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Characteristics of Produced Water Discharged to the Gulf of Mexico Hypoxic Zone

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Acknowledgments

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  - Todd Kimmell
  - Abbey Rechner
- Industry support
  - Mike Parker, ExxonMobil
  - Kent Satterlee, Shell

Topics for Discussion

- What is produced water?
- What is oxygen demand and the hypoxic zone?
- Why was produced water sampled?
- How was the sampling program designed and implemented?
- What were the results?
- How do platform discharges compare to other nutrient input sources?

What is Produced Water?

- Water that comes to the surface with oil and gas
- Waste that contains many chemical constituents
  - Salt content (salinity, total dissolved solids [TDS], electrical conductivity)
  - Oil and grease
    - *Composite of many hydrocarbons and other organic materials*
  - Toxicity from various natural inorganic and organic compounds or chemical additives
  - NORM
  - Some oxygen demanding materials

Produced Water Volume

- Largest volume waste stream from oil and gas production
  - Worldwide estimate – 77 billion bbl/year (2003 SPE paper)
  - U.S. offshore – >1 billion bbl/year
  - U.S. onshore (more than 850,000 wells)
    - *15-20 billion bbl/yr*

Ratio of Water to Oil

- Worldwide estimate – 2:1 to 3:1
- U.S. estimate – 7:1
- Many older U.S. wells have ratios > 50:1
  - This often determines profitability of well

Number of U.S. Producing Wells in 2002

Type of Well	Oil	Gas	Total
Onshore (low production)	402,072	245,961	648,033
Onshore (high production)	113,225	134,794	247,019
Offshore	3,700	3,245	6,948
Total	519,000	383,000	902,000

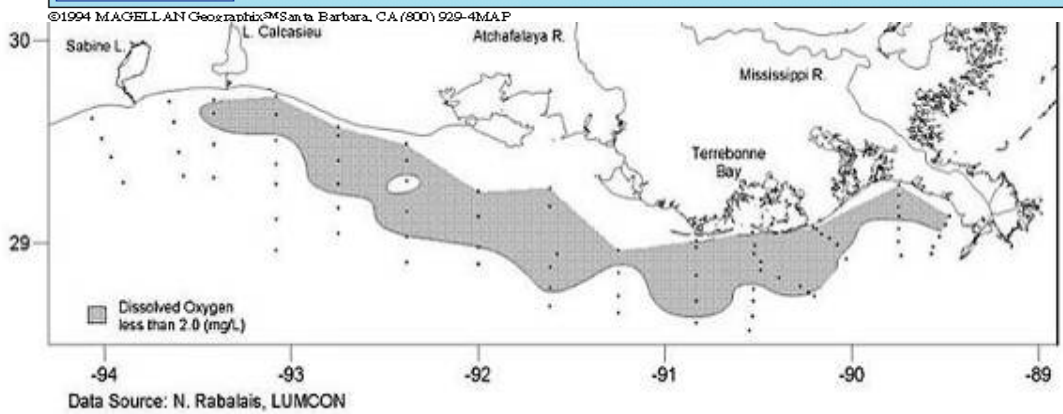
Source: U.S. Department of Energy, Energy Information Administration and Interstate Oil and Gas Compact Commission

What Is Oxygen Demand?

- The amount of oxygen that is consumed through microbial biodegradation of materials in a water sample
  - Typically measured as biochemical oxygen demand (BOD_5)
  - Can be caused by many chemical constituents
    - *Carbon*
    - *Nitrogen*
    - *Phosphorus*
- High oxygen demand can deplete oxygen in surface or bottom waters
  - Creates an unhealthy environment for marine life

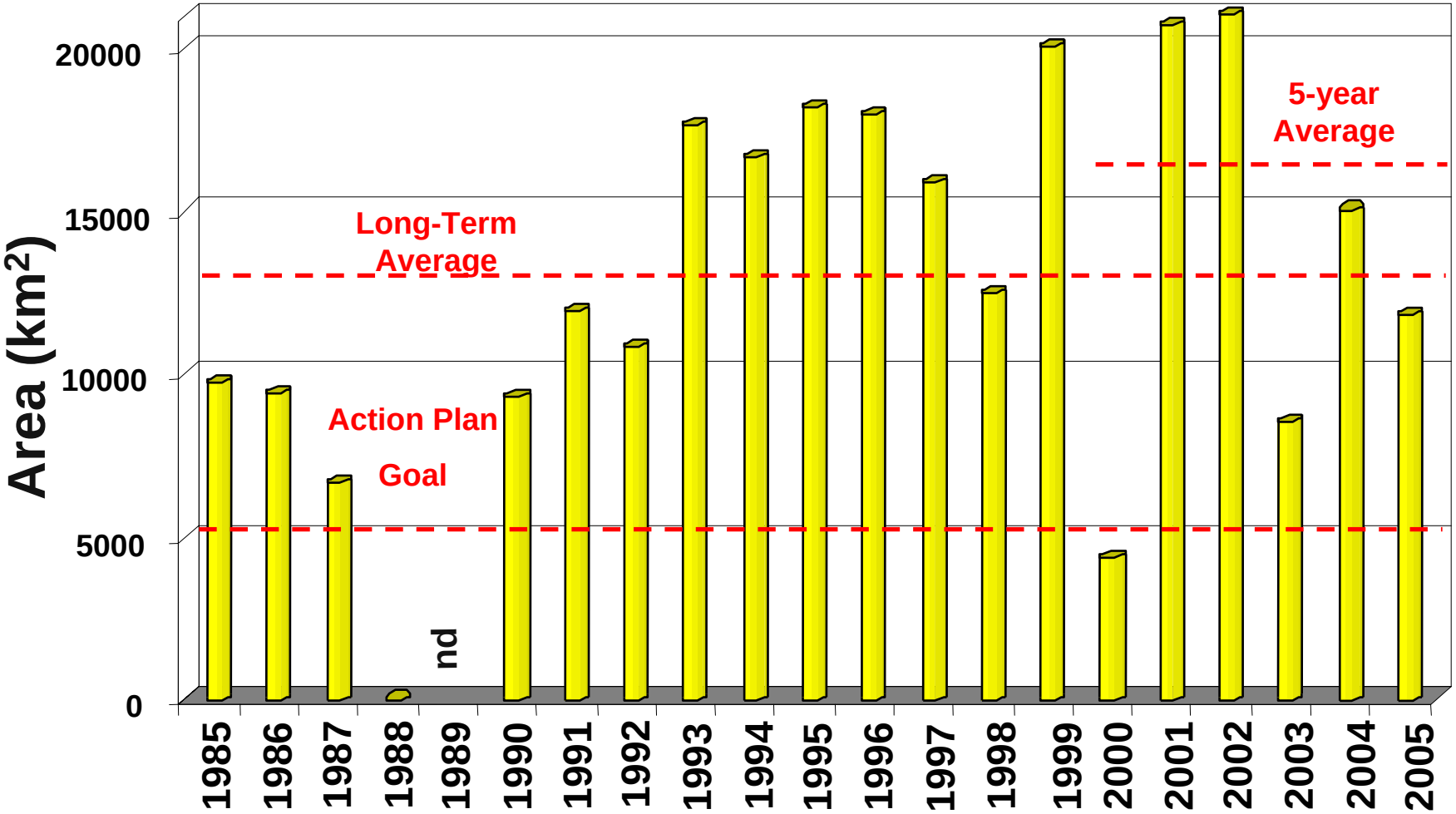
Study of Produced Water Discharges to the Gulf of Mexico Hypoxic Zone

- Each year, a large hypoxic zone (dissolved oxygen <2.0 mg/L) forms in the near-shore Gulf of Mexico.
- Primary contribution is nutrient inputs from Mississippi River and Atchafalaya River.
- Nutrients cause rapid growth of phytoplankton.
- Later these die off and sink to the bottom where they are decomposed by microorganisms.
  - This depletes the available oxygen.



Size of Zone Appears to Be Increasing

Estimated Size of Bottom-Water Hypoxia in Mid-Summer



(updated from Rabalais et al. 2002)

Basis for Study

- No good data existed on the oxygen-demanding properties of produced water.
- EPA did not want to continue produced water discharges indefinitely without having data and analysis to show the level of impact caused by the discharges.
- EPA issued a permit in late 2004 requiring sampling either:
  - At all platforms in hypoxic zone
  - Through a coordinated sampling program involving many platforms

Project Goals

- Provide information on the concentration of nutrient and oxygen demanding chemicals present in Gulf of Mexico produced water discharges.
- Estimate loadings of those parameters from all platforms in the hypoxic zone.
- Compare loadings to other sources of pollutants that contribute
  to hypoxic zone.

Objectives of Sampling Program

- Sample a representative subset of the produced water discharges in the study area.
- Determine average and range of BOD and nutrients from produced water discharges.
- Estimate variability within the same discharge.
- Follow good scientific procedures.
- Complete study by August 2005.

The Players and Their Roles

EPA – Issued permit; will decide future regulatory actions based on the study results

MMS – Responsibility for offshore activities; maintains extensive data collections and sponsors research

DOE – Concerned about maintaining energy supplies from offshore production; funded sampling program support and Argonne's work

Argonne – DOE contractor; designed sampling program; coordinated sampling, interpreted results, and prepared report

API – funded the laboratory analytical work

Offshore Operators Committee – assisted with selection of sampling locations; many member companies were sampled or offered to be sampled

Two analytical laboratories – one coordinated preparation of sample kits and delivery of samples to second lab; second lab conducted tests

Companies Participating in Hypoxic Zone Study

Apache	Dominion	J.M. Huber	Remington
Arena Offshore	El Paso	Kerr-McGee	Seneca Resources
ATP Oil & Gas	Energy Resource Technol	Linder	Shell Offshore
BHP Billiton	Eni	Marathon	Spinnaker
Bois dArc Offshore	EOG Resources Inc.	Mariner Energy	SPN Resources
BP	Exxon Mobil	Murphy	Stone Energy
Callon Petroleum	Forest Oil	Newfield	Houston Exploration
Calpine	Gryphon Exploration	Nexen	Unocal
Century Exploration	Helis	Northstar Gulfsands	W&T Offshore
Chevron	Hunt Oil Company	PetroQuest Energy	
Devon	Hunt Petroleum (AEC)	Pioneer	

Sample Design and Schedule

- Sampled 10% of approximately 500 discharges in the hypoxic zone.
  - 16 platforms sampled three times.
  - 34 platforms sampled one time.
- Parameters tested

Measure Indirect Oxygen Demand

ammonia
nitrate
nitrite
total Kjeldahl nitrogen (TKN)
total phosphorus
orthophosphate

Measure Direct OxygenDemand

BOD
TOC

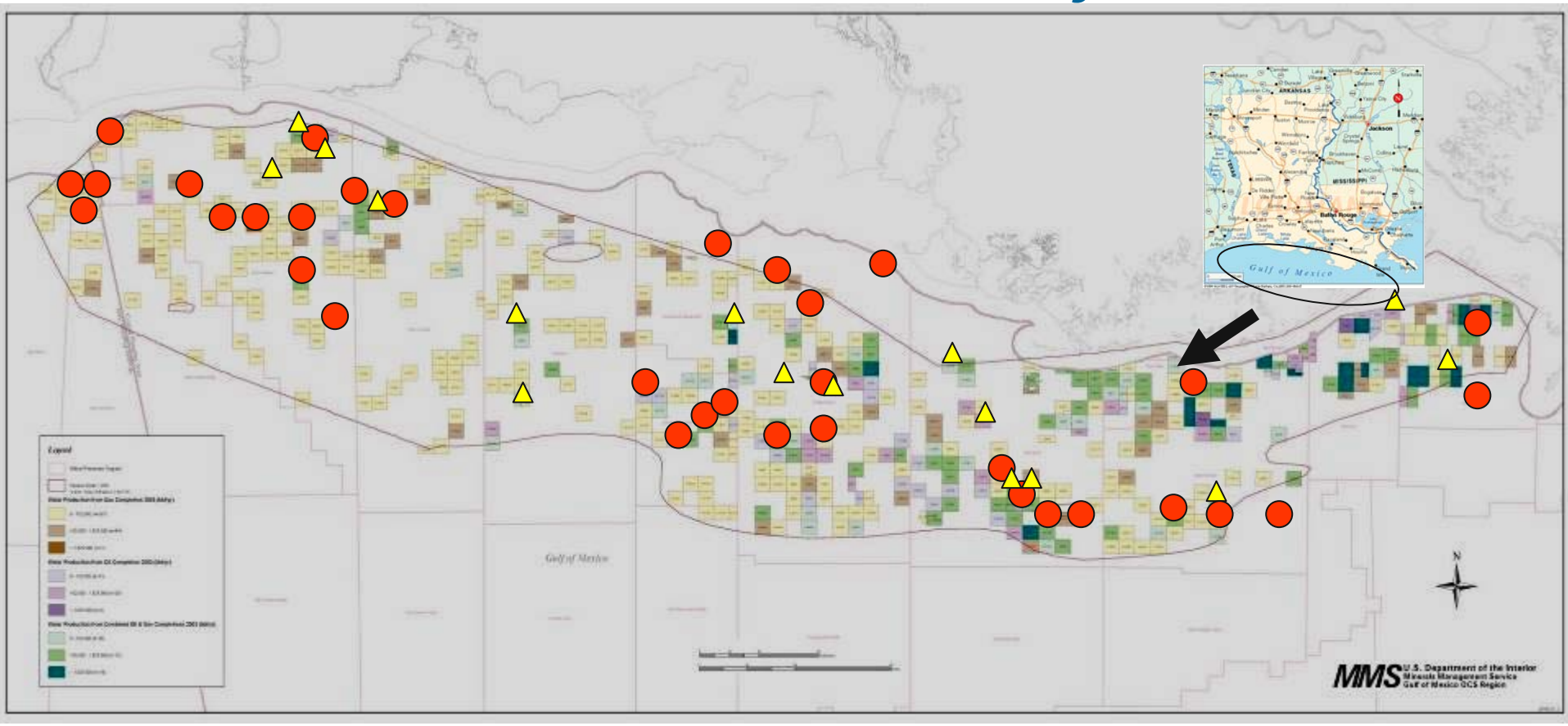
Other Parameters

pH
conductivity
salinity
temperature

Selection of Sampling Sites

- For the 16 sites tested three times, subdivide hypoxic zone lease blocks into three water production rate classes (< 500 bbl/day, 500 – 5000 bbl/day, >5000 bbl/day) and three hydrocarbon production type classes (oil completions, gas completions, both types of completions).
  - Select at least one facility from each of the nine subcategories.
- For the 34 sites tested one time, select locations at random.
- Issue
  - Neither EPA nor MMS had accurate data of number and identity of produced water discharges.
  - Decided to use MMS data on leases that produce both water and oil or gas (496 leases in study area).

Location of Platforms Sampled for Hypoxic Zone Produced Water Study



Platforms sampled one time and selected at random

Platforms sampled three times and selected based on discharge volume and type of hydrocarbon produced

Sample Collection and Transportation

- Sample kits were delivered to shore bases in advance of sampling date.
- Platform personnel collected samples according to instructions and placed them in a cooler with ice.
- Coolers were taken to helicopter pilot who delivered them to the shore bases.
- Laboratory couriers collected coolers at shore bases and delivered to lab.
- All transfers were documented on Chain of Custody form
- Issues
  - Tests must be started within 48 hours of sample collection
  - Complex scheduling and coordination
    - *Weather could impact schedule*

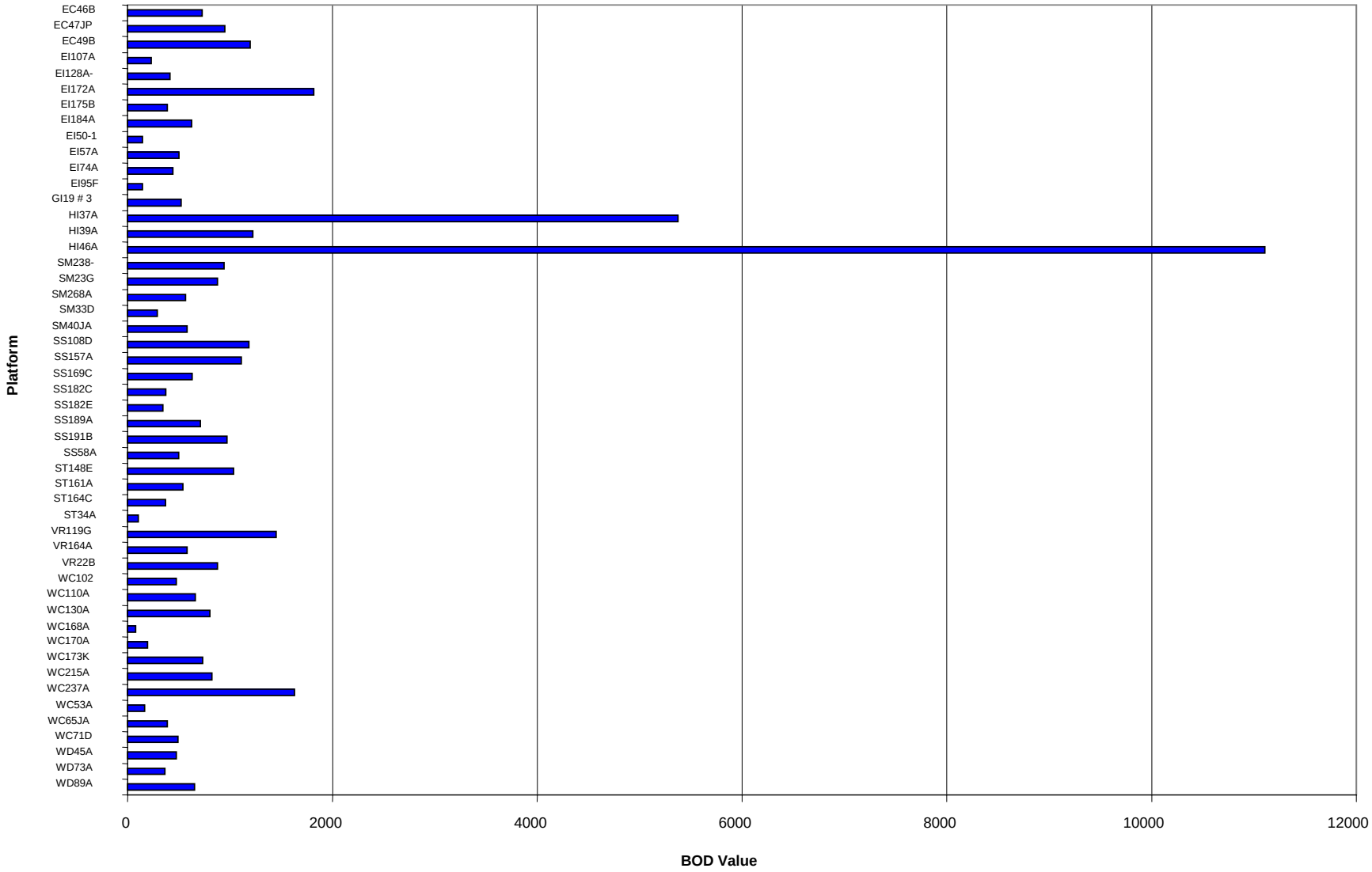
QA/QC Measures

- QA plan was developed before sampling began.
  - Sampling measures
    - *Blanks*
    - *Duplicates*
  - Analytical measures
    - *Calibration*
    - *Matrix samples*
    - *Blanks*

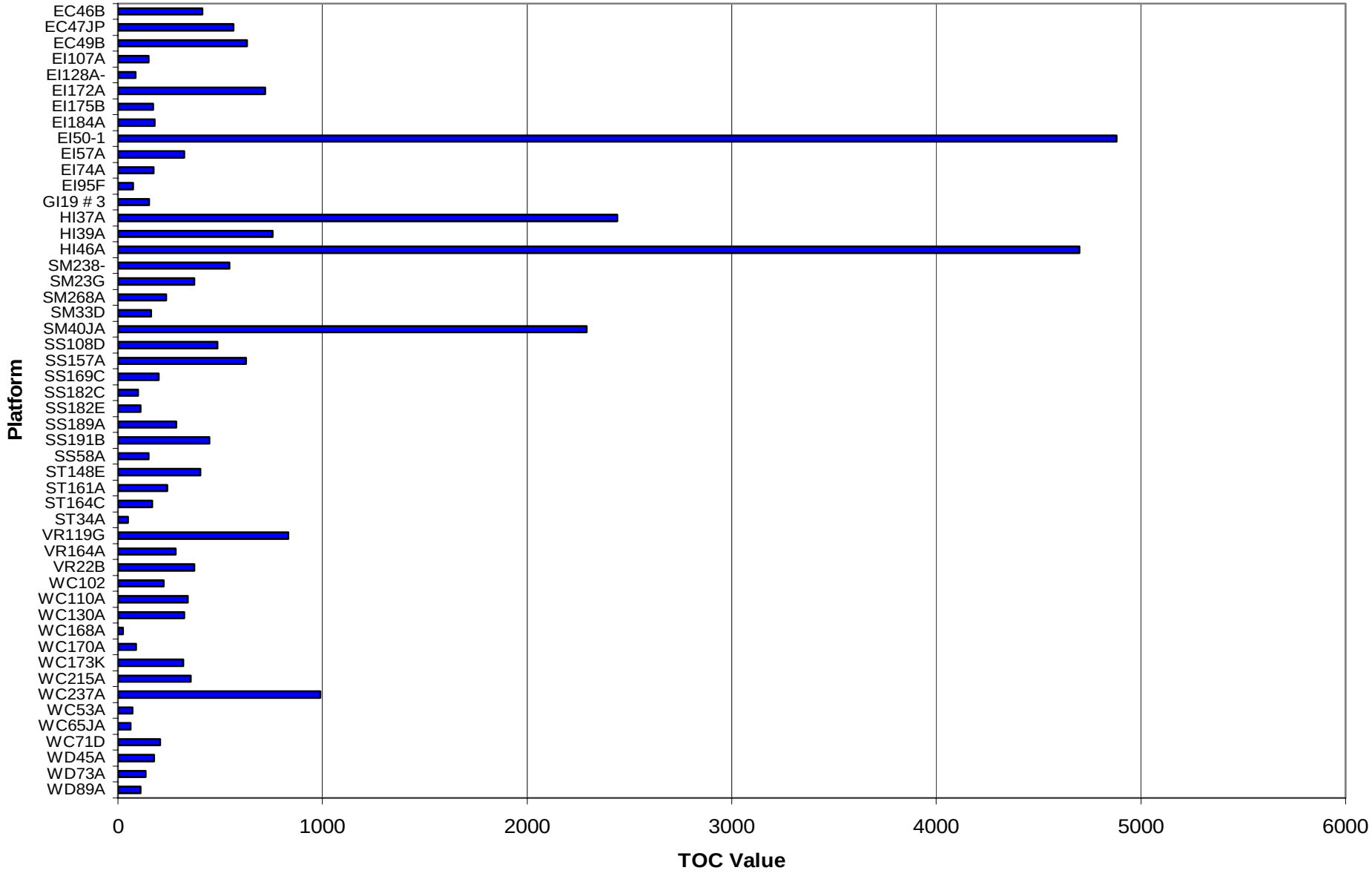
Summary of Analytical Data

Parameter	Mean	Median	Maximum	Minimum
BOD, mg/L	957	583	11,108	80
Dissolved BOD, mg/L	498	432	1,128	132
Suspended BOD, mg/L	76	57	146	16
TOC, mg/L	564	261	4,880	26
Dissolved TOC, mg/L	216	147	620	67
Suspended TOC, mg/L	32	13	127	5
Nitrate, mg/L	2.15	1.15	15.80	0.60
Nitrite, mg/L	0.05	0.05	0.06	0.05
Ammonia, mg/L	74	74	246	14
TKN, mg/L	83	81	216	17
Orthophosphate, mg/L	0.43	0.14	6.60	0.10
Total phosphorus, mg/L	0.71	0.28	7.90	0.10
Conductivity, umhos/cm	87,452	86,480	165,000	360
Salinity, ppt	100	84	251	0
Temperature, ^{o}C	38	32	80	20
pH, SU	6.29	6.50	7.25	1.77

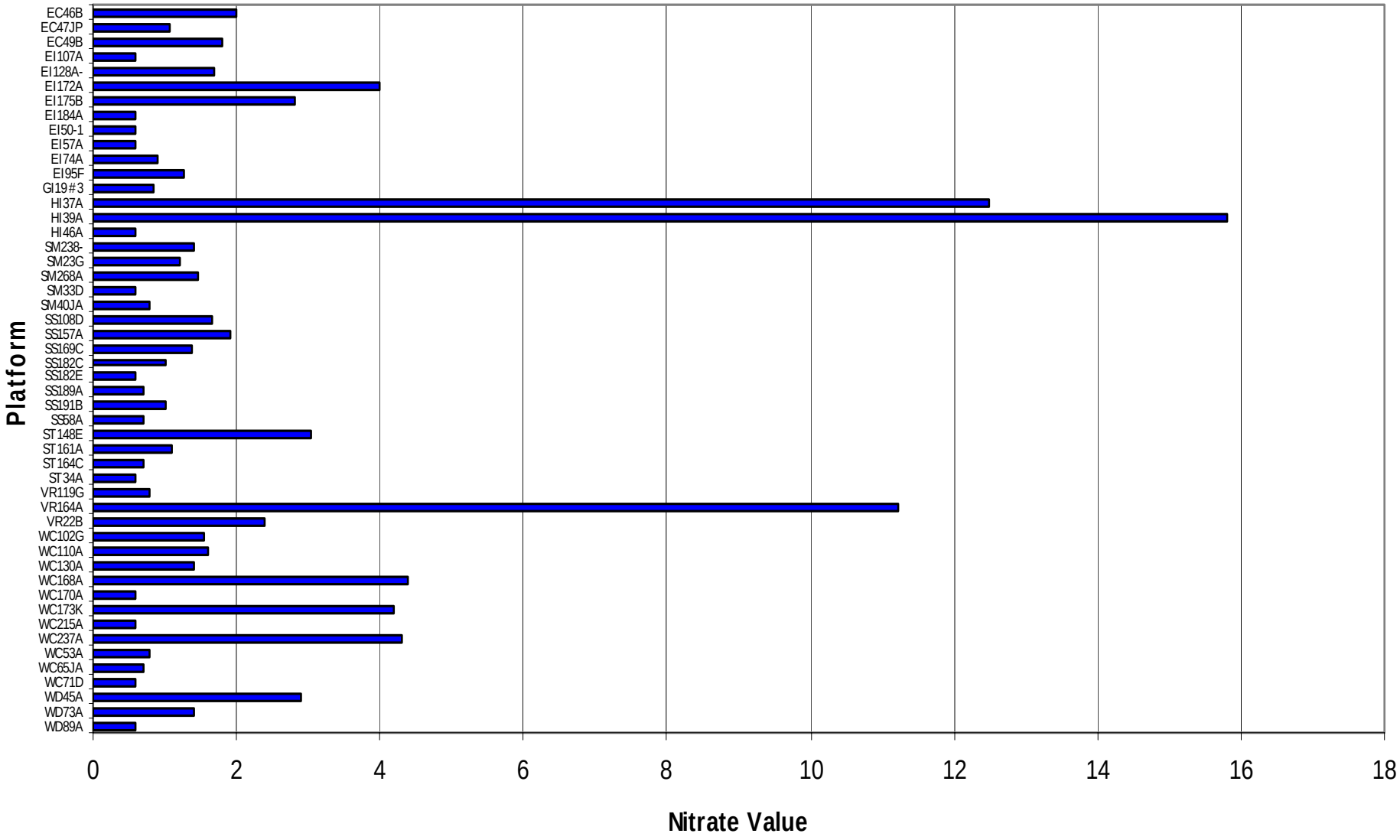
BOD Results from All Platforms (in mg/L)



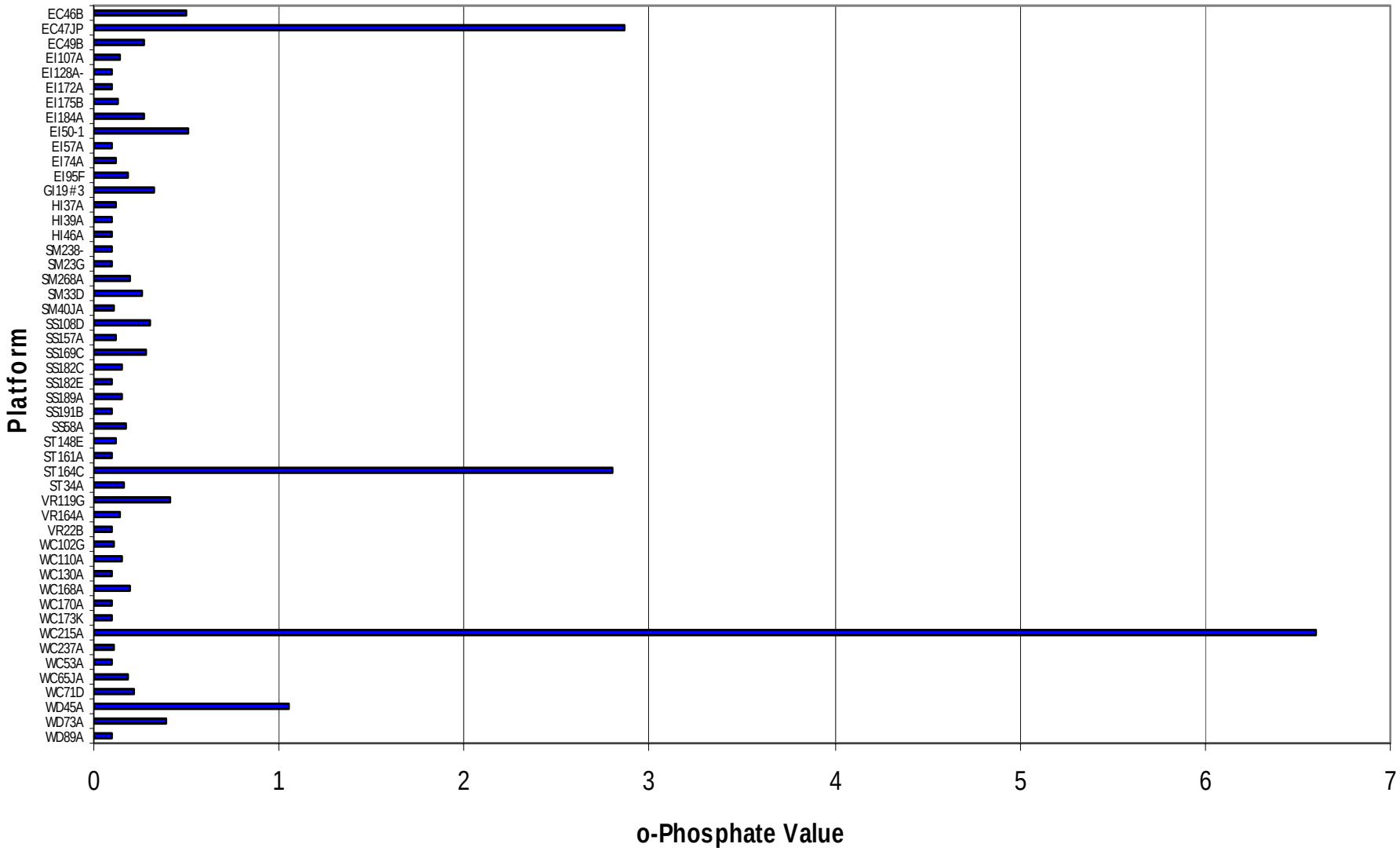
TOC Results from All Platforms (in mg/L)



Nitrate Results from All Platforms (in mg/L)



Orthophosphate Results from All Platforms (in mg/L)



Total Phosphorus Results from All Platforms (in mg/L)

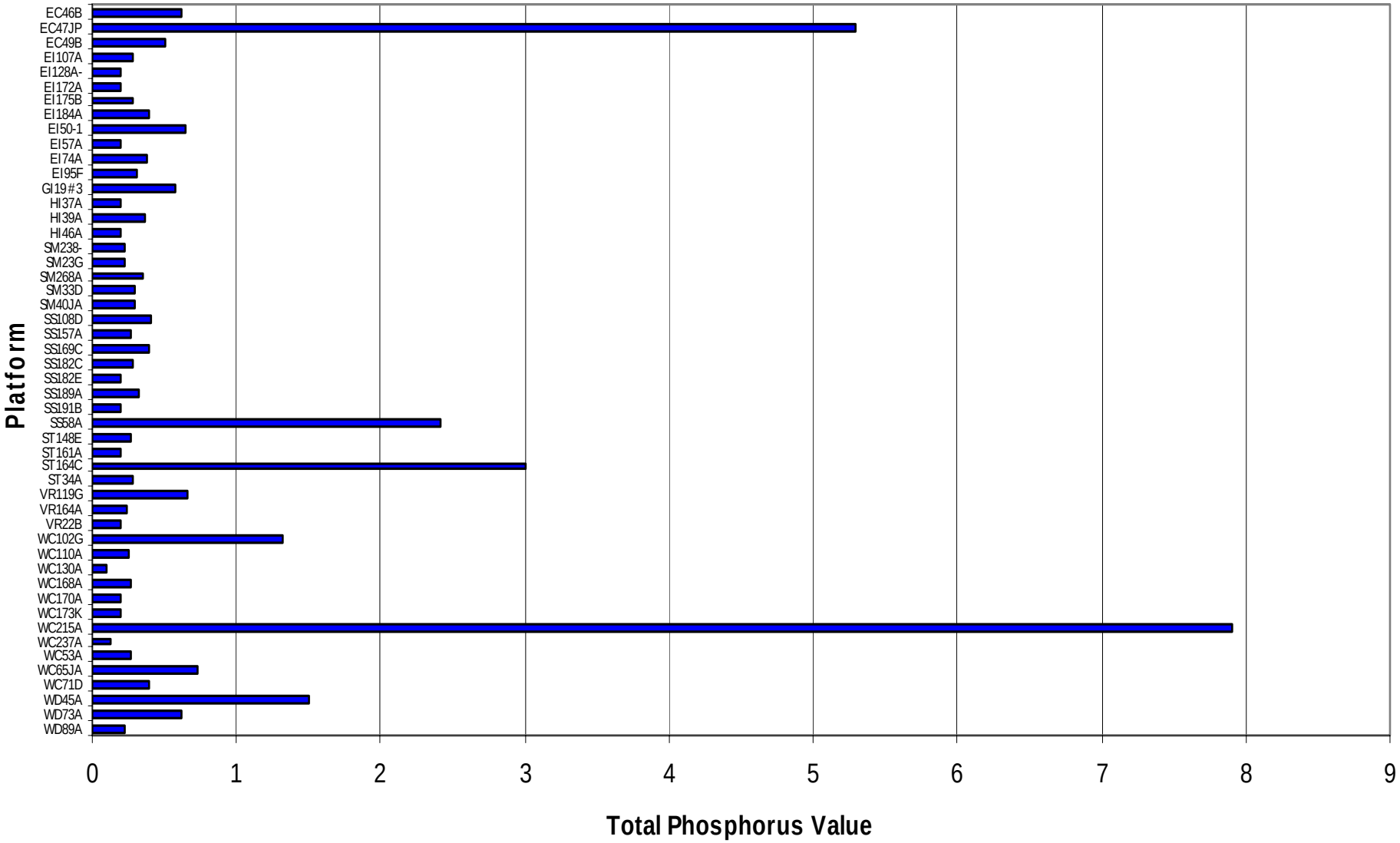


Table ES-2 – Loading Estimates for 50 Platforms and Entire Hypoxic Zone

Parameter	Loading from Sampled Platforms (lb/day)	Estimated Loading for Entire Hypoxic Zone (lb/day)
BOD	36,000	104,000
TOC	14,100	40,700
Nitrate	68.3	197
Nitrite	3.07	9
Ammonia	4,770	13,800
TKN	5,140	14,900
Orthophosphate	22.6	65
Total phosphorus	37.6	109

- **The mass loadings from offshore oil and gas discharges to the entire hypoxic zone were estimated by multiplying the 50-platform loadings by the ratio of total water generated to 50-platform discharge volume.**

Table 23 – Comparison of Nutrient Loadings from Produced Water Discharges and Riverine Inputs

Nutrient	Mean Flux (lb/yr) from Mississippi and Atchafalaya Rivers (Goolsby et al. 1999)	Estimated Annual Mass Loading (lb/yr) from Produced Water Discharges to the Hypoxic Zone	Ratio of Produced Water Loading to Riverine Loading
Ammonia	68,355,000	5,030,000	[a]
Organic N	1,278,900,000	389,000 (calculated as TKN – ammonia)	[a]
Nitrate	2,100,000,000	71,900	[a]
Nitrite	0	3,285	[a]
Total N	3,460,000,000	5,500,000	0.00159
Orthophosphate	92,100,000	23,700	[a]
Particulate phosphate	209,000,000	0	[a]
Total P	301,000,000	39,800	0.00013

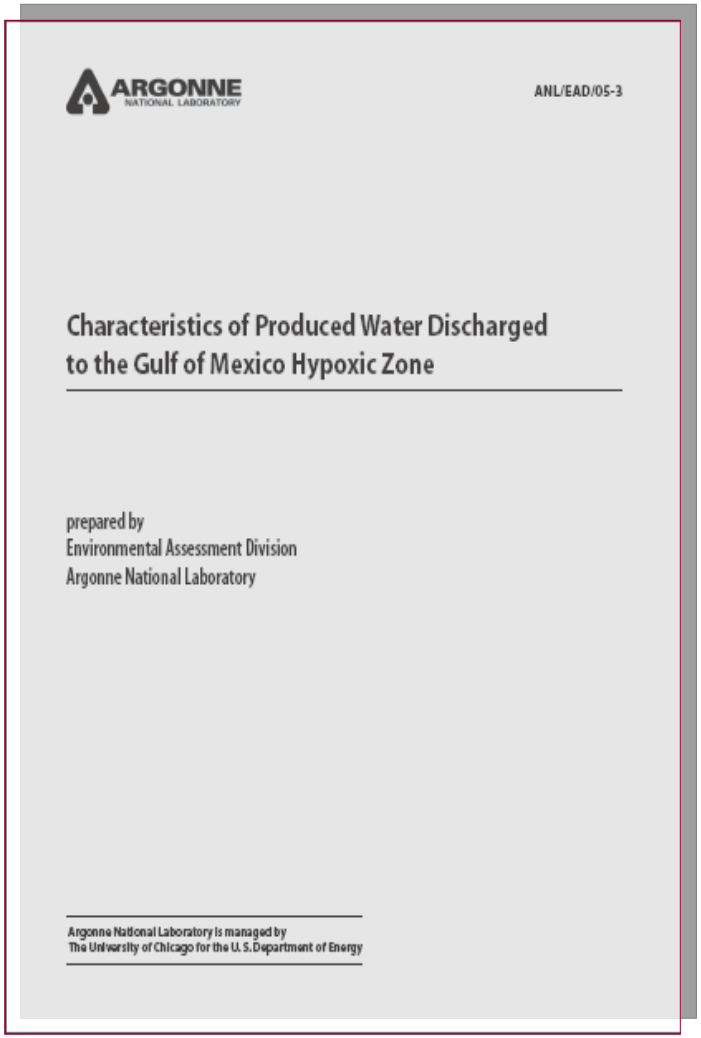
[a] The key ratios are total nitrogen and total phosphorus. Ratios for the other component comparisons are not shown.

nitrogen - 0.16%

phosphorus 0.013%

The Argonne Report Was Completed

- The hypoxic zone report was completed in August 2005 and subsequently submitted to EPA.



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prepared by
Environmental Assessment Division
Argonne National Laboratory

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The University of Chicago for the U.S. Department of Energy

Download report at:
www.ead.anl.gov/pub/dsp_detail.cfm?PubID=1874

What Happened Next?

- EPA hired three modelers to run different water quality models:
  - Vic Bierman, Limno-Tech
  - Zdravko Justic, Louisiana State University
  - Donald Scavia, University of Michigan
- The data from the Argonne report were used as inputs.

Addressing Uncertainty

- In early 2006, Argonne was asked by modelers to help them evaluate uncertainty of hypoxia data.
  - Had to develop range of model inputs based on data from 50 platforms
  - Used box and whisker plot technique to identify outliers

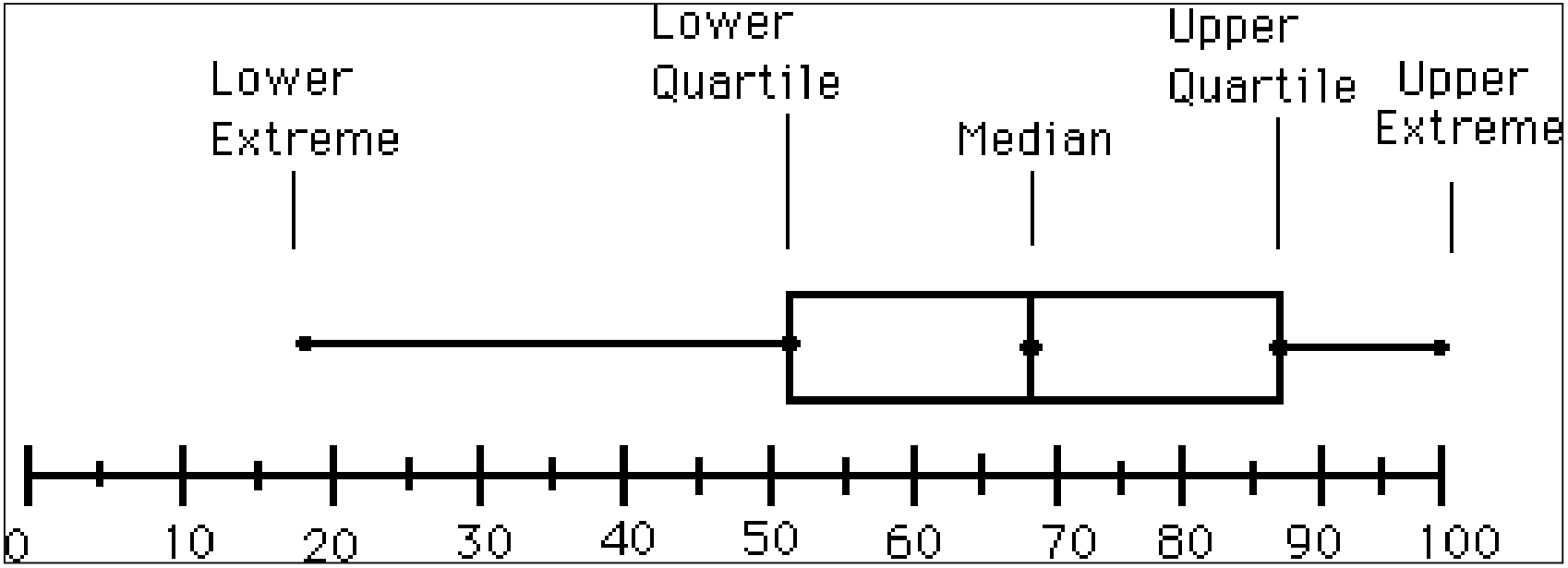


Table 1 – Calculation of sensitivity range values for BOD

BOD5 (mg/L)
80
103
147
148
167
198
234
289
344
365
372
376
389
392
415
442
477
479
494
499
503
521
543
569
582
583
628
632
654
663
711
732
736
804
826
876
879
940
954
974
1,038
1,108
1,186
1,200
1,224
1,448
1,632
1,821
5,378
11,108

Step 1: Calculate the flow weighted mean.

total loading	36,000 lb/day
total flow	175,000 bbl/day
flow-weighted average concentration	588 mg/L

Step 2: The 50 data values are ordered from lowest to highest (see list to the left).

Step 3: The quartile values are calculated.

lowest value		80
lower quartile		390
median		583
Upper quartile		925
highest value		11,108
outlier threshold (upper quartile plus 3 times the ICR)		2,529

Step 4: Any data values exceeding 2,529 mg/L are dropped from the data set. In this case, the two highest values are dropped.

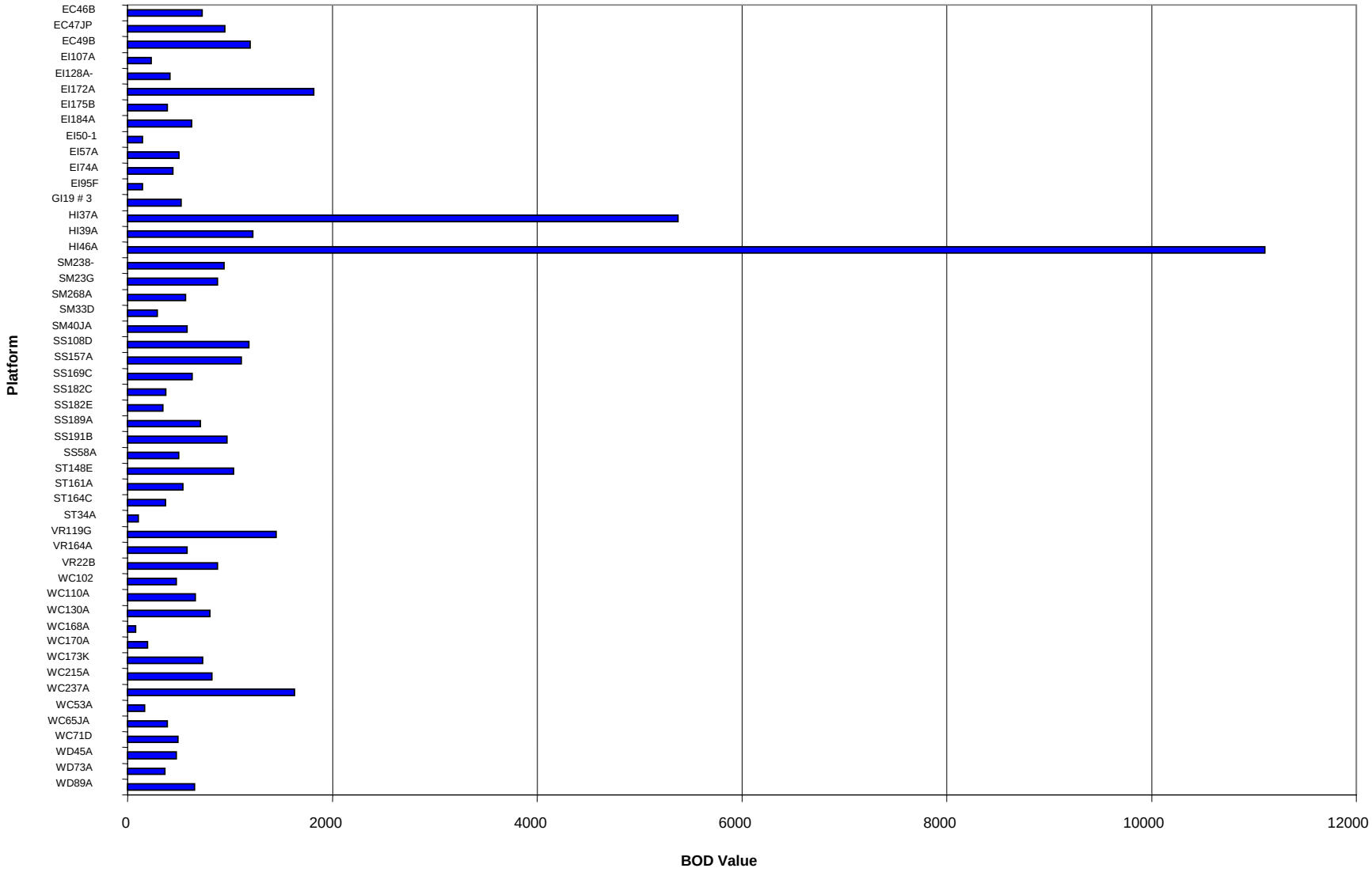
Step 5: Calculate the 95th percent confidence interval.

Standard Deviation	394
No. of data values	48
95% Conf. Int.	112

Step 6: Calculate the upper and lower ends of the range = flow-weighted average plus or minus the 95th percent confidence interval.

Range = 476 – 700 mg/L

BOD Results from All Platforms (in mg/L)



Conclusions

- Designing and conducting the sampling program was a cooperative effort among many players.
- The program was complex but was completed in a short time frame to meet EPA needs.
- These data from 50 platforms represent the most complete and comprehensive effort ever undertaken to characterize the amount and potential sources of the oxygen demand in offshore oil and gas produced water discharges.

Conclusions (cont.)

- The program emphasized good science and responsible QA/QC.
  - Results were scientifically sound.
- Discharges of oxygen-demanding pollutants and nutrients are collectively large, but they represent less than 1% of the contribution of the same pollutants from the Mississippi and Atchafalaya Rivers.

Reference

Rabalais, N.N., R.E. Turner, and W.J. Wiseman, Jr. 2002. Gulf Of Mexico hypoxia, a.k.a "The dead zone". Annu. Rev. Ecol. Syst. 33:235-63.