A Preliminary Phosphate Study of Selected Sites Along the Shanghai Tributary of the Yangtze River; Undergraduate International Student's Freshman Project in an Interconnected World (Student Poster-Paper)

Mr. Junyi Ying, Shanghai

Junyi Ying (Eric), a senior high school student in Shanghai, China, spent two weeks actively engaged in a research project involving the colorimetric analysis of phosphates in designated locations along the Shanghai tributary of the Yangtze River. Ying is a student at Shanghai Guanghua College. He is an excellent student seeking to pursue a career in chemistry at a major US University commencing the 2018-2019 academic year.

He has received several outstanding accommodations for his work in honors chemistry at Shanghai Guanghua College.

Mr. Cyrus Safai

Cyrus is an undergraduate student majoring in Mechanical Engineering at Salt Lake Community College (SLCC). Cyrus has teamed up and worked with a group of four other students from Mechanical, Civil, Electrical, and Computer engineering departments on the Vertical, Hydroponic, Smart Garden With Global and Universal (Space) Applications. He has worked at the SLCC Slick Science Summer Camp for the past 7 years.

Mr. Junior onyeagba

Junior Onyeagba, a former student at Salt Lake Community College, who is currently attending the University of Utah with the purpose of attaining a Bachelor's degree in Biology with cell and molecular emphasis. Junior has worked with phosphate over a year now with the intention of finding a more effective way to measure the concentration of phosphate in waterbodies using Flow Injection Analysis.

Dr. Nick M. Safai, Salt Lake Community College

Dr. Nick M. Safai has been an ASEE officer and member for the past 24 years. He has been the six-time elected as the Program Chair of the ASEE International Division for approximately the past 13 years. Nick has had a major role in development and expansion of the division. Under his term as the International Division Program Chair the international division expanded, broadened in topics, and the number of sessions increased from a few technical sessions to over eighteen sessions in the recent years. The ASEE International Division by votes, has recognized Nick's years of service through several awards over the past years. Nick has been the recipient of multiple Service awards (examples: 2010, 2006, 2004, 1996), Global Engineering Educators award (example: 2007, 2005), Best Paper award (examples: 2010, 2005, 2004, 1995) and other awards from the International Division for exceptional contribution to the international division of the American Society for Engineering Education. Examples of some Awards from other Professional Organizations: • American Society of Civil Engineers (ASCE): Engineering Educator of the Year Award 2004. • Utah Engineers Council, UEC: Engineering Educator of the Year 2005 award, in recognition of outstanding achievements in the field of engineering and for service to society. • SLC Foundation; Salt lake City, Utah: Teaching Excellence Award 2004. • American Society of Civil Engineers (ASCE): Chapter faculty Advisor recognition award 2002. • Computational Sciences and Education; recognition for outstanding contributions and for exemplary work in helping the division achieve its goals1998. • Engineering Division; recognition for outstanding contributions and for exemplary work in helping the division achieves its goals 1995. • Science and Humanities; recognition for outstanding contributions and for exemplary work in helping the fields achieve its May 1994. • Math & Physical Sciences; appreciation for academic expertise February 1994.

Academics: Nick Safai received his PhD degree in engineering from the Princeton University, Princeton, New Jersey in 1979. He also did a one year post-doctoral at Princeton University after receiving his degrees from Princeton University. His areas of interest, research topics, and some of the research

studies have been; • Multi-Phase Flow through Porous Media • Wave propagation in Filamentary Composite Materials • Vertical and Horizontal Land Deformation in a De-saturating Porous Medium • Stress Concentration in Filamentary Composites with Broken Fibers • Aviation; Developments of New Crashworthiness Evaluation Strategy for Advanced General Aviation • Pattern Recognition of Biological Photomicrographs Using Coherent Optical Techniques Nick also received his four masters; in Aerospace Engineering, Civil Engineering, Operation Research, and Mechanical Engineering all from Princeton University during the years from 1973 through 1976. He received his bachelor's degree in Mechanical engineering, with minor in Mathematics from Michigan State. Nick has served and held positions in Administration (Civil, Chemical, Computer Engineering, Electrical, Environmental, Mechanical, Manufacturing, Bioengineering, Material Science), and as Faculty in the engineering department for the past twenty seven years.

Industry experience: Consulting; since 1987; Had major or partial role in: I) performing research for industry, DOE and NSF, and II) in several oil industry or government (DOE, DOD, and NSF) proposals. Performed various consulting tasks from USA for several oil companies (Jawaby Oil Service Co., WAHA Oil and Oasis Co., London, England). The responsibilities included production planning, forecasting and reservoir maintenance. This production planning and forecasting consisted of history matching and prediction based on selected drilling. The reservoir maintenance included: water/gas injection and gas lift for selected wells to optimize reservoir production plateau and prolonging well's economic life.

Terra Tek, Inc., Salt Lake City, UT, 1985-1987; Director of Reservoir Engineering; Responsible of conducting research for reservoir engineering projects, multiphase flow, well testing, in situ stress measurements, SCA, hydraulic fracturing and other assigned research programs. In addition, as a group director have been responsible for all management and administrative duties, budgeting, and marketing of the services, codes and products.

Standard oil Co. (Sohio Petroleum Company), San Francisco, California, 1983-85; Senior Reservoir Engineer; Performed various tasks related to Lisburne reservoir project; reservoir simulation (3 phase flow), budgeting, proposal review and recommendation, fund authorizations (AFE) and supporting documents, computer usage forecasting, equipment purchase/lease justification (PC, IBM-XT, Printer, etc.), selection/justification and award of contract to service companies, lease evaluation, economics, reservoir description and modeling, lift curves, pressure maintenance (gas injection analysis, micellar-flooding, and water-flooding), Special Core Analysis (SCA), PVT correlations, petrophysics and water saturation mapping.

Performed reservoir description and modeling, material balance analysis. Recovery factors for the reservoir. Administrative; coordination and organization of 2 and 6 week workplans, 1982 and 1983 annual specific objectives, monthly reports, recommendation of courses and training program for the group. Chevron Oil Company, 1979- 1983; Chevron Overseas Petroleum Inc. (COPI), San Francisco, California 1981-1983. Project Leader/Reservoir Engineer, Conducted reservoir and some production engineering work using the in-house multiphase model/simulators. Evaluation/development, budgeting and planning for international fields; Rio Zulia field – Columbia, Pennington Field – Offshore Nigeria, Valenginan, Grauliegend and Rothliegend Reservoir – Netherlands. Also represented COPI as appropriate when necessary.

Chevron Geo-Sciences Company, Houston, TX, 1979-1980 Reservoir Engineer Applications, Performed reservoir simulation studies, history matching and performance forecasting, water-flooding for additional recovery (Rangeley Field – Colorado, Windalia Field – Australia), steam-flooding performances (Kern River, Bakersfield, California), gas blowdown and injection (Eugene Island Offshore Louisiana) on domestic and foreign fields where Chevron had an interest, using Chevron's CRS3D, SIS and Steam Tube simulator programs.

Chevron Oil Field Research Co. (COFRC), La Habra 1978-1979, California. Research Engineer, Worked with Three-Phase, Three-Dimensional Black Oil Reservoir Simulator, Steam Injection Simulator, Pipeflow #2. Also performed history matching and 20-year production forecast including gas lift and desalination plants for Hanifa Reservoir, Abu Hadriya Field (ARAMCO).

Dr. David Richardson, Salt Lake Community College

Education background for Dave Richardson:

B.A. in Chemistry and Mathematics from Oakwood College

M.S. in Organic Chemistry from Purdue University

Ph.D. in Physical Organic Chemistry from Utah State University, Dissertation topic: Proton Magnetic Resonance Spectroscopy of Alcoholic Metal Solvation

Dave Richardson has more than thirty years of teaching and administrative experience in a variety of institutions including Salt Lake Community College, Riverside Community College, Oakwood College, Alabama A and M University, University of Alabama, and Kentucky State University.

In 2007, Richardson retired as Vice President for Academic Affairs from Salt Lake Community College. Since his retirement, he has been actively involved in education as an interim dean in the School of Business and an Interim Dean for the Library. Also, since he retired, he has been an adjunct chemistry professor at the College. In addition to his professional activities, Dave and his son, Dave, Jr., created Next Level Outreach (NLO), a non-profit organization established for coordinating domestic and international mission service projects.

Dave is Vice President of the Utah Chinese Center, a non-profit organization that exists for the purpose of helping bridge relationships between China and the United States.

Dave has completed the second edition of his comprehensive organic chemistry book that is scheduled for publication in an ”i-book” format, and he looks forward to serving the College once again as the Interim Dean for the School of Humanities and Social Sciences.

Dr. Peter Joseph Iles, Salt Lake Community College
Dr. Rajan P Kochambilli, Salt Lake Community College

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Junyi Ying
Student from Shanghai, China
Cyrus Safai
Junior Onyeagba
Students: Salt Lake Community College

In Collaboration with

Dr. Nick M. Safai: Professor
Dr. Peter Iles, Professor
Dr. David Richardson, Interim Dean
Dr. Rajan Kochambilli, Instrumentation coordinator

Salt Lake Community College, Salt Lake City, Utah

(Student Poster-Paper ASEE Annual Conference)

Abstract:

This paper discusses the proposed quantitative analyses of phosphate along selected sites of the Yangtze River (the Shanghai tributary). Phosphates are major nutrients in the eco-system; consequently, excessive phosphates result in algal bloom that changes dissolved oxygen levels in the aquatic system. The research initiative identifies five sites selected for their differences in population densities and land utilization. Samples from each site will be analyzed for phosphate content to ascertain if there are correlations between population densities and land utilization with respect to phosphate content. Samples were acquired from sparsely populated environments, industrial environments, and densely populated area. The samples were en-route to the United States; consequently, analyses of the sample started early February and have been performed for phosphates during February which are included in this paper. The early research projects of this nature / type during the freshman year of the student college-years motivates and increases the student's interest in science and engineering disciplines and encourages them to pursue further education in these fields.

This paper will focus on the Preliminary Phosphate Study (FIA) and discuss the results of the experiments and the detection conditions performed. Future work would involve measurement of other nutrients such as nitrate and potassium levels and comparisons made to see if there is correlation between the nutrients and the sites tested so far in this work. Also future paper would discuss and present how this type of early research study increases interest, teamwork, leadership abilities in the freshman minority and international students.

Background:

The study presented in this paper discusses the research performed by an international student dealing with the data collected from his hometown, while studying science and engineering at a College in the USA, performing the research under the direction and guidance of the faculty at the college in the USA.

The research project involves an international student from China, studying the amount of phosphates and any other toxic material in Zhejiang River (within 10-20 miles of Shanghai, China) and its environmental impact on rural and urban areas, and any other possible unforeseen and unexpected impacts. Food and its availability is of major concern in various regions of the world, especially in the underdeveloped communities. Furthermore if the water is used downstream for farming, there might be additional concerns. This also impacts the quality and life of aquatic creatures (especially fish) and wildlife. The water samples are taken at various locations of the river. They are then shipped to the college in the USA. The laboratory experiments are performed to analyze each sample at this college. The laboratory results are analyzed and conclusions are drawn based on the data from the lab experiments.

Introduction:

Five total sites were considered, three sets of samples were obtained from the Shanghai tributary of the Yangtze River from each of the following proximal locations: *The Bund*; Lanzhou Road and Yanshupu Road; and the Forest Park Region. Samples were collected just along the sides of the *Bund*, Lanzhou Road, and Yanshupu Road sites. Samples were collected at approximately 10.0 m (cut significant figures) from sites of the Ship Factory, the Shanghai Grain Oil Industry Company, and the Forest Park Region. These sites were selected because of their population densities and use by the indigenous populations.

The densely populated area along Lanzhou and Yangshupu Roads along the Yangtze River provide a site that might contribute to a greater concentration of phosphates contributed by the cluster of people who reside in the area.

The Bund and Forest Park (1 km^2), primarily used by the tourism industry, are sparsely populated areas void of residential housing. The phosphate concentrations in these areas might be lower since they have no indigenous populations but have visitors who are discouraged from leaving any waste at the sites.

The Ship Factory is one of the 500 largest industrial enterprises in China and has more than seventy years of industrial history with in the Shanghai geographic region. The Grain Oil Industry Company produces edible oil and rice. These sites might contribute to greater phosphate concentrations resulting from industrial waste.

The phosphate concentrations will be charted to determine if there is a difference between population densities and land utilization.

Data Collection Areas:

To investigate the phosphate content in various locations of the Shanghai tributary of the Yangtze River fifteen (30.0 mL cut) samples were collected close to Lanzhou and Yangshupu Roads, residential areas; the Bund and Forest Park, tourist attractions and non-residential areas; and Ship Factory and Grain Oil Industry Company, industrial areas.

Samples:

Five samples were collected from each area providing a total of fifteen (30.0 mL cut) water samples. All containers and instruments that came in contact with the samples were previously cleaned with ultra-pure water to avoid contamination. Water samples were filtered to remove large particles.

Experimental and Methodology:

Phosphate estimations in the water samples were done using the following chemistry:

$$PO_4^{3-} + 12MoO_4^{2-} + 27H^+ \rightarrow H_3PO_4(MoO_3)_{12} + 12H_2O$$

The phosphomolybdic acid on reduction produces the blue color.

$$H_3PO_4(MoO_3)_{12} \text{ ------} \rightarrow \text{ phosphomolybdenum blue}$$

Flow Injection Analysis (FIA) detection conditions were at λ_{max} = 720 nm and background correction was set at at 414 nm (based on the UV spectrum) . The standard stock solution containing 0.2197g of oven–dried potassium dihydrogen orthophosphate in 500.0 ml of pure water was diluted to the required standard concentrations in the ppb range.

Ten (10) g of Ammonium molybdate was dissolved in 1.0 L pure water containing 35 mL concentrated sulphuric acid . Two-tenths (0.2) g Tin(II) chloride and 2 g hydrazinium sulphate were dissolved in 1 L pure water containing 28 mL of concentrated sulphuric acid to prepare the reducing agent. The reagents were introduced into the flow system (Figure 1) using a peristaltic pump (Gilson miniplus* 3). Samples were introduced through an injection valve (Valco Instruments Co. Inc). 250μL injection loop.

Equipment & Software Involved:

- Agilent Cary 8454 UV Vis Spectrophotometer
- Chemstation Software G1117AA

- Gilson miniplus* 3
- Valco Instruments Co. Inc. , using the 6 port loop injection valve.

Absorption was measured using an Agilent Cary 8454 UV-Vis Spectrophotometer running chemstation software G1117AA. FIA detection conditions were λ_{max} at 720 nm and background correction at 414 nm (based on the UV spectrum) . All solutions and reagents were prepared with ultra-pure water and all reagents were of AnalaR grade or equivalent.

Laboratory Set up and Testing:

The following figures illustrates the laboratory set up for these experiments, the room and the equipment involved.

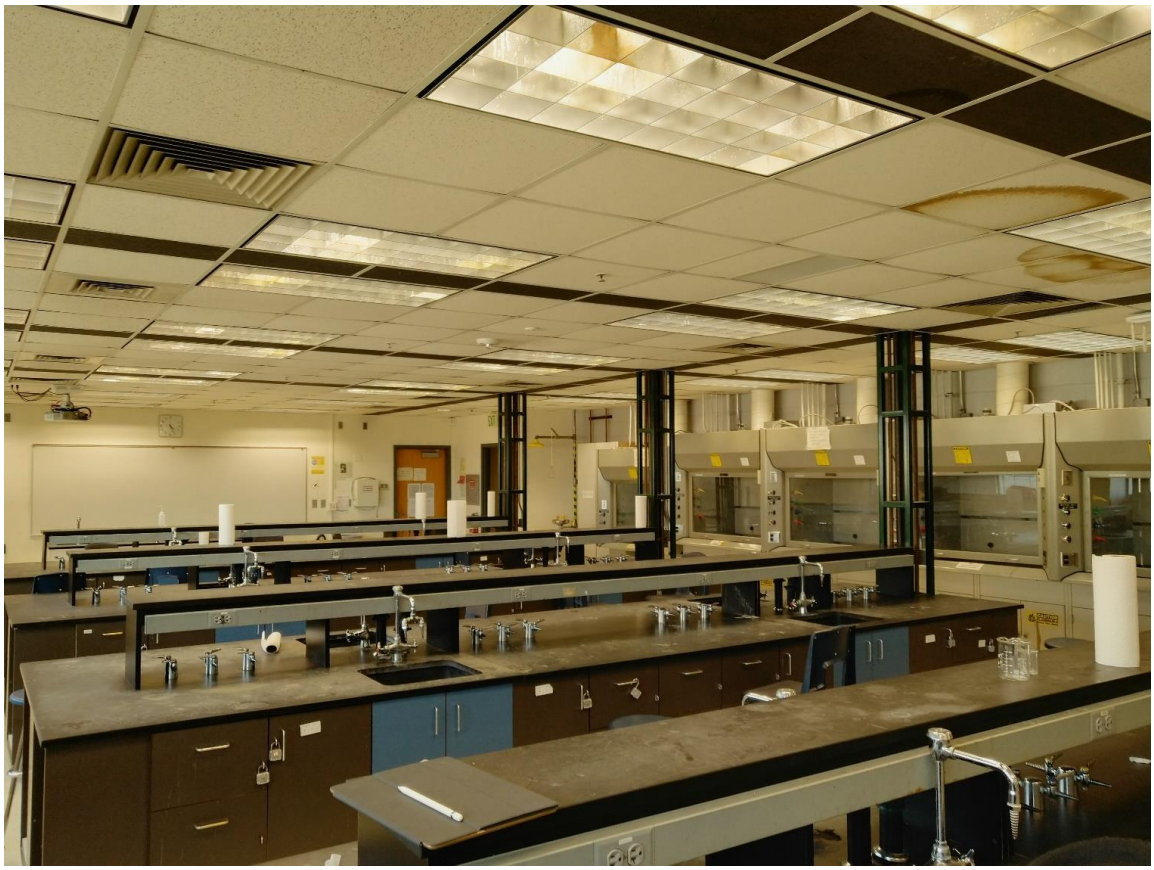


Figure 1: Shows the laboratory used for this study

Figure 2: International and Minority students running the experiment

The students and personnel were instructed to handle the waste material treated as containing heavy metal toxins. This was exercised throughout the study.

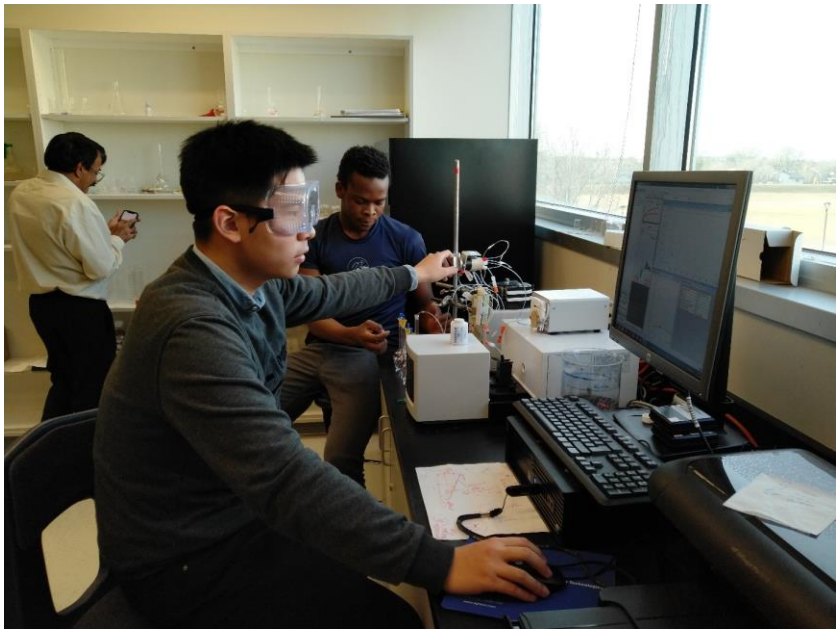


Figure 3: Personnel and International and Minority students at work

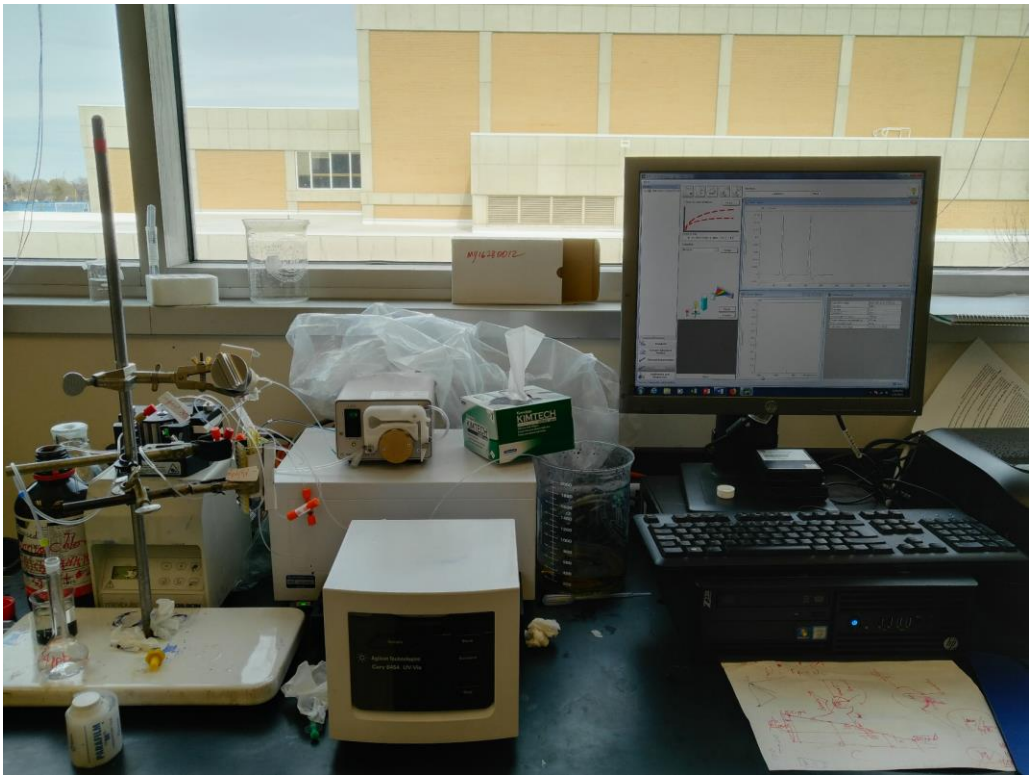


Figure 4: Illustrates FIA system and the UV-Vis Spectrophotometer

These early freshman students (first semester) needed to be first taught about each equipment, their operations and functions. The training of the lab procedures as well as becoming familiar with the equipment took several days. Students also ran a few test experiments using the water samples from the Salt Lake area. This is due to the fact that we could not afford losing the real samples from Shanghai, China unnecessarily. Therefore there would be no wasting of the Samples from Shanghai due to difficulty and complications in acquiring more samples.

Figure 5: Left and Right are Images of the Peristaltic Pump and FIA set up.

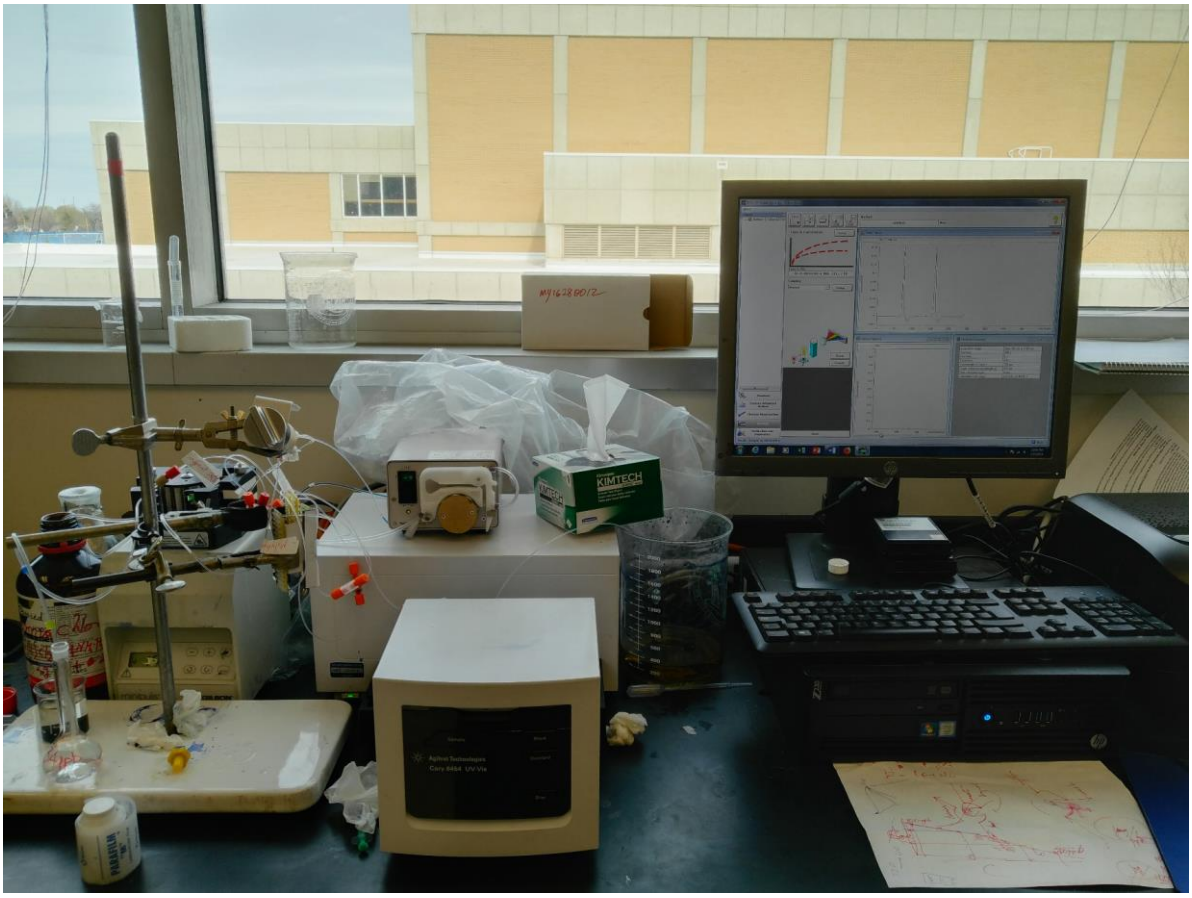
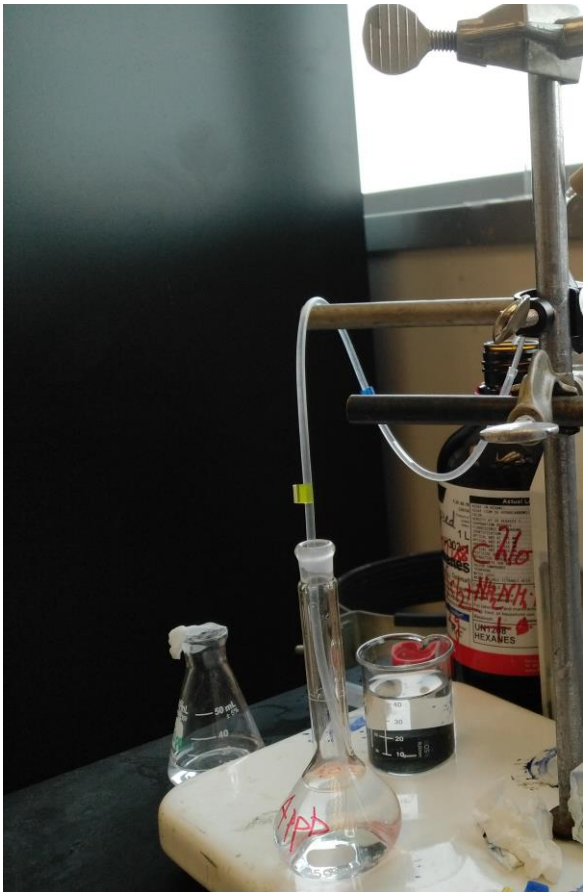


Figure 6: FIA system and Injector Wall in front of the Peristaltic Pump

The waste is collected in the container as shown and is discarded in a safe and according to the guideline, rules and standards as specified by the state.



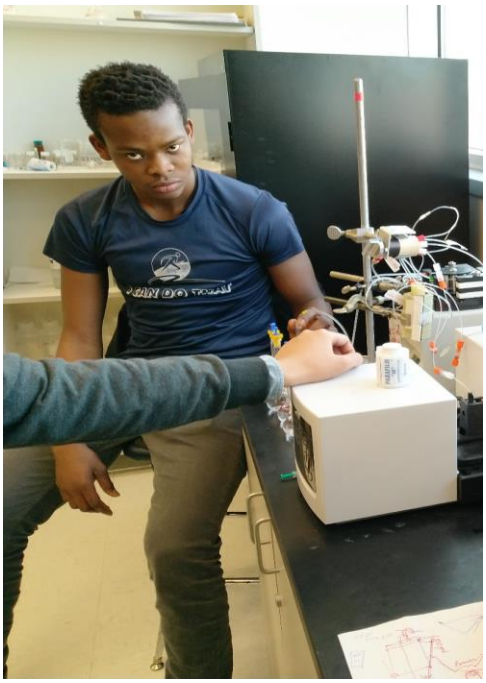
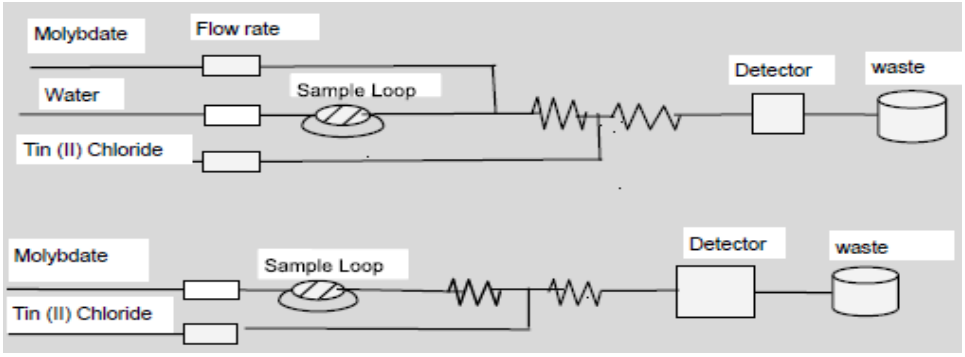


Figure 7: Left and Right photos are the NMR Machine in black, as is shown in the background in both photos.

Experiment Schematic:

The overall FIA manifolds schematic are illustrated below.



The sample analyses used the lower manifold in the diagram which is shown above.

The experiment in specific involved detector, waste, the sample loop, molybdate and tin (ll) chloride. The Flow Manifold schematic is illustrated in Figure 8, as shown below.

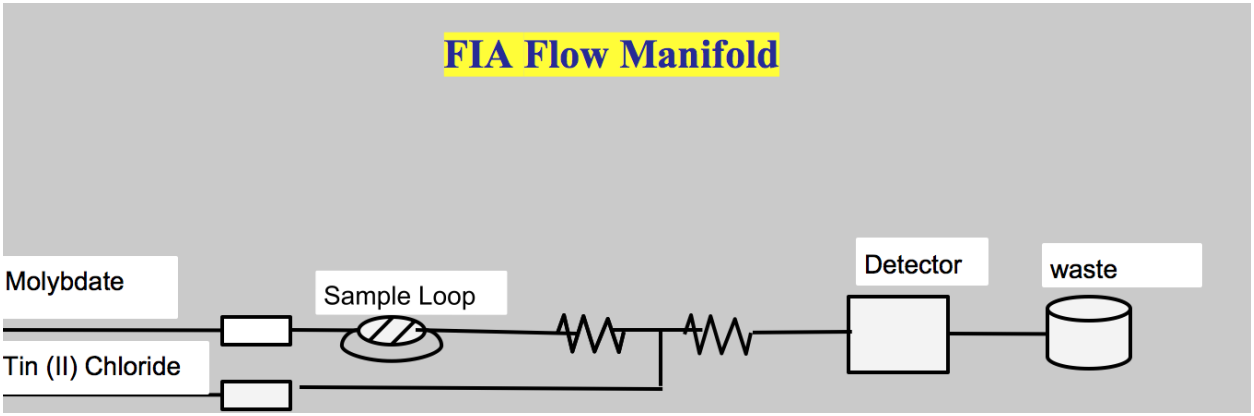


Figure 8. The FIA Flow Manifold is illustrated above

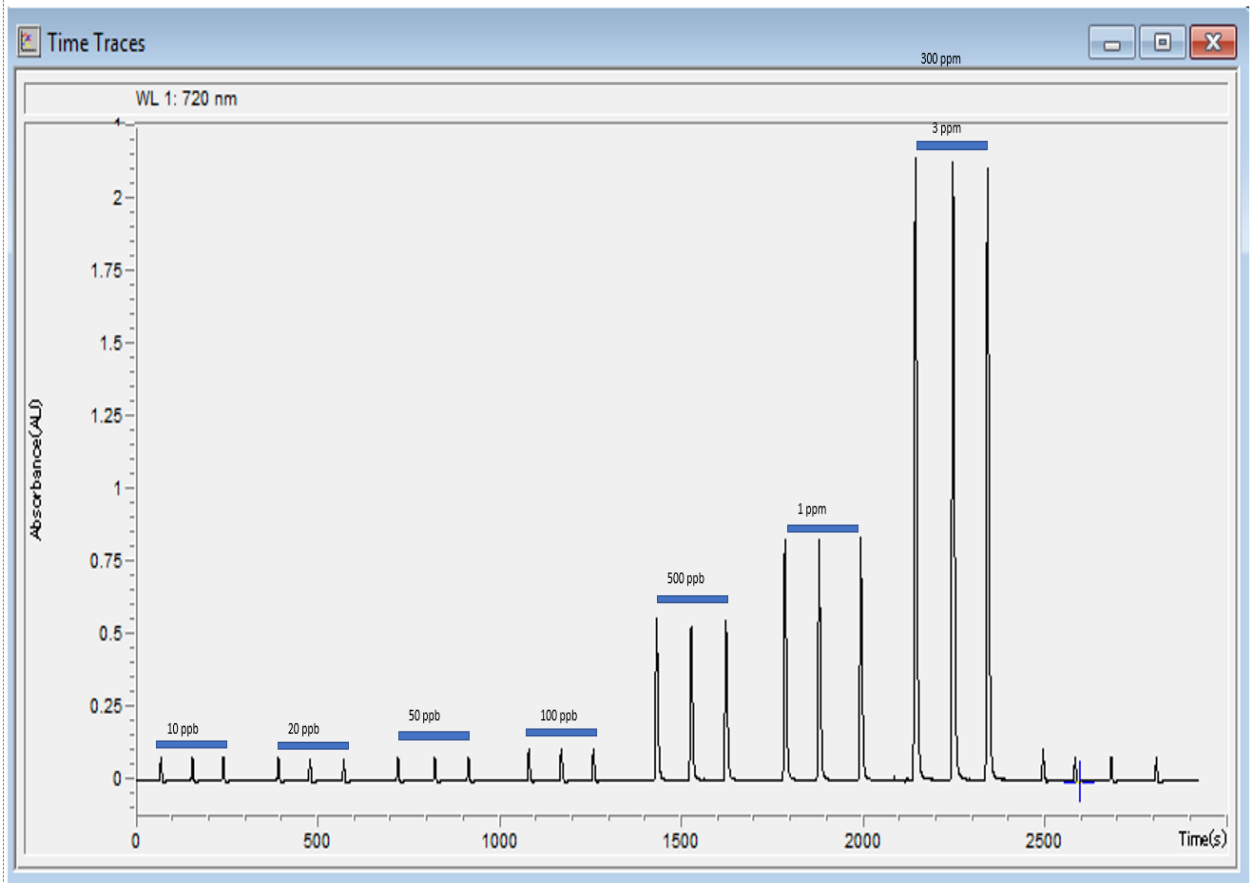
In the initial experiments, water was used as carrier. Both water and molybdate were pumped at 1.0 mL/min rate, while the Tin(II)chloride solution was maintained at 1.5 mL/min flow rate. Since the detection limit was high under these conditions, water flow was eliminated and the Molybdate solution was used as the carrier, avoiding further dilution and all tubing in the flow systems were 0.5 mm id resulting in better detection limits.

Results and Conclusions:

The samples were received in good condition with each sample properly sealed and labeled. However, calibration, system cleaning, purification and other procedures had to be first implemented before the actual experiments could be conducted.

A calibration and analysis method which allows detection of dissolved phosphate concentration in water resources to 10 ppb levels was developed. The samples needed filtration, since they were collected from the river sites and immediately sealed without any preliminary processing.

Initial runs were conducted with 30 uL cell having 10 mm pathlength at 15 speed on pump. This limited our detection limit to 50 ppb and all of the samples had levels close to the 50 ppb or lower concentrations. The sensitivity was not good enough to detect lower concentrations with the run conditions used as shown in the diagram below.



Peaks for of 10, 20, 50, 100, 500 ppb and 1,3 ppm samples at 15 speed and 30 µL concentrations of Phosphate ions.

The last run (quadruplicate) was done with one of the samples. So a study to increase sensitivity by varying the pump speed (flow rate) at different flow cell volumes was conducted.

The results in the table below show that the 80 µL cell with 10 mm path length and 5 speed at the pump gives best response to the phosphate concentrations. (The 30 µL flow cell had problems with small bubbles getting trapped in the measurement window.)

Cell volume	Path Length	speed	peak1	peak2	peak3	average
80µL	10mm	15	1.43058	1.42046	1.41552	1.422187
		10	1.79013	1.80489	N/A	1.79751
		5	1.92902	1.90756	N/A	1.91829
		3	1.70524	1.65633	N/A	1.680785

Cell volume	Path Length	speed	peak1	peak2	peak3	average
31µL	0.5mm	15	8.74E-02	8.66E-02	8.70E-02	8.70E-02
		10	0.103734	0.101431	N/A	0.102583
		5	0.114311	0.117311	N/A	0.115811
		3	0.13169	0.135155	N/A	0.133423
30µL	10mm	15	1.43129	1.42448	1.44387	1.433213
		10	1.53096	1.52945	N/A	1.530205
		5	1.53565	1.53034	N/A	1.532995
		3	1.50678	1.5135	N/A	1.51014
40µL	1mm	15	0.181046	0.17753	0.165813	0.174796
		10	0.225268	0.223938	N/A	0.224603
		5	0.245504	0.243107	N/A	0.244306
		3	0.259256	0.259868	N/A	0.259562

Repeat runs with different cell vol. and flow rates.

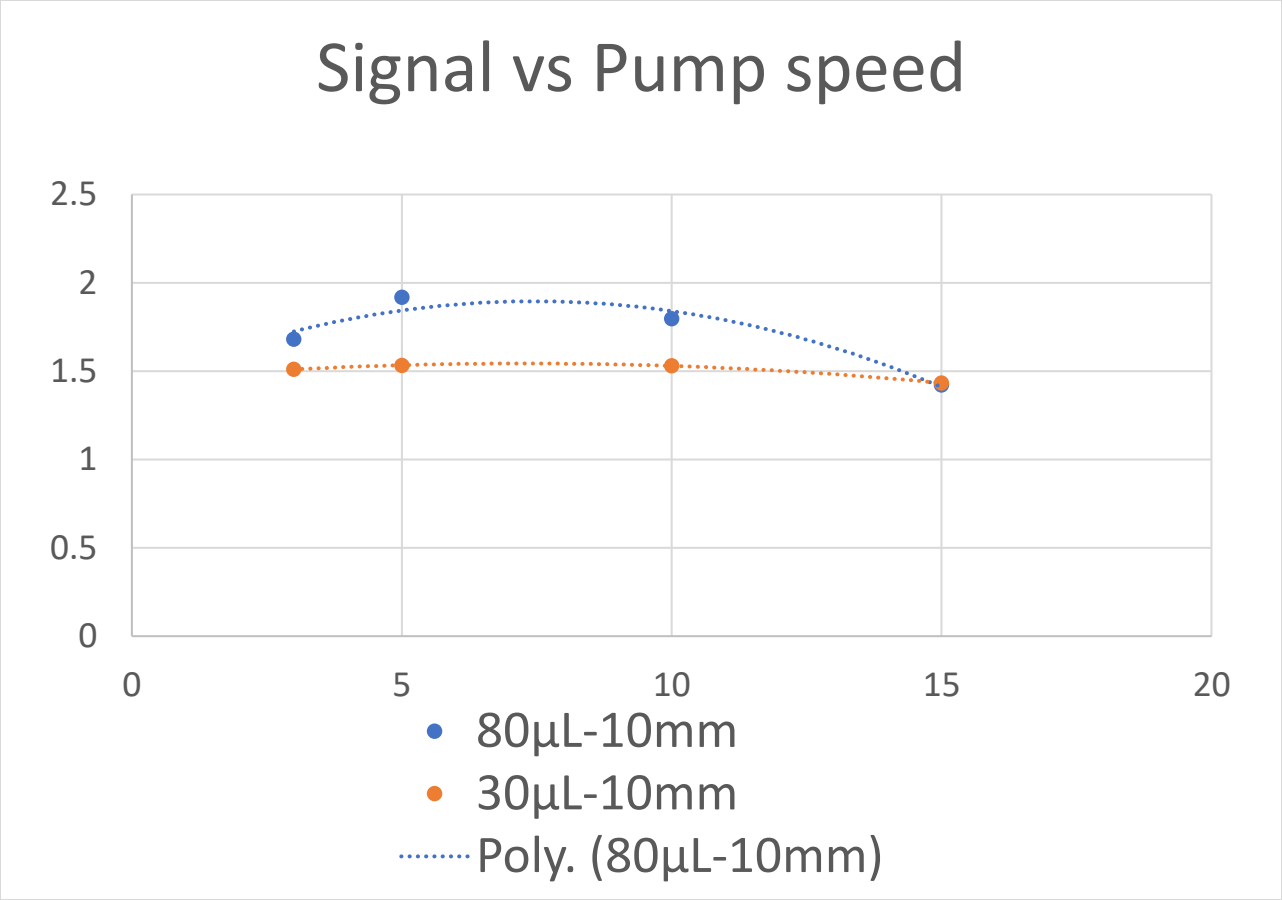
speed	80µL-10mm	31µL-0.5mm	30µL-10mm	40µL-1mm
3	1.680785	0.1334225	1.51014	0.259562
5	1.91829	0.115811	1.532995	0.244306
10	1.79751	0.1025825	1.530205	0.224603
15	1.422187	8.70E-02	1.4332133	0.174796

The highest response value is highlighted; these conditions were applied in further runs.

The highest response value was found to be at pump speed 5 and employing the 80µL flowcell and these conditions were applied for the analysis of the samples.

This highest response value is highlighted yellow in the above table. Also the precision by the Relative Standard Deviation of peak height from a full-page expanded print of the calibration peaks was measured to be 1-2% RSD.

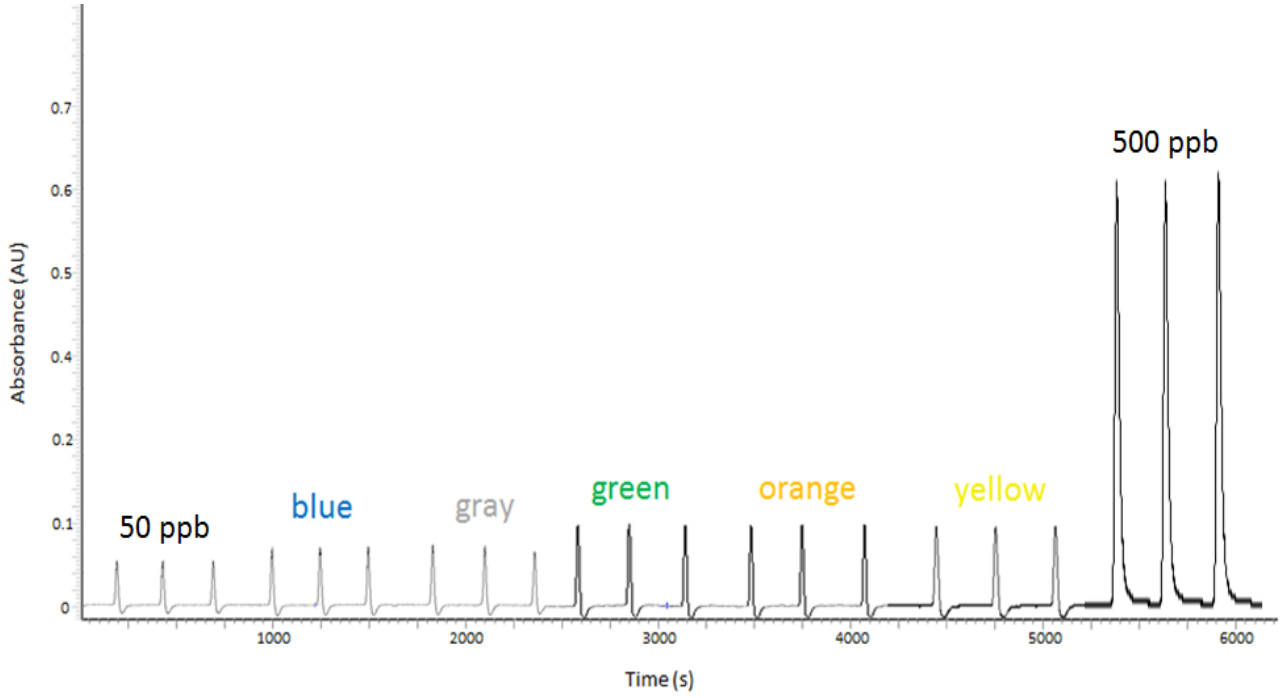
The signal versus the speed of the pump is illustrated in figure below. The highest response value was found to be at pump speed 5 and employing the 80µL flowcell, and these conditions were applied for the analysis of the samples



Calibration with 80 uL 10 mm path length flow cell using 5 speed at the pump is illustrated in the graph below.

The peak signal versus the concentration in parts per billion (ppb) is shown in the graph below, which it has exhibited an excellent linearity where the correlation coefficient squared was 0.9997.

The actual measurement with five unknown samples were conducted using the same parameters as the above calibration readings. Below are shown the results from Shanghai Tributary of the Yangtze River.



Key for the samples collected from each site.

兰州路区域（人口密集区） Lanzhou Rd. site (dense populated)

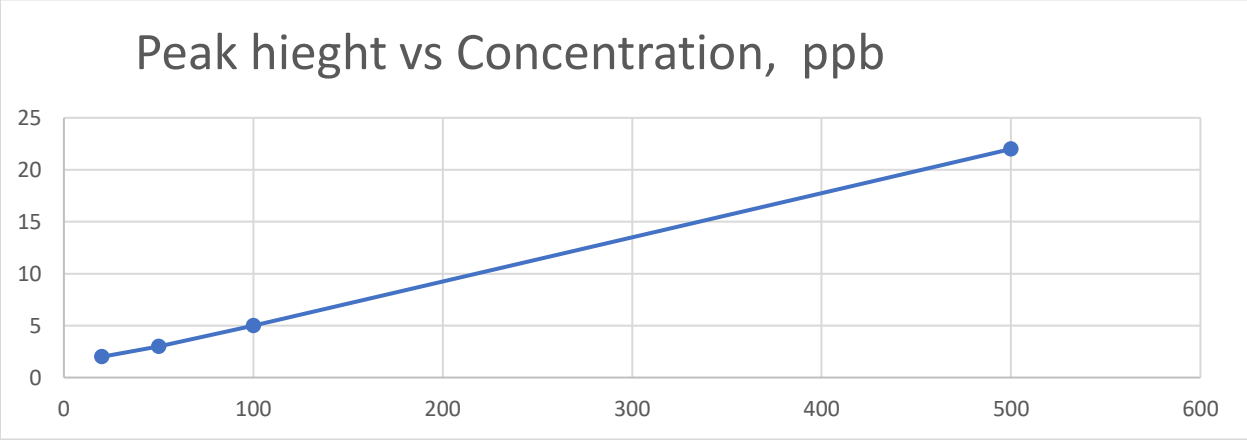
共青森林公园区域（人口稀少区）Gongqing Forest Park site (sparse populated)

粮油厂区域（工业区）grain and oil factory site (industrial)

外滩区域（人口稀少区） the Bund site (sparse populated)

浦东船厂区域（工业区） Pudong dockyard site (industrial)

The figure below illustrates clearly and shows calibration plot, used for the river samples, of absorbance versus concentration exhibited excellent linearity where the correlation coefficient squared was 0.9997.



The concentration for the five different sites where the samples were collected from are shown in Table 1 below.

ppb		Site
109		Lanzhou Rd (dense population)
109		Gongqing Forrest Park (sparse population)
152		Grain and oil factory (Industrial)
152		The Bund (sparse poplulation)
154		Pudong dockyard (industrial)

Table 1: Illustrates the concentration for the five different

In conclusion the results for the 5 river samples show higher values near industrial zones which is to be expected as more chemical activity from run off from the cleaning and maintenance of these sites is more probable. Future work could involve measurement of other nutrients such as nitrate and potassium levels and comparisons made to see if there is correlation between the nutrients and the sites tested so far in this work.

The new FIA highly sensitive method for phosphate developed by the chemistry department proved to be an ideal technique providing rapid, precise and reliable results and it was further shown to be easily adapted to these river samples.

References:

- Laura J Gimbert, Philip M Haygarth, Paul J. Worsfold. Talanta, Determination of nanomolar concentrations of phosphate in natural waters using flow injection analysis with a long path lenghtwaveguide capillary cell and solid-state spectrophotometric detection. 71 (2007) 1624-1628.

- Paul Worsfold, Ian McKelvie and Phil Monbet. Analytica Chimica, Determination of phosphorus in natural waters: A historical review. Acta 918 (2016) 8-20.

- Edward A Nagal, Ian D. Mckelvie, Paul Worsfold and Spas D. Kolev. Analytica Chimica The molybdenum blue reaction for the determination of orthophosphate revisited: Opening the black box,. Acta 890 (2015) 60-82.

- P. Monbet, I,D Mckelvie, A Saefumillah and P.J Worsfold, A protocol to assess the enzymatic release of dissolved organic phosphorus species in waters under environmentally relevant conditions. Environmental Science and Technology 41 (2007) 7479 – 7485.