang at the University of Maryland Center for Environmental Science provided clarity and guidance concerning the physics of mixing in sediment microcosms and statistical analyses, respectively. This work was supported, in part, by a grant from the National Science Foundation (1353766 DEB-1353766), and contracts with the City of Baltimore, MD (W070704 877) and the EPA Chesapeake Bay Program Office (075-239030). This is contribution number 5332 of the University of Maryland Center for Environmental Science Chesapeake Biological Laboratory.

References

- Aller, R.C. 1994. Bioturbation and remineralization of sedimentary organic matter: effects of redox oscillation. *Chemical Geology* 114: 331–345.
- An, S., and W.S. Gardner. 2002. Dissimilatory nitrate reduction to ammonium (DNRA) as a nitrogen link, versus denitrification as a sink in a shallow estuary (Laguna Madre/Baffin Bay, Texas). *Marine Ecology Progress Series* 237: 41–50.
- Andersen, F.Ø., and W. Helder. 1987. Comparison of oxygen microgradients, oxygen flux rates and electron-transport system activity in coastal marine-sediments. *Marine Ecology Progress Series* 37: 259–264. doi:10.3354/meps037259.
- Anderson, I.C., K.J. McGlathery, and A.C. Tyler. 2003. Microbial mediation of “reactive” nitrogen transformations in a temperate lagoon. *Marine Ecology Progress Series* 246: 73–84. doi:10.3354/meps246073.
- Anderson, I.C., J.W. Stanhope, A.K. Hardison, and K.J. McGlathery. 2010. Sources and fates of nitrogen in Virginia coastal bays. In *Coastal lagoons: critical habitats of environmental change*, ed. Michael J. Kennish and Hans W. Pearl, 43–72. Boca Raton: CRC Press. doi:10.1201/EBK1420088304-c3.
- Asmus, R.M., H.M. Jensen, K.M. Jensen, E. Kristensen, H. Asmus, and A. Wille. 1998. The role of water movement and spatial scaling for measurement of dissolved inorganic nitrogen fluxes in intertidal sediments. *Estuarine, Coastal and Shelf Science* 46: 221–232.
- Bailey, E.M., and W.R. Boynton. 2008. *Sediment oxygen and nutrient exchange measurements from Chesapeake Bay, tributary rivers and Maryland coastal bays: development of a comprehensive database and analysis of factors controlling patterns and magnitude of sediment-water exchanges*. Baltimore: Maryland Department of the Environment, TMDL Technical Development Program Ref. No. [UMCES] CBL 08-019. TS-542-08].
- Bailey, E.M., P.E. Smail, F. Rohland, B. Bean, M.A.C. Ceballos, M. Kaumeyer, and W.R. Boynton. 2003. *Monitoring of sediment oxygen and nutrient exchanges in the Potomac River Estuary in support of TMDL development*. Baltimore: Maryland Department of the Environment, Chesapeake Bay and Special Projects Ref. No. [UMCES] CBL 03-396.
- Bailey, E.M., M.S. Owens, Walter R. Boynton, J.C. Cornwell, E. Kiss, P.E. Smail, H. Soulen, E. Buck, and M.A.C. Ceballos. 2006. *Sediment phosphorus flux: pH interactions in the tidal freshwater Potomac River estuary*. Rockville: Interstate Commission on the Potomac River Basin Ref. No. [UMCES] CBL 06-005.
- Balzer, W., K. Grasshoff, P. Dieckmann, H. Haardt, and U. Petersohn. 1983. Redox-turnover at the sediment/water interface studied in a large bell jar system. *Oceanologica Acta* 6: 337–344.
- Banta, G.T., A.E. Giblin, J.E. Hobbie, and J. Tucker. 1995. Benthic respiration and nitrogen release in Buzzards Bay, Massachusetts. *Journal of Marine Research* 53: 107–135.
- Barnard, P.L., D.H. Schoellhamer, B.E. Jaffe, and L.J. McKee. 2013. Sediment transport in the San Francisco Bay Coastal System: an overview. *Marine Geology* 345: 3–17.
- Bartoli, M., M. Cattadori, G. Giordani, and P. Viaroli. 1996. Benthic oxygen respiration, ammonium and phosphorus regeneration in surficial sediments of the Sacca di Goro (Northern Italy) and two French coastal lagoons: a comparative study. *Hydrobiologia* 329: 143–159. doi:10.1007/BF00034554.
- Berelson, W.M., J. McManus, K.H. Coale, K.S. Johnson, T. Kilgorel, D. Burdige, and C. Pilskaln. 1996. Biogenic matter diagenesis on the sea floor: a comparison between two continental margin transects. *Journal of Marine Research* 54: 731–762.
- Berelson, W.M., J. McManus, S. Severmann, and C.E. Reimers. 2013. Benthic flux of oxygen and nutrients across Oregon/California shelf sediments. *Continental Shelf Research* 55: 66–75. doi:10.1016/j.csr.2013.01.009.
- Berg, P., H. Røy, F. Janssen, V. Meyer, B. Barker Jørgensen, M. Huettel, and D. De Beer. 2003. Oxygen uptake by aquatic sediments measured with a novel non-invasive eddy-correlation technique. *Marine Ecology Progress Series* 261: 75–83.
- Bosch, J.A., J.C. Cornwell, and W.M. Kemp. 2015. Short-term effects of nereid polychaete size and density on sediment inorganic nitrogen cycling under varying oxygen conditions. *Marine Ecology Progress Series* 524: 155–169. doi:10.3354/meps11185.
- Boucher, G., and R. Boucher-Rodoni. 1988. In situ measurement of respiratory metabolism and nitrogen fluxes at the interface of oyster beds. *Marine Ecology Progress Series* 44: 229–238.
- Boynton, J. E. 1985. The influence of current velocity on nutrient and oxygen exchanges between estuarine sediments and the water column. PhD thesis, University of Maryland, College Park, Maryland.
- Boynton, Walter R., and M. A. C. Ceballos. 2017. World flux data set 2016, Mendeley Data, v2. doi 10.17632/8gc3ys3jx6.2.
- Boynton, W.R., and W.M. Kemp. 1985. Nutrient regeneration and oxygen consumption by sediments along an estuarine salinity gradient. *Marine Ecology Progress Series* 23: 45–55.
- Boynton, W.R., and W.M. Kemp. 2000. Influence of river flow and nutrient loads on selected ecosystem processes: a synthesis of Chesapeake Bay data. In *Estuarine science: a synthetic approach to research and practice*, ed. J.E. Hobbie, 269–298. Washington, DC: Island Press.
- Boynton, W.R., W.M. Kemp, C.G. Osborne, K.R. Kaumeyer, and M.C. Jenkins. 1981. Influence of water circulation rate on in situ measurements of benthic community respiration. *Marine Biology* 65: 185–190. doi:10.1007/BF00397084.
- Boynton, W.R., W.M. Kemp, and C.W. Keefe. 1982. A comparative analysis of nutrients and other factors influencing estuarine phytoplankton production. In *Estuarine comparisons*, ed. Victor S. Kennedy, 69–90. New York: Academic Press.
- Boynton, W.R., J.D. Hagy, J.C. Cornwell, W.M. Kemp, S.M. Greene, J.E. Baker, and R.K. Larsen. 2008. Nutrient budgets and management actions in the Patuxent River Estuary, Maryland. *Estuaries and Coasts* 31: 623–651. doi:10.1007/s12237-008-9052-9.
- Bricker, S.B., B. Longstaff, W. Dennison, A. Jones, K. Boicourt, C. Wicks, and J. Woerner. 2007. *Effects of nutrient*

- enrichment in the nation's estuaries: a decade of change. Silver Spring: NOAA Coastal Ocean Program Decision Analysis Series No. 26.
- Burford, M.A., and A.R. Longmore. 2001. High ammonium production from sediments in hypereutrophic shrimp ponds. *Marine Ecology Progress Series* 224: 187–195.
- Caffrey, Jane M., N. Harrington, and B. Ward. 2002. Biogeochemical processes in a small California estuary. 1. Benthic fluxes and pore water constituents reflect high nutrient freshwater inputs. *Marine Ecology Progress Series* 233: 39–53. doi:10.3354/meps233039.
- Callender, E., and D.E. Hammond. 1982. Nutrient exchange across the sediment-water interface in the Potomac River estuary. *Estuarine, Coastal and Shelf Science* 15: 395–413.
- Carpenter, S.R., E.V. Armbrust, P.W. Arzberger, F.S. Chapin, J.J. Elser, E.J. Hackett, A.R. Ives, et al. 2009. Accelerate synthesis in ecology and environmental sciences. *Bioscience* 59: 699–701. doi:10.1525/bio.2009.59.8.11.
- Cerco, C.F. 1989. Measured and modelled effects of temperature, dissolved oxygen and nutrient concentration on sediment-water nutrient exchange. *Hydrobiologia* 174: 185–194. doi:10.1007/BF00008156.
- Cerco, C.F., and M.R. Noel. 2013. Twenty-one-year simulation of Chesapeake Bay water quality using the CE-QUAL-ICM eutrophication model. *Journal of the American Water Resources Association* 49: 1119–1133. doi:10.1111/jawr.12107.
- Clavero, V., J.J. Izquierdo, J.A. Fernández, and F.X. Niell. 2000. Seasonal fluxes of phosphate and ammonium across the sediment-water interface in a shallow small estuary (Palmones River, southern Spain). *Marine Ecology Progress Series* 198: 51–60.
- Cloern, J.E., S.Q. Foster, and A.E. Kleckner. 2014. Phytoplankton primary production in the world's estuarine-coastal ecosystems. *Biogeosciences* 11: 2477–2501.
- Clough, L.M., P.E. Renaud, and W.G. Ambrose. 2005. Impacts of water depth, sediment pigment concentration, and benthic macrofaunal biomass on sediment oxygen demand in the western Arctic Ocean. *Canadian Journal of Fisheries and Aquatic Sciences* 62: 1756–1765. doi:10.1139/f05-102.
- Cook, P.L.M., B.D. Eyre, R. Leeming, and E.C.V. Butler. 2004. Benthic fluxes of nitrogen in the tidal reaches of a turbid, high-nitrate subtropical river. *Estuarine, Coastal and Shelf Science* 59: 675–685. doi:10.1016/j.ecss.2003.11.011.
- Cornwell, J. C., and P. A. Sampou. 1995. Environmental controls on iron sulfide mineral formation in a coastal plain estuary. In *Geochemical transformations of sedimentary sulfur*, ed., 612:224–242. Washington D.C.: American Chemical Society.
- Cornwell, J.C., W.M. Kemp, and T.M. Kana. 1999. Denitrification in coastal ecosystems: methods, environmental controls, and ecosystem level controls, a review. *Aquatic Ecology* 33: 41–54. doi:10.1023/A:1009921414151.
- Cornwell, J.C., M.S. Owens, W.R. Boynton, and L.A. Harris. 2016. Sediment-water nitrogen exchange along the Potomac River estuarine salinity gradient. *Journal of Coastal Research* 32: 776–787. doi:10.2112/JCOASTRES-D-15-00159.1.
- Cowan, J.L.W., and W.R. Boynton. 1996. Sediment-water oxygen and nutrient exchanges along the longitudinal axis of Chesapeake Bay: seasonal patterns, controlling factors and ecological significance. *Estuaries* 19: 562–580. doi:10.2307/1352518.
- Cowan, J.L.W., J.R. Pennock, and W.R. Boynton. 1996. Seasonal and interannual patterns of sediment-water nutrient and oxygen fluxes in Mobile Bay, Alabama (USA): regulating factors and ecological significance. *Marine Ecology Progress Series* 141: 229–245.
- D'Elia, C.F., W.R. Boynton, and J.G. Sanders. 2003. A watershed perspective on nutrient enrichment, science, and policy in the Patuxent River, Maryland: 1960–2000. *Estuaries* 26: 171–185.
- Dade, W.B. 1993. Near-bed turbulence and hydrodynamic control of diffusional mass transfer at the sea floor. *Limnology and Oceanography* 38: 52–69.
- Dale, A.W., and R. Prego. 2002. Physico-biogeochemical controls on benthic-pelagic coupling of nutrient fluxes and recycling in a coastal upwelling system. *Marine Ecology Progress Series* 235: 15–28. doi:10.3354/meps235015.
- Dame, R.F., R.G. Zingmark, and E. Haskin. 1984. Oyster reefs as processors of estuarine materials. *Journal of Experimental Marine Biology and Ecology* 83: 239–247.
- Dame, R.F., N. Dankers, T. Prins, H. Jongsma, and A. Smaal. 1991. The influence of mussel beds on nutrients in the western Wadden Sea and Eastern Scheldt estuaries. *Estuaries* 14: 130–138.
- Denis, L., and C. Grenz. 2003. Spatial variability in oxygen and nutrient fluxes at the sediment-water interface on the continental shelf in the Gulf of Lions (NW Mediterranean). *Oceanologica Acta* 26: 373–389. doi:10.1016/S0399-1784(03)00017-3.
- Di Toro, D.M. 1980. The effect of phosphorus loadings on dissolved oxygen in Lake Erie. In *Phosphorus management strategies for lakes*, ed. R.C. Loehr, C.S. Martin, and W. Rast, 191–205. Ann Arbor: Ann Arbor Science.
- Diaz, R.J., and R. Rosenberg. 2008. Spreading dead zones and consequences for marine ecosystems. *Science* 321: 926–929. doi:10.1126/science.1156401.
- Eyre, B.D., and A.J.P. Ferguson. 2005. Benthic metabolism and nitrogen cycling in a subtropical east Australian estuary (Brunswick): temporal variability and controlling factors. *Limnology and Oceanography* 50: 81–96. doi:10.4319/lo.2005.50.1.0081.
- Faganeli, J., and N. Ogrinc. 2009. Oxidic-anoxic transition of benthic fluxes from the coastal marine environment (Gulf of Trieste, northern Adriatic Sea). *Marine and Freshwater Research* 60: 700–711. doi:10.1071/MF08065.
- Fanning, K.A., K.L. Carder, and P.R. Betzer. 1982. Sediment resuspension by coastal waters: a potential mechanism for nutrient re-cycling on the ocean's margins. *Deep Sea Research Part A, Oceanographic Research Papers* 29: 953–965.
- Fariás, L., L.A. Chuecas, and M.A. Salamanca. 1996. Effect of coastal upwelling on nitrogen regeneration from sediments and ammonium supply to the water column in Concepcion Bay, Chile. *Estuarine, Coastal and Shelf Science* 43: 137–155.
- Fenchel, T., and T.H. Blackburn. 1979. *Bacteria and mineral cycling*. London: Academic Press.
- Fennel, K., D. Brady, D. DiToro, R.W. Fulweiler, W.S. Gardner, A. Giblin, M.J. McCarthy, et al. 2009. Modeling denitrification in aquatic sediments. *Biogeochemistry* 93: 159–178.
- Fisher, T.R., E.R. Peele, J.W. Ammerman, and L.W. Harding. 1992. Nutrient limitation of phytoplankton in Chesapeake Bay. *Marine Ecology Progress Series* 82: 51–63.
- Fisher, T.R., A.B. Gustafson, K. Sellner, R. Lacouture, L.W. Haas, R.L. Wetzel, R. Magnien, D. Everitt, B. Michaels, and R. Karrh. 1999. Spatial and temporal variation of resource limitation in Chesapeake Bay. *Marine Biology* 133: 763–778.
- Fulweiler, R.W., and S.W. Nixon. 2009. Responses of benthic-pelagic coupling to climate change in a temperate estuary. *Hydrobiologia* 629: 147–156.
- Fulweiler, R.W., S.W. Nixon, and B.A. Buckley. 2010. Spatial and temporal variability of benthic oxygen demand and nutrient regeneration in an anthropogenically impacted New England estuary. *Estuaries and Coasts* 33: 1377–1390.
- Gao, Y., J.C. Cornwell, D.K. Stoecker, and M.S. Owens. 2012. Effects of cyanobacterial-driven pH increases on sediment nutrient fluxes and coupled nitrification-denitrification in a shallow fresh water estuary. *Biogeosciences* 9: 2697–2710.
- Gelesh, L., K. Marshall, W. Boicourt, and L. Lapham. 2016. Methane concentrations increase in bottom waters during summertime anoxia

- in the highly eutrophic estuary, Chesapeake Bay, U.S.A. *Limnology and Oceanography* 61: S253–S266. doi:10.1002/lno.10272.
- Giblin, A.E., C.S. Hopkins, and J. Tucker. 1997. Benthic metabolism and nutrient cycling in Boston Harbor, Massachusetts. *Estuaries* 20: 346–364.
- Giblin, Anne E., Nathaniel B. Weston, Gary T. Banta, Jane Tucker, and Charles S. Hopkins. 2010. The effects of salinity on nitrogen losses from an oligohaline estuarine sediment. *Estuaries and Coasts* 33: 1054–1068. doi:10.1007/s12237-010-9280-7.
- Grenz, C., J.E. Cloern, S.W. Hager, and B.E. Cole. 2000. Dynamics of nutrient cycling and related benthic nutrient and oxygen fluxes during a spring phytoplankton bloom in South San Francisco Bay (USA). *Marine Ecology Progress Series* 197: 67–80.
- Grenz, C., L. Denis, G. Boucher, L. Chauvaud, J. Clavier, R. Fichez, and O. Pringault. 2003. Spatial variability in sediment oxygen consumption under winter conditions in a lagoonal system in New Caledonia (South Pacific). *Journal of Experimental Marine Biology and Ecology* 285–286: 33–47.
- Hammond, D.E., C. Fuller, D. Harmon, B. Hartman, M. Korosec, L.G. Miller, R. Rea, S. Warren, W.M. Berelson, and S.W. Hager. 1985. Benthic fluxes in San Francisco Bay. *Hydrobiologia* 129: 69–90.
- Hansen, L.S., and T.H. Blackburn. 1992. Effect of algal bloom deposition on sediment respiration and fluxes. *Marine Biology* 112: 147–152. doi:10.1007/BF00349738.
- Hargrave, B.T. 1973. Coupling carbon flow through some pelagic and benthic communities. *Journal of the Fisheries Research Board of Canada* 30: 1317–1326. doi:10.1139/f73-212.
- Harrell Jr., F. E., C. Dupont, et al. 2016. *Hmisc: Harrell Miscellaneous. R package version 3.17-4*. URL: <https://CRAN.R-project.org/package=Hmisc>.
- Henriksen, K., T.H. Blackburn, B.Aa. Lomstein, and C.P. McRoy. 1993. Rates of nitrification, distribution of nitrifying bacteria and inorganic N fluxes in northern Bering-Chukchi shelf sediments. *Continental Shelf Research* 13: 629–651.
- Hopkinson, C.S., Jr. 1985. Shallow-water benthic and pelagic metabolism. *Marine Biology* 87: 19–32.
- Hopkinson, C.S., Jr. 1987. Nutrient regeneration in shallow-water sediments of the estuarine plume region of the nearshore Georgia Bight, USA. *Marine Biology* 94: 127–142.
- Hopkinson, C.S., A.E. Giblin, and J. Tucker. 2001. Benthic metabolism and nutrient regeneration on the continental shelf of Eastern Massachusetts, USA. *Marine Ecology Progress Series* 224: 1–19.
- Houde, E.D., and E.S. Rutherford. 1993. Recent trends in estuarine fisheries: predictions of fish production and yield. *Estuaries* 16: 161–176.
- Howarth, R.W. 1988. Nutrient limitation of net primary production in marine ecosystems. *Annual Review of Ecology and Systematics* 19: 89–110.
- Huettel, M., P. Berg, and J.E. Kostka. 2014. Benthic exchange and biogeochemical cycling in permeable sediments. *Annual Review of Marine Science* 6: 23–51.
- Jensen, M.H., E. Lomstein, and J. Sørensen. 1990. Benthic NH_4^+ and NO_3^- flux following sedimentation of a spring phytoplankton bloom in Aarhus Bight, Denmark. *Marine Ecology Progress Series* 61: 87–96. doi:10.3354/meps061087.
- Jensen, H.S., P.B. Mortensen, F.O. Andersen, E. Rasmussen, and A. Jensen. 1995. Phosphorus cycling in a coastal marine sediment, Aarhus Bay, Denmark. *Limnology and Oceanography* 40: 908–917.
- Jordan, T.E., Je.C. Cornwell, W.R. Boynton, and J.T. Anderson. 2008. Changes in phosphorus biogeochemistry along an estuarine salinity gradient: the iron conveyor belt. *Limnology and Oceanography* 53: 172–184. doi:10.4319/lo.2008.53.1.0172.
- Katsev, S., G. Chaillou, B. Sundby, and A. Mucci. 2007. Effects of progressive oxygen depletion on sediment diagenesis and fluxes: A model for the lower St. Lawrence River Estuary. *Limnology and Oceanography* 52: 2555–2568.
- Kemp, W.M., and W.R. Boynton. 1981. External and internal factors regulating metabolic rates of an estuarine community. *Oecologia* 51: 19–27.
- Kemp, W.M., and W.R. Boynton. 1992. Benthic-pelagic interactions: nutrient and oxygen dynamics. In *Oxygen dynamics in Chesapeake Bay: a synthesis of recent research*, ed. D.E. Smith, M. Leffler, and G.B. Mackiernan, 149–221. College Park: Maryland Sea Grant.
- Kemp, W.M., and W.R. Boynton. 2012. Synthesis in estuarine and coastal ecological research: what is it, why is it important, and how do we teach it? *Estuaries and Coasts* 35: 1–22. doi:10.1007/s12237-011-9464-9.
- Kemp, W.M., P.A. Sampou, J. Garber, J. Tuttle, and W.R. Boynton. 1992. Seasonal depletion of oxygen from bottom waters of Chesapeake Bay: roles of benthic and planktonic respiration and physical exchange processes. *Marine Ecology Progress Series* 85: 137–152.
- Kemp, W.M., J. Faganeli, S. Puskaric, E.M. Smith, and W.R. Boynton. 1999. Pelagic-benthic coupling and nutrient cycling. In *Ecosystems at the land-sea margin: drainage basin to coastal sea*, ed. T.C. Malone, A. Malej, L.W. Harding, N. Smolaka, and R.E. Turner, 295–339. Washington, D.C.: American Geophysical Union. Chapter 10.
- Kemp, W.M., W.R. Boynton, J.E. Adolf, D.F. Boesch, W.C. Boicourt, G. Brush, J.C. Cornwell, et al. 2005. Eutrophication of Chesapeake Bay: historical trends and ecological interactions. *Marine Ecology Progress Series* 303: 1–29. doi:10.3354/meps303001.
- Koop, K., Walter R. Boynton, F. Wulff, and R. Carman. 1990. Sediment-water oxygen and nutrient exchanges along a depth gradient in the Baltic Sea. *Marine Ecology Progress Series* 63: 65–77. doi:10.3354/meps063065.
- Kristensen, E. 1993. Seasonal variations in benthic community metabolism and nitrogen dynamics in a shallow, organic-poor Danish lagoon. *Estuarine, Coastal and Shelf Science* 36: 565–586. doi:10.1006/ecss.1993.1035.
- Krom, M.D., and R.A. Berner. 1980. Adsorption of phosphate in anoxic marine sediments. *Limnology and Oceanography* 25: 797–806. doi:10.4319/lo.1980.25.5.0797.
- Lansard, B., C. Rabouille, L. Denis, and C. Grenz. 2008. In situ oxygen uptake rates by coastal sediments under the influence of the Rhone River (NW Mediterranean Sea). *Continental Shelf Research* 28: 1501–1510. doi:10.1016/j.csr.2007.10.010.
- Li, M., Y.J. Lee, J.M. Testa, Y. Li, W. Ni, W.M. Kemp, and D.M. Di Toro. 2016. What drives interannual variability of hypoxia in Chesapeake Bay: climate forcing versus nutrient loading? *Geophysical Research Letters* 43: 2127–2134. doi:10.1002/2015GL067334.
- Lin, X., M.J. McCarthy, S.A. Carini, and W.S. Gardner. 2011. Net, actual, and potential sediment-water interface NH_4^+ fluxes in the northern Gulf of Mexico (NGOMEX): evidence for NH_4^+ limitation of microbial dynamics. *Continental Shelf Research* 31: 120–128. doi:10.1016/j.csr.2010.11.012.
- Link, H., P. Archambault, T. Tاملander, P.E. Renaud, and D. Piepenburg. 2011. Spring-to-summer changes and regional variability of benthic processes in the western Canadian Arctic. *Polar Biology* 34: 2025–2038. doi:10.1007/s00300-011-1046-6.
- Lyons, W.B., T.C. Loder, and S.M. Murray. 1982. Nutrient pore water chemistry, Great Bay, New Hampshire: benthic fluxes. *Estuaries* 5: 230–233.
- Macreadie, P.I., D.J. Ross, and A.R. Longmore. 2006. Denitrification measurements of sediments using cores and chambers. *Marine Ecology Progress Series* 326: 49–59.
- Marvin-DiPasquale, M., and D. Capone. 1998. Benthic sulfate reduction along the Chesapeake Bay central channel. I. Spatial trends and controls. *Marine Ecology Progress Series* 168: 213–228.

- Marvin-DiPasquale, M.C., W.R. Boynton, and D.G. Capone. 2003. Benthic sulfate reduction along the Chesapeake Bay central channel. II. Temporal controls. *Marine Ecology Progress Series* 260: 55–70.
- McGlathery, K.J. 2008. Seagrass Habitats. In *Nitrogen in the marine environment*, ed. D.G. Capone, D.A. Bronk, M.R. Mulholland, and E.J. Carpenter 2nd, 1037–1071. San Diego: Academic Press. doi:10.1016/B978-0-12-372522-6.00023-2.
- Middelburg, J.J., T. Vlug, and F.J.W.A. van der Nat. 1993. Organic-matter mineralization in marine systems. *Global and Planetary Change* 8: 47–58.
- Miller, W.D., L.W. Harding, and J.E. Adolf. 2006. Hurricane Isabel generated an unusual fall bloom in Chesapeake Bay. *Geophysical Research Letters* 33: 2–5.
- Miller-Way, T., G.S. Boland, G.T. Rowe, and R.R. Twilley. 1994. Sediment oxygen consumption and benthic nutrient fluxes on the Louisiana continental shelf: a methodological comparison. *Estuaries* 17: 809–815. doi:10.2307/1352749.
- Mortimer, C.H. 1941. The exchange of dissolved substances between mud and water in lakes. *Journal of Ecology* 29: 280–329.
- Mortimer, R.J.G., M.D. Krom, P.G. Watson, P.E. Frickers, J.T. Davey, and R.J. Clifton. 1998. Sediment-water exchange of nutrients in the intertidal zone of the Humber estuary, UK. *Marine Pollution Bulletin* 37: 261–279. doi:10.1016/S0025-326X(99)00053-3.
- Murrell, M.C., and J.C. Lehrter. 2011. Sediment and lower water column oxygen consumption in the seasonally hypoxic region of the Louisiana continental shelf. *Estuaries and Coasts* 34: 912–924. doi:10.1007/s12237-010-9351-9.
- Nedwell, D.B., and M. Trimmer. 1996. Nitrogen fluxes through the upper estuary of the Great Ouse, England: the role of the bottom sediments. *Marine Ecology Progress Series* 142: 273–286. doi:10.3354/meps142273.
- Nedwell, D.B., S.E. Hall, A. Andersson, Å.F. Hagström, and E.B. Lindström. 1983. Seasonal changes in the distribution and exchange of inorganic nitrogen between sediment and water in the Northern Baltic (Gulf of Bothnia). *Estuarine, Coastal and Shelf Science* 17: 169–179.
- Nedwell, D.B., T.R. Walker, J.C. Ellis-Evans, and A. Clarke. 1993. Measurements of seasonal rates and annual budgets of organic carbon fluxes in an Antarctic coastal environment at Signy Island, South Orkney Islands, suggest a broad balance between production and decomposition. *Applied and Environmental Microbiology* 59: 3989–3995.
- Nixon, S.W. 1981. Remineralization and nutrient cycling in coastal marine ecosystems. In *Estuaries and nutrients*, ed. B.J. Neilson and L.E. Cronin, 1st ed., 111–138. Clifton: Humana Press.
- Nixon, S.W. 1988. Physical energy inputs and the comparative ecology of lake and marine ecosystems. *Limnology and Oceanography* 33: 1005–1025.
- Nixon, S.W., C.A. Oviatt, and S.S. Hale. 1976. Nitrogen regeneration and the metabolism of coastal marine bottom communities. In *The role of terrestrial and aquatic organisms in decomposition processes*, ed. J.M. Anderson and A. McFadyen, 269–283. Blackwell: Blackwell Scientific Publications.
- Nowell, A.R.M., and P.A. Jumars. 1984. Flow environments and aquatic benthos. *Annual Review of Ecology and Systematics* 15: 303–328.
- Nunnally, C.C., G.T. Rowe, D.C.O. Thornton, and A. Quigg. 2013. Sedimentary oxygen consumption and nutrient regeneration in the northern Gulf of Mexico hypoxic zone. *Journal of Coastal Research* 63: 84–96. doi:10.2112/SI63-008.1.
- Pamatmat, M.M. 1971. Oxygen consumption by the seabed. IV. Shipboard and laboratory experiments. *Limnology and Oceanography* 16: 536–550. doi:10.4319/lo.1971.16.3.0536.
- Piepenburg, D., T.H. Blackburn, C.F. von Dorrien, J. Gutt, P.O.J. Hall, S. Hulth, M.A. Kendall, K.W. Opalinski, E. Rachor, and M.K. Schmid. 1995. Partitioning of benthic community respiration in the Arctic (northwestern Barents Sea). *Marine Ecology Progress Series* 118: 199–213.
- Piña-Ochoa, E., and M. Álvarez-Cobelas. 2006. Denitrification in aquatic environments: a cross-system analysis. *Biogeochemistry* 81: 111–130. doi:10.1007/s10533-006-9033-7.
- Porter, E.T., J.C. Cornwell, and L.P. Sanford. 2004. Effect of oysters *Crassostrea virginica* and bottom shear velocity on benthic-pelagic coupling and estuarine water quality. *Marine Ecology Progress Series* 271: 61–75. doi:10.3354/meps271061.
- Porter, E.T., M.S. Owens, and J.C. Cornwell. 2006. Effect of sediment manipulation on the biogeochemistry of experimental sediment systems. *Journal of Coastal Research* 22: 1539–1551.
- Porter, E.T., R.P. Mason, and L.P. Sanford. 2010. Effect of tidal resuspension on benthic-pelagic coupling in an experimental ecosystem study. *Marine Ecology Progress Series* 413: 33–53. doi:10.3354/meps08709.
- Pratihary, Anil K., S.W.A. Naqvi, H. Naik, B.R.R. Thorat, G. Narvenkar, B.R.R. Manjunatha, and V.P.P. Rao. 2009. Benthic fluxes in a tropical estuary and their role in the ecosystem. *Estuarine, Coastal and Shelf Science* 85: 387–398.
- Prins, T.C., and A.C. Smaal. 1994. The role of the blue mussel *Mytilus edulis* in the cycling of nutrients in the Oosterschelde estuary (The Netherlands). *Hydrobiologia* 283: 413–429.
- Provoost, P., U. Braeckman, D. Van Gansbeke, L. Moodley, K. Soetaert, J.J. Middelburg, and J. Vanaverbeke. 2013. Modelling benthic oxygen consumption and benthic-pelagic coupling at a shallow station in the southern North Sea. *Estuarine, Coastal and Shelf Science* 120: 1–11. doi:10.1016/j.ecss.2013.01.008.
- Rasmussen, H., and B. Barker Jørgensen. 1992. Microelectrode studies of seasonal oxygen uptake in a coastal sediment: role of molecular diffusion. *Marine Ecology Progress Series* 81: 289–303.
- Redfield, A.C. 1934. On the proportions of organic derivatives in sea water and their relation to the composition of plankton. In *James Johnstone memorial volume*, ed. J. Johnstone, R.J. Daniel, and University of Liverpool, 176–192. Liverpool: University of Liverpool Press.
- Rizzo, W.M., and R.R. Christian. 1996. Significance of subtidal sediments to heterotrophically-mediated oxygen and nutrient dynamics in a temperate estuary. *Estuaries* 19: 475–487. doi:10.2307/1352464.
- Rizzo, W.M., G.J. Lackey, and R.R. Christian. 1992. Significance of euphotic, subtidal sediments to oxygen and nutrient cycling in a temperate estuary. *Marine Ecology Progress Series* 86: 51–61.
- Rysgaard, S., B. Thamdrup, N. Risgaard-Petersen, H. Fossing, P. Berg, P.B. Christensen, and T. Dalsgaard. 1998. Seasonal carbon and nutrient mineralization in a high-Arctic coastal marine sediment, Young Sound, Northeast Greenland. *Marine Ecology Progress Series* 175: 261–276. doi:10.3354/meps175261.
- Sanford, L.P. 1997. Turbulent mixing in experimental ecosystems. *Marine Ecology Progress Series* 161: 265–293. doi:10.3354/meps161265.
- Sanford, L.P., and S.M. Crawford. 2000. Mass transfer versus kinetic control of uptake across solid-water boundaries. *Limnology and Oceanography* 45: 1180–1186.
- Sanford, L.P., W. Panageotou, and J.P. Halka. 1991. Tidal resuspension of sediments in the northern Chesapeake Bay. *Marine Geology* 97: 87–103.
- Sarthou, G., K.R. Timmermans, S. Blain, and P. Tréguer. 2005. Growth physiology and fate of diatoms in the ocean: A review. *Journal of Sea Research* 53: 25–22.
- Seitzinger, S.P. 1991. The effect of pH on the release of phosphorus from Potomac River sediments: implications for blue-green algal blooms. *Estuarine, Coastal and Shelf Science* 33: 409–418.
- Seitzinger, S.P., S.W. Nixon, and M.E.Q. Pilson. 1984. Denitrification and nitrous oxide production in a coastal marine. *Limnology and Oceanography* 29: 73–83.

- Seitzinger, S.P., J.A. Harrison, J.K. Böhlke, A.F. Bouwman, R. Lowrance, B. Peterson, C. Tobias, and G. van Drecht. 2006. Denitrification across landscapes and waterscapes: a synthesis. *Ecological Applications* 16: 2064–2090.
- Shim, J.H., Y.C. Kang, D.J. Kang, and M.W. Han. 2011. Fluxes and budgets of biogenic elements at the sediment-water interface of Marian Cove, King George Island. *Antarctic Science* 23: 358–368. doi:10.1017/S0954102011000137.
- Smith, K.L., Jr., and J.M. Teal. 1973. Deep-sea benthic community respiration: an in situ study at 1850 meters. *Science* 179: 282–283. doi:10.1126/science.179.4070.282.
- Smith, J., M.A. Burford, A.T. Revill, R.R. Haese, and J. Fortune. 2012. Effect of nutrient loading on biogeochemical processes in tropical tidal creeks. *Biogeochemistry* 108: 359–380. doi:10.1007/s10533-011-9605-z.
- Sohma, A., Y. Sekiguchi, T. Kuwae, and Y. Nakamura. 2008. A benthic-pelagic coupled ecosystem model to estimate the hypoxic estuary including tidal flat-model description and validation of seasonal/daily dynamics. *Ecological Modelling* 215: 10–39.
- Sørensen, J., B. Barker Jørgensen, and N.P. Revsbech. 1979. A comparison of oxygen, nitrate, and sulfate respiration in coastal marine sediments. *Microbial Ecology* 5: 105–115.
- Spooner, D.R., and W. Maher. 2009. Benthic sediment composition and nutrient cycling in an intermittently closed and open lake lagoon. *Journal of Marine Systems* 75: 33–45.
- Sun, M.Y., C. Lee, and R.C. Aller. 1993. Anoxic and oxic degradation of ¹⁴C-labeled Chlorophylls and a ¹⁴C-labeled diatom in Long-Island Sound sediments. *Limnology and Oceanography* 38: 1438–1451. doi:10.4319/lo.1993.38.7.1438.
- Sundbäck, K., and W. Graneli. 1988. Flux between sediment and water: a laboratory. *Marine Ecology Progress Series* 43: 63–69.
- Sundbäck, K., A. Miles, and E. Göransson. 2000. Nitrogen fluxes, denitrification and the role of microphytobenthos in microtidal shallow-water sediments: an annual study. *Marine Ecology Progress Series* 200: 59–76. doi:10.3354/meps200059.
- Sundbäck, K., F. Linares, F. Larson, A. Wulff, and A. Engelsen. 2004. Benthic nitrogen fluxes along a depth gradient in a microtidal fjord: the role of denitrification and microphytobenthos. *Limnology and Oceanography* 49: 1095–1107.
- Sundbäck, K., A. Miles, and F. Linares. 2006. Nitrogen dynamics in nontidal littoral sediments: role of microphytobenthos and denitrification. *Estuaries and Coasts* 29: 1196–1211.
- Sundby, B., C. Gobeil, N. Silverberg, and A. Mucci. 1992. The phosphorus cycle in coastal marine sediments. *Limnology and Oceanography* 37: 1129–1145.
- Taylor, D.I., C.A. Oviatt, and D.G. Borkman. 2011. Non-linear responses of a coastal aquatic ecosystem to large decreases in nutrient and organic loadings. *Estuaries and Coasts* 34: 745–757. doi:10.1007/s12237-010-9312-3.
- Testa, J.M., W.M. Kemp, W.R. Boynton, and J.D. Hagy III. 2008. Long-term changes in water quality and productivity in the Patuxent River estuary: 1985 to 2003. *Estuaries and Coasts* 31: 1021–1037. doi:10.1007/s12237-008-9095-y.
- Testa, J.M., Y. Li, Y.J. Lee, M. Li, D.C. Brady, D.M. Di Toro, W.M. Kemp, and J.J. Fitzpatrick. 2014. Quantifying the effects of nutrient loading on dissolved O₂ cycling and hypoxia in Chesapeake Bay using a coupled hydrodynamic-biogeochemical model. *Journal of Marine Systems* 139: 139–158. doi:10.1016/j.jmarsys.2014.05.018.
- Thereau, T.M., and E.J. Atkinson. 2015. *An introduction to recursive partitioning using the RPART routines*. Mayo Clinic Division of Biostatistics. Rochester: Mayo Foundation.
- Traykovski, P., R. Geyer, and C. Sommerfield. 2004. Rapid sediment deposition and fine-scale strata formation in the Hudson estuary. *Journal of Geophysical Research* 109: 1–20.
- Trimmer, M., R.J. Gowen, and B.M. Stewart. 2003. Changes in sediment processes across the western Irish Sea front. *Estuarine, Coastal and Shelf Science* 56: 1011–1019.
- Tucker, J., A.E. Giblin, C.S. Hopkinson, S.W. Kelsey, and B.L. Howes. 2014. Response of benthic metabolism and nutrient cycling to reductions in wastewater loading to Boston Harbor, USA. *Estuarine, Coastal and Shelf Science* 151: 54–68.
- Twilley, R.R., J. Cowan, T. Miller-Way, P.A. Montagna, and B. Mortazavi. 1999. Benthic nutrient fluxes in selected estuaries in the Gulf of Mexico. In *Biogeochemistry of Gulf of Mexico estuaries*, ed. T.S. Bianchi, J.R. Pennock, and R.R. Twilley, 163–209. New York: Wiley.
- Venables, W.N., and B.D. Ripley. 2002. *Modern applied statistics with S-Plus. 4th ed. Series: Statistics and Computing*. New York: Springer.
- Vidal, M., J. Romero, and J. Camp. 1989. Sediment-water nutrient fluxes: preliminary results of in situ measurements in Alfacas Bay, Ebro River Delta. *Scientia Marina* 53: 505–511.
- Vidal, M., J. A. Morgui, M. Latasa, J. Romero, and J. Camp. 1997. Factors controlling seasonal variability of benthic ammonium release and oxygen uptake in Alfacs Bay (Ebro Delta, NW Mediterranean). *Hydrobiologia* 350:169–178. doi:10.1023/A:1003096117678.
- Warnken, K.W., G.A. Gill, P.H. Santschi, and L.L. Griffin. 2000. Benthic exchange of nutrients in Galveston Bay, Texas. *Estuaries* 23: 647–661. doi:10.2307/1352891.
- Watson, P.G., and T. Frickers. 1995. Sediment-water exchange of nutrients in the southern North-Sea adjacent to the Humber Estuary. *Ophelia* 41: 361–384.
- Watson, P.G., P.E. Frickers, and R.J.M. Howland. 1993. Benthic fluxes of nutrients and some trace metals in the Tamar Estuary, SW England. *Netherlands Journal of Aquatic Ecology* 27: 135–146. doi:10.1007/BF02334776.
- Webb, K.L., and C.F. D’Elia. 1980. Nutrient and oxygen redistribution during a spring neap tidal cycle in a temperate estuary. *Science* 207: 983–985.
- Welsh, D.T. 2003. It’s a dirty job but someone has to do it: the role of marine benthic macrofauna in organic matter turnover and nutrient recycling to the water column. *Chemistry and Ecology* 19: 321–342. doi:10.1080/0275754031000155474.
- Wijsman, J.W.M., P.M.J. Herman, and M.T. Gomoiu. 1999. Spatial distribution in sediment characteristics and benthic activity on the northwestern Black Sea shelf. *Marine Ecology Progress Series* 181: 25–39. doi:10.3354/meps181025.
- Wolaver, T., G. Whiting, B. Kjerfve, J. Spurrier, H. McKellar, R. Dame, T. Chrzanowski, J. Zingmark, and T. Williams. 1985. The flume design- a methodology for evaluating material fluxes between a vegetated salt marsh and the adjacent tidal creel. *Journal of Experimental Marine Biology and Ecology* 91: 281–291.
- Wulff, F., A. Stigebrandt, and L. Rahm. 1990. Nutrient dynamics of the Baltic Sea. *Ambio* 19: 126–133.
- Zimmerman, A.R., and R. Benner. 1994. Denitrification, nutrient regeneration and carbon mineralization in sediments of Galveston Bay, Texas, USA. *Marine Ecology Progress Series* 114: 275–288. doi:10.3354/meps114275.