Challenges in observing long term trends in nutrients:

Ocean Station P as an example

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IOS Nutrient Methods:

- Technicon AutoAnalyzer and modified methods to suit concentration ranges
- Thoroughly reviewed then published methods (technical report)
- Updated to Astoria autoanalyzer in 2009, same chemistries

- Changed from fresh to salt water baseline for PO_4 in 1989: -0.1 μM since.
- Fresh sample analysis almost all Line P cruises starting in 1987
- Use of best available reference materials to confirm standards (Sagami CKS, Acculute, MNSK from OSI, RMNS)
- consistent personnel, Chemistry group helpful in maintaining data quality
  - calibrated balances, good quality deionized water, specialized labs.

TECHNICAL REPORTS OF THE METEOROLOGICAL RESEARCH INSTITUTE NO. 58

2006 Inter-laboratory Comparison Study of a **R**eference **M**aterial for **N**utrients in **S**eawater

TECHNICAL REPORTS OF THE METEOROLOGICAL RESEARCH INSTITUTE No. 60

2008 Inter-laboratory Comparison Study of a Reference Material for Nutrients in Seawater

Z scores for 2006 **RMNS** Inter-lab Comparison – top 10 of 51

Rank	Lab	NO_3 Z	PO_4 Z	Si Z	Av Z	SD Z
1	The Netherlands (van Ooijen)	0.67	0.37	0.63	0.56	0.27
2	**Canada (IOS, Barwell-Clarke)**	**0.77**	**0.60**	**0.35**	**0.57**	**0.25**
3	France (Kerouel)	0.97	0.42	0.43	0.61	0.47
4	Canada (IOS, White)	1.17	0.45	0.22	0.61	0.62
5	France (Youenou)	0.47	0.80	0.75	0.67	0.46
6	Japan (Nagai)	0.83	0.55		0.69	0.47
7	Japan (Kasai)	0.82	0.78	0.57	0.71	0.51
8	Japan (Masuda)	0.80	1.07		0.93	0.59
9	Canada (BIO, Yeats)	1.22	1.20	0.48	0.97	1.44
10	USA (Scripps, Becker)	0.43	0.65	1.83	0.97	0.78

The *Z-score for each analysis, Z_{par}, is defined as:*

$$Z_{par} = ABS((C_{par} - C_{consensus})/P_{par})$$

C_{par} is the concentration measured by a laboratory for the parameter of interest;
$C_{consensus}$ is the consensus mean sample concentration for the parameter of interest;
P_{par} is the standard deviation of the sample concentration for the parameter of interest.

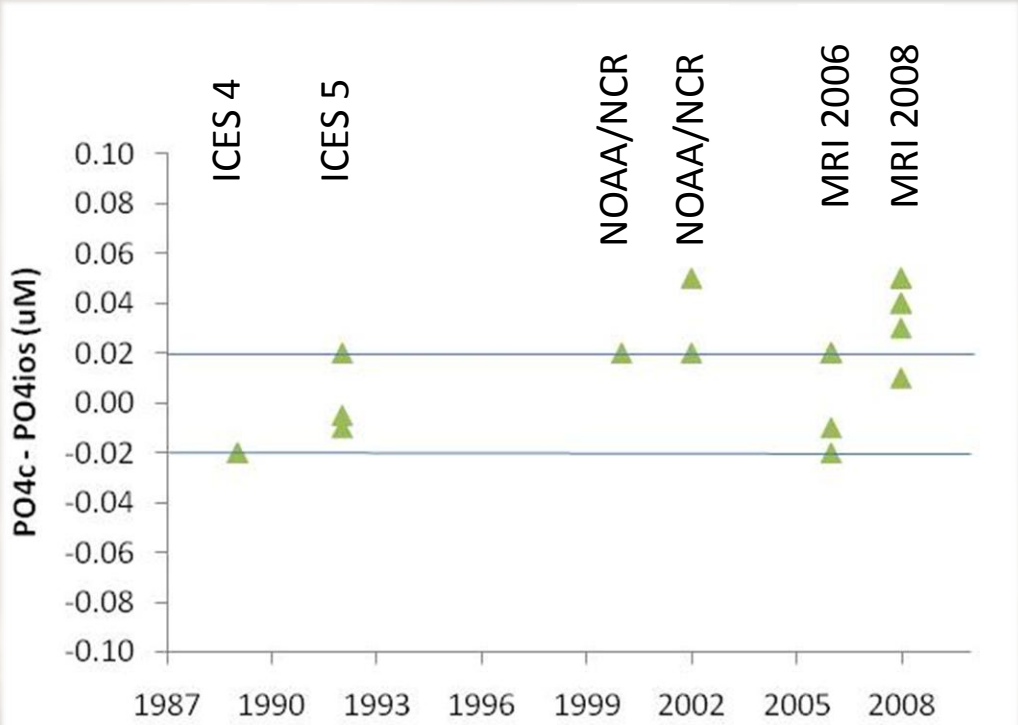
Z scores for 2008 **RMNS** Inter-lab Comparison – top 10 of 56

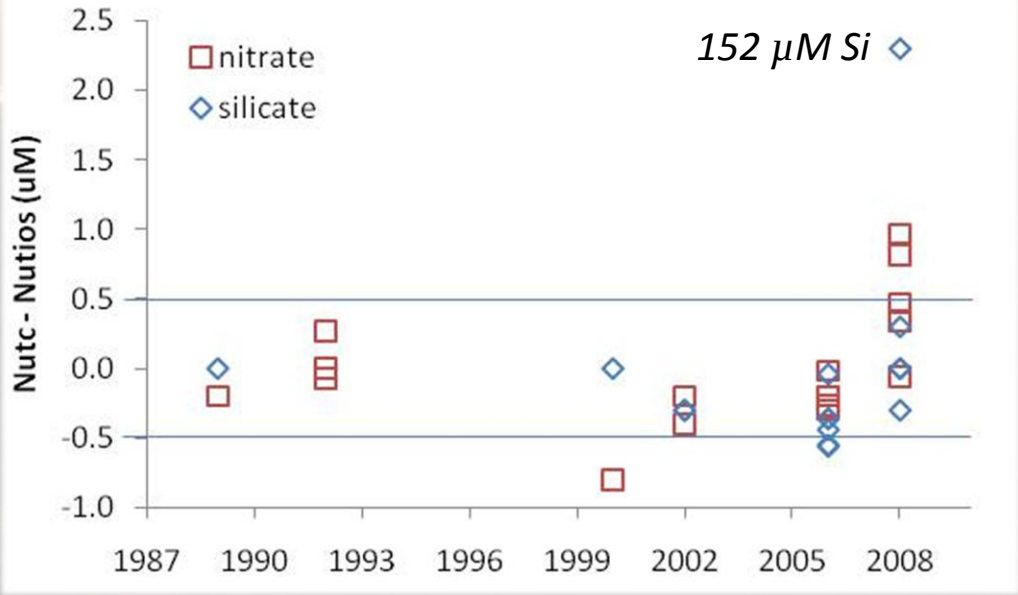
Rank	Lab	NO_3 Z	PO_4 Z	Si Z	Av Z	SD Z
1	France (Keroul)	0.15	0.28	0.30	0.24	0.20
2	The Netherlands (van Ooijen)	0.15	0.43	0.53	0.37	0.26
3	Japan (Saito)	0.70	0.43	0.17	0.43	0.33
4	**Canada IOS (Barwell-Clarke)**	**0.65**	**0.30**	**0.73**	**0.56**	**0.47**
5	Canada IOS (White)	0.77	0.43	0.53	0.58	0.31
6	Japan (Ishida)	0.70	0.72	0.37	0.59	0.60
7	Japan (Murata)	0.38	0.58	0.82	0.59	0.35
8	Japan (Ogawa)	0.58	0.17	1.03	0.59	0.44
9	France (Munaron)	1.10	0.15	0.90	0.72	0.59
10	Japan (Hirayama)	0.82	0.85	0.50	0.72	0.36

IOS still ranked well, but a slightly high Z score for Si needs attention.

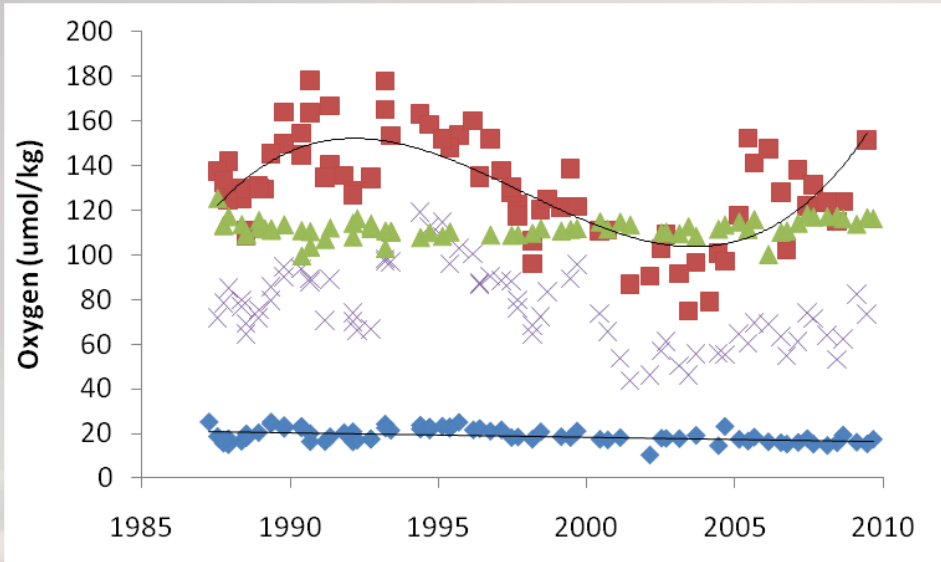
IOS Intercalibrations –

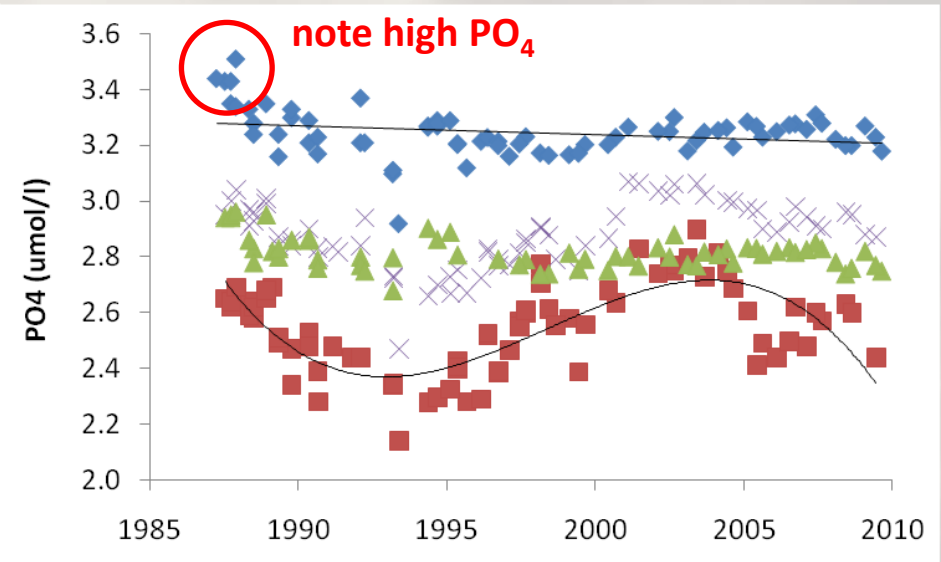
Difference between Consensus and IOS values are plotted.

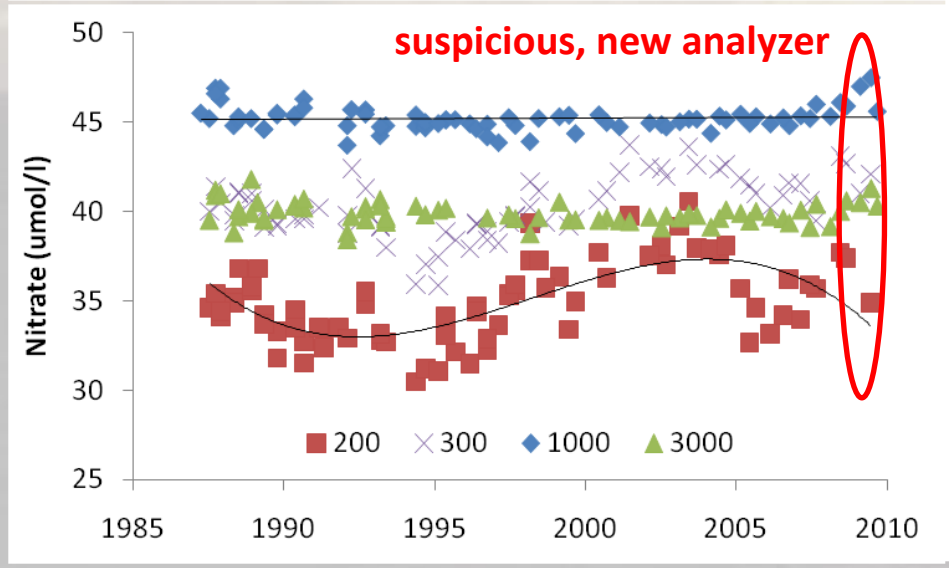


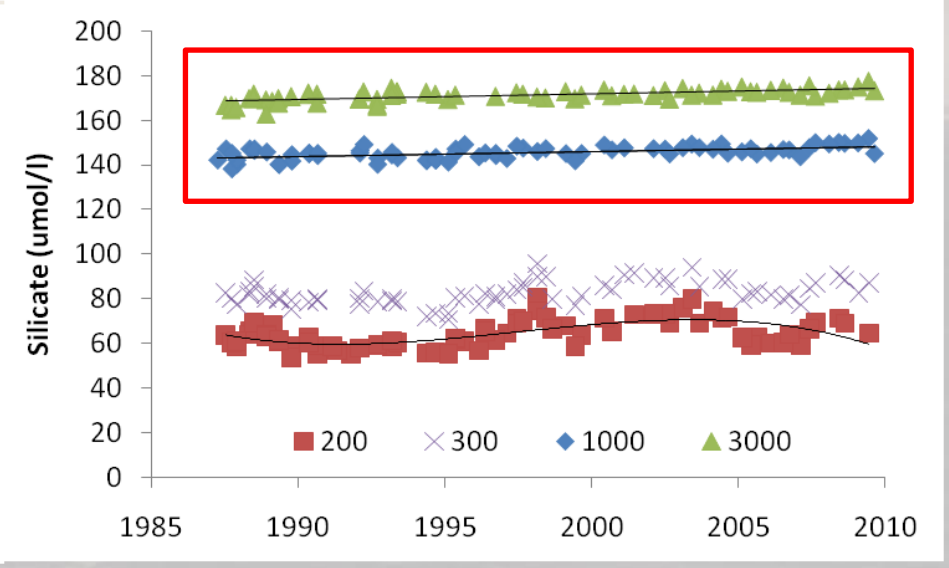


Ocean Station P trends for Oxygen and Nutrients

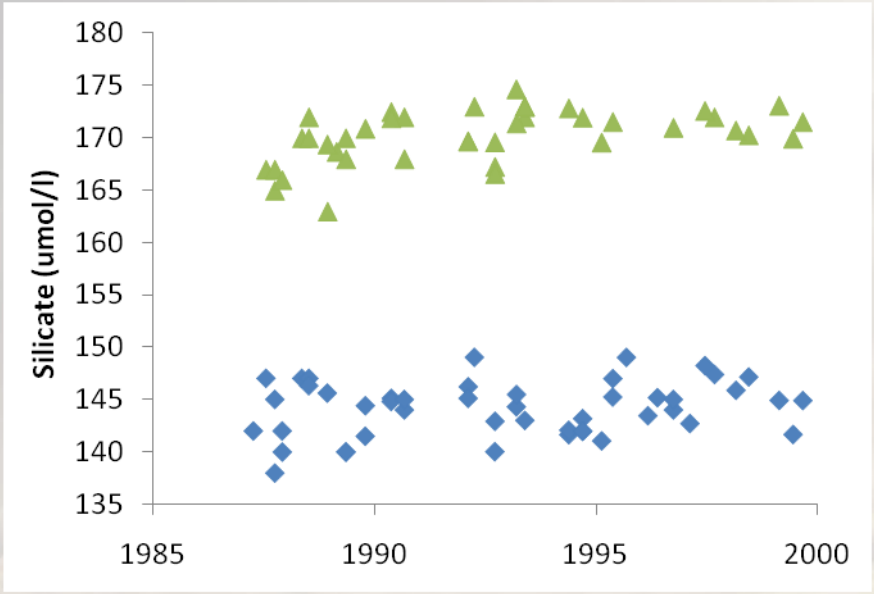


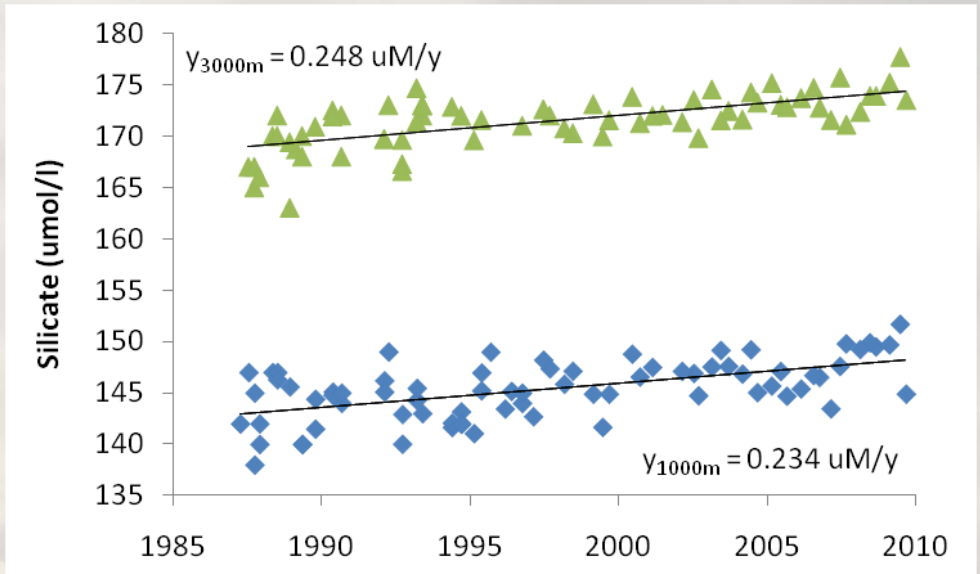


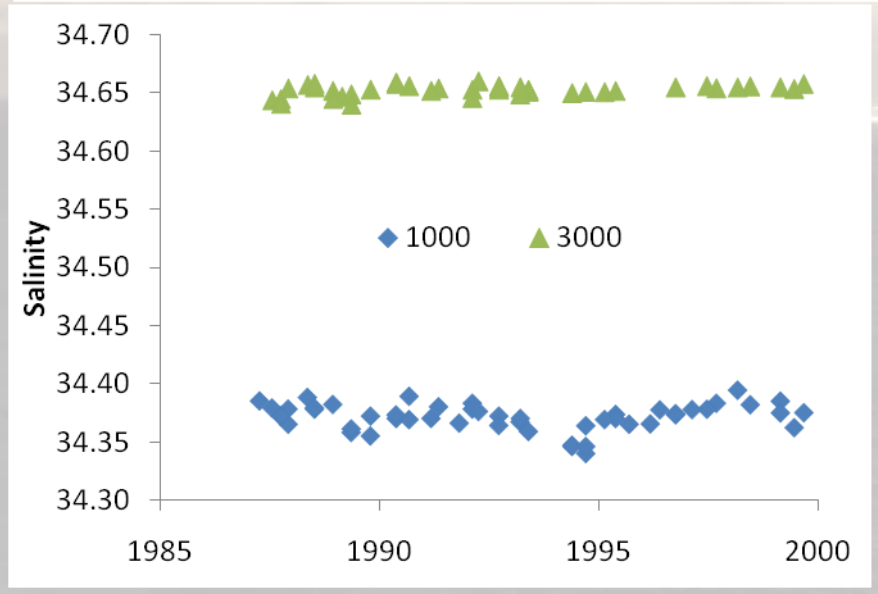


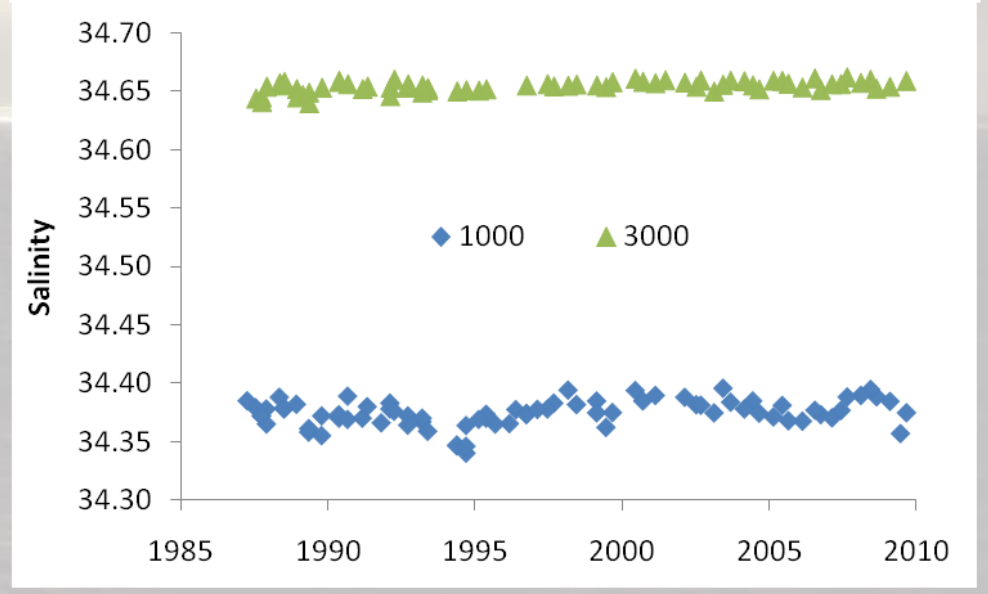


Trends take time to emerge

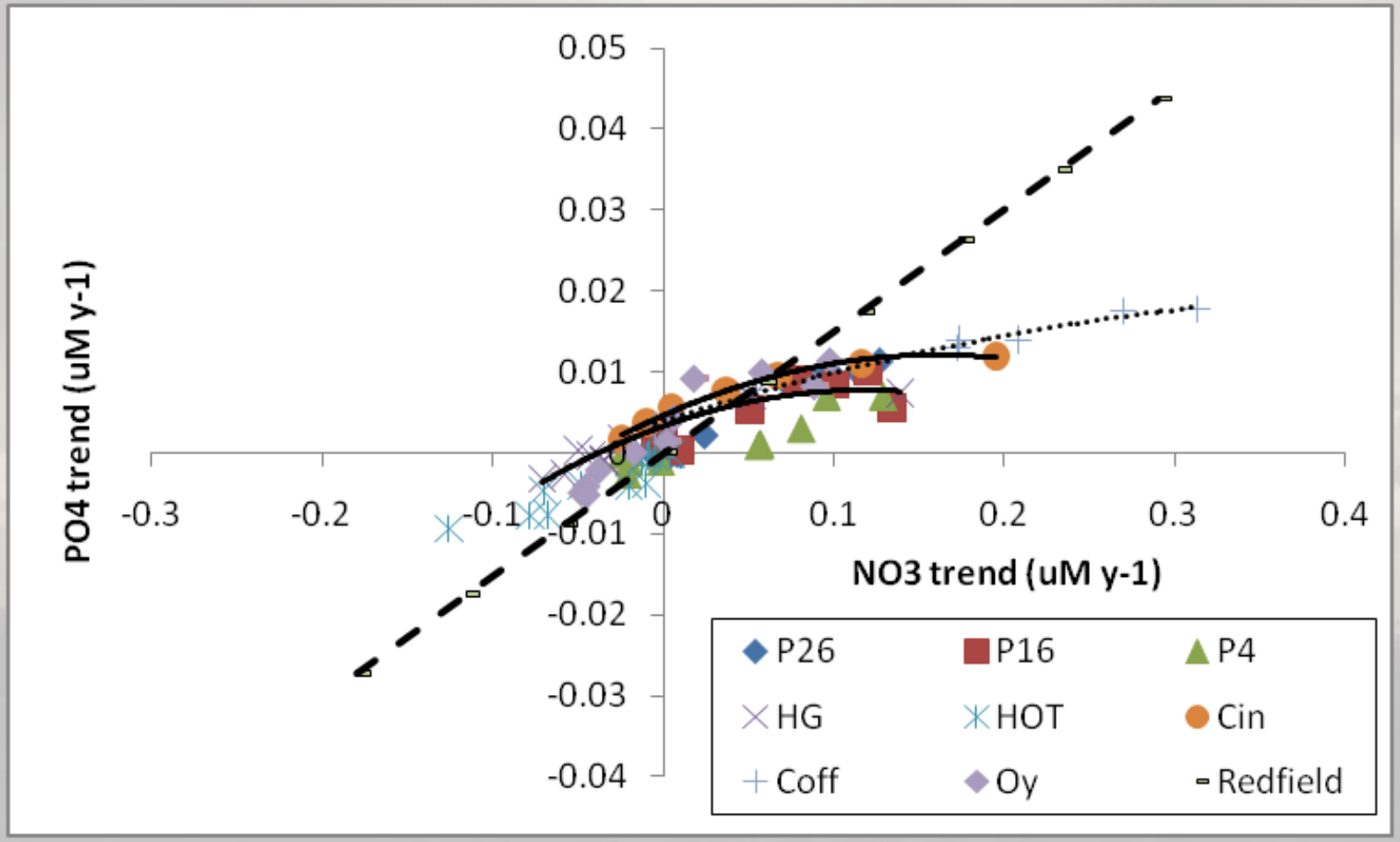








Trends for Time-Series Stations in the North Pacific (waters below the mixed layer)



Deviations from Redfield ratios may be caused by:

- a faster turnover of P vs N in the shallow ocean
- P source but N sink near anoxic sediments

Quality data requires:

- well defined methods (e.g. Strickland and Parsons)
- well maintained laboratory, limited access helps
- constant method testing, especially with new personnel
- use of certified reference materials
- laboratory intercalibrations
- **data available on-line**

(e.g. WOCE, St P, A-line, CalCOFI, HOT...)