Phosphate Time Series Data Obtained from an Autonomous Programmable Flow Injection (pFI) Analyzer at CeNVOOS Moss Landing Shore Station during February 2022 (pFI-SI-LOV project)

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Project
» Collaborative Research: Developing Automated Nutrient and Trace Metal Methodology using Programmable Flow Injection (pFI-SI-LOV)

Contributors	Affiliation	Role
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Abstract
In this dataset, we report phosphate (PO4) data obtained with our recently developed programmable Flow Injection (pFI) analyzer. The dataset represents a six-day hourly phosphate time series obtained in February 2022 using an autonomous pFI analyzer deployed at the Central & Northern California Ocean Observing System (CeNCOOS) Moss Landing Shore Station. During this 6-day deployment, we configured the pFI analyzer to create a four-point calibration curve (0, 0.5, 1.5 and 3.0 µmol L-1 PO4) every 12 hours using a single MQ phosphate standard (3.0 µmol L-1 PO4). In the intervals between these calibrations, the pFI was programmed to withdraw and analyze a sample from the seawater intake line hourly.

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Coverage

Location: Moss Landing Shore Station, Central California
Spatial Extent: **Lat**:36.8004 **Lon**:-121.7884
Temporal Extent: 2022-02-01 - 2022-02-07

Methods & Sampling

We deployed a pFI analyzer at the Central and Northern California Ocean Observing System (CeNCOOS) Moss Landing shore station in February 2022. The instrument was equipped with an auxiliary diaphragm pump and sample loop for hourly phosphate analysis of samples withdrawn from the station's seawater intake line. The samples were then analyzed using a pFI analyzer running on the assay described in Murphy and Riley (1962), adapted for pFI use. During this 6-day deployment, we configured the pFI analyzer to create a four-point calibration curve (0, 0.5, 1.5 and 3.0 µmol L-1 PO4) every 12 hours using a single MQ phosphate standard (3.0 µmol L-1 PO4). In the intervals between these calibrations, the pFI was programmed to withdraw and analyze a

sample from the seawater intake line hourly. The calibration procedure involved aspirating a fixed volume of the concentrated standard into one of the holding coils and simultaneously dispensing a variable volume of diluent (MQ carrier) to set the appropriate dilution factor.

Data Processing Description

The pFI analyzer was calibrated every 12 hours with working phosphate standards prepared in MQ water (0-3 µmol L-1). To calculate phosphate concentrations at each depth, we took the mean of the baseline corrected absorbance at 880 nm minus the reference absorbance at 1050 nm. Phosphate concentrations were then calculated using the slope and intercept of the MQ calibration curves.

The instrument was controlled and the data was processed using FloZF software (v 5.2).

Quality flags represented in the primary data file

- 1 = good
- 2 = bad*
- 3 = below detection limit

Data were flagged when the data were inconsistent with adjacent depths and visual observation of the absorbance spectra confirmed an issue during the analysis.

BCO-DMO Processing Description

- Units removed from parameter names in primary data file
- Spaces in parameter names replaced with underscores ("_")

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Related Publications

Lebrec, M., & Grand, M. M. (2024). Programmable flow injection: a versatile technique for benchtop and autonomous analysis of phosphate and silicate in seawater. Frontiers in Marine Science, 11. https://doi.org/10.3389/fmars.2024.1354780
Results

Murphy, J., & Riley, J. P. (1962). A modified single solution method for the determination of phosphate in natural waters. Analytica Chimica Acta, 27, 31–36. doi:10.1016/s0003-2670(00)88444-5
Methods

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Parameters

Parameter	Description	Units
Latitude	Latitude of ship location when underway sample was made with the pFI analyzer in decimal degrees; a positive value indicates a Northern coordinate.	decimal degrees
Longitude	Longitude of ship location when underway sample was made with the pFI analyzer in decimal degrees; a negative value indicates a Western coordinate.	decimal degrees
Time_UTC	Date and time when underway sample was made with the pFI analyzer in UTC.	unitless
pFI_PO4	Phosphate concentration withdrawn and analyzed by the programmable Flow Injection (pFI) analyzer.	micromoles per liter (umol/L)
pFI_flag	Phosphate concentration flag. 1 = good, 2 = bad, 3 = below detection limit.	unitless

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Instruments

Dataset-specific Instrument Name	miniSIA-2 (GlobalFIA, USA)
Generic Instrument Name	Flow Injection Analyzer
Dataset-specific Description	Samples were analyzed autonomously at the station using a pFI analyzer (miniSIA2, GlobalFIA, USA). This instrument was furnished with two High Flow milliGAT pumps with stainless steel heads, a plexiglass 8-port Lab-On-Valve, a 20 cm Long Path Linear Flow cell equipped with a Tungsten-Halogen lamp and a VIS-NIR Flame spectrophotometer (Ocean Insight, USA). The instrument was controlled and the data processed using FloZF software (v 5.2).
Generic Instrument Description	An instrument that performs flow injection analysis. Flow injection analysis (FIA) is an approach to chemical analysis that is accomplished by injecting a plug of sample into a flowing carrier stream. FIA is an automated method in which a sample is injected into a continuous flow of a carrier solution that mixes with other continuously flowing solutions before reaching a detector. Precision is dramatically increased when FIA is used instead of manual injections and as a result very specific FIA systems have been developed for a wide array of analytical techniques.

Dataset-specific Instrument Name	VIS-NIR Flame spectrophotometer (Ocean Insight, USA)
Generic Instrument Name	Spectrophotometer
Dataset-specific Description	Samples were analyzed autonomously at the station using a pFI analyzer (miniSIA2, GlobalFIA, USA). This instrument was furnished with two High Flow milliGAT pumps with stainless steel heads, a plexiglass 8-port Lab-On-Valve, a 20 cm Long Path Linear Flow cell equipped with a Tungsten-Halogen lamp and a VIS-NIR Flame spectrophotometer (Ocean Insight, USA). The instrument was controlled and the data processed using FloZF software (v 5.2).
Generic Instrument Description	An instrument used to measure the relative absorption of electromagnetic radiation of different wavelengths in the near infra-red, visible and ultraviolet wavebands by samples.

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Project Information

Collaborative Research: Developing Automated Nutrient and Trace Metal Methodology using Programmable Flow Injection (pFI-SI-LOV)

NSF Award Abstract:

Progress and discovery in the understanding of the chemical processes that regulate the growth of phytoplankton in the marine environment is limited by the ability of oceanographers to measure nutrients and trace metals at relevant spatial and temporal scales. This project aims to develop a new generation of autonomous and highly sensitive nutrient and trace metal analyzers for shipboard use and deployment at coastal monitoring stations, with potential for incorporation into existing autonomous observing platforms (e.g., gliders, autonomous underwater vehicles). Such a development will generate new insights into nutrient dynamics at a range of spatial and temporal scales and provide a new capability to obtain high resolution data sets for nutrients and trace metals in remote areas and environments where sample volumes are limited (e.g., brines, pore waters).

This project will develop novel automated methods for nutrients (phosphate and silicate) and trace metals (aluminium, manganese) using a technology called programmable Flow Injection (pFI). pFI is a microfluidic technique, which allows to automate conventional wet chemical analysis using microliter volumes of sample and reagents while significantly reducing the generation waste. In order to bring low levels of trace metals and nutrients that characterize remote ocean regions into the analytical window of pFI, concentration techniques will also be developed and coupled to spectrophotometric and fluorescence detection. The developed methodologies will be intercalibrated with standard oceanographic methods by participating in a GO-SHIP research cruise and a Hawaii Ocean Time-series cruise of opportunity. The long-term, unattended operation of the pFI analyzers will be evaluated at the Central California Ocean Observing System (CenCOOS) Moss Landing Shore station, where autonomous pFI analyzers will be deployed to undertake a year-long, hourly time series of phosphate and silicate. The data obtained from the shore station will be made publicly available and will complement existing monitoring data from this location, illuminating the connection between deep ocean nutrient dynamics and biological activity in coastal upwelling systems. The newly developed pFI analyzers will be assembled using commercially available components and open source software to facilitate uptake of this new methodology by the chemical oceanography community at large. This project will also support the training and exchange of at least two graduate students at the University of Hawaii at Mānoa and the Moss Landing Marine Laboratories, who will represent the next generation of specialists in the development and application of pFI methodologies to chemical oceanography.

This award reflects NSF's statutory mission and has been deemed worthy of support through evaluation using the Foundation's intellectual merit and broader impacts review criteria.

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Funding

Funding Source	Award
NSF Division of Ocean Sciences (NSF OCE)	OCE-1924539

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