

## Corrections to Nitrate and Phosphate for Deep-Water Cruises from 2009 to 2012

In early 2013 it was discovered that there were offsets in nitrate and phosphate data collected between 2009 and 2012 compared to data archived previous to 2009. Silicate data from those years did not have an offset. This document describes the source of the offsets and steps taken to correct the data.

Prior to 2007, a Technicon AA II instrument was used for nutrient analysis. An Astoria system was purchased in spring 2007 and has been used at IOS for the analysis of Water Property nutrient samples since June 2007. However, for the 2007 and 2008 cruises that involved deep nutrient sampling (Line P and West Coast Vancouver Island) the Technicon was still used.

Initially there were problems with the nitrate column provided by Astoria. After many months of trial and error it was re-designed to be more similar to the Technicon cadmium column, which had been in use for many years. Further modifications – decreasing the sample time and increasing the wash time – reduced the carryover (or tailing of peaks, i.e. the portion of the previous sample not completely washed-out). This resulted in a carryover < 3% (Astoria's recommendation). This 45:75 seconds sample:wash ratio and micro-connections to the cadmium column stabilized the carryover.

The Astoria is calibrated with mid-range Sagami standards for nitrate and silicate (as was done with the Technicon – 20.0 µM Nitrate and 100 µM Silicate – made in 30.5% NaCl). The phosphate standards are produced by Kanson Technos Inc. of Japan from natural seawater containing a range of nutrient concentrations. Our calibrations usually agree to within 1% of the Sagami standards for nitrate (20.0 µM) and silicate, but not as well with deeper, higher concentrations for nitrate and phosphate.

When the offset was noted, tests were run to determine how to ensure future analysis results are good and to determine how to correct the offsets for the affected 2009-2012 data. All three nutrients are analyzed at the same sample:wash ratio but silicate is not affected by that ratio and therefore does not have an offset to archived values. Various sample:wash ratios were tested and the ratio of 90:90 seconds that was used for the Technicon produced results for nitrate and phosphate that agreed with older archived values. Nutrients from cruise 2013-01 (February Line P) had already been analyzed at the 45:75 seconds ratio, so were quickly re-analyzed (within 10 days) at the 90:90 ratio. The re-analyzed samples agreed to archived values.

Comparing the 45:75 versus 90:90 results from the re-analysis of cruise 2013-01 produced linear fits as follows:

$$\text{Nitrate Corrected} = 0.9812 * \text{Nitrate Original} + 0.1709 \quad R^2 = 0.9997$$

$$\text{Phosphate Corrected} = 1.0115 * \text{Phosphate Original} + 0.0453 \quad R^2 = 0.9969$$

These corrections bring the post-2009 data into agreement with the archived pre-2009 data. Since the 45:75 ratio had been used exclusively since February 2009, it was possible to correct all the affected post-2009 cruises using these relationships.