

# Major (Al), minor (Mn, Ba), and trace metal (Cd, Ag, Mo) data from Multitracers sediment trap samples

**Website:** <https://www.bco-dmo.org/dataset/865386>

**Data Type:** Cruise Results, Other Field Results

**Version:** 1

**Version Date:** 2023-10-25

## Project

» [A Sediment Trap Study to Determine if the Flux of Silver to the Seafloor is Related to Export Productivity](#) (Ag Flux and Export Productivity)

Contributors	Affiliation	Role
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## Abstract

This dataset includes major (Al), minor (Mn, Ba), and trace metal (Cd, Ag, Mo) concentrations from Multitracers sediment trap samples.

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## Coverage

**Spatial Extent:** N:42.192 E:-125.761 S:40.087 W:-132

**Temporal Extent:** 1987-09-22 - 1990-09-17

## Methods & Sampling

The following methodology section is from McKay (in prep), with minor modifications.

### Sample collection

During the Multitracers Project (September 1987 to July 1991) bottom-moored sediments traps were deployed at three stations (Nearshore, Midway, and Gyre) in the Northeast Pacific Ocean. This dataset provides major (Al), minor (Ti, Ba, Mn), and trace element (Cd, Ag, Mo) data for the Nearshore and Gyre stations. The data are for the first 2 years of the project, where "year" refers to the time a trap mooring was deployed until it was recovered and not a calendar year (e.g., Year 1 is September 1987 to September 1988 and Year 2 is September 1988 to September 1989). In addition, there are data for the Nearshore site in Year 3 (September 1989 and March 1990). Sediment trap samples were obtained from the Oregon State University Marine and Geology Repository.

Each mooring had sediment traps deployed at 500 m (Year 1 only), within the OMZ at 1000 m, just below the OMZ at 1500 and/or 1750 m, and 500 m above the bottom (near-bottom traps; ~2300 m at the Nearshore site and ~3200 m at the Gyre site). In Years 1 and 2 most traps, with the exception of the 1500 m trap, had 6

sample cups (C1 to C6) that were open for 30 to 33 days (C1), 60 days (C2 to C5), and 87 to 94 days (C6). The 1500 m trap at both sites had 13 cups that were open for ~30 days each. In Year 3 all Nearshore traps had 6 cups, which were open for 30 days (C1 to C5) and 23 days (C6, near-bottom trap only). No traps were deployed at the Gyre site in Year 3.

In Year 1 the 500 m trap at the Nearshore station failed after the third cup, presumably due to clogging during a high flux event. There is also evidence that the 500 m trap at the Gyre site under-collected material (i.e., lower fluxes at 500 m compared to 1000 m). For these reasons, the 500 m traps were not deployed at either site in subsequent years. The 1500 m traps also failed at both sites in Year 1. Fortunately, traps were also deployed at 1750 m and they functioned correctly.

The trap sample cups were filled with unfiltered seawater collected from the near-bottom trap depth at each site and poisoned with 15g/L of sodium azide. To compare the effects of different "preservatives" a pair of traps were deployed at the Nearshore site (1750 m) in Year 3; one set of cups was poisoned with sodium azide and the others preserved with formalin. No special trace metal clean sampling procedures were utilized during the Multitracers Project; however, the traps were constructed out of plastic and fiberglass thus reducing possible trace metal contamination.

When the sediment traps were recovered the sample cups were removed, sealed, and not opened until they were ready to be processed in the laboratory. Once back at the lab the samples were allowed to sit undisturbed until the particulate material had settled. Once opened the supernatant was poured off and then used to rinse the particulate fraction through a 2 mm sieve. The  $\geq 2$  mm size-fraction was transferred to a bottle containing formalin and refrigerated for future use. The  $< 2$  mm size-fraction, which was used in this study, was split into 10 aliquots. Between 1 and 4 aliquots were frozen for future use. The other 6 to 9 aliquots were centrifuged and the supernatant was discarded. These samples were then rinsed with buffered distilled water and centrifuged; this step was carried out twice. Finally, the samples were freeze-dried and then homogenized.

### Analytical methods

Sample preparation for major (Al), minor (Mn, Ba), and trace (Cd, Ag, Mo) metal analysis involved placing ~50 mg of sample into teflon reaction vessels and pretreating overnight at room temperature with a mixture of concentrated, quartz-distilled HNO<sub>3</sub> (1 ml) and HCl (1 ml). The following day concentrated, quartz-distilled HNO<sub>3</sub> (2 ml), BDH Aristar Ultra HF (2 ml), and Milli-Q water (2 ml) were added and the samples were digested using a CEM MARS microwave digestion system. This was followed by 3 cycles of acid evaporation using the same system. After the final evaporation, samples were diluted with 10 ml of 5% quartz-distilled HNO<sub>3</sub> and heated for 24 hr at 60°C to remove fluorides complexes (Muratli et al., 2012). The concentrations of Ag, Cd, and Mo in these digests were analyzed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a Thermo Scientific X-Series II instrument located in the Keck Collaboratory at Oregon State University. No column chemistry was carried out prior to ICP-MS analysis. Instead, a collision cell was utilized to reduce the formation of oxides that interfere with the analysis of Ag-109 (Nb oxides and Zr oxides and oxyhydroxides) and Cd-114 (Sn oxides). However, it was still necessary to measure the oxide formation, which was typically <5 %, and apply a small oxide correction to the data. The same digests were used to analyze the major and minor element concentrations by ICP-OES (Prodigy, Teledyne Instruments) in the Keck Collaboratory. Metal concentrations were calculated using an external standard calibration curve.

Precision and accuracy were determined using the National Research Council of Canada sediment standards MESS-3 and PACS-2, which were put through the same digestion and analytical procedures as the samples. In general, precision was better than 8% and accuracy was within error for all metals except Al (see the "Table 1" [Supplemental File](#) (PDF)). The Al values for both sediment standards are slightly (~4 to 5 %) lower than their certified values.

The non-lithogenic (i.e., excess) concentrations of the metals were estimated using Eq. (1), where  $x_{sM}$  is the excess concentration of the metal,  $M_{smp}$  is the metal concentration in the sample,  $Al_{smp}$  is the aluminum concentration in the sample, and  $(M/Al)_{lith}$  is the metal/Al ratio in lithogenic material.

$$[x_{sM}] = [M_{smp}] - [Al_{smp}] * (M/Al)_{lith}$$

This method of calculating excess concentrations relies on measuring or assuming a reasonable lithogenic value for each metal. In this study, the average shale values reported in Brumsack (2006) were used (i.e., 8.83 wt% Al; 580 µg/g Ba; 850 µg/g Mn; 0.13 µg/g Cd; 0.07 µg/g Ag; 1 µg/g Mo). In addition, because variations in trace metal concentrations can be driven by changes in the concentrations of major components (e.g., dilution by lithogenic material in late fall and winter) all metal data have been converted from concentrations to fluxes using the total particulate flux data provided by Dr. Collier.

### Known problems/issues

(1) Year 1 data for the 500 m sediment traps at both sites (i.e., Nearshore samples MT31584 to MT31586 and Gyre samples MT31607 to MT31612) are problematic because evidence (e.g., lower total mass fluxes compared to the 1000 m trap) suggest these shallow traps under-collected settling particulate material.

(2) The 1500 m trap at the Nearshore site in Year 1 (samples MT31396 to MT31401) should have had samples for 13 cups; however, only 6 samples were collected. It is unclear whether the trap failed after cup 6, meaning this cup was open for 237 days, or the trap was programmed improperly and thus each cup was actually open for twice as long. Flux data suggest the latter.

(3) At times fluxes were low and not enough sample was available for an analysis. This was most common at the Gyre site.

(4) The midway (MS) sediment trap samples were not analyzed as a part of this study. Also, there was no Gyre sediment trap samples collected in Year 3.

## Data Processing Description

### Data Notes:

C = cup (e.g., cup 1 is C1)

NS-1 to 3 = Nearshore sediment trap mooring site, years 1 to 3 (see below\*)

Gyre-1 to 2 = Gyre sediment trap mooring site, years 1 to 2 (see below\*)

MTT samples (column 1) = a bulk sample collected from a failed trap

nd = not determined

na = not applicable / available

\* A year refers to the time from when a trap mooring is deployed to when it is recovered and the samples are collected. It does not refer to a calendar year. Traps are named based on the "year" of the project they were recovered.

## BCO-DMO Processing Description

- converted dates for YYYY-MM-DD format;
- renamed fields to conform with BCO-DMO naming conventions.

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## Data Files

File
<b>865386_v1_mckay_trace_metals.csv</b> (Comma Separated Values (.csv), 31.40 KB) MD5:cf4bf0d33b1fb4c1bd4700ebbbc26946
Primary data file for dataset ID 865386, version 1.

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## Supplemental Files

File	
<b>Multitracers_Cruise_Information.pdf</b>	(Portable Document Format (.pdf), 399.10 KB) MD5:52268c14befc6f33fac8c68aa154ca9a
This file contains information about the Multitracers cruises, including cruise IDs, start and end dates, stations where traps were deployed, and deployment and recovery dates. Some information is not known for some cruises (represented by "na" or "?").	
<b>Table 1</b>	
filename: Table1.pdf	(Portable Document Format (.pdf), 271.75 KB) MD5:6185be4a50391bd2abf9db0e820066fe
Table 1: Metal Data for the NRC Sediment Standards MESS-3 and PACS-2.	
Associated with "Multitracers Metal Concentration Data" (dataset 865386; PI: Jennifer McKay)	

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## Related Publications

Brumsack, H.-J. (2006). The trace metal content of recent organic carbon-rich sediments: Implications for Cretaceous black shale formation. *Palaeogeography, Palaeoclimatology, Palaeoecology*, 232(2-4), 344-361.

doi:[10.1016/j.palaeo.2005.05.011](https://doi.org/10.1016/j.palaeo.2005.05.011)

*Methods*

Lyle, M., Zahn, R., Prahl, F., Dymond, J., Collier, R., Pisias, N., & Suess, E. (1992). Paleoproductivity and carbon burial across the California Current: The multitracers transect, 42°N. *Paleoceanography*, 7(3), 251-272.

doi:10.1029/92pa00696 <https://doi.org/10.1029/92PA00696>

*Methods*

McKay (in prep). Particulate Trace Metal (Cd, Ag, Mo) fluxes to the Deep Northeast Pacific Ocean.

*Results*

Muratli, J. M., McManus, J., Mix, A., & Chase, Z. (2012). Dissolution of fluoride complexes following microwave-assisted hydrofluoric acid digestion of marine sediments. In *Talanta* (Vol. 89, pp. 195-200). Elsevier BV.

<https://doi.org/10.1016/j.talanta.2011.11.081>

*Methods*

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## Parameters

Parameter	Description	Units
Sample_ID	sample identifier	unitless
Sample_Description	sample description	unitless
Mooring_ID	mooring identifier	unitless
Sample_Type	sample type	unitless
Latitude	latitude	degrees North
Longitude	longitude	degrees East
Water_Depth	water depth	meters (m)
Trap_Depth	trap depth	meters (m)
Cup_num	cup number	unitless
Date_Cup_Opened	date when cup was opened; format: YYYY-MM-DD	unitless
Days_Cup_Open	number of days cup was open	days
Cup_vol	cup volume	milliliters (ml)
Area	area	square meters (m2)

Wt_in_cup	weight in cup	grams (g)
Wt_Fract	weight fraction	unitless
Total_Flux_mg_cm2_y	total flux	milligrams per square centimeter per year (mg/cm2/y)
Total_Flux_mg_m2_d	total flux	milligrams per square meter per day (mg/m2/d)
Al	aluminum (Al) percent weight	wt percent
Ti	titanium (Ti) percent weight	wt percent
Ba	barium (Ba) concentration	micrograms per gram (ug/g)
Mn	manganese (Mn) concentration	micrograms per gram (ug/g)
Mo	molybdenum (Mo) concentration	micrograms per gram (ug/g)
Ag	silver (Ag) concentration	micrograms per gram (ug/g)
Cd	cadmium (Cd) concentration	micrograms per gram (ug/g)
Total_Al_flux	total Al flux	milligrams per square meter per day (mg/m2/d)
Total_Ti_flux	total Ti flux	milligrams per square meter per day (mg/m2/d)
Total_Ba_flux	total Ba flux	micrograms per square meter per day (ug/m2/d)
Total_Mn_flux	total Mn flux	micrograms per square meter per day (ug/m2/d)
Total_Mo_flux	total Mo flux	micrograms per square meter per day (ug/m2/d)
Total_Ag_flux	total Ag flux	nanograms per square meter per day (ng/m2/d)
Total_Cd_flux	total Cd flux	nanograms per square meter per day (ng/m2/d)
Excess_Ba_flux	excess Ba flux	micrograms per square meter per day (ug/m2/d)
Excess_Mn_flux	excess Mn flux	micrograms per square meter per day (ug/m2/d)
Excess_Mo_flux	excess Mo flux	nanograms per square meter per day (ng/m2/d)
Excess_Ag_flux	excess Ag flux	nanograms per square meter per day (ng/m2/d)
Excess_Cd_flux	excess Cd flux	nanograms per square meter per day (ng/m2/d)

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## Instruments

<b>Dataset-specific Instrument Name</b>	Thermo Scientific X-Series II Inductively Coupled Plasma Mass Spectrometer
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Mass Spectrometer
<b>Dataset-specific Description</b>	Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a Thermo Scientific X-Series II instrument located in the Keck Collaboratory at Oregon State University
<b>Generic Instrument Description</b>	An ICP Mass Spec is an instrument that passes nebulized samples into an inductively-coupled gas plasma (8-10000 K) where they are atomized and ionized. Ions of specific mass-to-charge ratios are quantified in a quadrupole mass spectrometer.

<b>Dataset-specific Instrument Name</b>	Teledyne Instruments, Prodigy Inductively Coupled Plasma - Optical Emission Spectrometer
<b>Generic Instrument Name</b>	Inductively Coupled Plasma Optical Emission Spectrometer
<b>Generic Instrument Description</b>	Also referred to as an Inductively coupled plasma atomic emission spectroscope (ICP-AES). These instruments pass nebulised samples into an inductively-coupled gas plasma (8-10000 K) where they are atomised and excited. The de-excitation optical emissions at characteristic wavelengths are spectroscopically analysed. It is often used in the detection of trace metals.

<b>Dataset-specific Instrument Name</b>	bottom-moored sediment traps
<b>Generic Instrument Name</b>	Sediment Trap
<b>Generic Instrument Description</b>	Sediment traps are specially designed containers deployed in the water column for periods of time to collect particles from the water column falling toward the sea floor. In general a sediment trap has a jar at the bottom to collect the sample and a broad funnel-shaped opening at the top with baffles to keep out very large objects and help prevent the funnel from clogging. This designation is used when the specific type of sediment trap was not specified by the contributing investigator.

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## Project Information

### A Sediment Trap Study to Determine if the Flux of Silver to the Seafloor is Related to Export Productivity (Ag Flux and Export Productivity)

#### *NSF Award Abstract:*

Intellectual Merit: Since work conducted in the early 1980's, there has been a growing interest in improving our understanding of the relationship between the particle flux of Ag and export productivity in the ocean. Despite tantalizing positive correlations between sedimentary Ag and more traditional paleoproxies, such as organic carbon, opal and biogenic Ba, there has yet to be a comprehensive study undertaken to evaluate in detail the relationship between the flux of particulate Ag and export productivity in the ocean. If the sinking flux of Ag can be shown to reliably track export productivity, as will be evaluated in this study, then the geochemical community will have a new tracer to provide important new insights and constraints on past changes in

paleoproductivity. In particular, this project will test the hypothesis that Ag can be used to trace the flux of biogenic particulate organic matter exported from the surface ocean to the sediments; furthermore, this project will evaluate the potential use of Ag as a proxy tracer of past changes in productivity. A secondary objective is to determine whether sedimentary redox conditions affect the accumulation of Ag in sediments. This work will be accomplished by analysis of Ag in a suite of archived sediment trap and sediment samples collected from a range of oceanographic locations. The data obtained from this research will aid in the development of a new paleoproductivity proxy (Ag) that can be utilized to improve paleoceanographic reconstructions.

Broader Impacts: In regards to broader impacts, this research will provide the scientific community with a better understanding of the biogeochemical cycling of Ag, an element that is toxic to marine organisms, as well as the cycling of redox-sensitive trace metals. The study will support an early scientist, and provide training for one graduate student and two undergraduate students.

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## Funding

Funding Source	Award
<a href="#">NSF Division of Ocean Sciences (NSF OCE)</a>	<a href="#">OCE-1234465</a>

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