National Environmental Monitoring Conference

15 – 19 Aug 2011, Bellevue, WA, USA

Monitoring and fractionation of low-level phosphorus in water and environment

Wei Ning YAP, Kok Yong LIM, Wei ZHANG, Zhongxian GUO

PUB Singapore

Outline

- Introduction
  - Phosphorus (P) as nutrient and pollutant
  - Various forms of P
- Common analytical methods
- ICP-OES optimization
- Monitoring
  - Total P and Dissolved P
  - Reservoirs
  - Sediments
  - Detergents

Introduction

Phosphorus as nutrient

- Essential nutrient for all life forms
- Active roles in DNA, RNA, ADP and ATP

Freshwater guideline	Total Phosphorus (ug/L)
Ultra-oligotrophic	< 4
Oligotrophic	4 – 10
Mesotrophic	10 – 20
Meso-eutrophic	20 – 35
Eutrophic	35 – 100
Hyper-eutrophic	>100

Canadian Water Quality Guidelines, Phosphorus, February 2005

Introduction

Phosphorus as a pollutant

- Eutrophication of freshwater with undesirable changes:
  - ❖ Excessive algae growth
  - ❖ Reduced water clarity
  - ❖ Unpleasant odour and taste
  - ❖ Low dissolved oxygen
  - ❖ Changes in fish populations or fish kills
  - ❖ Toxins from bluegreen algae
- PO_4 > 1.0 mg/L may interfere with coagulation in treatment
- Total P at < 60 µg/L, to prevent algae bloom

Introduction

Sources

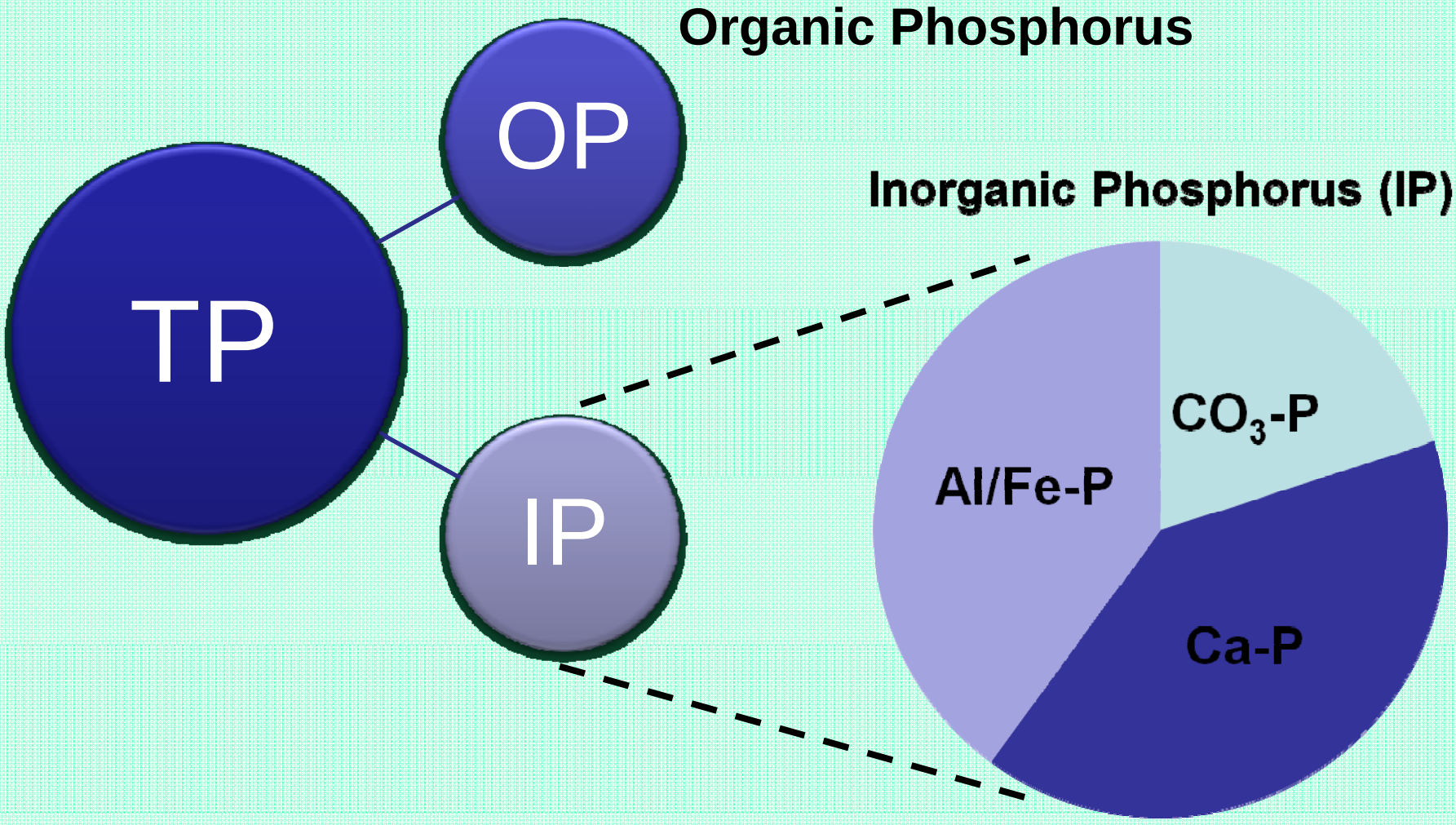
- Industries, food, pharmaceuticals, detergents, agricultural sites, leach from reservoir sediment sink

Regulation in water

	Phosphate (mg/L)
Stream not flowing into lake/reservoir	<0.10
Stream flowing into lake/reservoir	< 0.05
Within lake/reservoir	<0.025

*Federal criteria (USEPA, 1986)

Forms of phosphorus in environmental samples



Common analytical methods

Methods	Features	Detection Limits (DLs)
IC	Orthophosphate (PO_4^-) Anion-exchange column Conductivity detector	High µg/L
ICP-OES	TP & Dissolved P Element emission line (P 214.917 nm)	µg/L
ICP-MS	TP & Dissolved P m/z = 31	Sub-µg/L

Common analytical methods

Spectrophotometry involves two steps:

i. Digestion
ii. Colorimetric

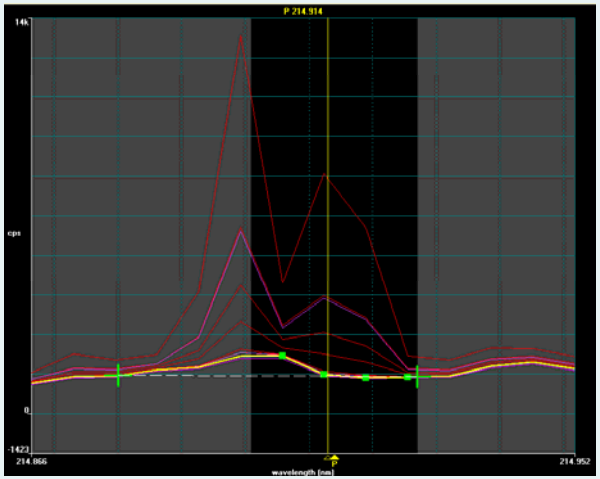
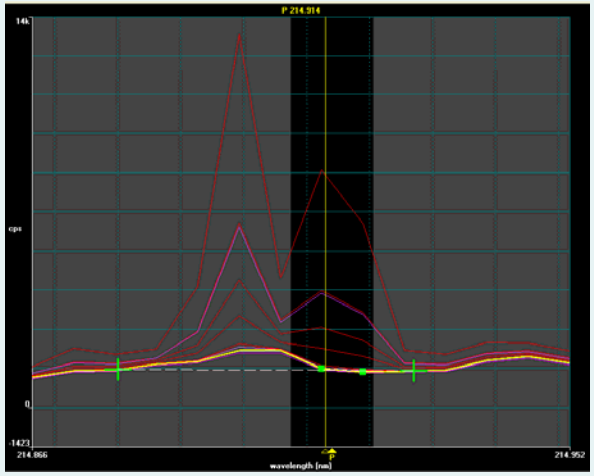
Methods	Features	Detection Limits (DLs)
Ascorbic acid	Fe^{3+}, Cu, SiO_2, turbidity and color	High µg/L
Vanadomolybdo-phosphoric Acid	SiO_2, arsenate Fe^{3+} > 100 mg/L	High µg/L
Stannous Chloride	SiO_2, arsenate Fe^{3+} > 100 mg/L	High µg/L

Method adopted

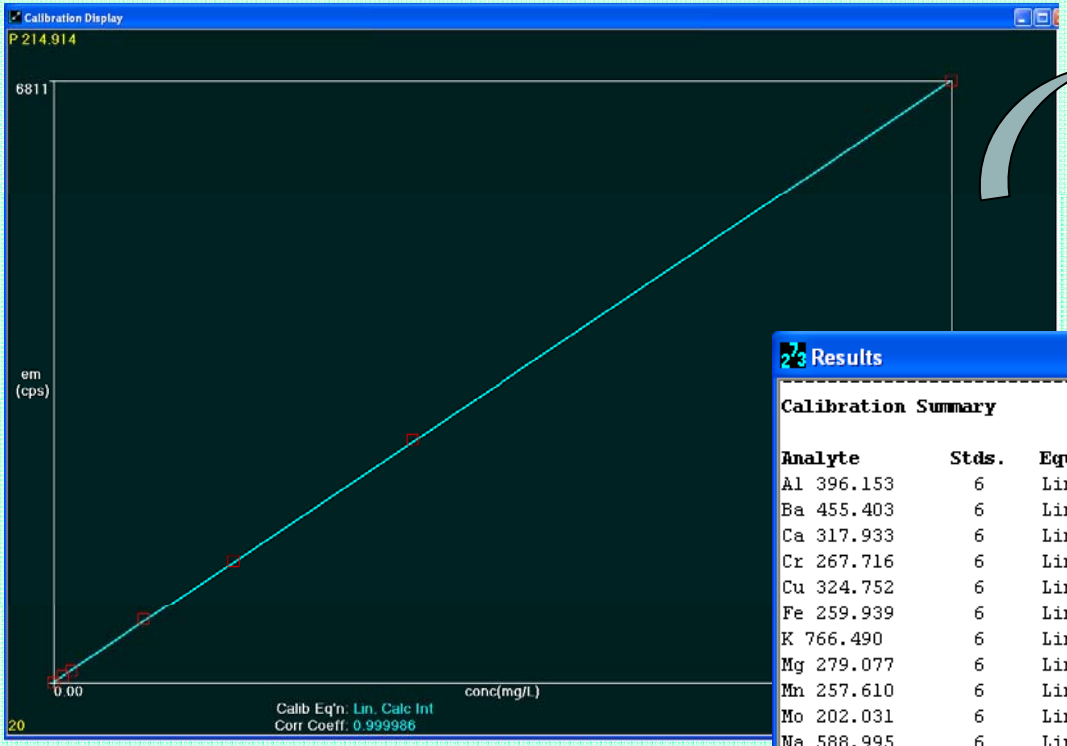
- ICP-OES
  - Better sensitivity (MDL: 3 µg/L) than spectrometry and IC
  - Multi-element capabilities
  - Higher sample throughput/productivity
  - Phosphorus emission lines at 177.434, 178.221, 213.617 and 214.914 nm
  - A less expensive approach per analysis
  - Fewer interference than quadrupole ICP-MS (without collision-reaction cell)

Method Adopted

- ICP-OES optimization

	Before	After
Nebulizer flow (L/min)	0.80	0.65
RF power (W)	1300	1350
Spectral correction, P at 214.917 nm Probable interference: *Cu (with emission lines at 213.598 nm and 214.897 nm).*	Peak area - 4 points 	Peak area – 2 points 

Method Adopted



6 points calibration
(lowest point: 0.05 mg/L)

Results

Calibration Summary

Analyte	Stds.	Equation	Intercept	Slope	Curvature	Corr. Coef.
Al 396.153	6	Lin, Calc Int	828.6	109600	0.00000	0.999975
Ba 455.403	6	Lin, Calc Int	8386.1	501900	0.00000	0.999935
Ca 317.933	6	Lin, Calc Int	-567.0	101800	0.00000	0.999993
Cr 267.716	6	Lin, Calc Int	95.1	51560	0.00000	0.999997
Cu 324.752	6	Lin, Calc Int	-2097.0	301600	0.00000	0.999981
Fe 259.939	6	Lin, Calc Int	445.8	119200	0.00000	0.999995
K 766.490	6	Lin, Calc Int	311.1	3598	0.00000	0.999855
Mg 279.077	6	Lin, Calc Int	78.0	9680	0.00000	0.999981
Mn 257.610	6	Lin, Calc Int	4975.4	625900	0.00000	0.999989
Mo 202.031	6	Lin, Calc Int	-40.5	8547	0.00000	0.999998
Na 588.995	6	Lin, Calc Int	1040.4	17850	0.00000	0.999913
Ni 232.003	6	Lin, Calc Int	34.3	12720	0.00000	0.999996
Sr 421.552	6	Lin, Calc Int	4080.2	755500	0.00000	0.999988
Zn 213.857	6	Lin, Calc Int	118.7	77070	0.00000	0.999996
Sn 189.927	6	Lin, Calc Int	9.4	2952	0.00000	0.999996
Co 228.616	6	Lin, Calc Int	201.9	65430	0.00000	0.999995
Li 670.784	6	Lin, Calc Int	842.6	120600	0.00000	0.999978
B 208.957	6	Lin, Calc Int	235.2	15280	0.00000	0.999935
Pb 220.353	6	Lin, Calc Int	48.7	4438	0.00000	0.999979
P 214.914	6	Lin, Calc Int	12.3	1362	0.00000	0.999986

Linear dynamic range
up to 5.0 mg/L P

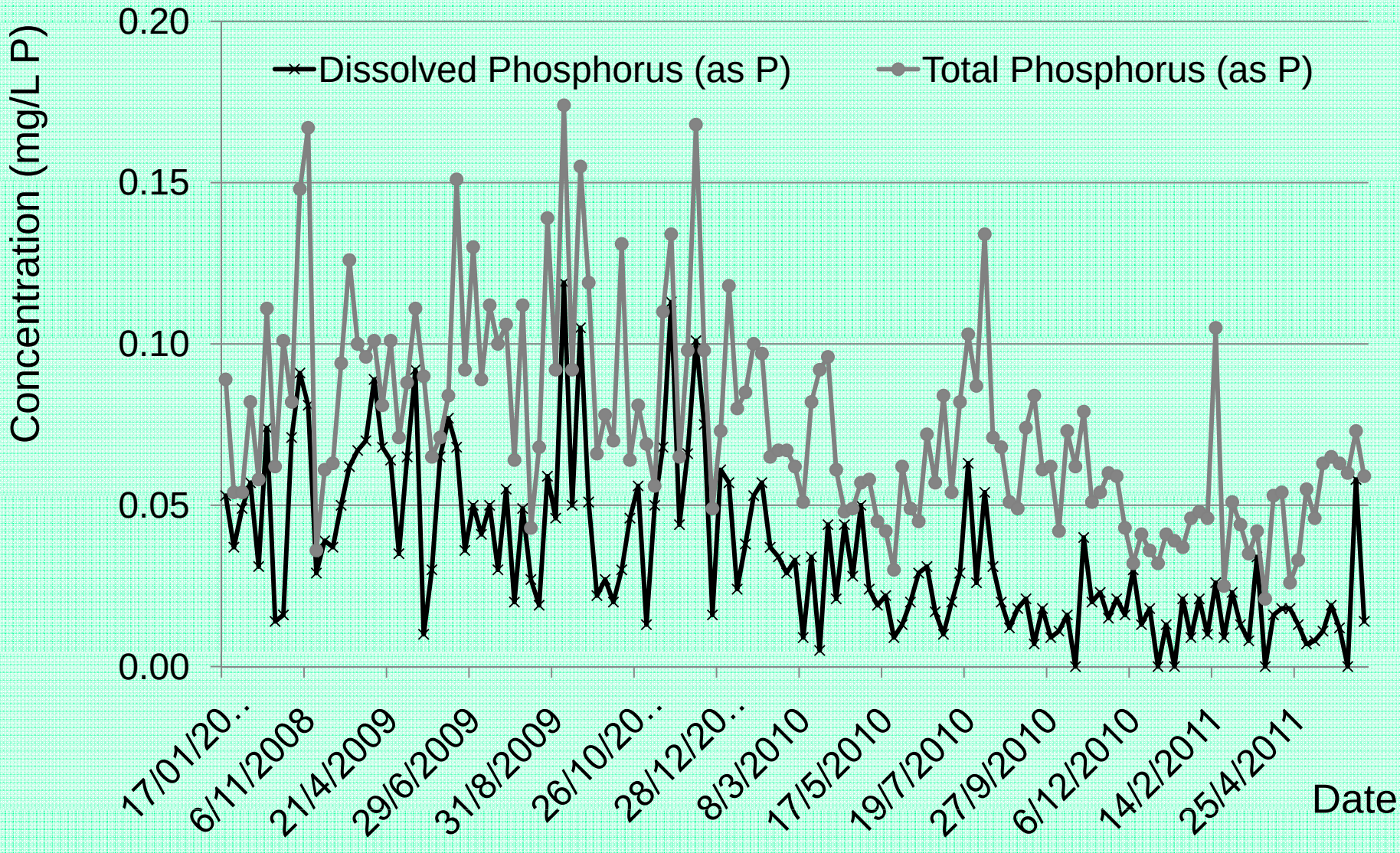
Corr. Coefficient >0.999

Reservoir and Catchment Water

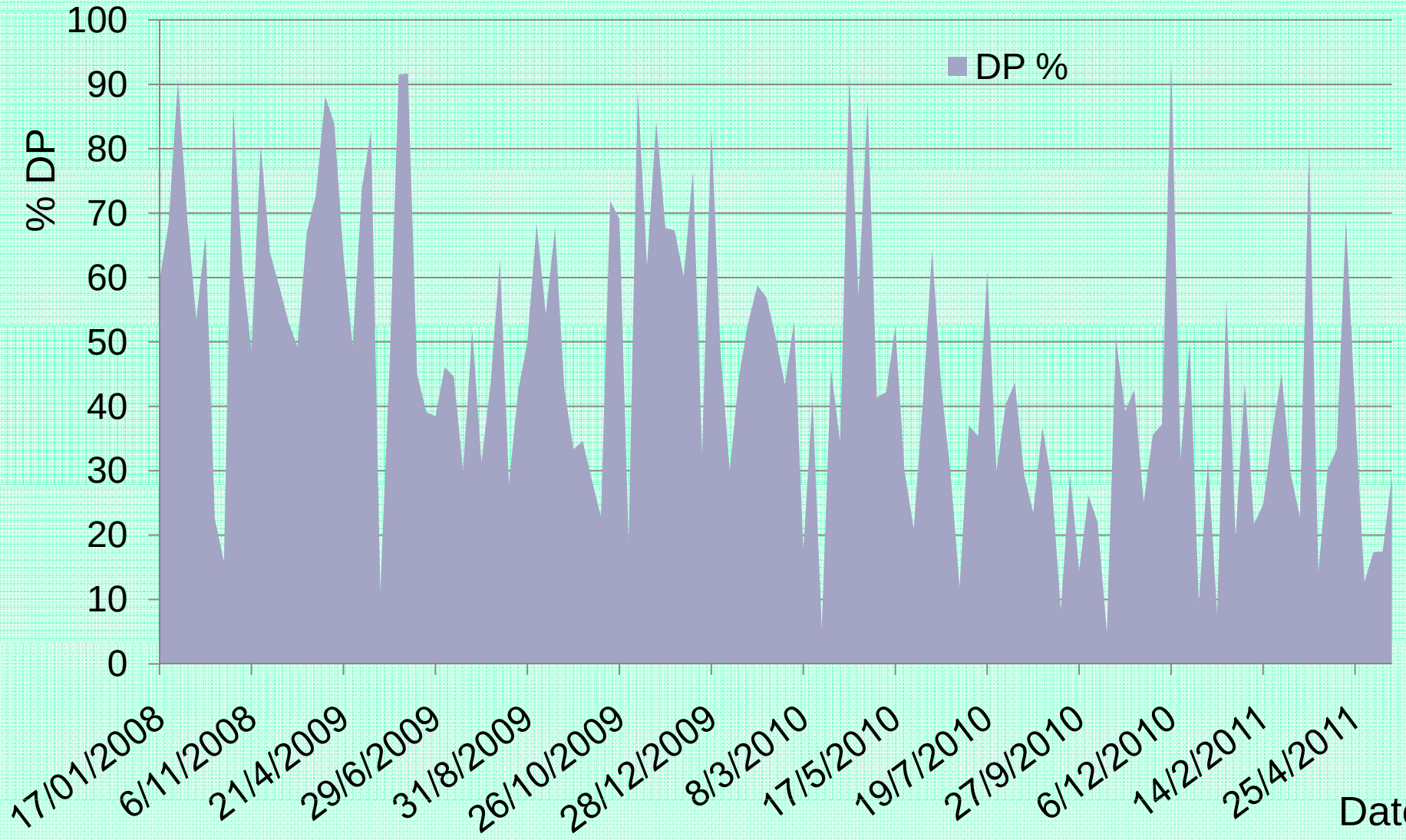
- Total Phosphorus (TP)
  - Acid digestion
  - 50 mL of sample into digestion vessel
  - 1.5 mL conc. HNO_3 (3% v/v HNO_3)
  - 0.5 mL conc. HCl (1% v/v HCl)
  - Digest for 4 h at 95^{o}C hot block
  - Top up to 50 mL with DI water

- Dissolved Phosphorus (DP)
  - Filter 50 mL of sample through 0.45 µm filter membrane (Nylon)
  - Steps as per that of TP

Monitoring of Reservoir Water Quality



Monitoring of Reservoir Water Quality



Sediment

Some forms of P in sediment may release into river and lakes.

- Sequential extraction procedures
  i. Hieltjes-Lijklema[1]
  ii. Williams[2]
  iii. Golterman
  iv. Ruttenberg

- Hieltjes and Lijklema method
  – 1.0 M NH_4Cl, extract for 2 h, 2 times
  – 0.1 M NaOH, extract for 17 h
  – 0.5 M HCl, extract for 24 h

[1]A. H. M. Hieltjes and L. Lijklema, *J. Environ. Qual., 1980,* **3,** 405
[2]J. D. Williams, T. Mayer and J. O. Nriagu, *Soil Sci. Soc. Am. J.,* 1980, **44,** 462

Phosphorus extraction from sediment

- Hieltjes and Lijklema scheme

Dried sample (1.0 gm)

Loosely-bound P (Exchangeable P)	
1.0 M NH_4Cl (50 mL)	2 h x 2

Al / Fe-bound P	
0.1 M NaOH (50 mL)	17 h

Ca-bound P	
0.5 M HCl (50 mL)	24 h

Sediment

- Hieltjes and Lijklema scheme

  - Each extractant was adjusted to pH 7.0
  - Centrifuged at 300 rpm for 30 min
  - Each filterate was forced through 0.45 µm membrane
  - Further dilutions before introduction into ICP-OES for phosphorus analysis

Fractionation of Phosphorus in Sediments

(mg/kg, dry weight)	Marina A	Marina B	Marina C	Punggol	Upper Pierce
Total P	520	1060	462	3580	204
Loosely bound P	21.4	6.5	18.2	665	1.81
Fe/Al bound P	140	590	93	2275	157
Ca bound P	197	280	196	386	15.0
Organic P	162	184	156	255	30.2
Water content (%)	73.5	79.9	69.5	63.9	44.5
Fe	39,200	40,200	32,700	29,700	3,180
Al	89,000	81,500	58,500	79,900	1,650
Ca	9,260	7,190	18,800	7,520	211

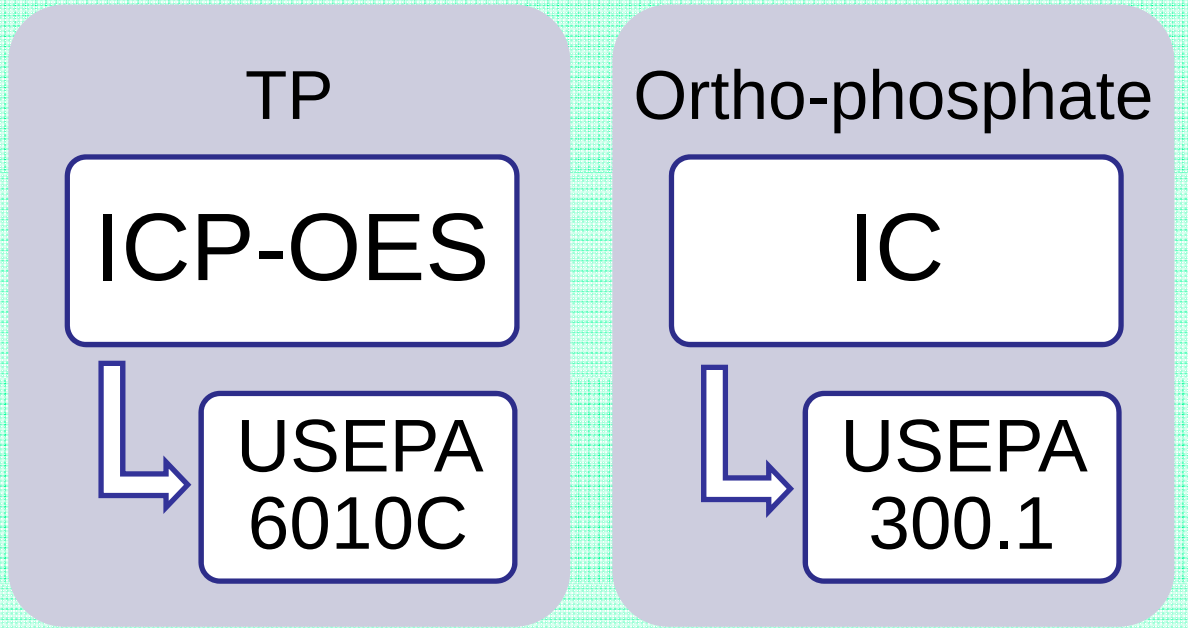
Fractionation of Phosphorus in Sediments

Composition (%)	Marina A	Marina B	Marina C	Punggol	Upper Pierce
TP (mg/kg)	520	1060	462	3580	204
Loosely bound P	4.12	0.61	3.94	18.6	0.89
Fe/Al bound P	26.9	55.7	20.1	63.5	77.0
Ca bound P	37.9	26.4	42.4	10.8	7.35
Organic P	31.2	17.4	33.8	7.11	14.8

Detergents

- Phosphorus-containing detergents: a potential pollutant, discharged to drainage system
- To determine the concentration of ortho-phosphate and total phosphorus present in commercial detergents

Method used



Detergent

- Determination of Total Phosphorus (TP) by ICP-OES
- Sample digestion
- Operating conditions
  - PerkinElmer Optima 5300DV
  - Argon flow: 15 L/min
  - Auxiliary flow: 0.2 L/min
  - Nebulizer flow: 0.65 L/min
  - RF Power: 1350 W
  - Axial view
  - P (214.914 nm)

Detergents

- Determination of Ortho-phosphate (PO_4) by IC with conductivity detection
- Operating conditions
  - Dionex ICS-3000
  - Guard column, Dionex IonPac AG9-HC, 4 x 50 mm
  - Separation column, Dionex IonPac® AS9-HC, 4 x 250 mm
  - ASRS 45 mA
  - Sample loop of 50 µL
  - Eluent, 9.0 mM Na_2CO_3 at 1.00 mL/min

Detergents (powder form)

Sample	TP (mg/kg)	OP (mg/kg)
UIC (Bio)	8.32	7.73
Attack	60.2	52.2
Fairprice detergent	93.2	28.7
Downy	44.4	1.30

Detergents (liquid form)

Sample	TP (mg/L)	OP (mg/L)
Kiwi Kleen	5.68	2.56
Mama Lemon	156	106
Amorall	61.9	46.9
Essence	3.85	3.75
Woolite	381	25.4
UIC (liquid)	56.4	8.32
Dynamo	516	5.74

Conclusions

- ICP-OES (USEPA Method 6010C) with sample preparation: Good for the testing of total P and dissolved P in reservoir and catchment freshwater.
- Better than spectrometry, especially in the case of low levels of P
- Phosphorus in sediments can be fractionated by sequential extraction and ICP-OES analysis
- Levels of phosphorus in household detergents varied much

Acknowledgement

- Special thanks to PUB colleagues
  - Sampling team
  - Inorganic Chemistry Laboratory


Thank You~~~
Water for All
Conserve, Value, Enjoy
PUB