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Supporting Information for

Estuarine Sediments Exhibit Dynamic and Variable Biogeochemical Responses to Hypoxia

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Additional Supporting Information (File uploaded separately)

Introduction

As part of our manuscript we are including nine data tables and figures as supporting information. All tables contain data relevant to our three-year study (2011-2013) on the effect of water-column hypoxia on sediment biogeochemistry in a shallow temperate estuary (Waquoit Bay, East Falmouth, Massachusetts, USA). In order to provide ecological context for our study there are descriptive datasets that characterize the waters (Table S1) and sediments (Table S2) used in our experiments. In addition, we include statistical results from regression analyses used to determine relationships between environmental conditions and the time it took for the cores to reach hypoxia in our experimental set-up (Table S3). We show sediment variability across our sampling sites (Figure S4) and provide statistical results from our correlation analyses examining relationships between sediment characteristics measured (Table S5), sediment flux rates (Table S6) and the response of fluxes to hypoxia (Table S7). We also include a table (Table S8) that summarizes the literature used to create the conceptual model (Figure 7, main text) of key biogeochemical fluxes under varying oxygen conditions. And finally, we include a table that summarizes our analysis of water-column nutrient ratios under normoxic and hypoxic conditions (Table S9). In the following section, there are links to full sediment characteristic and nutrient and gas flux datasets used in this study.

Additional Data Sources

Complete sediment characteristic and flux datasets from this study are published on figshare, where they may be viewed and downloaded. The sediment characteristic dataset includes sediment porosity, density, %carbon, %nitrogen and molar carbon to nitrogen ratios up to 4 cm at 1 cm sample increments. The flux datasets include net fluxes of nutrients and dissolved gases across the sediment-water interface under hypoxic and normoxic conditions. The flux data are the primary focus of our manuscript, and evaluation of these data informed our main conclusions.

Sediment characteristic dataset: https://doi.org/10.6084/m9.figshare.7371017.v1
Hypoxic flux dataset: https://doi.org/10.6084/m9.figshare.7371110.v1
Normoxic flux dataset: https://doi.org/10.6084/m9.figshare.7371095.v2

Captions for Supporting Tables & Figures

Table S1. Water conditions in the field and in cores at the start of the incubation experiments for each sampling date. Sediments were collected from four stations (CRE (Childs River Estuary), MP (Metoxit Point), SB (South Basin), SLP (Sage Lot Pond)) during the summer and early fall on 7 dates between 2011-2013. Abbreviations are as follows: oxygen (O_2), ammonium (NH_4^+), nitrite + nitrate (NO_x), nitrite (NO_2^-), silica (DSi), phosphate (PO_4^{3-}), di-nitrogen gas (N_2-N), nitrous oxide (N_2O), and methane (CH_4). The N_2O concentrations and fluxes from 6-Aug-2012 were 2-3 orders of magnitude greater than the other dates and are outliers in the N_2O flux dataset and designated with a star (*). On 2 dates in 2012 there was an issue with the instrument analysis of N_2, therefore they are designated as having a measurement issue (m.i.) and were not able to be used in our analyses. Nutrient and greenhouse gas parameters were not measured (n.m.) prior to 2012.

Table S2. Sediment surface characteristics. Sediment composition, porosity, percent carbon (%C) and nitrogen (%N), chlorophyll *a* (Chl *a*), and benthic invertebrate abundances across four stations in Waquoit Bay, East Falmouth, Massachusetts, USA: Childs River Estuary (CRE), Metoxit Point (MP), South Basin (SB), and Sage Lot Pond (SLP). Values represent the range measured or the mean (plus or minus the standard error). Surface sediment porosity, %C and %N are from 0-1cm.

Table S3. Relationship between the time to hypoxia and water column and sediment parameters for individual cores in our incubation experiments. Time to hypoxia is defined as the amount of time it took cores to reach oxygen concentrations below the hypoxic threshold of 3 mg L^{-1} (94 µM). Statistical results are for single variable linear regression models comparing time to hypoxia and each parameter. Kendall Rank Correlation (Kendall's tau(τ)) was used to evaluate model strength. The corresponding probability (p) values for statistical significance are also shown for each model test. Bold font signifies a significant relationship (α=0.05). We ranked models with similar sample sizes using information-based statistics (Akaike Information Criterion (AIC)).

Figure S4. Sediment characteristics in Waquoit Bay. Surface sediment (a) density, (b) porosity, (c) percent carbon, (d) percent nitrogen, and (e) carbon to nitrogen molar ratio, across the four sampling stations (Childs River Estuary (CRE), Metoxit Point (MP), South Basin (SB) and Sage Lot Pond (SLP)). Solid bars represent station means minus from samples collected over 0-1cm and lines represent the standard error. Letters above the bars denote significant differences between stations (Wilcoxon/Kruskal-Wallis, df=3, and paired Wilcoxon, α=0.05).

Table S5. Relationships between surface sediment characteristics. Statistical results are for single variable linear regression models comparing each sediment parameter measured to each other. Model strength was evaluated using Kendall Rank Correlation (Kendall's Tau(τ)). Bold font signifies a significant relationship (α=0.05). Sediments samples are from 0-1cm.

Table S6. Relationships between surface sediment characteristics and biogeochemical flux rates at the sediment-water interface. Statistical results are for single variable linear regression models comparing sediment parameters to each (normoxic) flux rate. Model strength was evaluated using Kendall Rank Correlation (Kendall's Tau(τ)). Bold font signifies a significant relationship (α=0.05). Sediments samples are from 0-1cm.

Table S7. Relationships between surface sediment characteristics and the hypoxic response of biogeochemical fluxes at the sediment-water interface. The hypoxic response is defined here as the difference between normoxic and hypoxic fluxes rates. Statistical results are for single variable linear regression models comparing sediment parameters to each (normoxic) flux rate. Model strength was evaluated using Kendall Rank Correlation (Kendall's Tau (τ)). Bold font signifies a significant relationship (α=0.05). Sediments samples are from 0-1cm.

Table S8. Summary of references for conceptual model (Figure 7) describing effects of hypoxia on key biogeochemical processes and net fluxes at the sediment-water interface. Full citations are in the main text.

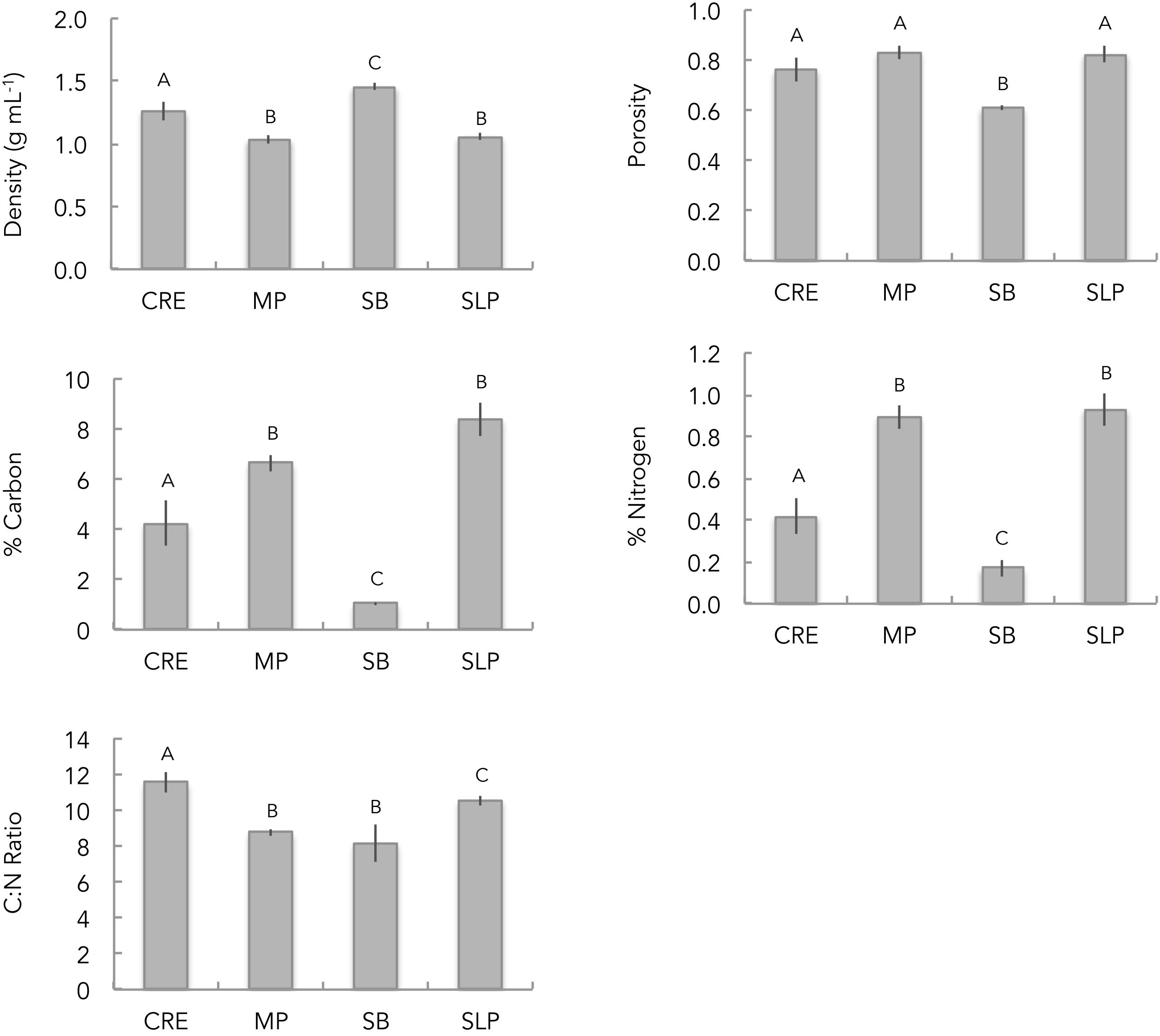
Table S9. Final nutrient ratios under normoxic and hypoxic conditions. Ratios are based on the final molar nutrient concentrations measured at the end of the core incubations for dissolved nitrogen (N), phosphorus (P), and silica (Si), using the median plus or minus the median absolute deviation. The difference represents the percent that the hypoxic median varies from the normoxic. p values on plots are from non-parametric tests of difference between normoxic and hypoxic flux rates for the statistically distinct station groups. Bold font signifies a significant relationship (α=0.05).

Field Sample Collection Dates	Station	Field Water Conditions				Initial Water Conditions - Cores								
		Temperature (°C)		Salinity (psu)		O_2 (mg/L)	NH_4^+ (µM)	NOx (µM)	NO_2^- (µM)	DSi (µM)	PO_4^{3-} (µM)	N_2 (µM)	N_2O (nM)	CH_4 (nM)
		Surface	Bottom	Surface	Bottom									
29-Jul-2011	CRE	22.0	26.1	28.1	28.6	5.99 ±0.02	n.m.	n.m.	n.m.	n.m.	n.m.	417.9 ±0.2	n.m.	n.m.
	SLP	24.4	24.6	29.7	29.9	7.55 ±0.25	n.m.	n.m.	n.m.	n.m.	n.m.	410.3 ±0.6	n.m.	n.m.
24 Aug 2011	MP	24.6	25.3	29.8	29.7	8.28 ±0.03	n.m.	n.m.	n.m.	n.m.	n.m.	409.1 ±0.2	n.m.	n.m.
	SB	23.9	24.8	30.5	31.3	8.54 ±0.03	n.m.	n.m.	n.m.	n.m.	n.m.	407.8 ±0.8	n.m.	n.m.
	SLP	22.9	23.4	28.5	28.9	7.26 ±0.07	n.m.	n.m.	n.m.	n.m.	n.m.	410.0 ±0.4	n.m.	n.m.
11-Oct-2011	MP	19.0	21.0	29.0	30.0	8.16 ±0.09	n.m.	n.m.	n.m.	n.m.	n.m.	443.7 ±0.4	n.m.	n.m.
	SB	18.5	18.3	30.8	30.9	8.37 ±0.04	n.m.	n.m.	n.m.	n.m.	n.m.	440.0 ±0.8	n.m.	n.m.
11-Jul-2012	CRE	22.2	27.9	3.5	29.7	5.18 ±0.03	11.3 ±1.6	<0.035	0.024 ±0.008	33.8 ±2.1	0.85 ±0.03	391.7 ±2.7	10.7 ±0.1	372 ±55
	MP	27.2	25.9	30.6	31.3	7.06 ±0.03	11.5 ±1.8	<0.035	0.014 ±0.004	17.7 ±2.0	1.27 ±0.05	367.7 ±0.4	11.9 ±0.9	838 ±263
	SB	28.1	27.9	30.8	30.6	6.69 ±0.10	8.5 ±0.8	<0.035	<0.006	8.2 ±0.2	0.86 ±0.05	380.2 ±0.4	9.8 ±1.0	70 ±3
6-Aug-2012	SLP	29.4	28.5	30.4	30.4	5.61 ±0.12	14.5 ±1.8	<0.035	0.039 ±0.007	22.3 ±0.6	0.75 ±0.16	m.i.	175* ±21.4	79 ±4
2-Oct-2012	MP	18.3	19.2	29.1	29.6	7.24 ±0.25	15.7 ±6.4	<0.035	<0.006	8.2 ±4.2	0.51 ±0.12	m.i.	7.9 ±0.9	148 ±40
	SB	18.8	18.9	31.1	31.3	7.10 ±0.18	5.0 ±0.5	0.039	<0.006	7.4 ±0.1	0.82 ±0.08	m.i.	9.8 ±1.8	30 ±7
23-Sep-2013	CRE	22.6	22.6	27.2	27.3	6.51 ±0.09	2.8 ±0.3	<0.035	<0.006	14.8 ±0.4	0.03 ±0.01	445.3 ±0.2	10.5 ±0.5	380 ±84
	MP	20.9	19.9	29.7	29.7	7.83 ±0.03	6.6 ±0.6	<0.035	<0.006	8.5 ±0.7	0.23 ±0.03	433.5 ±1.0	9.3 ±0.8	385 ±91
	SLP	19.8	19.7	29.6	29.7	7.86 ±0.02	4.3 ±0.1	<0.035	<0.006	10.4 ±0.5	0.21 ±0.01	435.9 ±1.0	8.8 ±0.2	40 ±2

Station	Sediment Characteristics								
	Silt + Clay[1] (%)	Sand[1] (%)	Density[2] (g/mL)	Porosity[2]	C[2] (%)	N[2] (%)	C:N[2]	Chl *a*[3] (mg m^{-2})	Benthic Organism Abundance[4] (individuals m^{-2})
CRE	9-14	86-91	1.26 ± 0.07	0.76 ± 0.05	4.2 ± 0.9	0.42 ± 0.09	11.6 ± 0.6	90-120	3093 ± 441
MP	-	-	1.03 ± 0.03	0.83 ± 0.03	6.6 ± 0.3	0.89 ± 0.06	8.8 ± 0.2	-	-
SB	-	-	1.45 ± 0.03	0.61 ± 0.01	1.0 ± 0.1	0.17 ± 0.04	8.2 ±1.0	-	-
SLP	2-9	91-97	1.06 ± 0.03	0.82 ± 0.03	8.4 ± 0.7	0.93 ± 0.08	10.5 ± 0.3	50-90	24213 ± 3277

[1]Carmichael and Valiela 2004, 2005 ; [2]This study and Foster and Fulweiler 2014 ; [3]Lever and Valiela 2005 ; [4]Fox et al. 2009

Parameters	Number of Cores	Evaluation of Bi-variate Models			
		Kendall τ	p value	AIC	Ranking
Water Column					
Temperature	51	**-0.42**	**<0.0001**	360.3	1
Intitial Oxygen Concentration	51	**0.25**	**0.0119**	376.8	3
Sediment					
Density	51	**0.34**	**0.0005**	370.8	2
Porosity	47	-0.03	0.7760		
Percent Carbon	29	-0.21	0.1066		
Percent Nitrogen	28	-0.24	0.0719		
Carbon : Nitrogen Ratio	28	-0.13	0.3418		



Density (g mL-1)
2.0
1.5
1.0
0.5
0.0
A
B
C
B
CRE
MP
SB
SLP
Porosity
1.0
0.8
0.6
0.4
0.2
0.0
A
A
B
A
CRE
MP
SB
SLP
% Carbon
10
8
6
4
2
0
A
B
C
B
CRE
MP
SB
SLP
% Nitrogen
1.2
1.0
0.8
0.6
0.4
0.2
0.0
A
B
C
B
CRE
MP
SB
SLP
C:N Ratio
14
12
10
8
6
4
2
0
A
B
B
C
CRE
MP
SB
SLP

Sediment Parameter	Sediment Parameter	Kendall's Tau	p value	n
Density	**Porosity**	**-0.2017**	**0.0483**	47
Density	**%C**	**-0.5224**	**<0.0001**	29
Density	**%N**	**-0.5235**	**0.0001**	28
Porosity	**%C**	**0.5180**	**0.0002**	27
Porosity	**%N**	**0.4406**	**0.0018**	26
%N	**%C**	**0.8154**	**<0.0001**	28

Sediment Parameter	Normoxic Rate	Kendall's Tau	p value	n
Density	**O_2 Uptake**	**-0.3512**	**0.0003**	51
Density	**NH_4^+ Flux**	**-0.3797**	**0.0050**	28
Density	DSi Flux	-0.0932	0.4888	28
Density	PO_4^{3-} Flux	-0.3546	0.0118	26
Density	N_2-N Flux	0.1171	0.3019	39
Density	N_2O Flux	0.0221	0.8873	22
Density	**CH_4 Flux**	**-0.3003**	**0.0323**	26
Porosity	O_2 Uptake	0.0075	0.9415	47
Porosity	NH_4^+ Flux	0.2240	0.1118	26
Porosity	DSi Flux	0.0093	0.9472	26
Porosity	PO_4^{3-} Flux	0.1064	0.4709	24
Porosity	N_2-N Flux	0.0996	0.4083	35
Porosity	N_2O Flux	0.0860	0.6019	20
Porosity	CH_4 Flux	-0.0513	0.7279	24
%N	**O_2 Uptake**	**0.3479**	**0.0096**	28
%N	**NH_4^+ Flux**	**0.4269**	**0.0071**	21
%N	DSi Flux	0.1435	0.3645	21
%N	PO_4^{3-} Flux	0.2463	0.1415	19
%N	N_2-N Flux	0.0525	0.7396	21
%N	N_2O Flux	0.0268	0.8787	18
%N	CH_4 Flux	0.3175	0.0513	20
%C	**O_2 Uptake**	**0.2956**	**0.0244**	29
%C	**NH_4^+ Flux**	**0.3198**	**0.0430**	21
%C	DSi Flux	-0.0095	0.9518	21
%C	PO_4^{3-} Flux	0.2047	0.2208	19
%C	N_2-N Flux	0.0694	0.6517	22
%C	N_2O Flux	-0.0600	0.7316	18
%C	CH_4 Flux	0.1693	0.2987	20

Sediment Parameter	Hypoxic Response (Normoxic minus Hypoxic)	Kendall's Tau	p value	n
Density	**O_2 Uptake**	**-0.2827**	**0.0036**	51
Density	NH_4^+ Flux	-0.2583	0.0551	28
Density	DSi Flux	0.0559	0.6779	28
Density	PO_4^{3-} Flux	-0.0684	0.6271	26
Density	N_2-N Flux	0.1566	0.1816	36
Density	N_2O Flux	-0.1513	0.3830	18
Density	CH_4 Flux	0.0464	0.7407	26
Porosity	O_2 Uptake	0.0093	0.9269	47
Porosity	**NH_4^+ Flux**	**0.2764**	**0.0494**	26
Porosity	DSi Flux	0.2143	0.1277	26
Porosity	PO_4^{3-} Flux	0.1207	0.4122	24
Porosity	N_2-N Flux	0.1670	0.1830	32
Porosity	N_2O Flux	0.3193	0.0865	16
Porosity	**CH_4 Flux**	0.0293	0.8424	24
%N	**O_2 Uptake**	**0.3564**	**0.0081**	28
%N	NH_4^+ Flux	0.2775	0.0796	21
%N	DSi Flux	-0.0287	0.8561	21
%N	PO_4^{3-} Flux	0.1361	0.4197	19
%N	N_2-N Flux	0.2026	0.2403	18
%N	N_2O Flux	0.1340	0.4879	15
%N	**CH_4 Flux**	0.1164	0.4749	20
%C	**O_2 Uptake**	**0.2935**	**0.0256**	29
%C	NH_4^+ Flux	0.2476	0.1164	21
%C	DSi Flux	-0.1619	0.3046	21
%C	PO_4^{3-} Flux	0.1534	0.3619	19
%C	N_2-N Flux	0.2164	0.1955	19
%C	N_2O Flux	0.1429	0.4579	15
%C	CH_4 Flux	0.0000	1.0000	20

Conceptual Models	Hypoxic Effect on Net Flux Rate	Proposed Mechanism(s) and Notes	References
Nitrogen Cycling Dynamics			
Ammonium Regeneration (NH_4^+)	Enhanced	DNRA increase and nitrification decrease	Caffrey & Kemp 1990, Kemp et al. 1990, An & Gardner 2002, Gardner & McCarthy 2009, McCarthy et al. 2015
	Diminished	Adsoption coefficient (K*) increases with reducing conditions in marine sediments. Total benthic metabolism may be diminshed under anoxia - increasing preservation of organic matter, slowing re-mineralization, and decreasing nutrient availabilty.	Hansen & Blackburn 1991, Kristensen & Holmer 2001, Canfield et al. 2005, Morse & Morin 2005, Jessen et al. 2017
	No effect	Nitrification (coupled to denitrification) can occur at very low oxygen concentrations, nitrifier affinity for oxygen increases at low concentrations, systems with repeated hypoxia exposure can promote nitrifier adaptations. DNRA could stimulate nitrifiers with ammonium source.	Goreau et al. 1980, Hansen et al. 1981, Henriksen et al. 1981, Bodelier et al. 1996, Kester et al. 1997, Hietanen 2007, Gardner et al. 2006, Carini et al. 2010, York et al. 2010, Bristow et al. 2016, Zakem and Follows 2016
Nitrous Oxide Flux (N_2O)	Enhanced	Nitrifiers release more N_2O by-product when oxygen availability is low. DNRA could stimulate nitrifiers with increased ammonium.	Goreau et al 1980, Jorgensen et al. 1984, Bange et al. 1996, Kester et al. 1997, Naqvi et al. 2000, Gardner et al. 2006, Silvennoienen et al. 2008, Naqvi et al. 2010, Stein 2011, Kozlowski et al. 2016
Denitrification (N_2)	Enhanced		McCarthy et al. 2015
	Diminished	Nitrification (coupled to denitrification) inhibited by lower oxygen availability, sulfidic conditions favor DNRA over denitrification for nitrate reduction	Kemp et al. 1990, Tuominen et al. 1998, An & Gardner 2002, Childs et al. 2002, Kemp et al 2005, Gardner & McCarthy 2009
	No effect	Nitrification (coupled to denitrification) can occur at very low oxygen concentrations, nitrifier affinity for oxygen increases at low concentrations, systems with repeated hypoxia exposure can promote nitrifier adaptations	Goreau et al. 1980, Hansen et al. 1981, Henriksen et al. 1981, Bodelier et al. 1996, Kester et al. 1997, Hietanen 2007, York et al. 2010, Bristow et al. 2016, Zakem and Follows 2016
Phosphorous Dynamics			
Phosphate Flux (PO_4^{3-})	Enhanced	Under oxic conditions, metal oxyhydroxides produce a zone at surface of sediments with high adsorbing capacity. Under low oxygen conditions, phosphate released from metal oxides reaction with sulfides and microbial respiration.	Mortimer 1942, Davison & Seed 1983, Millero et al. 1987, Sundby et al. 1992, Griffioen 1994, Jensen et al. 1995, Cowan & Boynton 1996, Anschutz et al. 1998, Conley et al. 2007, Slomp & Van Cappellen 2007
Carbon Dynamics			
Organic Matter Re-mineralization	Diminished	Decomposition is more effective with oxygen and microbial growth yield is greater under aerobic conditions. Diminished benthic metabolism increases preservation of organic matter, slows re-mineralization, and decreases nutrient availability.	Hansen & Blackburn 1991, Kristensen & Holmer 2001, Canfield et al. 2005, Jessen et al. 2017
Methane Flux (CH_4)	Enhanced	Methanogenesis rates enhanced by low oxygen conditions. Methanogenesis move vertically towards sediment surface as other electron acceptors used up.	Damgaard et al. 1998
	No effect / Diminishe	Anaerobic oxidation of methane stimulated by sulfate reducers and ammonium oxidizing nitrifiers.	Hyman & Wood 1983, Jones & Morita 1983, Canfield et al. 2005
Silicon Dynamics			
Silica Flux (DSi)	Enhanced		Villnas et al. 2012, Lehtimaki et al 2016
	Diminished	Decrease in in-fauna activity (which has a positive relationship to sediment silica flux). Decrease in overall benthic metabolism and re-mineralization. Silica fluxes correlated to sediment oxygen uptake and to nutrient fluxes - suggesting Silica connected to sediment respiration and remineralization rates.	Aller 1980, Aller 1981, Aller & Yingst 1985, Hansen & Blackburn 1991, Marinelli 1992, Kristensen & Holmer 2001, Canfield et al. 2005, Bartoli et al 2009, Raimonet et al. 2013, Jessen et al. 2017
Waquoit Bay Conditions			
Nitrogen Cycling Parameters		Rates for sediment net denitrification (N_2 fluxes), ammonium flux, N_2O flux, under normoxic conditions	Foster & Fulweiler 2014, Foster & Fulweiler 2016
		Rates for DNRA, denitrification, N fixation, anammox	Newell et al. 2016
		Proportion of ammonium processed through nitrification-denitrification	York et al. 210
		Low water column nitrate concentrations	LaMontagne et al. 2003, NOAA
Phosphate Cycling Parameters		Phosphate flux rates under normoxic conditions	Foster & Fulweiler 2016
		Iron oxides at the groundwater-estuary interface have a substantial impact on phosphorous geochemistry.	Charette 2002, Testa et al. 2002

Ratio	Final Concentrations		Difference	Wilcoxon/Kruskal-Wallis
	Normoxic	Hypoxic		p value
N:P	34.6 ± 15.8	17.5 ± 5.8	**49% (Lower)**	**0.0008**
Si:P	49.6 ± 25.8	25.4 ± 14.4	**49% (Lower)**	**0.0035**
N:Si	0.62 ± 0.3	0.64 ± 0.2	No Difference	0.4233