DEPARTMENT OF
ECOLOGY
State of Washington

Addendum 6 to Quality Assurance Project Plan

Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores

January 2017
Publication No. 17-03-105

Publication Information

Addendum

This addendum is on the Department of Ecology's website at https://fortress.wa.gov/ecy/publications/SummaryPages/1703105.html

This addendum is an addition to an original Quality Assurance Project Plan. It is not a correction (errata) to the original plan.

Data for this project will be available on Ecology's Environmental Information Management (EIM) website at www.ecy.wa.gov/eim/index.htm. Search Study ID WHOB006.

Activity Tracker code

Ecology's Activity Tracker code for this addendum is 17-014.

Original Publication

Quality Assurance Project Plan: Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores.

Publication No. 06-03-113
https://fortress.wa.gov/ecy/publications/summarypages/0603113.html

Author and Contact Information

William Hobbs
Environmental Assessment Program
Washington State Department of Ecology
PO Box 47600
Olympia, WA 98504-76000

For more information contact: Communications Consultant, phone 360-407-6764.

Addendum 6 to
Quality Assurance Project Plan

Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores

January 2017

Approved by:

Signature:	Date:
Steve Hood, Client, Water Quality Program, BFO	
Signature:	Date:
Doug Allen, Client's Section Manager, Water Quality Program, BFO	
Signature:	Date:
William Hobbs, Author / Project Manager, EAP	
Signature:	Date:
Debby Sargeant, Author's Unit Supervisor, EAP	
Signature:	Date:
Jessica Archer, Author's Section Manager, EAP	
Signature:	Date:
Dale Norton, Study Area Section Manager, EAP	
Signature:	Date:
Joel Bird, Director, Manchester Environmental Laboratory	
Signature:	Date:
Bill Kammin, Ecology Quality Assurance Officer	

Signatures are not available on the Internet version.
BFO: Bellingham Field Office
EAP: Environmental Assessment Program

3.0 Background

The Washington State Department of Ecology (Ecology) program to monitor Persistent, Bioaccumulative, and Toxic Chemicals (PBTs) has been assessing the chemical deposition trends to lakes through dated sediment cores for the last ten years. The program selects three new lakes a year to study the historical deposition of PBTs. Previous Quality Assurance Project Plans (QAPPs) have covered many of the details relevant to this project (Coots, 2006; Mathieu, 2015).

In 2015, Ecology collected a sediment core from Lake Whatcom in Bellingham, Whatcom County. Sediments were analyzed for lead radioisotopes (dating), elemental lead (Pb), mercury (Hg), total organic carbon (TOC), and brominated flame retardants (BFRs). Results from this study are presented in a separate publication (Mathieu and McCall, 2016). Dating of the sediment core provided a reliable age-depth model to estimate specific years associated with each sediment layer.

Lake Whatcom has been under study by Ecology since the 1990s. Issues of low dissolved oxygen in the lake, linked to inputs of phosphorus, led to a total maximum daily load (TMDL) study (Pickett and Hood, 2008). An implementation strategy was then compiled to reduce phosphorus inputs through permitting (Hood, 2013). In addition, an extensive period of modeling took place concurrent with and following the initial investigation (Berger and Wells, 2005; Cadmus Group and CDM, 2007; Butcher, 2008). A key component of the water quality model for Lake Whatcom is understanding the internal loading of phosphorus from the lake sediments.

The goal of this project is to provide Ecology's modeling group with an understanding of the pool of residual total phosphorus (TP) that has accumulated in the recent (upper 10 cm = ~ post-1950) sediments of Lake Whatcom. To meet this goal, Ecology will analyze archived sediment core samples for TP and summarize the potential mass of TP within discrete sediment layers. Secondly, additional information that can be gained about the depositional history of sediments and phosphorus to the core location (sediment core profiles) would provide a more holistic picture of the history of Lake Whatcom.

3.1 Study area and surroundings

3.1.3 Parameters of interest

The main parameter of interest is TP in sediments. The deposition of phosphorus to lake bottom sediments reflects TP inputs and internal cycling of TP within the lake. Sediment TP in cores has therefore been used in the past as an indicator of historical changes in the nutrient enrichment of lakes that may lead to excessive algal growth or issues of low dissolved oxygen (Anderson et al., 1993; Engstrom, 2005; Engstrom et al., 2009). However, sediment TP is often used as part of a multi-proxy or multiple lines-of-evidence approach. The reason is that phosphorus in lake sediments is not stable and can migrate to upper sediment layers under changes in the redox or oxygen content of the sediments (Mortimer, 1942; Søndergaard et al., 1993; Rydin, 2000). Phosphorus is generally bound in large part to oxi-hydroxides of iron and manganese which are redox-sensitive metals; therefore, as the oxidation state of the metals changes, phosphorus can be released. Due to lack of resources, we will not be using a multi-proxy approach for TP inputs, and therefore the historical trend of TP down the sediment core has limitations.

Additional parameters will be analyzed in the sediments to allow for a broader understanding of the inputs to the lake and past productivity of the lake. The organic, carbonate, and mineral fractions of the sediments will be analyzed in order to decipher the inorganic flux of material into the lake since ~ 1850 to present. The inorganic flux represents changes in the lake catchment land-use and erosion of tributary rivers and creeks that lead to changes in the inputs of inorganic sediment. The sediments also will be analyzed for organic carbon (C) and nitrogen (N) to infer past productivity and estimate the source of the organic material. The ratio of C:N in lake sediments is often used to decipher between a terrestrial C and aquatic C source, based on the knowledge that terrestrial C is more refractory (Kaushal and Binford, 1999).

3.1.4 Results of previous studies

The sediment core from the northern basin (Basin 1) of Lake Whatcom was collected in the summer of 2015. Since being collected, the sediments have been dated and analyzed for mercury, lead and flame retardants (brominated flame retardants; PBDEs). These data are published in Mathieu and McCall (2016) and will not be presented here, with the exception of the radioisotopic dating. The dating of the sediments using 210-Po and 210-Pb by alpha spectroscopy, established a reliable age-depth model for the 2015 sediment core (Figure 1). The constant-rate-of-supply model was used to establish rates of sediment deposition from the 210-Pb activity (Appleby and Oldfield, 1978). The age-depth model therefore provides a reliable timeline on which to measure TP concentrations.

Additional studies from Lake Whatcom sediment cores also have included detailed investigations of mercury deposition (Paulson, 2004; Paulson and Norton, 2008). The ultimate conclusion from much of this work was that the deposition of mercury to Lake Whatcom was not dominated by local sources, but rather regional or extra-regional sources likely contributed the majority of mercury.

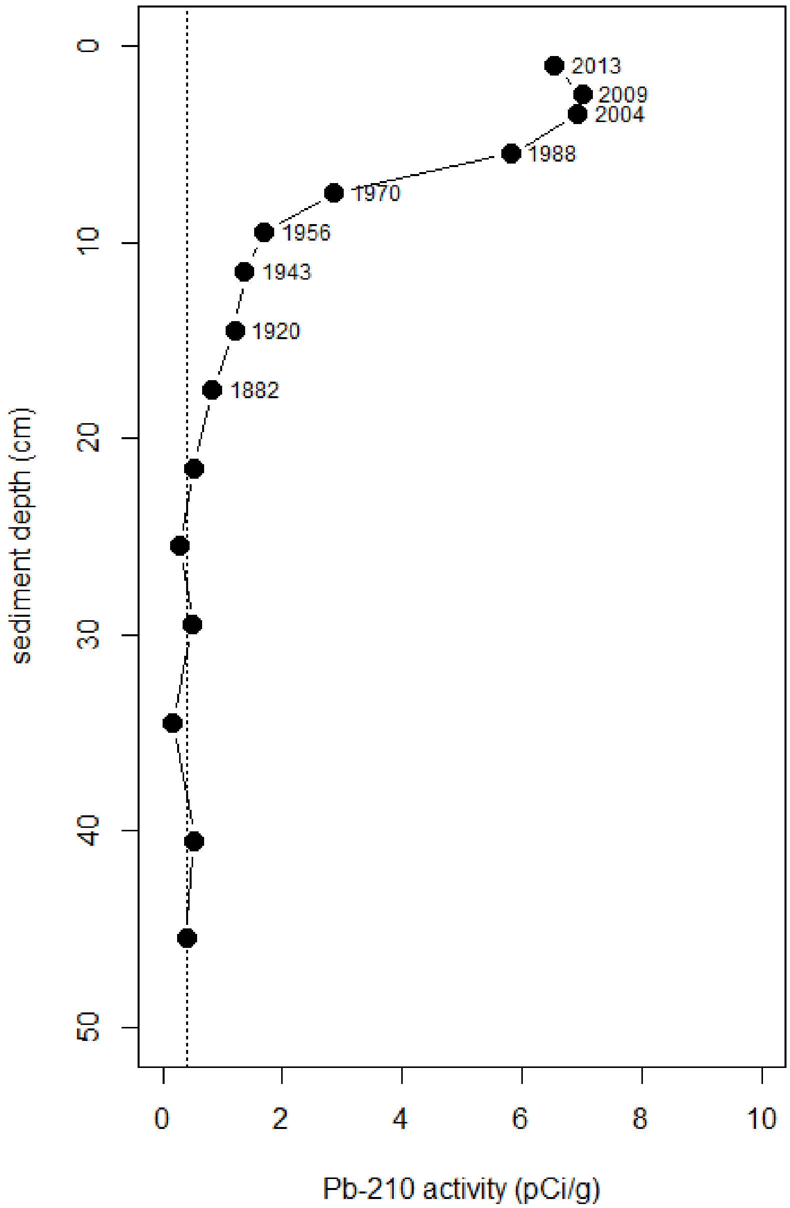

Figure 1: Lead-210 activity with depth in the 2015 sediment core.

Modeled ages are shown adjacent to samples.

Dashed vertical line represents the background or supported ^{210}Pb.

4.0 Project Description

This project relies on a previously collected sediment core from Lake Whatcom (Mathieu and McCall, 2016). The goal of the Mathieu and McCall (2016) study was to establish a depositional history of mercury, lead, and flame retardants.

4.1 Project goal

The goal of this study is to provide the Ecology modeling group working on Lake Whatcom with an understanding of the pool of residual TP that has accumulated in the recent (last ~ 20 years) sediments.

4.2 Project objectives

The specific objectives of the study are to:

- Analyze multiple sediment core intervals for TP and provide a statistical summary for the periods pre-1900, 1900-1950, and 1950-present; estimate the mass of TP within Basin 1 for each period.
- Analyze multiple sediment core intervals for organic carbon, nitrogen, and sediment composition (mineral, carbonate, or organic).
- Interpret the profile of analyzed parameters relative to previous work in Basin 1 (Paulson, 2004).

5.0 Organization and Schedule

5.1 Key individuals and their responsibilities

This project was requested and initiated by Steve Hood, Water Quality Program, Bellingham Field Office.

Table 1: Organization of project staff and responsibilities.

Staff (all are EAP except client)	Title	Responsibilities
Steve Hood, WQP, BFO Phone: 360-407-7146	EAP Client	Clarifies scope of the project. Provides internal review of the QAPP, approves the budget and approves the final QAPP.
William Hobbs, TSU, SCS Phone: 360-407-7512	Project Manager	Writes the QAPP. Oversees submission of samples to laboratory. Conducts QA review of data, analyzes and interprets data, and reviews data in EIM. Writes the draft report and final report.
Melissa McCall, TSU, SCS Phone: 360-407-7384	Project Assistant	Enters project data into EIM.
Debby Sargeant, TSU, SCS Phone: 360-407-6771	Unit Supervisor for the Project Manager	Provides internal review of the QAPP, approves the budget, and approves the final QAPP. Reviews draft of report.
Jessica Archer, SCS Phone: 360-407-6596	Section Manager for the Project Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Dale Norton, WOS Phone: 306-407-6765	Section Manager for the Study Area	Reviews the project scope and budget, the draft QAPP, and approves the final QAPP.
Joel Bird, MEL Phone: 360-871-8801	Director	Reviews and approves the final QAPP.
William R. Kammin Phone: 360-407-6964	Ecology Quality Assurance Officer	Reviews and approves the draft QAPP and the final QAPP.

EAP: Environmental Assessment Program; WQP: Water Quality Program; BFO: Bellingham Field Office;
TSU: Toxic Studies Unit; SCS: Statewide Coordination Section; WOS: Western Operations Section;
MEL: Manchester Environmental Laboratory; EIM: Environmental Information Management database;
QAPP: Quality Assurance Project Plan

5.3 Organization chart

See Table 1 for the description of the organization chart.

5.4 Project schedule

The schedule for the project is described in Table 2.

Table 2: Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	Due date	Lead staff
Laboratory analyses completed	March 2017	
Environmental Information System (EIM) database		
EIM Study ID	ID number WHOB006	
Product	Due date	Lead staff
EIM data loaded	March 2017	Melissa McCall
EIM data entry review	April 2017	Siana Wong
EIM complete	May 2017	Melissa McCall
Final report		
Author lead / Support staff	William Hobbs	
Schedule		
Draft due to supervisor	April 2017	
Draft due to client/peer reviewer	May 2017	
Draft due to external reviewer(s)	June 2017	
Final (all reviews done) due to publications coordinator	July 2017	
Final report due on web	August 31, 2017	

5.5 Limitations on schedule

There are no foreseen limitations on the project schedule.

5.6 Budget and funding

MEL will conduct analyses of TP, carbon, and nitrogen. The analysis of sediment organic, carbonate, and mineral fractions through loss-on-ignition (LOI) will be carried out by Ecology's Toxics Studies Unit staff with no associated lab costs.

Table 3: Laboratory budget

Parameter	Field Samples (# of samples)	QA Samples* (# of samples)	Total Number of Samples	Cost per Sample	MEL Subtotal	Contract Lab Subtotal	MEL Contract Fee
TP	25	3	28	$50	$1,400	---	---
C and N	25	25	50	$50	$2,500	---	---
				MEL subtotal	**$3,900**	**---**	**---**
				Lab Grand Total	**$3,900**		

* Includes only QA samples that are not free of charge with the analysis.

6.0 Quality Objectives

6.2 Measurement Quality Objectives

Table 4: Measurement quality objectives.

Analyte	LCS (recovery)	Lab Duplicates (RPD)	Method Blanks	Matrix Spike (recovery)	Matrix Spike Duplicates (% recov.)	Surrogate Standards (% recov.)	Lowest Concentration of Interest
TP	85 - 115%	<20%	< LOQ	75-125%	<20%	NA	5.0 mg/kg
C and N	NA	<20%	< LOQ	NA	NA	NA	0.1%
LOI	NA	<20%	NA	NA	NA	NA	1.0%

LCS: Laboratory control samples
LOI: loss-on-ignition

7.0 Sampling Process Design (Experimental Design)

7.1 Study design

This project will analyze TP, carbon, and nitrogen in archived sediment from the Lake Whatcom sediment core collected in 2015. Up to 25 sediment intervals will be analyzed, depending on availability of archived material. Sediment intervals will be selected based on the age-depth model to provide an estimate of TP in sediment for discrete periods of time (pre-1900, 1900-1950, and 1950 present). Sediments have been stored frozen since the time of collection which is appropriate for the long-term storage of lake sediments. The holding time for metals in sediments that are frozen is two years (MEL, 2016).

9.0 Measurement Methods

9.2 Lab procedures table

Table 5: Laboratory procedures.

Analyte	Number of Samples	Expected Range of Results	Reporting Limit	Analytical Method	Method Description
TP	25	<0.1 - 10 mg/kg	5.0 mg/kg	EPA 6020	ICP-MS
C and N	50	<0.1 – 5% C; <0.1 – 2% N	0.1%	EPA 440.0	CHN
LOI	25	1 – 80%	1%	ASTM D7348-13	LOI

LOI: loss-on-ignition

9.3 Sample preparation method(s)

Sediment samples for analysis of carbon and nitrogen will be fumigated using 1N hydrochloric acid to oxidize carbonates and provide a measure of organic carbon and nitrogen (Komada et al., 2008).

9.4 Special method requirements

The sediments will be assessed for organic, carbonate, and mineral fractions using an LOI technique (Dean, 1974; Heiri et al., 2001). This level of assessment of the lake sediments is one step above visual assessment and will be carried out by Toxic Studies Unit staff at the EAP operations center. The LOI method is based on the loss of mass of the sediments following drying (105ºC) and heating in a muffle furnace (550ºC – organic matter; 1000ºC – carbonates).

10.0 Quality Control (QC) Procedures

10.1 Table of field and lab QC required

Table 6: QC samples, types, and frequency.

Parameter	Matrix	Field		Laboratory			
		Blanks	Duplicates*	LCS	Method blanks	Analytical duplicates	Surrogates
TP	sediment	n/a	3	1/batch	1/batch	1/batch	n/a
C and N	sediment	n/a	n/a	n/a	1/batch	each sample	n/a
LOI	sediment	n/a	3	n/a	n/a	n/a	n/a

*Field duplicates are split samples; Batch = 20 samples or fewer

15.0 References

Anderson, N.J., Rippey, B., and Gibson, C.E., 1993. A comparison of sedimentary and diatom-inferred phosphorus profiles: implications for defining pre-disturbance nutrient conditions. Hydrobiologia, *253*(1-3), 357-366.

Appleby, P.G. and F. Oldfield, 1978. The calculation of lead210 dates assuming a constant rate of supply of unsupported ^{210}Pb to the sediment. Catena 5:1-8.

Berger, C.J. and S.A. Wells, 2005. Lake Whatcom Water Quality Model. Prepared by Portland State University for Washington State Department of Ecology, Olympia, WA. Publication Number 09-10-007. https://fortress.wa.gov/ecy/publications/summarypages/0910007.html

Butcher, J., 2008. Lake Whatcom Models Review. Prepared by Tetra Tech for Washington State Department of Ecology, Olympia, WA. Publication Number 09-10-013. https://fortress.wa.gov/ecy/publications/summarypages/0910013.html

Cadmus Group Inc. and CDM, 2007. Final Model Report for the Lake Whatcom Watershed TMDL Model Project. Prepared for U.S. Environmental Protection Agency Region 10 and Washington State Department of Ecology, Olympia, WA. Publication Number 09-10-010. https://fortress.wa.gov/ecy/publications/summarypages/0910010.html

Coots, R., 2006. Quality Assurance Project Plan: Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores. Washington State Department of Ecology, Olympia, WA. Publication Number 06-03-113. https://fortress.wa.gov/ecy/publications/summarypages/0603113.html

Dean, W.E. Jr., 1974. Determination of carbonate and organic matter in calcareous sediments and sedimentary rocks by loss on ignition: Comparison with other methods. J. Sed. Petrol. 44: 242–248.

Engstrom, D.R., J.E. Almendinger, and J.A. Wolin, 2009. Historical changes in sediment and phosphorus loading to the upper Mississippi River: mass-balance reconstructions from the sediments of Lake Pepin. Journal of Paleolimnology 41:563 – 588.

Heiri, O., A. Lotter, and G. Lemcke, 2001. Loss on ignition as a method for estimating organic and carbonate content in sediments. Journal of Paleolimnology 25:101-110

Hood, S., 2013. Lake Whatcom Watershed Total Phosphorus and Bacteria Total Maximum Daily Loads: Volume 2. Water Quality Improvement Report and Implementation Strategy. Washington State Department of Ecology, Olympia, WA. Publication Number 13-03-012. https://fortress.wa.gov/ecy/publications/summarypages/1303012.html

Kaushal, S. and M.W. Binford, 1999. Relationship between C: N ratios of lake sediments, organic matter sources, and historical deforestation in Lake Pleasant, Massachusetts, USA. Journal of Paleolimnology 22:439-442.

Komada, T., M.R. Anderson, and C.L. Dorfmeier, 2008. Carbonate removal from coastal sediments for the determination of organic carbon and its isotopic signatures, δ13C and Δ14C: comparison of fumigation and direct acidification by hydrochloric acid. Limnology and Oceanography Methods, 6:254-262.

Mathieu, C., 2015. Addendum 5 to Quality Assurance Project Plan: Depositional History of Mercury in Selected Washington Lakes Determined from Sediment Cores. Washington State Department of Ecology, Olympia, WA. Publication Number 15-03-113. https://fortress.wa.gov/ecy/publications/SummaryPages/1503113.html

Mathieu, C. and M. McCall, 2016. PBT Chemical Trends Determined from Age-Dated Lake Sediment Cores, 2015 Results. Washington State Department of Ecology, Olympia, WA. Publication Number 16-03-046.
https://fortress.wa.gov/ecy/publications/SummaryPages/1603046.html

MEL, 2016. Manchester Environmental Laboratory Lab Users Manual, Tenth Edition. Manchester Environmental Laboratory, Washington State Department of Ecology, Manchester, WA.

Mortimer, C.H., 1942. The exchange of dissolved substances between mud and water in lakes. The Journal of Ecology, 147-201.

Paulson, A.J., 2004. Sources of mercury in sediments, water, and fish of the Lakes of Whatcom County, Washington: U.S. Geological Survey Scientific Investigations Report 2004-5084, 98 p.

Paulson, A.J. and D. Norton, 2008. Mercury Sedimentation in Lakes in Western Whatcom County, Washington, USA and its Relation to Local Industrial and Municipal Atmospheric Sources. Water, Air, and Soil Pollution 189: 5-19.

Pickett, P. and S. Hood, 2008. Lake Whatcom Watershed Total Phosphorus and Bacteria Total Maximum Daily Loads: Volume 1. Water Quality Study Findings. Washington State Department of Ecology, Olympia, WA. Publication Number 08-03-024.
https://fortress.wa.gov/ecy/publications/summarypages/0803024.html

Rydin, E., 2000. Potentially mobile phosphorus in Lake Erken sediment. Water Research, 34, 2037-2042.

Søndergaard, M., Kristensen, P., and Jeppesen, E., 1993. Eight years of internal phosphorus loading and changes in the sediment phosphorus profile of Lake Søbygaard, Denmark. Hydrobiologia, 253(1-3), 345-356.

16.0 Appendix

Appendix. Whatcom Lake sediment core summary

Table A-1: Estimated dry mass, sediment interval age, and availability of remaining material for the Whatcom Lake core.

Depth (cm)	Interval thickness (cm)	% Solids	Porosity	Dry mass (g/cm^2)	Cumulative dry mass (g/cm^2)	Associated year w/ mid point	Archive
0-2	2	**0.127**	0.948875	0.276076	0.27607584	2013	
2-3	1	0.144	0.941349	0.158358	0.43443361	2009	
3-4	1	**0.161**	0.933644	0.179162	0.6135953	2004	
4-5	1	0.1805	0.924576	0.203644	0.81723903	***1996***	x
5-6	1	**0.2**	0.915254	0.228814	1.04605259	1988	
6-7	1	0.2015	0.914526	0.230779	1.27683161	***1979***	x
7-8	1	**0.203**	0.913797	0.232749	1.50958035	1970	
8-9	1	0.19825	0.916102	0.226526	1.73610623	***1963***	x
9-10	1	0.1935	0.918391	0.220345	1.95645165	1956	
10-11	1	0.18875	0.920664	0.214207	2.17065855	***1949***	x
11-12	1	**0.184**	0.922922	0.20811	2.37876847	1943	
12-13	1	0.1813	0.924183	0.204705	2.58347357	***1935***	x
13-14	1	0.1787	0.92544	0.201313	2.78478672	***1928***	x
14-15	1	**0.176**	0.926691	0.197934	2.98272074	1920	
15-16	1	0.1710	0.929025	0.191632	3.17435317	***1907***	x
16-17	1	0.1660	0.931343	0.185375	3.3597283	***1894***	x
17-18	1	**0.161**	0.933644	0.179162	3.53888999	1882	
18-19	1	0.1595	0.934331	0.177306	3.71619612	***1865***	x
19-20	1	0.158	0.935017	0.175454	3.89165059	***1849***	x
20-21	1	0.1565	0.935701	0.173607	4.06525728	***1833***	x
21-22	1	**0.155**	0.936384	0.171763	4.23702006	*1817*	x
22-23	1	0.15475	0.936498	0.171456	4.40847589		x
23-24	1	0.1545	0.936611	0.171149	4.57962488		x
24-25	1	0.15425	0.936725	0.170842	4.75046714		x
25-26	1	**0.154**	0.936839	0.170536	4.92100278	*1754*	x
26-27	1	0.1555	0.936157	0.172377	5.09337977		x
27-28	1	0.157	0.935473	0.174222	5.26760195		x
28-29	1	0.1585	0.934788	0.176071	5.44367321		x
29-30	1	**0.16**	0.934102	0.177924	5.62159743	*1690*	x
30-31	1	0.1632	0.932633	0.18189	5.80348766		x
31-32	1	0.1664	0.931158	0.185874	5.98936176		x
32-33	1	0.1696	0.929676	0.189876	6.1792377		x
33-34	1	0.1728	0.928187	0.193896	6.37313357		x
34-35	1	**0.176**	0.926691	0.197934	6.57106759	*1603*	x
35-36	1	0.177636	0.925924	0.200006	6.77107366		x
36-37	1	0.179273	0.925154	0.202083	6.97315658		x
37-38	1	0.180909	0.924383	0.204165	7.17732119		x
38-39	1	0.182545	0.923611	0.206251	7.38357233		x

Depth (cm)	Interval thickness (cm)	% Solids	Porosity	Dry mass (g/cm^2)	Cumulative dry mass (g/cm^2)	Associated year w/ mid point	Archive
39-40	1	0.184182	0.922836	0.208343	7.59191487	*1508*	x
40-41	1	0.185818	0.92206	0.210439	7.80235368		x
41-42	1	0.187455	0.921281	0.21254	8.01489367		x
42-43	1	0.189091	0.920501	0.214646	8.22953975		x
43-44	1	0.190727	0.91972	0.216757	8.44629685		x
44-45	1	0.192364	0.918936	0.218873	8.66516992		x
45-46	1	**0.194**	0.91815	0.220994	8.88616393	*1392*	x

Bold = measured solids
Bold italic = interpolated
Blue italic = extrapolated