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The Biogeochemistry of Card Sound, Florida circa 1972

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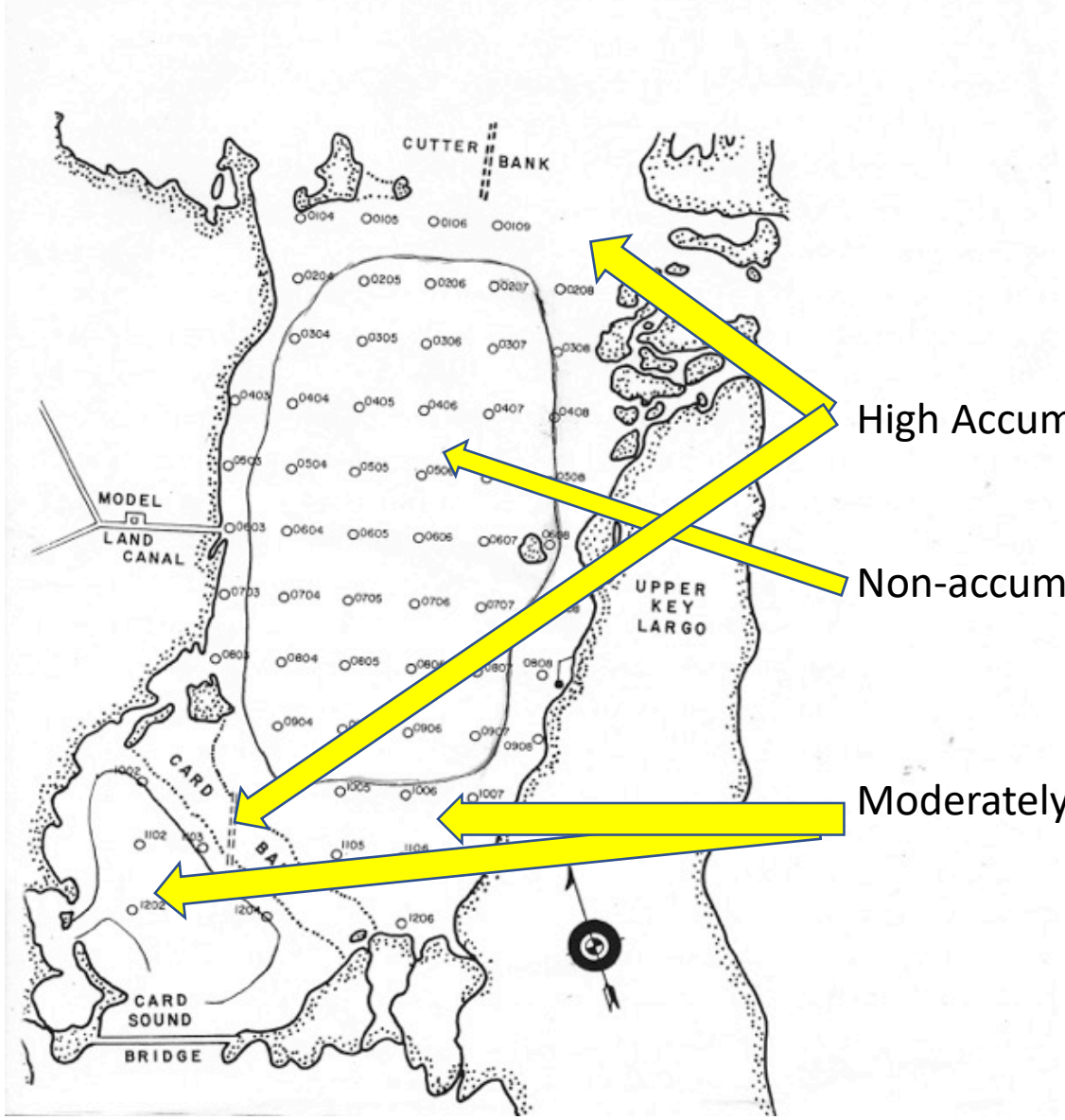
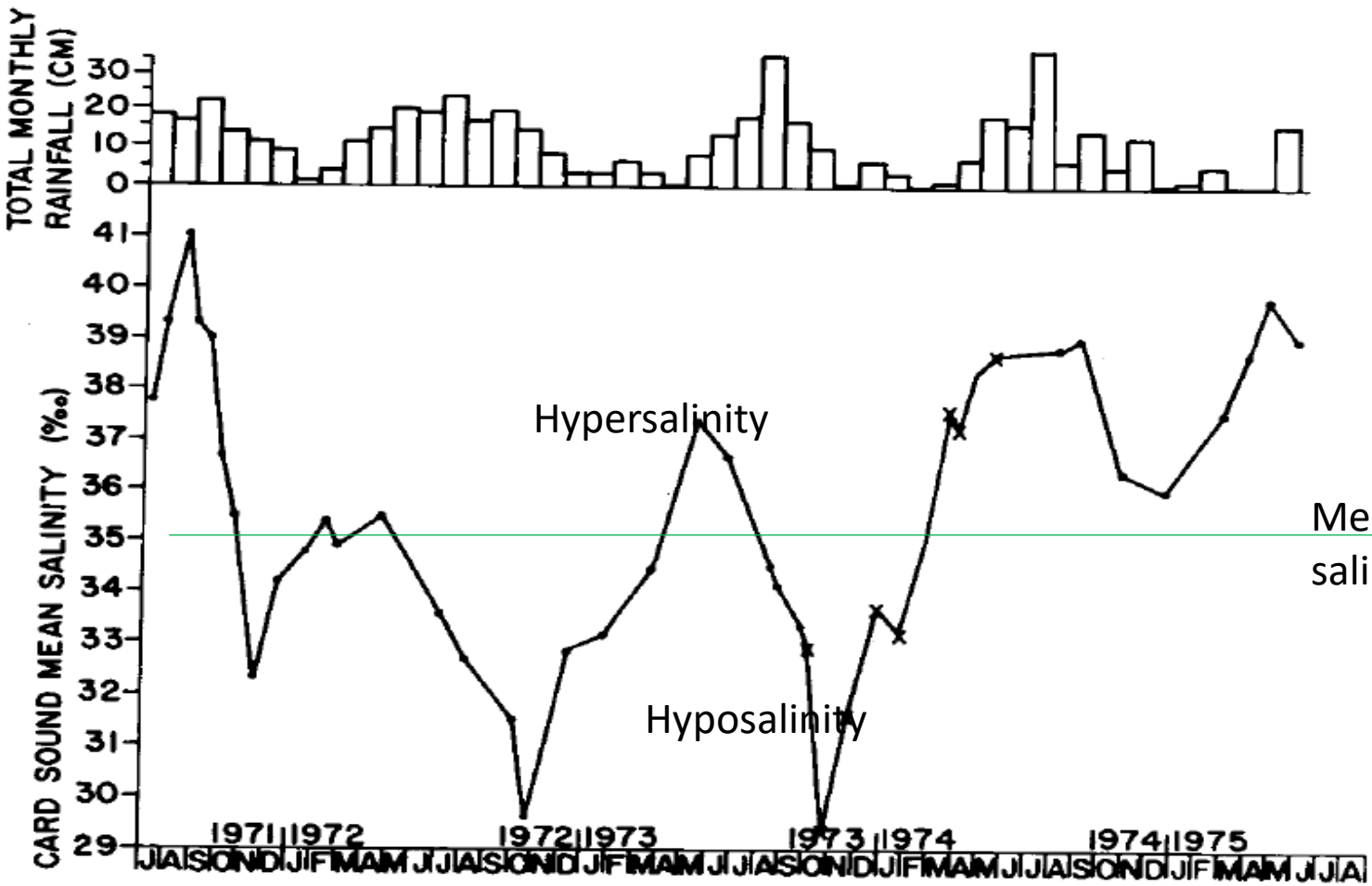
April 26, 2018


Miami
Everglades
Biscayne Bay
Card Sound
Reefs
Barnes Sound
Florida Bay
Straights of Florida


Biscayne Bay
Caesar Creek
Cutter Bank
FPL Turkey Point
Cooling Channels
Broad Creek
Card Sound
Angelfish Creek
Little
Card Sound
Card Bank
Card Sound Bridge
Barnes Sound
Straights of Florida



Active Sediment Depths and Sampling Stations within Card Sound and Little Card Sound


TOTAL MONTHLY RAINFALL (CM)
30
20
10
0
CARD SOUND MEAN SALINITY (‰)
41
40
39
38
37
36
35
34
33
32
31
30
29
Hypersalinity
Hyposalinity
Mean oceanic salinity
1971 1972
1972 1973
1973 1974
1974 1975
J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A S O N D J F M A M J J A

Sample Collection Methodology

- Sediment and organisms – collected with polyethylene gloves, polyethylene tubes [sediment], trowels [biota] by snorkel divers, labeled in sealed whirl-pacs, iced, stored frozen in lab
- Water samples - collected in pre-nitric acid washed polyethylene 1 L bottles. Phytoplankton samples collected in 8 L acid pre-washed polyethylene bottles. Direct pole collection for shallow water samples, deep samples, diver opened bottle at collection depth. Polyethylene gloves used at all times. All samples immediately iced, then frozen in lab

Chemical Preparation Methodology

- Ammonium pyrrolidine dithiocarbamate (APDC) synthesized from redistilled A.C.S. grade pyrrolidine and carbon disulfide
- Fuming nitric acid was redistilled in glassware
- All analysis and wash water was Millipore ^{R} filtered, followed by double distillation in pure silica ware and always below detection limits for all the trace elements analyzed
- All acid digestion occurred in silica flasks with silica ball tops
- All extraction occurred in pure polyethylene separatory funnels

Laboratory Analysis Methodology

- Dried NBS orchid leaves # 1517, frozen samples [sediment, biota, seawater] thawed, freeze dried, weighted sample digested with 1 M H_2NO_3
- Dried residue re-solubilized in 0.1 M H_2NO_3 and made up to 500 ml with double distilled pure water
- APDC chelation and methyl isobutyl ketone [A.C.S. grade] [MIBK] added to separatory funnels, shaken vigorously for 5 minutes, decanted and a second APDC extraction performed.
- APDC & MIBK decanted into silica flasks, dried to residue, solubilized and digested with 0.1 M H_2NO_3, made up to 5ml volume, transferred into polyethylene sealed containers.
- Eppendorf pipetted 10 to 20 ul samples of above into hollow graphite tube of apparatus. All samples analyzed in triplicate at < 5% SD.
- Flame atomic absorption spectrophotometry (dual beam) was used for most iron analysis.
- Other elements used the Atom Reservoir Atomic Absorption mode incorporating a Perkin Elmer (HGA-70) heated graphite atomizer with a deuterium arc background corrector and a variable ash temperature (ARAA/HGA-70/D_2/T_v).
- Matrix interferences from major ions - Na^{+}, Mg^{+2}, Ca^{+2}, Cl^{-1} and SO_4^{-2} and others was virtually eliminated through the APDC chelation and ketone extraction.
- Standard solutions from ultrapure nitrate salts of Fe, V, Cd, Co, Cu, Zn, Pb and Ag where made and run into the analyzer both prior to and at the end of sample runs. Graphite tubes were changed routinely.

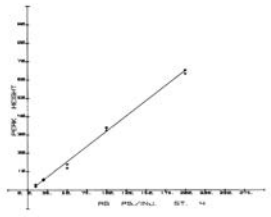
	THIS PAPER'S METHOD Segar & Gilio (1973)	NBS SRM 1571	ACCURACY Segar & Gilio (1973)	ICP-MS (Note 2) Valentina et. al.(2003)
	Results ug/g	NBS Certified ug/g	Percent	% Recovery co-ppt
Fe	260 ± 20	270 (Note 1)	96	97.7
Cu	11 ±1	12 ± 2	92	84 -93.3
Zn	24 ±2	25 ± 3	96	
Cd	0.11 ±0.03	0.11 ± 0.02	100	86.4
Pb	44 ±5	45 ± 3	98	96.7

(Note 1) Nitric acid digestion resulted in a silica solid residue yielding 270 ug/g not 300. Error due to silica contaminant of 30 ug/g. Full solubilization with perchloric acid yield 300 ug/g (Cali, 1977). Hence, accurate SRM-1571 Orchard Leaves is 270 ug/g. based on the biological sample only.

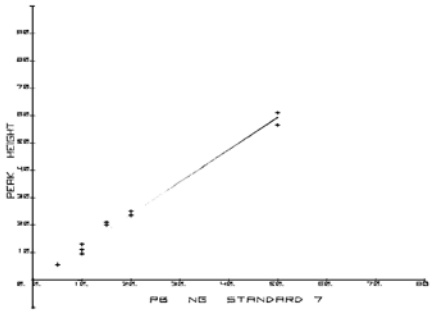
(Note 2) Inductively Coupled Plasma Mass Spectroscopy ICP-MS (4500 HP), from Valentina, et. al., (2003)

Accuracy of Orchard Leaf Testing Methods

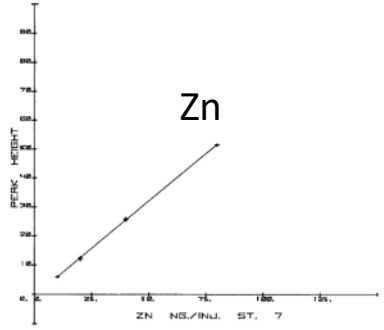
Ag

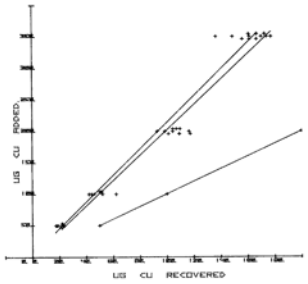


V

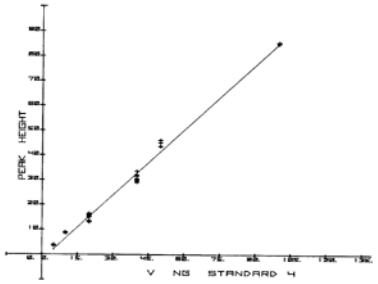


Zn

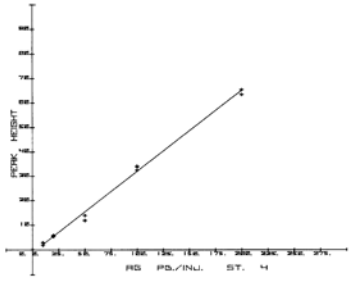




Cu



Pb



Cd

Standard run curves for calibration and during sample analysis

Epiphytes

*Thalassia testudin*um

Halicona molitba

Ircinia fasiculata

Halimeda incrassata

Penicillus capitatus

Laurencia poitei

Biota species Included in this study

Trace element inventory for Card Sound, Florida

NOTES: (1) Calculated from concentration data elements in Card Sound, from Pellenbarg (1973). Includes total sediment depth and total element concentrations.

(2) Josselyn (1975).

(3) Calculated from Bach (1975). Includes Halimeda incrassate (5.5), H. monile (1.5), and H. opunta (1.4).

(4) Calculated from Bach (1975). Includes Penicillus capitatus (1.7), Rhipocephalus phoenix (0.51), and Udotea flabellum (0.48).

Compartment	Biomass g dry wt./m²	V mg/m²	Fe mg/m²	Cu mg/m²	Zn mg/m²	Cd mg/m²	Pb mg/m²
Sediments (1)	3.4×10^5	8.0×10^3	6.3×10^5	670	1400	23	340
Water	3.0×10^6	2.6	52	12	26	.21	1.5
BIOTA							
Macrophyta							
Thalassia testudium	1.67×10^2	1.4	53	0.27	3.0	0.033	0.12
Laurencia poitei	6.1 (2)	0.23	2.6	0.073	0.21	0.0012	0.0036
Halimeda group	8.7 (3)	0.023	2.2	0.0068	0.036	0.0016	0.012
Penicillus group	3.1 (4)	0.015	1.7	0.0037	0.037	0.00034	0.0034
Microphyta							
Epiphytes	10	.96	4.2	0.21	1.5	0.002	0.0059
Phytoplankton	0.28	0.0092×10^{-2}	0.064	0.0034	0.050	0.0076×10^{-3}	0.0092×10^{-2}
Macrofauna							
Sponges	1.1×10^2	0.032	89	0.19	2.1	0.030	0.014
Detritivores + Carnivores	0.18×10^2	0.021×10^{-2}	0.011	0.002	0.075	0.055×10^{-3}	0.011×10^{-2}
BIOTA TOTAL	310	2.7	150	0.76	7.0	0.068	0.16

CARD SOUND COMPARTMENTS for Trace Metals During 1972

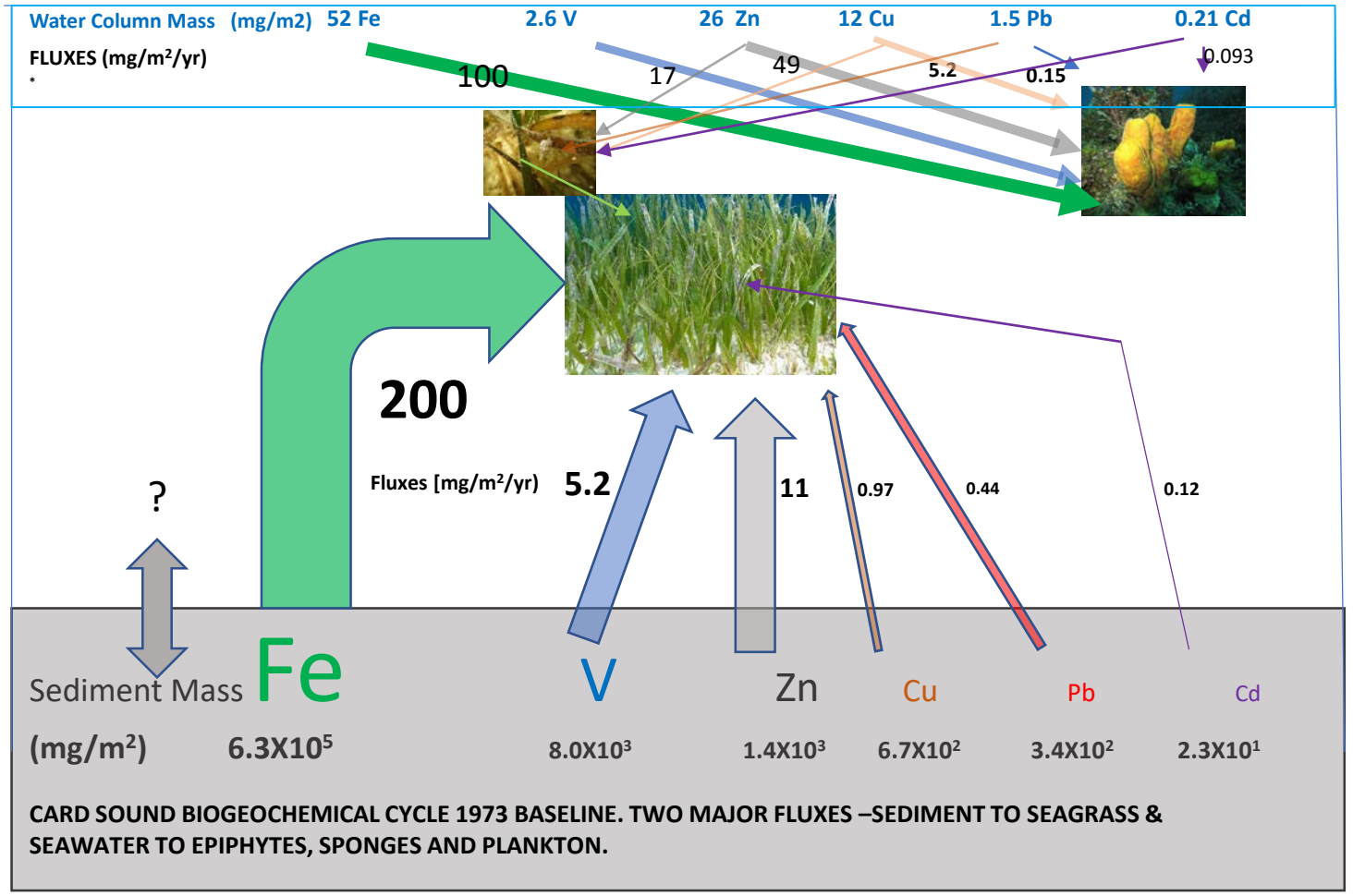
Water (mg/m2)	52 Fe	2.6 V	26 Zn	12 Cu	1.5 Pb	0.21 Cd
Biological Standing Stock (Sea grass, Epiphytes, Macroalgae, phytoplankton, sponges, detritivores, carnivores)						
(mg/m2/yr)	**320 Fe**	**24 V**	**61 Zn**	**6.4 Cu**	**0.62 Pb**	**0.19 Cd**
Entire Sediment	Fe	V	Zn	Cu	Pb	Cd
(mg/m2)	$6.3X10^5$	$8.0X10^3$	$1.4X10^3$	$6.7X10^2$	340	23

SOURCE – CARD SOUND WATER --→ Biota ---> Sediment

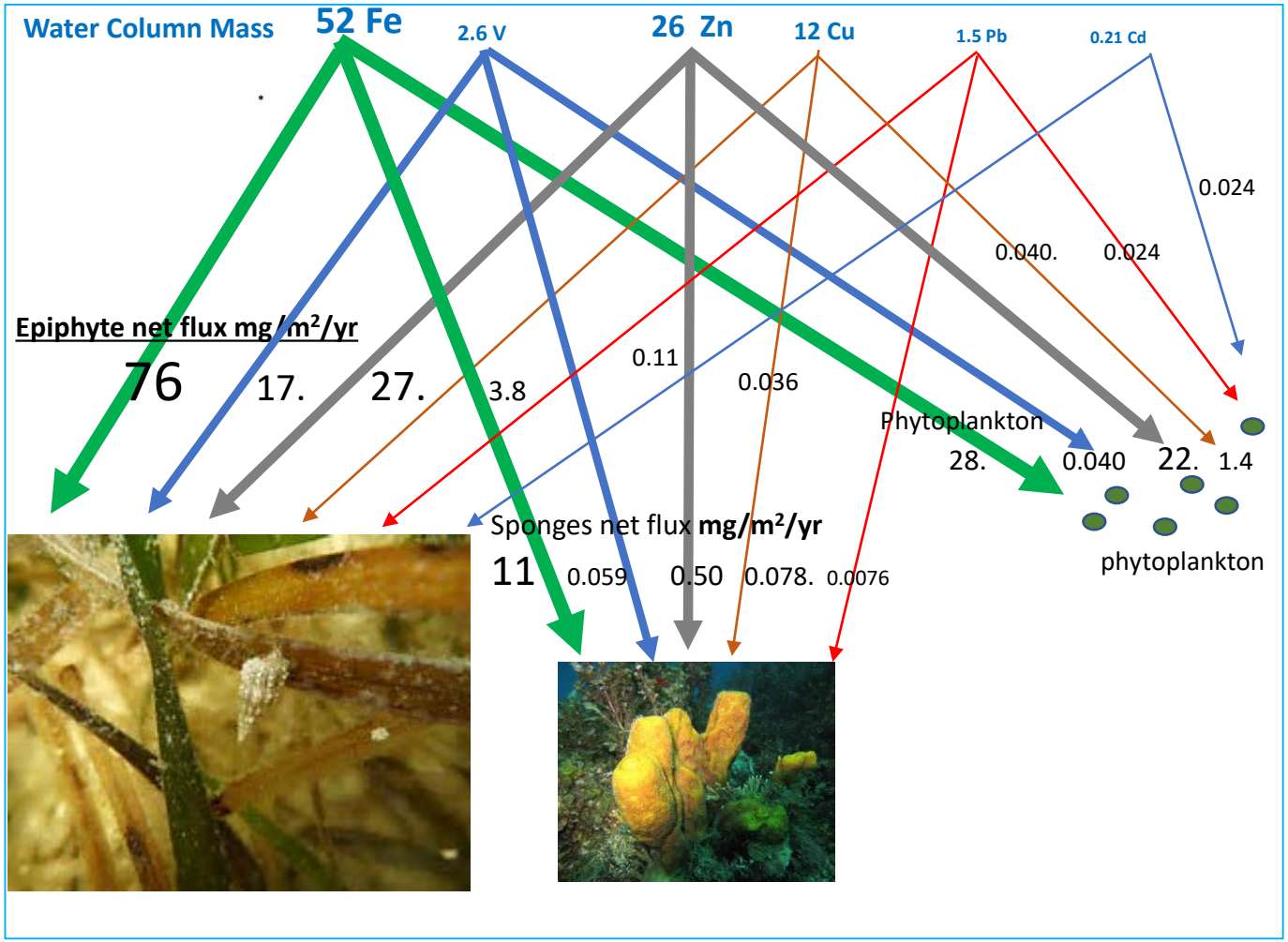
MINOR SINK: EPIPHYTES, SPONGES AND PLANKTON.

Compartment	Annual Net Production $g/m^2/yr$	V $mg/m^2/yr$	Fe $mg/m^2/yr$	Cu $mg/m^2/yr$	Zn $mg/m^2/yr$	Cd $mg/m^2/yr$	Pb $mg/m^2/yr$
Macrophyta							
Thalassia blades	609.	5.2	200.	0.97	11.	0.12	0.44
Laurencia poetei	11.	1.1	4.6	0.13	0.37	0.0022	0.0065
Penicillus group	4.2 (1)	0.021	2.4	0.0052	0.052	0.00047	0.0047
Halimeda group	8.6 (2)	0.021	2.0	0.0060	0.032	0.00014	0.010
∑ Sub-comp	630	6.3	210	1.1	13.	0.12	O.46
Microphyta							
Epiphytes	180.	17.	76.	3.8	27.	0.036	0.11
phytoplankton	120.	0.040	28.	1.4	22.	0.024	0.040
∑ Sub-comp	300	17.	100	5.2	49.	0.060	0.15
Macrofauna							
Sponges	21.	0.059	11.	0.078	0.50	0.0092	0.0076
Detritivores + Carnivores	6.6 (3)	0.0051	0.27	0.049	0.18	0.0043	0.0026
∑ Sub-comp	28.	0.12	11.	0.13	0.68	0.14	0.010
Total for Biota	960.	24.	320.	6.4	61.	0.19	0.62

Trace Element Net Biological Incorporation in Card Sound - 1972



Trace Element Potential Biogeochemical Fluxes Within Card Sound During 1972



Trace Metal Fluxes to Biota within Card Sound Water Column During 1972

Element	Water Column (Kg)	Turnover (days)	Bio flux (days)
Fe	3,000	50	49
Zn	1,500	25	9.5
Cu	670	13	1.0
Pb	88	44	0.096
Cd	12	60	0.027

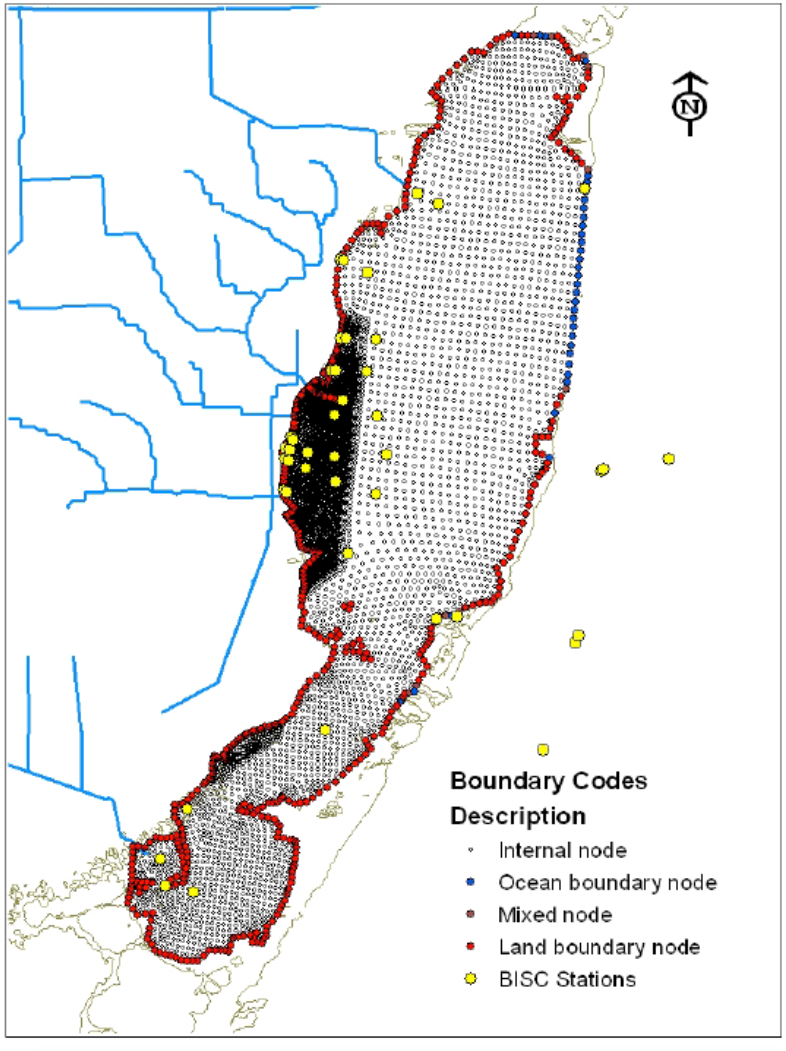
Trace Metal Mass, Turnover and Bio Flux Times Within Card Sound Water 1972

EFDC Modeling of Card Sound Circulation

- Mine data from WWW
- Stabenau (2015, GitHub), NOAA, NCDC, USGS, Bader & Roessler (1972)
- Develop Grid and Inputs (Met, Tidal BCs, Depths)
- Run model for October 1972 and save results (water levels and flows) at 15-minute intervals for key locations (boundaries and Within Card Sound)
- Inject Conservative Tracer at Card Sound Ocean Boundaries and estimate time to steady-state at Card Sound Bridge
- Runs - Base Case (tidal forcing and basic met only), add Winds, add FPL intake from Biscayne Bay and discharges to Biscayne Bay and Card Sound, add Canal discharges to Biscayne Bay and Card Sound
- Use Spreadsheet to calculate boundary fluxes, based on EFDC predicted flows and ebb and flood tide water quality monitoring by Author at boundaries (October 17-19, 1972)

EXPERIENCE YOUR AMERICA

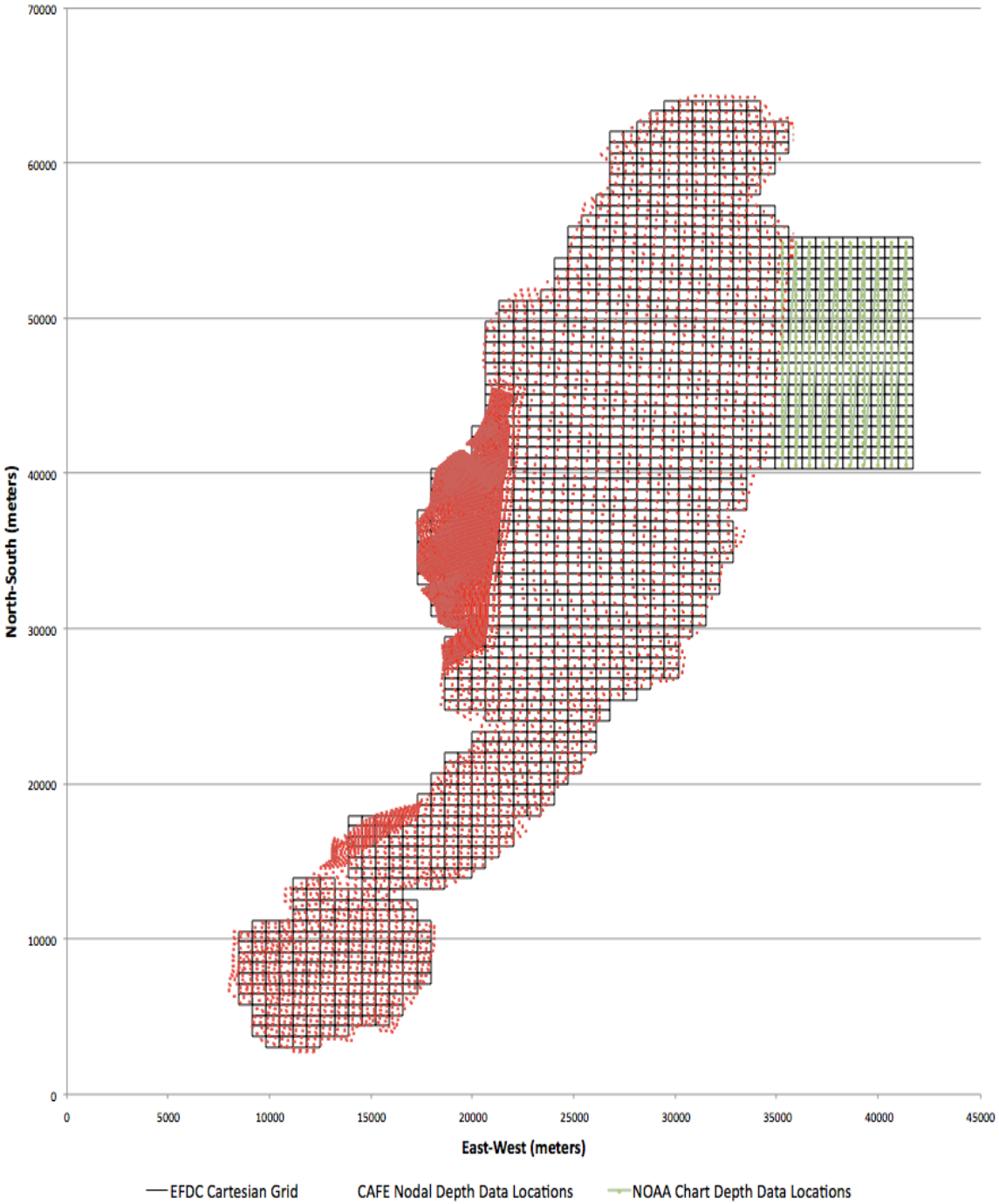
Biscayne Bay Simulation Model (BBSM)

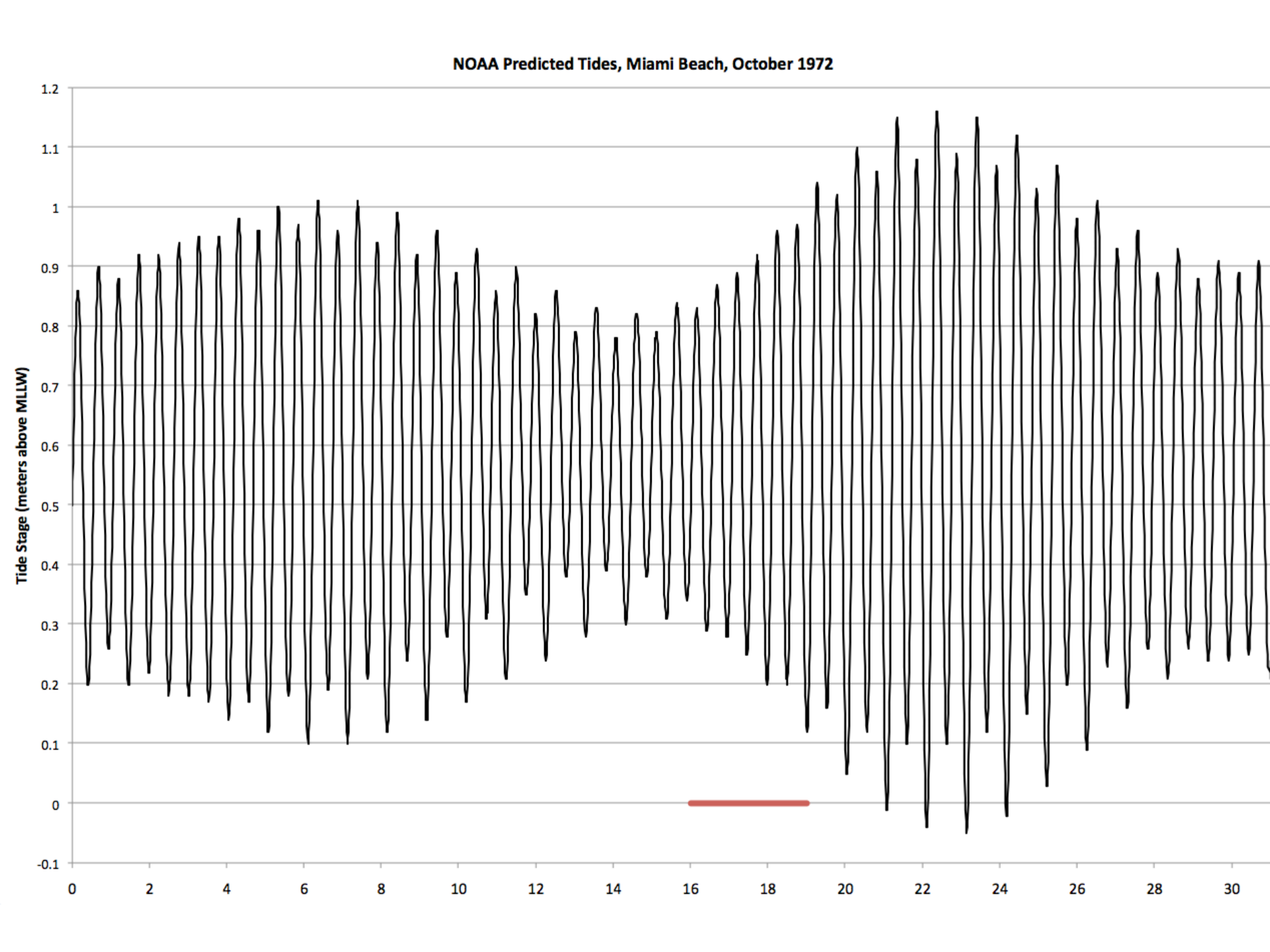


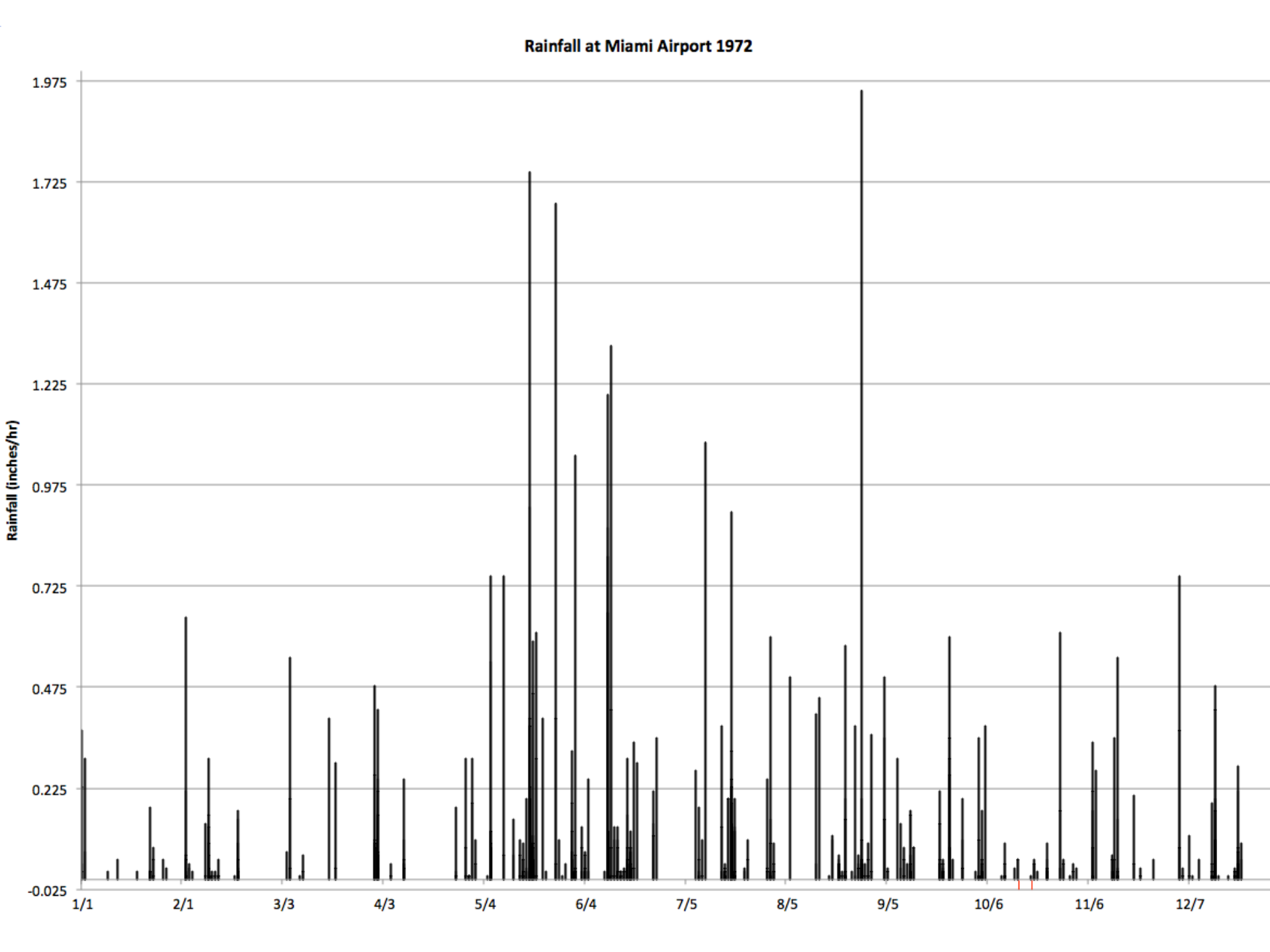
Predicting salinity regime under alternate discharge scenarios

BBSM 2D model with:

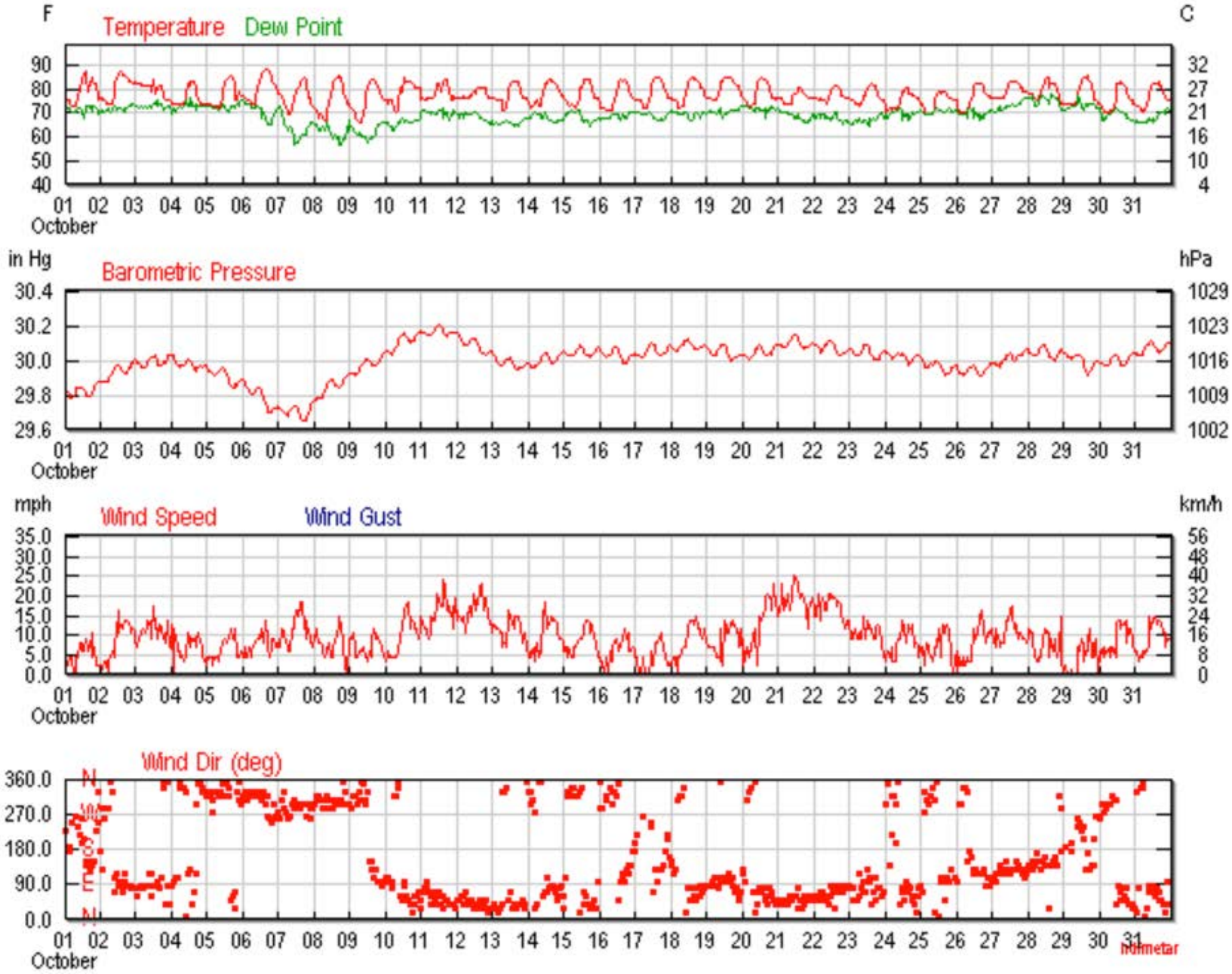
- Advection and diffusion
- Rain and evaporation
- Wind stress
- Bottom friction
- Tidal mixing
- Surface water inflows*
- Model or observation based boundary conditions

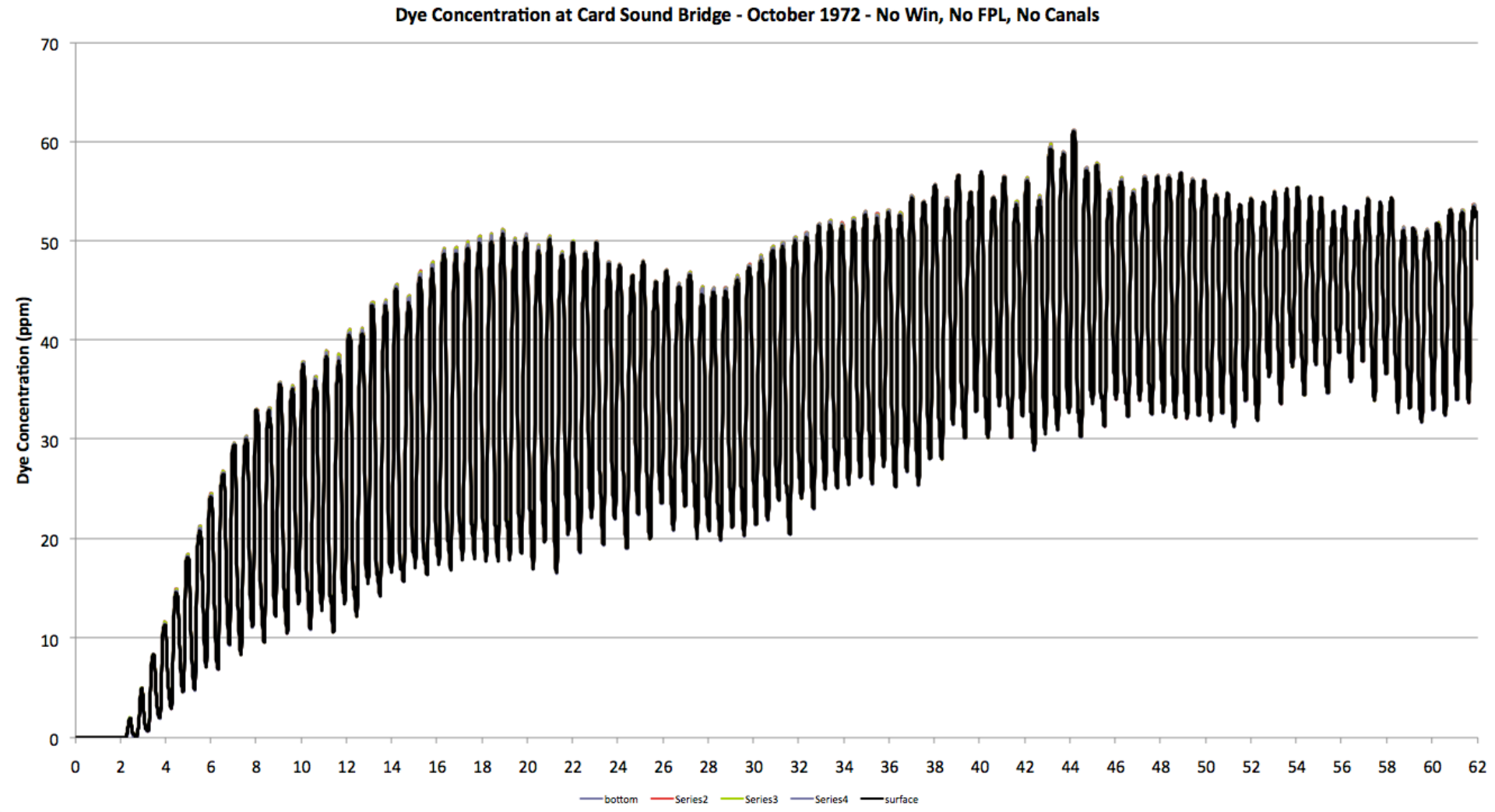

Card Sound and Biscayne Bay EFDC Grid - CAFE Node and NOAA Chart Depth Data Coverage
North-South (meters)
70000
60000
50000
40000
30000
20000
10000
0
0
5000
10000
15000
20000
25000
30000
35000
40000
45000
East-West (meters)
EFDC Cartesian Grid
CAFE Nodal Depth Data Locations
NOAA Chart Depth Data Locations

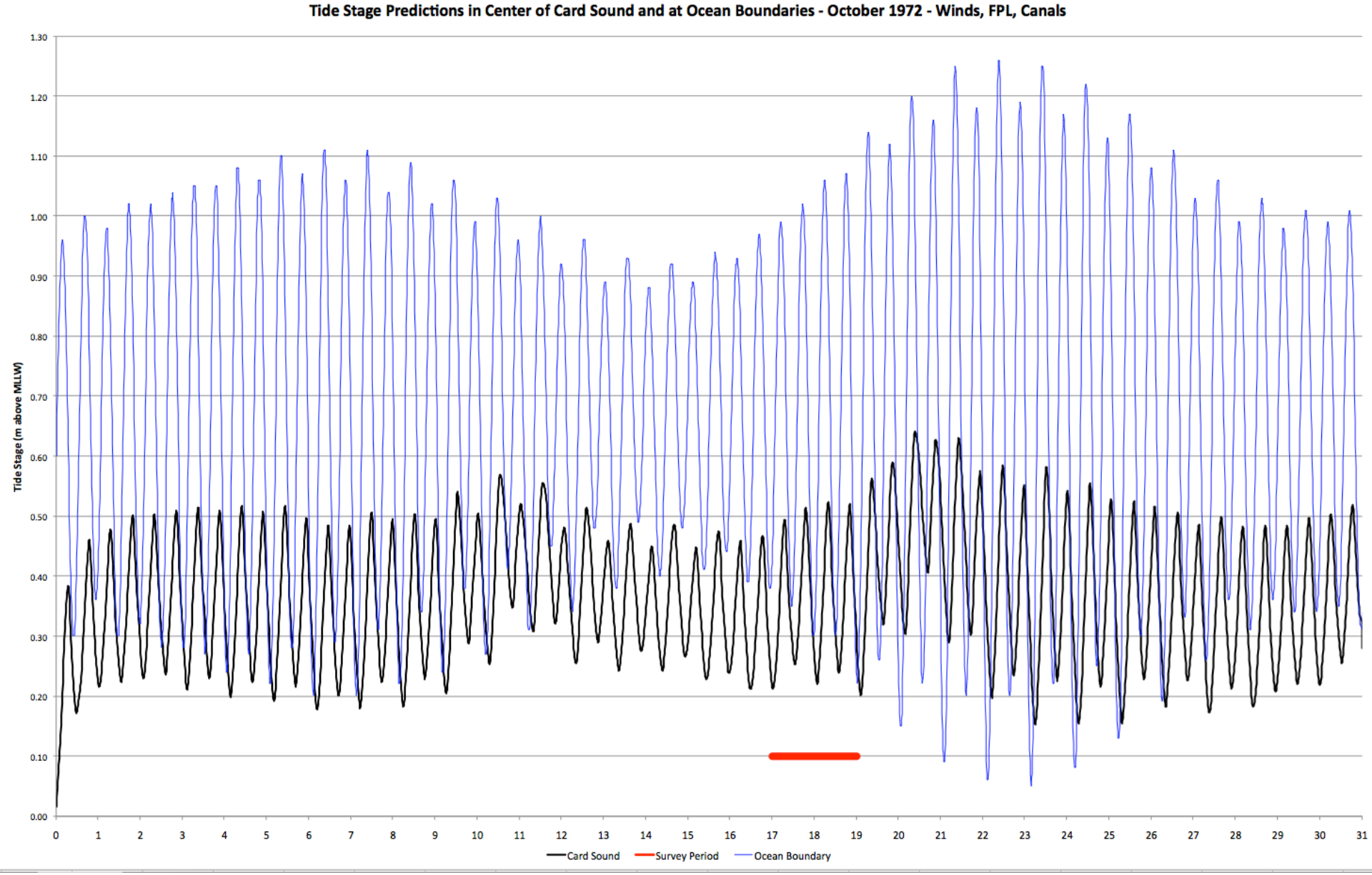

NOAA Predicted Tides, Miami Beach, October 1972
Tide Stage (meters above MLLW)
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
2
4
6
8
10
12
14
16
18
20
22
24
26
28
30

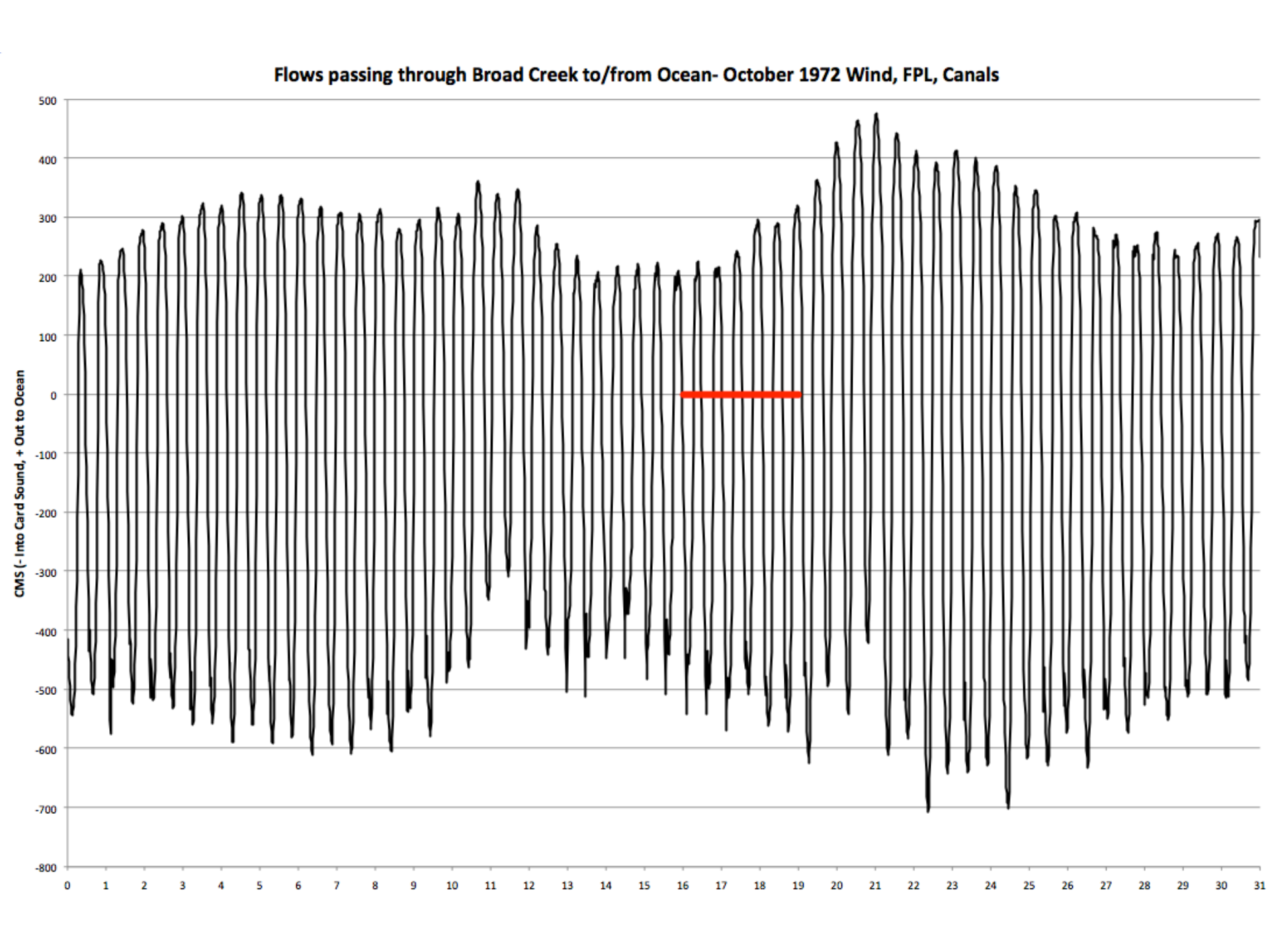

Rainfall at Miami Airport 1972
Rainfall (inches/hr)
1.975
1.725
1.475
1.225
0.975
0.725
0.475
0.225
-0.025
1/1
2/1
3/3
4/3
5/4
6/4
7/5
8/5
9/5
10/6
11/6
12/7

Meteorological Data at Miami Airport During October 1972




Dye Concentration at Card Sound Bridge - October 1972 - No Win, No FPL, No Canals
Dye Concentration (ppm)
70
60
50
40
30
20
10
0
0 2 4 6 8 10 12 14 16 18 20 22 24 26 28 30 32 34 36 38 40 42 44 46 48 50 52 54 56 58 60 62
bottom
Series2
Series3
Series4
surface


Tide Stage Predictions in Center of Card Sound and at Ocean Boundaries - October 1972 - Winds, FPL, Canals
Tide Stage (m above MLLW)
1.30
1.20
1.10
1.00
0.90
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
0 1 2 3 4 5 6 7 8 9 10 11 12 13 14 15 16 17 18 19 20 21 22 23 24 25 26 27 28 29 30 31
Card Sound
Survey Period
Ocean Boundary


Flows passing through Broad Creek to/from Ocean- October 1972 Wind, FPL, Canals
CMS (- Into Card Sound, + Out to Ocean
500
400
300
200
100
0
-100
-200
-300
-400
-500
-600
-700
-800
0
1
2
3
4
5
6
7
8
9
10
11
12
13
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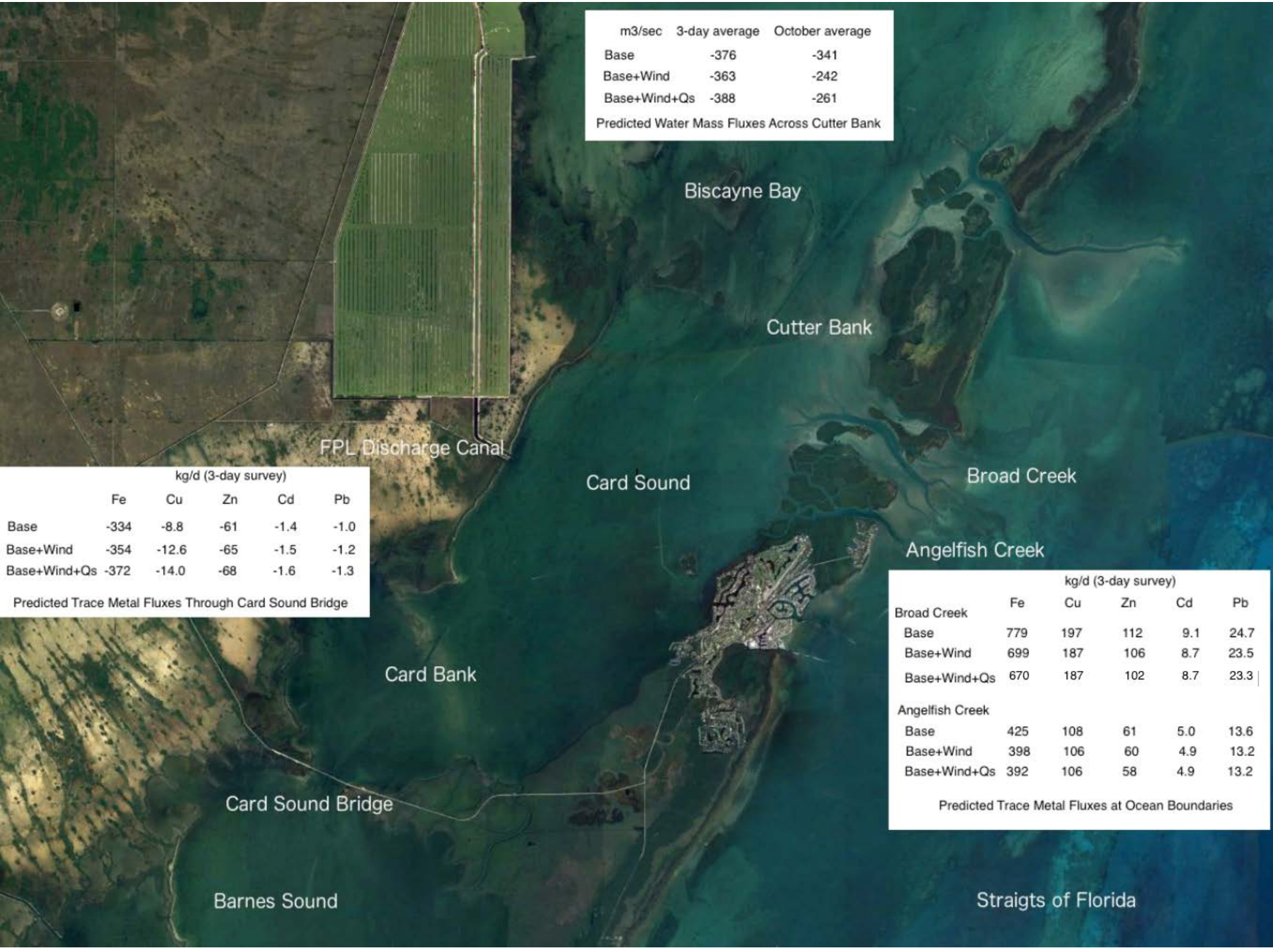
28
29
30
31



m3/sec	3-day average	October average
Base	-376	-341
Base+Wind	-363	-242
Base+Wind+Qs	-388	-261

Predicted Water Mass Fluxes Across Cutter Bank

kg/d (3-day survey)

	Fe	Cu	Zn	Cd	Pb
Base	-334	-8.8	-61	-1.4	-1.0
Base+Wind	-354	-12.6	-65	-1.5	-1.2
Base+Wind+Qs	-372	-14.0	-68	-1.6	-1.3

Predicted Trace Metal Fluxes Through Card Sound Bridge

kg/d (3-day survey)

	Fe	Cu	Zn	Cd	Pb
Broad Creek					
Base	779	197	112	9.1	24.7
Base+Wind	699	187	106	8.7	23.5
Base+Wind+Qs	670	187	102	8.7	23.3
Angelfish Creek					
Base	425	108	61	5.0	13.6
Base+Wind	398	106	60	4.9	13.2
Base+Wind+Qs	392	106	58	4.9	13.2

Predicted Trace Metal Fluxes at Ocean Boundaries

Summary of Author's Research and Future Goals

- Established High Quality database of Card Sound Water, Biota and Sediments, prior to significant Anthropogenic Impacts (Over 45 years ago)
- Increased Knowledge of Trace Metal Cycling Within an Important Florida Estuary
- Suggests lines of Future Research

  > Use Author's database and knowledge to Develop Comprehensive 3-d Model of Circulation and trace element cycling within Card Sound and adjacent waters

  > Extend Model Boundaries to Include Coastal and Offshore Waters (Florida Current)

  > Develop high quality database of Current Conditions within Card Sound

  > Use Enhanced Modeling Framework to Study Anthropogenic Impacts, such as

  Impacts of Current FPL Turkey Point Nuclear Plant Discharges and its Cooling Canals

  Impacts of Coastal Development on Fish and Shellfish Nurseries

  Impacts of Climate Change and SLR