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OFP mooring and sample collection:

The Oceanic Flux Program (OFP) time-series began in 1978 at the Hydrostation S hydrographic time-series site ($32^0$05'N, $64^0$15'W), located approximately 45 km southeast of Bermuda. The time-series was originally called the SCIFF (Seasonal Changes in Isotopes and Flux of Foraminifera) program. The SCIFF mooring consisted of a single 1.54m^2 conical sediment trap located at 3200m water depth (total water depth 4200m). The 1.54m^2 trap had only a single collection cup under the trap funnel, and the mooring was recovered every two months to change the sample. In 1984, the SCIFF mooring was relocated farther offshore to $31^0$50'N, $64^0$10'W (OFP site A, 4400m water depth) and the program was renamed the Oceanic Flux Program time-series. Between 1984-1989, samples were collected with the 1.54m^2 traps. In addition to 3200m depth, sampling was also conducted at 500m and 1500m depths.

In 1989, the 1.54m^2 traps were replaced by the newly introduced 0.5m^2 Parflux conical sediment traps (McLane Labs, Falmouth MA) having a rotating carousel to allow for multiple samples to be collected during a single deployment. The introduction of the Parflux trap (PARFLUX Mark 7G-13, Mark 7G-21 and currently Mark 78G-21) enabled the sampling period to be reduced from a nominal two month duration to a nominal two week duration.

The OFP sample collection has been nearly continuous since 1989 at all three trap depths with the exception of two hiatuses due to loss of the mooring: the first in 1996 and the second in 2010. After the 2010 accident, the OFP mooring site was permanently moved to $31^0$55'N, $64^0$05'W (OFP Site B)

Trap cups are manufactured of polyethlyene and filled with seawater brine (~40 ppt). Between 1984-1989, the 500 and 1500m traps were poisoned with sodium azide and the 3200m trap brine was not poisoned. In 1989, the poison was switched to mercuric chloride.

Since 1996, the brine has been made by freezing Sargasso Sea deep water collected from a depth of 3000m using trace metal clean GoFlo bottles (General Oceanics, Miami FL) and poisoned with ultra-high purity mercuric chloride at a concentration of 200 mg l^{-1}. An intercalibration exercise conducted in 1995 determined that there was no difference in fluxes of bulk constituents between unpoisoned and mercuric chloride poisoned traps at 3200m depth (Conte et al. 1998).

Between Oct 1992 to Jan 1996, in an attempt to prevent large swimmers from entering the cups, 3-4mm sized plastic mesh screens were installed in the orifices of sample collection cups in the 500m and 1500m traps. The screens appear to have been prevented larger flux material from entering the cups, and so the 500m and 1500m fluxes for this period undersampled the flux. Use of the screens was discontinued in Jan 1996.

Beginning in July 2007, a mesh screen (Titanium Grade 1, 1/2" opening, 0.063" wire diameter) was installed on the top of the honeycomb baffle of the sediment trap deployed at 500m to exclude large swimmers from entering the trap cone.

Since 1995, as a precaution against metal contamination from the mooring, the galvanized mooring chain directly above the traps was replaced with 316 Stainless chain and all exposed metal terminations on the trap bridles have been epoxy coated.

Additional details on the OFP mooring and sample collection are described in Deuser *et al.* (1981) and Conte *et al.* (2001, 2018).

OFP analytical methodology:

Cleaning procedures: Prior to 1996, trap cups and analytical glassware were cleaned in general laboratory cleaning solutions, soaked in 1N HCl, and then rinsed with distilled water. Since 1996, all glass and Teflonware has been precleaned in a NoChromix(Godax Labs)/sulfuric acid oxidizing solution; the glassware is then combusted overnight at 375^{0}C. Beginning in 1998, we added more stringent cleaning of trap cups and other plasticware specifically for trace metal analyses: Precleaned virgin LDPE trap cups and sample processing plastics and Teflonware are soaked 6 hrs in 6 N HNO_3, transferred to 4 N HCl for 12 hrs, and then rinsed with deionized water. Trap cups are then filled with 0.4 NHCl and leached for an additional 4-5 d. Cups are stored filled with MilliQ water until used.

Sample processing: Samples are stored in their collection cups and refrigerated prior to analysis. Between 1978 to 1995, samples were wet-sieved through a series of stainless steel sieves (1000, 500, 125 and 37□m mesh) into a glass beaker. Material on the sieves was rinsed into preweighed glass petri dishes using distilled water. The largest two size fractions were examined under a dissecting microscope to remove swimmers, and then all four fractions were oven dried at 45^{0}C before weighing. The remaining <37μm material was concentrated using a flow through centrifuge before drying at 45^{0}C and weighing. In 1996, the use of the 37 □m mesh sieve was discontinued, and the 37-125μm and <37μm size fractions replaced by a single <125μm size fraction.

In 1996, other modifications were made to sample processing methods to allow for trace organic and elemental determinations. Samples are split under a laminar flow hood using a McLane rotary splitter (McLane Laboratory, Falmouth, MA) equipped with a Teflon-coated splitting tray and spigots. Before splitting, the sample is briefly centrifuged in its collection cup to separate the particles from the overlying supernatant. About 50 ml of supernatant is removed for analysis of dissolved constituents and part of the remaining supernatant is removed to use for rinsing during the sample sieving process. After the supernatant is sampled, the sample is resuspended and quickly passed through 1000 and 500μm solvent-rinsed 316 stainless steel sieves to remove large swimmers and/or large flocculent material. The >1000μm fraction is then rinsed into a pre-weighed Teflon petri dish, swimmers removed under a stereomicroscope (Zeiss Stemi SV-11), photographed (see below) and the sample oven dried at 50^{0}C. The 500-1000μm fraction is rinsed into a Teflon petri dish, swimmers picked and then recombined with the <500μm fraction. The total <1000μm picked material is then split into ten subsamples using the rotary splitter. Three tubes (30%) are set aside for trace organic analyses and one tube (10%) is collected in a Teflon centrifuge tube for trace elemental analyses. The remaining six splits (60%) are recombined and fractionated into 500-1000, 125-500, and <125μm size fractions. The 500-1000μm and 125-500μm fractions are rinsed into preweighed glass petri dishes using deionized water, quantitatively photographed using a Zeiss Stemi SV-11 stereomicroscope in conjunction with an Olympus Q-Color 5 (5.0 MP) camera as described in Shatova *et al.* (2012, *J. Plankton Res.* 34, 905-921). In 2016, the camera was upgraded to an Olympus DP73-1-51 (17.0 MP) camera and Olympus CELLSENS (1.13) imaging software. The sample fractions in their petri dishes and then oven dried at 50^{0}C for dry weight determination (±0.01mg accuracy). The <125μm fraction,

collected into a Teflon beaker, is transferred to a preweighed Teflon test tube, concentrated by centrifugation and then freeze dried for dry weight determination.

Bulk analytical methods:

The carbonate and organic carbon/nitrogen data reports the composition of the <125 um size fraction, which comprises 82±7% of the 3200m mass, 76±9% of the 1500m mass, and 52±20% of the 500m mass. The conversions to flux assume that the composition of the total mass is the same as the <125 um fraction. The average per cent carbonate in the <125 um and <1000 um size fractions was compared in selected samples and found not to be significantly different, indicating that this is a reasonable assumption.

Carbonate: Prior to 1995, carbonate was determined manometrically on a vacuum line system (Deuser *et al.* 1981). Since 1995, carbonate has been analyzed by coulometry (UIC Inc., Joliet, IL). Samples (2-3mg each) are run in duplicate. If the spread between duplicate runs is >5%, a triplicate sample is run. Well-characterized deep-sea sediment standards as well as $CaCO_3$ standards are analyzed with each set of sample runs to ensure intercalibration of results. Typical sample c.v. is ~3%.

Organic carbon and nitrogen: Prior to about 1992, organic carbon was determined manometrically on the same vacuum line as used for carbonate after combustion of preacidified samples (Deuser *et al.* 1981). Between 1992 and 1995, total carbon and nitrogen were determined on a Perkin Elmer 240 CHN instrument; organic carbon was calculated as the difference between total and carbonate carbon. Between 1995-2004, organic carbon and nitrogen were determined directly on pre-acidified samples using either a Carlo Erba or Perkin Elmer 240 CHN instrument.

Samples for direct organic carbon and carbonate analysis are acidified to remove carbonates using a modified Verrado *et al.* (1990) method. Approximately 1-2 mg of sample material is weighed into solvent rinsed aluminum combustion boats secured in a Teflon well plate and the carbonate removed using multiple sulfurous acid applications until no fizzing is observed under a magnifier.

Since 2004, concentrations of organic carbon and nitrogen, as well as their isotopic compositions, have been analyzed by mass spectrometry using either a Europa 20-20 or GV Isoprime mass spectrometer. Mass spectrometry determinations include re-analysis of archived samples as well as recently collected samples. The C and N concentrations for older samples that also have isotopic data have been quantified by mass spectrometry. Each sample is analyzed in duplicate. If the coefficient of variation is >5% or the $\delta^{13}C$ of the sample is questionably low (an indication of incomplete acidification), a triplicate is run. Certified standards, and working standards of sediment-trap material (including several OFP samples from the 1980s) and sediments are run with each sample batch for intercalibration. Typical sample c.v. is ~3%.

Samples collected pre-2000 that have isotopic data have been re-analyzed using the acidification and mass spectrometric methods described above and this is the data reported.

Phosphorus: Prior to 2005, particulate phosphorus in the <37 um and <125 um size fractions was analyzed using a modified Aspilla method (Aspilla *et al.* 1976), and samples were quantified using a spectrophotometer. For samples collected 2000 onwards, phosphorus in the total <1000um fraction has been analyzed using a more sensitive and precise fusion/HR-ICPMS method (Huang *et al.* 2007). Comparison of <125 um samples analyzed by both the Aspilla and fusion/HR-ICPMS methods indicate no difference between the two (ibid). Typical sample c.v. for

replicate runs is <5%.

Dissolved phosphorus in the supernatant has been analyzed using the phosphomolybdate blue complex reaction (Koroleff *et al.* 1976) for samples collected since 2000. For samples collected prior to 2005, samples were analyzed on a spectrophotometer. After 2005, samples have been analyzed using a Lachat autosampler (QuikChem FIA^+ 8000 series, XYZ Autosampler 500 Series) with artificial seawater (40 ppt) as the carrier. Standard curves are constructed from standards that are prepared using brine from the dipped trap cup blanks (i.e. sample cups filled with mercuric chloride brine solution that are deployed on the traps but do not sample), with dilutions matched to that of the samples. Typical sample c.v. for replicate runs is ~2%.

Opal: Prior to 1992, opal in the <37um and 37-125um size fractions in selected 3200m samples was analyzed using the method of Newton *et al.* (1994), which is based on opal dissolution in 2M Na_2CO_3 and assumes an estimated opal composition of $SiO_2*0.4H_2O$ (Mortlock and Froelich 1989) to convert Si to opal. For samples collected 2000 onwards, biogenic silica has been estimated from the difference between total Si, quantified using fusion/HR-ICPMS method (Huang et al. 2007), and the lithogenic silica, estimated from the [Al] by assuming an average composition of deep pelagic sediments (8.4% Al and 25.0% Si, Li and Shoemaker 2003). Biogenic Si is then converted to opal using an estimated opal composition of $SiO_2*0.4H_2O$ (Mortlock and Froelich 1989).

Lithogenic material: For samples collected from 2000 onwards, lithogenic material has been estimated from the [Al], measured by fusion/HR-ICPMS (Huang *et al.* 2007), and assuming that the lithogenic material composition approximates that of the average composition of deep sea sediments (8.4% Al, Li and Showmaker 2003).

Further details on opal and lithogenic determinations are provided in Conte et al. (2019)

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