

BASF Corporation

Groundwater/Surface Water Interface Work Plan

**Point Hennepin
Wayne County, Michigan**

May 17, 2024

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Prepared By:

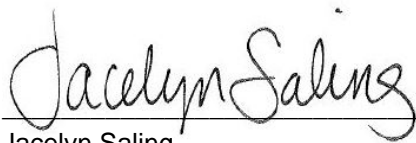
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Acronyms and Abbreviations

Arcadis	Arcadis of Michigan, LLC
BASF	BASF Corporation
COC	contaminant of concern
CSM	conceptual site model
DBO	distiller blowoff
EC	electrical conductivity
EGLE	Department of Environment, Great Lakes, and Energy
GSI	groundwater to surface water interface
MS/MSD	matrix spike/matrix spike duplicate
NREPA	Natural Resources and Environmental Protection Act
PDMS SPME	polydimethylsiloxane solid phase microextraction
QA/QC	quality assurance and quality control
Site	Point Hennepin, located in Wayne County, Michigan
sVOCs	semivolatile organic compounds
TOC	total organic carbon
VOCs	volatile organic compounds
Work Plan	Groundwater/Surface Water Interface Investigation Work Plan

1 Introduction

On behalf of BASF Corporation (BASF), Arcadis of Michigan, LLC (Arcadis) prepared this Groundwater/Surface Water Interface (GSI) Investigation Work Plan (Work Plan) for Point Hennepin, located in Wayne County, Michigan (Site; Figure 1). Point Hennepin is a 225-acre island located in the Detroit River located immediately north of Grand Ile and east of Wyandotte, Michigan. The objective of this Work Plan is to outline an approach to evaluate GSI compliance at the Site. The overarching goal for the Site is to obtain site closure through the Michigan Department of Environment, Great Lakes, and Energy (EGLE) voluntary Part 201 program that incorporates a sustainable perimeter groundwater management approach in harmony with utilization of the Site as a wildlife refuge. Work to establish the Site as a permanent wildlife refuge will occur separately, but in conjunction with Site closure under Part 201. The general approach and rationale for this GSI Investigation Work Plan were presented to the EGLE at a meeting held in April 2024.

1.1 Objective and Approach

Point Hennepin is an island in the Detroit River upon which distiller blowoff (DBO) was placed in slurry form from the 1920s until approximately 1951. The slurried material was allowed to dry and currently the material of DBO-origin is primarily a soil-like material that provides substrate for vegetation on the island. A geophysical investigation completed in 2021 and 2022 (Arcadis 2022) in combination with a hydraulic investigation completed in 2023, identified perimeter areas of higher and lower priority of potential groundwater and surface water (i.e., Detroit River) interaction based on several lines of evidence including electrical conductivity response, relative groundwater and surface water levels, hydraulic gradients, and specific conductivity and temperature (Arcadis 2024). The areas identified as higher priority are the focus of this Work Plan.

Groundwater sampling from wells on the island has historically been conducted at the Site, however, the most recent data is nearly 20 years old and was not collected in the higher priority areas. This Work Plan includes collecting updated groundwater sampling data from the existing perimeter piezometers to screen higher priority areas relative to GSI criteria to identify an appropriate GSI compliance approach.

Two phases of sampling are proposed: groundwater sampling (Phase 1) and GSI sampling (Phase 2). Phase 1 will include a groundwater sampling program using existing shoreline piezometers in high priority areas (Figure 2), as identified by the Hydraulic Investigation (Arcadis 2024). Results will be used to assess current potential contaminant of concern (COC) concentrations, pH, geochemistry, and microbial processes in groundwater at these perimeter locations. Results of the perimeter groundwater sampling program will support design of the details of Phase 2 sampling, which will assess conditions relative to GSI compliance under the Part 201 regulations. Note that exceedances of GSI criteria at the perimeter do not indicate a GSI compliance concern, but rather informs the development of the GSI compliance approach and next steps for data collection.

The following activities will be performed under this Work Plan:

- Phase 1 Groundwater Sampling
 - Attempt retrieval of pressure transducer lost down PZ-11 during the Hydraulic Evaluation (Arcadis 2024)
 - Deploy pressure transducers in PZ-11, SMW-1, SMW-2, and SW-05 to collect groundwater elevation data if pressure transducer retrieval is not possible in PZ-11 (Figure 2)

- Sample 10 piezometers near shoreline in higher priority areas at a quarterly frequency (Figure 2)
- Phase 2 GSI Sampling Work Plan (follows the execution and data interpretation associated with Phase 1)
 - Update the Conceptual Site Model (CSM) with respect to the biological and geochemical data collected. The updated CSM will be provided with the Phase 2 GSI Compliance Sampling Work Plan.
 - Evaluate results of the Phase 1 groundwater sampling against GSI criteria, as applicable
 - Determine applicable GSI compliance approach which may include one or more of the following:
 - Mixing zone
 - Alternative monitoring points
 - Ecological assessments
 - Modeling assessments
 - Natural attenuation
 - Passive or active remediation
 - Prepare the proposed data development approach for the Phase 2 investigation by describing specific tasks to be completed.

1.2 Applicable Regulatory Framework

This Work Plan was developed to support Site closure via Part 201 of Michigan’s Natural Resources and Environmental Protection Act (NREPA) with a focus on GSI compliance in areas of the site perimeter that are assessed to be priority areas of groundwater venting to the Detroit River. Pursuant to Section 324.20220e of NREPA, BASF is developing a response activity to assess and accordingly address potential venting groundwater from the Site. The primary exposure pathway at the Site is the GSI because the potential exists for groundwater above relevant criteria from the Site to discharge to the Detroit River. The approach presented in this Work Plan was developed in consideration of EGLE (2018) guidance as a step to inform the development of a GSI compliance approach. Exceedances of GSI criteria at the perimeter that may be identified during the execution of this work plan do not indicate a GSI compliance concern, but rather informs the development of the GSI compliance approach and next steps for data collection.

2 Phase 1 Investigation Activities

This section describes field activities to be conducted as part the Phase 1 investigation and associated data analysis to inform the Phase 2 GSI compliance assessment.

2.1 Pressure Transducer Retrieval and/or Deployment

During the 2023 Hydraulic Evaluation, pressure transducers were deployed at all piezometers, stilling wells, and a subset of upland monitoring wells across the site to collect high frequency water level and temperature data. Approximately one month into the monitoring period, the pressure transducer in PZ-11 was lost down the piezometer and could not be recovered. The lack of data over the monitoring period resulted in the channel area that separates Point Hennepin from Grosse Ile being identified as a data gap. Although the pressure transducer fell to the bottom of the piezometer, it is presumed to have still been collecting data over the monitoring period. If

it can be retrieved, then the hydraulic evaluation will be completed using the data logged on the recovered pressure transducer.

Pressure transducer retrieval will be attempted at PZ-11 using vacuum methods or similar. If retrieval attempts fail, then non-vented pressure transducers will be deployed in PZ-11, SMW-1, SMW-2, and SW-05 to collect water level data, temperature, and/or specific conductivity data for a total of 3 months. A barometric pressure transducer will be deployed at the Site to measure atmospheric pressure during the monitoring period. The barometric pressure measurements will be used to compensate and evaluate the influence of and correct for barometric pressure induced changes to groundwater levels. Manual water levels to a survey reference point will be collected during pressure transducer deployment and download events (monthly). This data set will allow for hydraulic evaluation which mimics what was completed in the 2023 Hydraulic Evaluation (Arcadis 2024).

If the hydraulic analysis for the channel area suggests that it is a high priority area, associated piezometers will be included in the Phase 1 groundwater sampling program, as appropriate.

2.2 Groundwater Sampling

Groundwater samples will be obtained from 10 existing shoreline piezometers in high priority areas (Figure 2). This will include the following piezometer pairs:

- Southwestern portion of Point Hennepin
 - PZ-01S/D, PZ-02S/D, and PZ-03S/D
- East central portion of Point Hennepin
 - PZ-08S/D and PZ-09S/D

Prior to sampling, the piezometers will be opened and allowed to equilibrate. A depth to water measurement will be collected to determine the water level in the piezometer. All piezometers will be sampled with a peristaltic pump capable of low flow rates to complete low flow sampling methodology. If there is sufficient water column in the piezometer, the pump intake will be placed at the midpoint of the screen. The field parameters including temperature, pH, dissolved oxygen, oxygen reducing potential, specific conductance, and turbidity will be measured at timed intervals during the purge. Purging of the piezometers will continue until field parameters have stabilized over three (3) consecutive readings.

Following stabilization, groundwater samples will be placed into laboratory supplied sample containers for analysis. The groundwater samples will be submitted under chain of custody protocols to a Michigan certified lab and analyzed for the list of analytes provided in Table 1. Analytes will include:

- Iron and Manganese
 - Iron and manganese can support microbial activity driven by any biologically available carbon in the groundwater system. That includes interactions with sulfate and trivalent nitrogen.
 - If sulfate reduction takes place dissolved iron will react with sulfide (potentially toxic to microbial activity) to form insoluble iron sulfides.
 - Ferric iron can stimulate denitrification.
- Background Cations – Calcium, Magnesium, Sodium and Potassium
 - Allows for the assessment of the ion balance in the sample. It also provides information on the forensic history of the groundwater such as groundwater flow paths, interactions with fill, and interactions with infiltrating rainfall.

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- Background Major Anions – Alkalinity, Chloride, Sulfate, and Sulfide
 - Allow for the assessment of the ion balance of the sample and provides a forensic history.
 - Alkalinity can potentially indicate microbial activity, and autotrophic microbial populations require carbon dioxide for growth, which alkalinity can provide.
 - Ammonia nitrifying microbes are autotrophic.
 - Sulfate participates in microbial sulfate reduction
 - This in turn impacts iron chemistry and can have effect on trivalent nitrogen.
 - Total and Dissolved Sulfide
 - Dissolved Sulfide in hydrogen sulfide or the sulfide anion (depending on pH) the daughter product of sulfate reduction.
 - Total Sulfide is colloidal iron sulfide from the reaction of ferrous iron and sulfide, both can induce denitrification.
- Tracer Ion – Bromide
 - Supports the forensic evaluation of the groundwater such as groundwater flow paths, interactions with fill, and interactions with infiltrating rainfall.
- Nitrate/Nitrite
 - Nitrate is the daughter product of ammonia nitrification.
 - Nitrite is also an ammonia system reaction daughter product, but more importantly it is critical for the anaerobic Anammox process that directly converts ammonia to nitrogen gas (N₂).
- Ammonium
 - The ionized form of trivalent nitrogen (vs. Ammonia) – determined by the concentration of total ammonia and the pH of the sample at the time of sample processing.
- Metals (filtered and unfiltered) with filtered samples representing dissolved concentrations and unfiltered samples total concentrations.
 - In addition to the GSI implications, metals can participate in microbial processes when present as oxyanionic complexes such as: Arsenic; Chromium; Selenium; and Manganese.
- VOCs
 - In addition to GSI implications, some of these compounds can participate in microbial processing.
 - Reduction dehalogenation of chlorinated VOCs.
 - As a microbial carbon source.
- sVOCs
 - Lower molecular weight species can serve as a carbon source for microbial processing.
- Total Organic Carbon (TOC)
 - TOC provides a total assessment of dissolved carbon in the groundwater that may not be detected by the VOC and sVOC analysis.
 - The TOC provides a more accurate assessment of carbon that may be available for microbial processing in the groundwater system.
- QuantArray – Biogeochemical Profile

- This is a series of methods using deoxyribonucleic acid (DNA) analysis to identify specific microbial populations and their respective process dynamics that may be taking place in the groundwater system.
 - Nitrogen system (ammonia, nitrification, denitrification, and Anammox)
 - Sulfate and Iron Reducers
 - Methanogens
 - Aerobes
- The profile also provides a quantitative estimate of the population numbers of the respective microbes detected.
- Biological Oxygen Demand (BOD)
 - Identifies the stoichiometric oxygen demand for chemical species in the water that will react via biological processes. BOD is also an indicator of historical microbial activity or the potential for the stimulation of indigenous microbes for ammonia processing.
- Chemical Oxygen Demand
 - Similar to BOD but also includes reactions from inorganic species such as iron sulfides or ferrous iron that would consume oxygen if it were to be added to the system.
- Dissolved Gas Analysis – Carbon Dioxide, Methane, and Nitrogen
 - Carbon Dioxide and Methane are indicators of microbial activity.
 - Nitrogen is a byproduct of nitrification/denitrification or the Anammox process.

Groundwater sampling will be conducted quarterly for one year. The hydraulic investigation demonstrated seasonal variability is notable that could significantly impact the groundwater (and potentially contaminant) flux to the Detroit River, therefore, a full year of quarterly monitoring is recommended to capture this variability. After one year, the data collected will be evaluated to determine if further sampling is necessary or if it is sufficient to inform Phase 2. If additional data collection needs become apparent prior to the completion of one year of quarterly sampling, recommendations will be discussed with EGLE in parallel with the groundwater sampling.

In addition, surface water samples will be collected from the eastern and western side of the island in order to calculate GSI criteria. Samples will be collected utilizing either a peristaltic pump or a dipper sampler and placed in laboratory supplied sample containers for analysis. Grab samples will be screened for field parameters listed above and submitted to a Michigan certified lab and analyzed for total hardness (milligram per liter as CaCO₃) using method SM 2340B. The following quality assurance/quality control (QA/QC) samples will be collected during each sampling event:

- Trip blanks will be placed in each cooler that contains groundwater samples being analyzed for VOCs.
- Duplicate, matrix spike/matrix spike duplicate (MS/MSD), and equipment blank samples will be collected at a frequency of one per 20 samples and will be analyzed for the same COCs as the parent sample.

2.3 Data Analysis and Interpretation

Following retrieval of the PZ-11 pressure transducer or after 3 months of water level monitoring, if required, data collected from the pressure transducers will be processed by removing shifts in water levels. These shifts typically result from the movement of the instruments that may occur when accessed. The data will also be calibrated with instrument water level measurements to water elevation with manual water levels measured at the respective well

from a known survey reference point. Specific conductivity and/or temperature data will also be evaluated at each location, as applicable, as additional lines of evidence to support the hydraulic analysis. These data, in combination with the sampling program data results, will aid in understanding the potential groundwater flux of COCs around the island. If the hydraulic analysis for the channel area suggests that it is a high priority area, associated piezometers will be included in the Phase 1 groundwater sampling program, as appropriate.

Following each groundwater sampling event, low flow sampling logs will be reviewed for completeness and accuracy. As analytical data is received, results will be reviewed, interpreted, and used as guidance for Phase 2. After one year, the data collected will be evaluated to determine if further sampling is necessary or if it is sufficient to inform Phase 2.

3 Phase 2 GSI Sampling Work Plan

Information and understandings developed under Phase 1 will be incorporated into an updated CSM, with a specific focus on GSI conditions at the Site. The groundwater results from Phase 1 groundwater sampling will be compared against GSI criteria, as applicable, to evaluate if specific COCs exceed relevant criteria. These potential exceedances will be assessed on an individual COC basis. Results from the Phase 1 data analysis will be used to identify an appropriate GSI compliance assessment approach for each COC to be included in the updated CSM. The updated CSM will provide the basis to identify an appropriate GSI compliance demonstration approach for each COC under the Part 201 regulations, which may include (but are not limited to):

- Mixing zones for COCs that are not bioaccumulative and do not exceed the final acute value for aquatic life;
- Alternative monitoring points designed to measure COCs in groundwater that is venting at the GSI;
- Ecological assessments to evaluate the likelihood of adverse ecological effects as a result of exposure of aquatic life and/or wildlife to COCs in venting groundwater;
- Modeling assessments to determine compliance with the GSI pathway using scientifically valid modeling approaches that are calibrated and verified with site-specific field data;
- Natural attenuation demonstration in accordance with published reference documents;
- Passive or active remediation where treatment is required to reduce concentrations of COCs to below applicable GSI criteria prior to groundwater venting to surface water.

Note that exceedances of GSI criteria at the perimeter do not indicate a GSI compliance concern, but rather informs the development of the GSI compliance approach and next steps for data collection. Additional data collection may be needed to support the GSI compliance approach and a Phase 2 work plan will be prepared to describe the specific data development activities. Data development activities may include (but are not limited to):

- Collect data/information required to request a calculation of mixing zone-based GSI criteria consistent with Procedure RRD-32
- The use of alternative monitoring points for the collection and analysis of groundwater venting at the GSI.
- Complete ecological assessments to evaluate ecological effects to aquatic life and/or wildlife with respect to venting groundwater
- Collect Site-specific data needed to calibrate potential modelling efforts
- Obtain lines of evidence to demonstrate natural attenuation in accordance with published approaches
- Acquire data to evaluate or design a potential passive or active remedy

If alternative monitoring points are identified as a potential GSI compliance approach (i.e., alternatives to using shallow groundwater piezometers installed on land along the site shoreline), sampling of groundwater venting at the GSI may be recommended. A potential method for this sampling includes using sediment high resolution (i.e., with closely-spaced sampling ports for specific depth intervals below the sediment surface) passive profiler (passive profiler). This device has demonstrated reliability in measuring a wide range of COCs and it has also been used to estimate groundwater upwelling velocity (Jackson et al. 2022). This method serves as one potential alternative that may be proposed in the Phase 2 Work Plan. Specific details about the monitoring approach, including locations, number of samples, and COCs to be monitored, will be described in the Phase 2 Work Plan.

While various methods of construction are described in the literature, if passive sampler profilers are proposed, the passive profiling device would be constructed from stainless steel and features multiple sets of equilibrium cells positioned approximately every 2 centimeters (cm). These cells sample analyte concentrations in porewater at various depths by using a pre-filled reservoir of water within the equilibrium cells that equilibrates with the porewater through a micro-porous membrane. The cells have replaceable membranes that are secured by a stainless-steel cover plate, with each cell opening protected by a mesh. Each equilibrium cell is pre-loaded with a known concentration of bromide, serving as a performance reference tracer to evaluate the equilibrium status with the groundwater.

If sampling of sVOCs with relatively low water solubilities is needed based on the Phase 1 results, polydimethylsiloxane (PDMS) solid phase microextraction (SPME) fibers will be utilized as passive samplers to sample these compounds from the upwelling groundwater. The SPME fibers are attached to the mesh on the equilibrium cover plate (see Figure 3). When deployed, sVOCs continuously diffuse into the SPME fiber until equilibrium is achieved. C-13 labeled or deuterated sVOCs may be introduced in the SPME fibers at low concentrations and analyzed to monitor the equilibrium process.

Additionally, the device includes multiple sets of “velocity” cells situated at the top, the bottom, and between two sets of equilibrium cells. Each set of velocity cells has four cells of various surface area opening-volume ratios. These cells come preloaded with bromide solutions and gradually release the bromide as conservative tracers into the surrounding environment through the membrane. This allows for the measurement of tracer flux and subsequent analysis of groundwater upwelling velocity to ensure that the monitoring points are located in areas that are representative of the groundwater venting to surface water. The number of sets of equilibrium cells and velocity cells, and cells in each set will be determined in coordination with the manufacturer.

If microbial community assessment is needed based on the Phase 1 results, micro-scale bio-trap cells may be added for microbial community analysis.

An example configuration of this type of sampling device is presented on Figure 3.

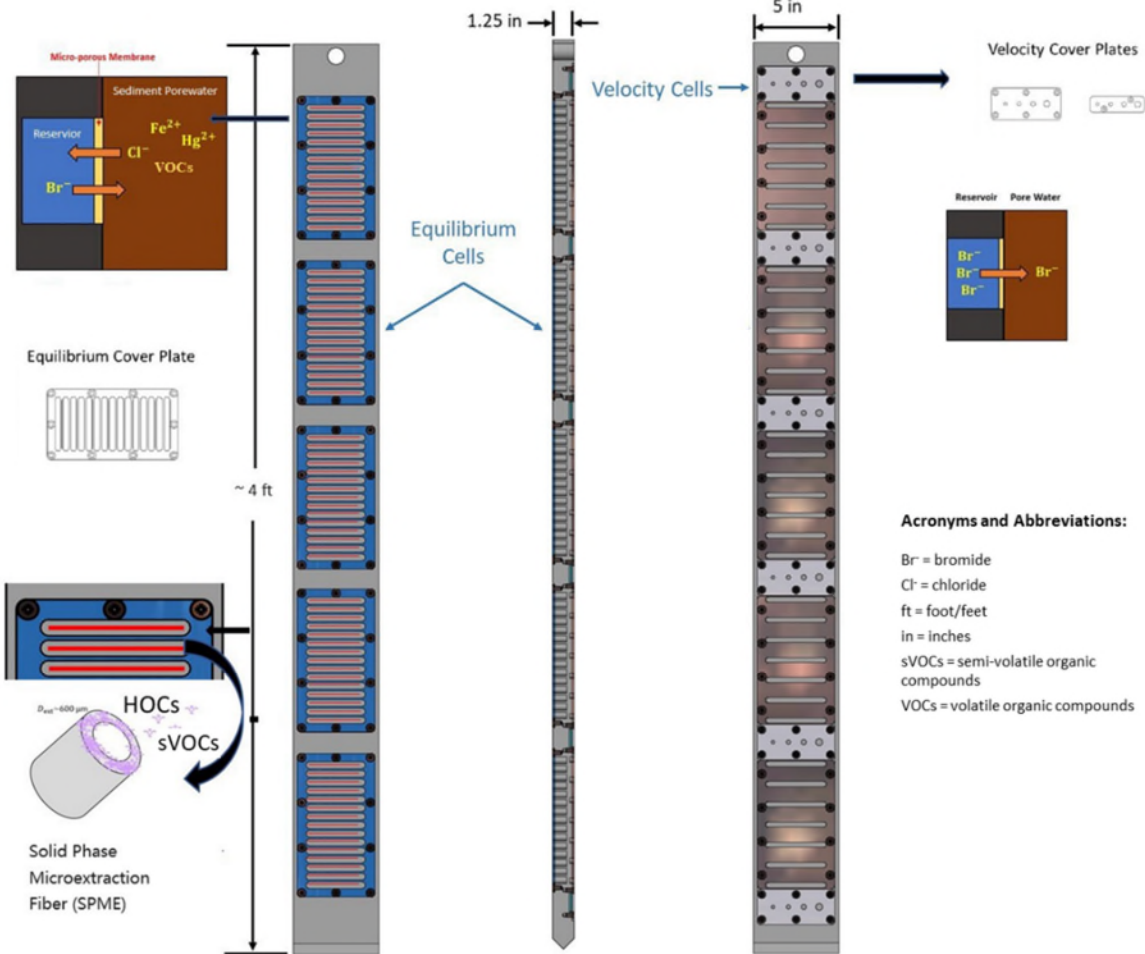


Figure 3. Sediment High Resolution Passive Profiler (Adapted from Jackson et al. 2022)

The passive profiler devices would be installed using the weight of a Vibracore head to push them into the sediment/substrate materials present in the GSI venting area, or by driving them in using manual force if sediments are soft. Prior to field deployment, the equilibrium and velocity cells of the passive profiler will be filled with bromide solutions. During the deployment, the samplers will be placed up to 3.5 feet below sediment surface for a duration of nominally 28 days to represent groundwater upwelling flux measurements. Conductivity may be measured at the water bottom above the sediment-water interface to inform the data analysis and modeling. Procedures for the passive profiler installation and retrieval are included in Appendix A. Sampling number, locations, and schedule will be informed by the hydraulic investigation findings (Arcadis 2024) and Phase 1 results and will be provided to EGLE prior to implementation for review.

After retrieval, the reservoir water from each cell (cell water) and the SPME fibers attached to the mesh on the equilibrium cover plate will be collected from the devices. The equilibrium cell water samples and SPME fibers will be submitted to a Michigan certified laboratory and analyzed for a subset of the analytes listed in Table 1 to be selected based on the Phase 1 sampling results.

If the results from Phase 1 indicate that passive profilers are not ideal for the Site-specific conditions (i.e. the analytes requiring further assessment and/or based on the CSM), a different methodology for collecting alternative monitoring point samples will be proposed to EGLE for review following the Phase 1 implementation, data analysis, and interpretation.

4 Reporting

The results from Phase 1 activities described in this Work Plan will be provided in a report for EGLE review. The Phase 1 report will include the summary of activities and supporting documentation. The data evaluation will include charted data and supporting tables and figures to support the development of the GSI compliance approach. Additional proposed activities will be described in the Phase 2 work plan. The proposed Phase 2 CSM update, GSI compliance approach and associated data collection requirements will be described in a work plan to be provided following review of the Phase 1 results with EGLE.

5 Implementation Schedule

Quarterly groundwater sampling activities discussed in this Work Plan will begin upon concurrence from EGLE. Results of the Phase 1 sampling will be discussed in quarterly meetings with the EGLE during the execution of the Phase 1 to keep EGLE updated on the ongoing work. If additional data collection needs become apparent prior to the completion of Phase 1 (i.e. one year of quarterly sampling), recommendations will be discussed with EGLE during the quarterly meetings in parallel with the ongoing groundwater sampling.

Report preparation will begin after all analytical data have been received and the GSI compliance approach has been developed.

6 References

- Arcadis. 2024. Hydraulic Investigation Summary Report. Point Hennepin, Wayne County, Michigan. February 8.
- EGLE. 2018. Groundwater-Surface Water Pathway Compliance Options. Remediation and Redevelopment Division Resource Materials. April 23.
- Jackson, A., Reible, D., Garza-Rubalcava, U., Hatzinger, P., & Lavorgna, G. 2022. High resolution passive profiling to monitor contaminated sediments in support of remediation evaluation and risk characterization. Environmental Security Technology Certification Program (ESTCP). <https://www.serdp-estcp.org/Program-Areas/Environmental-Restoration/Contaminated-Sediments/ER-201734>

Table

Analyte		Analysis Method	Purpose		
Geochemistry (Filtered and Unfiltered)	Alkalinity	Alkalinity (2320B or 310)	Geochemistry, Microbial Processes		
	Ammonium	Ammonium-Total Ammonia (350.1)	GSI Evaluation		
	Total Ammonia				
	Calcium	Metals (ICP SW 6010) Individual Metals	Geochemistry		
	Iron		Microbial Processes		
	Magnesium		Geochemistry		
	Manganese		Microbial Processes		
	Potassium		Geochemistry		
	Sodium		Geochemistry		
	Chloride		Chloride (SM4500-CL or EPA 325)	Geochemistry	
	Bromide	EPA Method 300.0	Forensic		
	Nitrate	Nitrate-Nitrite -Nitrogen (EPA 353.2)	Geochemistry		
	Nitrite		Geochemistry		
	Sulfide	SM4500	Geochemistry		
	Sulfate	Sulfate (EPA 375.4, D516, 4500, or 9038)	Geochemistry		
Metals (Filtered and Unfiltered)	Arsenic	Metals (ICPMS SW 6020)	GSI Evaluation, Microbial Processes		
	Cadmium	Metals (ICP SW 6010)	GSI Evaluation		
	Chromium		GSI Evaluation, Microbial Processes		
	Copper		GSI Evaluation		
	Lead		GSI Evaluation		
	Barium		GSI Evaluation		
	Nickel		GSI Evaluation		
	Selenium		GSI Evaluation, Microbial Processes		
	Silver		GSI Evaluation		
	Vanadium		GSI Evaluation		
	Zinc		GSI Evaluation		
	Volatile Organic Compounds		Volatile Organic Compounds (GC/MS) (SW 8260)	GSI Evaluation, Microbial Processes	
	Semivolatile Organic Compounds BNA (Base Neutral and Acid Extractables)		Semivolatile Organic Compounds (GC/MS) (SW 8270)	GSI Evaluation	
Total organic carbon			EPA 415.1 or SM5310	Microbial Processes	
Biogeochemical (BGC) Profile		QuantArray®	Microbial Processes		
Biochemical Oxygen Demand (BOD5)		Biochemical Oxygen Demand (SM5210B)	Microbial Processes		
Chemical Oxygen Demand		Chemical Oxygen Demand (E410.4)	Microbial Processes		
Dissolved Gas Analysis	Carbon Dioxide	RSKSOP-175	Microbial Processes		
	Methane				
	Nitrogen				
	Oxygen				

Note:

Microbial process evaluation analysis will be conducted once to determine current conditions, with potential for additional sampling based on initial results.

Acronyms and Abbreviations:

EPA = Environmental Protection Agency

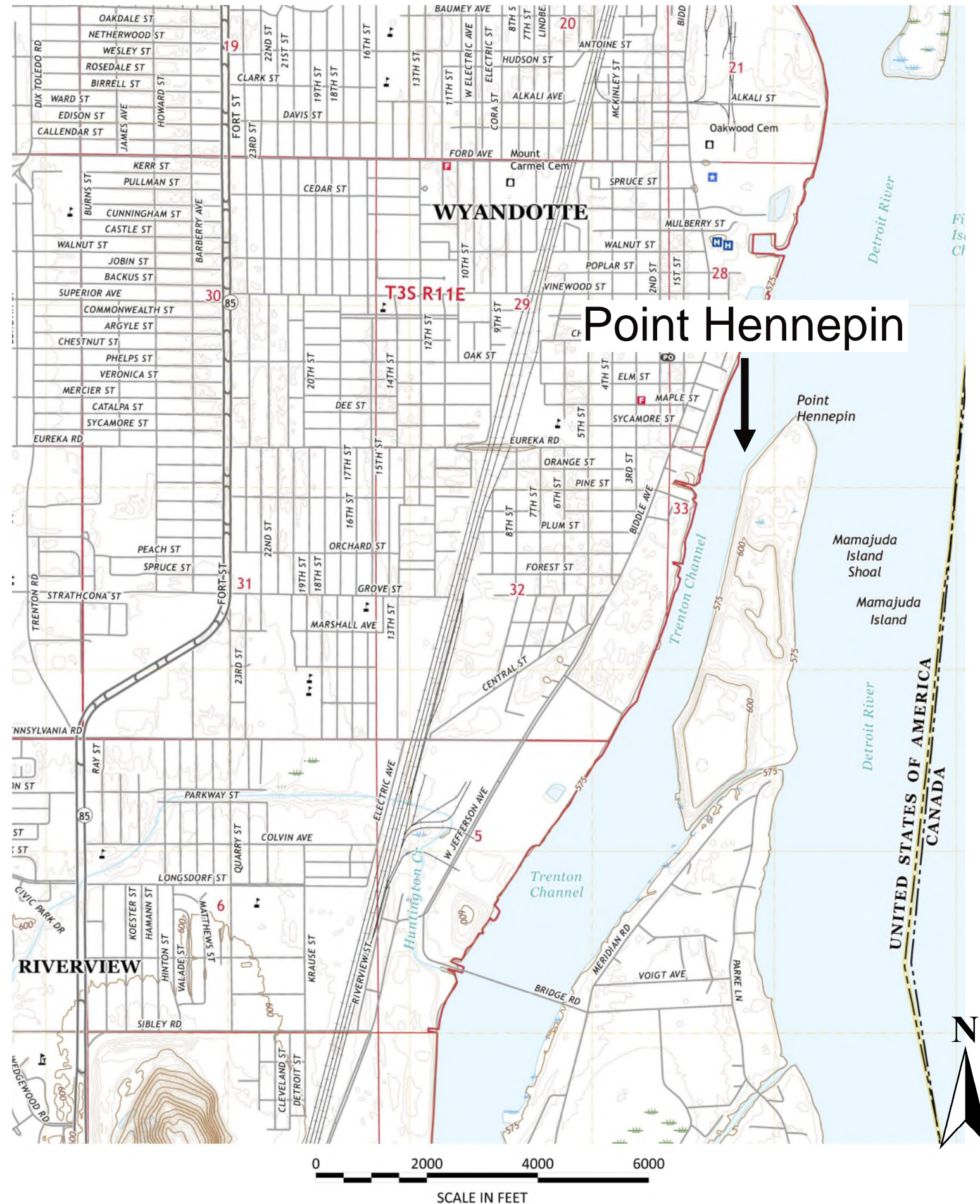
GC = gas chromatography

ICP = inductively coupled plasma

MS = mass spectrometry

RSKSOP = standard operating procedure developed by the R.S. Kerr EPA Laboratory in Ada, Oklahoma

Figures



Point Hennepin

2019 Quad
 Wyandotte Quadrangle Michigan-Wayne
 County
 7.5-Minute Series

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 Groundwater/Surface Water Interface Work Plan

SITE LOCATION MAP

 **ARCADIS** | FIGURE 1



Path: T:\ENVI\PT_Hennepin\PT_Hennepin_2023.aprx\RevFig9 PriorityAreas Last Saved By: AKENS 3/25/2024

LEGEND

- GOLDER 2021 BORING LOCATION
- EXISTING MONITORING WELL
- EXISTING MONITORING WELL (NON-VERIFIED LOCATION)
- ▲ PIEZOMETER
- ⊕ STILLING WELL
- ◆ HPT/ECT BORING LOCATIONS
- TOPOGRAPHIC CONTOURS (FEET NAVD88)

— HIGH PRIORITY AREAS (DASHED WHERE INFERRED)

LOWER PRIORITY AREAS (DASHED WHERE INFERRED)

DATA GAP AREA

FEC IN mS/m

530 35

NOTES:

1. Projection: North American Datum of 1983 Universal Transverse Mercator
2. Basemap source: Google Satellite, accessed 3/25/2024
3. Priority based on surface water responses in groundwater data, horizontal gradient directions, groundwater and surface water levels, and geophysics data.

ABBREVIATIONS:

ECT = electrical conductivity tool
HPT = hydraulic profiling tool
FEC = Formation bulk electrical conductivity of sediments beneath river bottom
mS/m = milliSiemens per meter
NAVD 88 = North American Vertical Datum of 1988

0 500 1,000
GRAPHIC SCALE IN FEET

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PRIORITY AREAS

FIGURE
2

Appendix A

Technical Methodology

Sediment High-Resolution Passive Profiler

The sediment high-resolution passive profiler (passive profiler) is a passive profiler device able to measure geochemistry parameters, metals, semi-volatile organic compounds (sVOCs), and volatile organic compounds (VOCs) at various depths. This is a potential method that may be used due to its capability to measure several parameters based on project-specific requirements via passive sampling technique. It has been successfully used at various sites, including Canal Creek, Grand Calumet River, Abraham Creek, and the Quantico Embayment (Jackson et al. 2022). It is available in different configurations depending on the project-specific goals.

This method serves as an example to illustrate its potential use in Phase 2. If it is selected, specific details about the monitoring approach, including locations, number of samples, and chemicals to be monitored, will be described in the Phase 2 Work Plan. In such case, this appendix will be updated and submitted to the Michigan Department of Environment, Great Lakes, and Energy for review and approval. Sampling will commence following approval of sampling locations and the updated appendix.

Sampling Device Configurations

The passive profiler sampling device, engineered from high-quality stainless steel, incorporates configurations designed to analyze dissolved species in upwelling groundwater at varying depths within sediment layers (Exhibit A-1). This section elaborates on the structural components and functionalities of the equilibrium cells, solid phase microextraction (SPME) fibers, and velocity cells, alongside their roles in tracing and analyzing dissolved contaminants and groundwater dynamics. The device features the components below.

Equilibrium Cells

The device boasts several sets of equilibrium cells, designated as Exhibit A-1. Each set comprises cells with spacing adjusted on a project-specific basis. This arrangement allows for the sampling of analyte concentrations across different sediment depths. Inside each equilibrium cell, a reservoir of water interacts with groundwater through a micro-porous membrane. This interaction facilitates the equilibration of analytes between the cell water and the upwelling groundwater, accurately reflecting the chemical composition in the groundwater. The opening of each cell, located just beyond the membrane, is protected by a stainless-steel or nylon mesh. This mesh, in conjunction with the membrane, is firmly secured beneath a stainless-steel cover plate, ensuring the integrity of the sampling process. A known concentration of bromide is pre-loaded into the equilibrium cells, acting as a performance reference tracer. This tracer aids in assessing the equilibrium state between the cell's internal water and the surrounding upwelling groundwater, enhancing the reliability of the sampling process.

SPME fibers

For sampling sVOCs with relatively low water solubility, the device may employ polydimethylsiloxane (PDMS) SPME fibers. These fibers, adept at passive sampling, are affixed to the mesh at the selected equilibrium cell openings. The SPME fibers can be assembled at an equivalent or lower resolutions compared to the equilibrium cells, depending on the needs for sampling profile depth. They uptake target analytes from the groundwater until equilibrium is reached. The process is monitored using C-13 labeled or deuterated compounds introduced into the fibers as performance reference compounds, providing a precise measure of the equilibrium state and the concentration of target analytes.

Velocity Cells

The velocity cells are positioned at multiple locations – the top, bottom, and between two sets of equilibrium cells. Each set houses four cells, differentiated by their surface-volume ratios. These cells are initially loaded with bromide solutions, which they release into the surrounding sediment as conservative tracers over time. The gradual diffusion of bromide allows for the measurement of tracer flux, offering valuable insights into groundwater upwelling flow rates and groundwater upwelling dynamics.

Micro-biotrap Cells

The microbial community can be assessed with micro-scale bio-trap cells that include Bio-Sep beads situated in a modified chamber, which is isolated from the sediments by a mesh. These beads gather microbial communities, which are then analyzed to determine their composition using the QuantArray procedure. This involves quantitative polymerase chain reaction (qPCR) analysis to identify a wide range of organisms/genes. Additionally, in certain scenarios, the activity of microbes can also be gauged through compound-specific isotope analysis (CSIA) of the contaminants captured by the Bio-Sep beads.

The exact number of cell sets, as well as the number of cells in each set, are determined through a collaborative process with the device's manufacturer, ensuring the sampling device meets the specific requirements of the project. The device facilitates understanding of aqueous chemistry and groundwater dynamics through the sampling profile of analytes and tracers with depth.

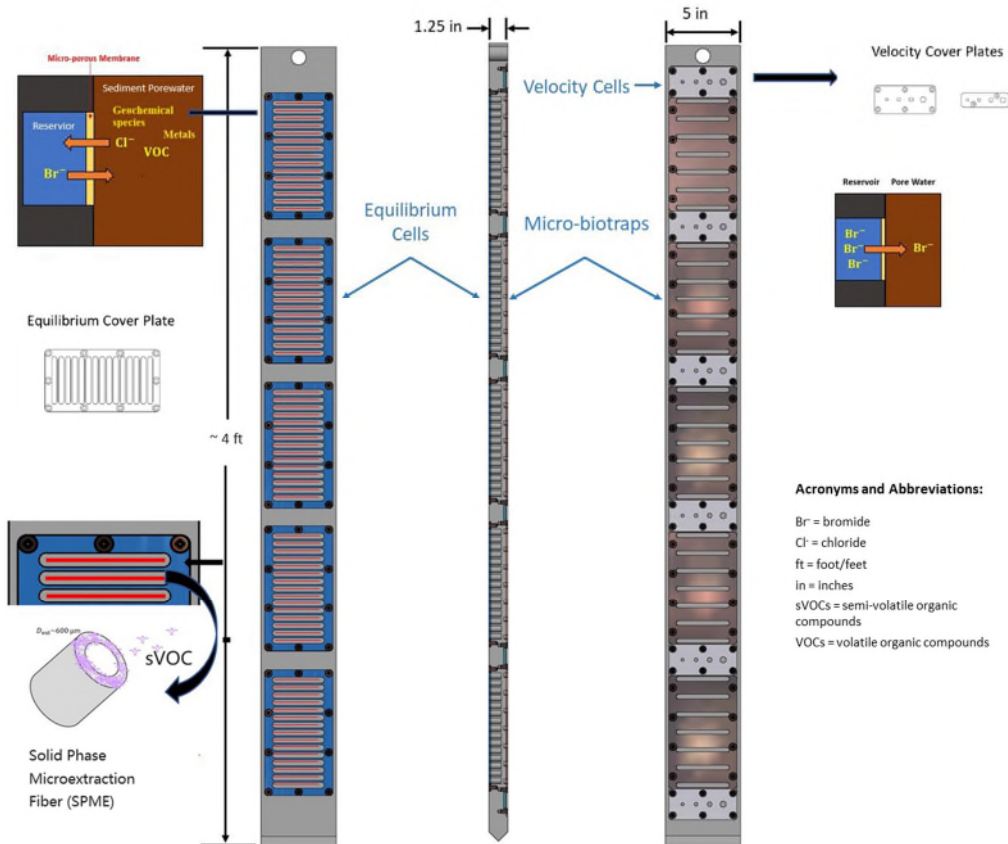


Exhibit A-1. Sediment High Resolution Passive Profiler (Adapted from Jackson et al. 2022)

Field Sampling Procedures

This section includes a brief description of procedures for the decontamination, preparation, deployment, retrieval, and demobilization of the passive profilers. Each phase includes:

- **Pre-sampling Decontamination** – This step includes cleaning the passive profiler from contaminants that could skew sampling results. It includes thorough cleaning with low phosphate detergent, rinsing with tap and deionized water, and methanol rinsing as final step to remove residual water. The profiler is then dried and wrapped in plastic sheeting for protection.
- **Preparation** - The profiler is prepared with a bromide solution to indicate the mass exchange between bromide and chloride. The bromide solution will be selected based on the environmental background concentrations and the recommendations of the profiler developer, typically ranging from 100-1000 milligram per liter (mg/L). This step involves submerging the cleaned profiler in a bromide solution, ensuring no air bubbles are trapped, assembling it with a Viton gasket, nylon membrane, and protective meshes, and securing it with screws. The profiler is kept submerged in the bromide solution until deployment to maintain the initial bromide concentration.
- **Deployment** - This involves positioning the profiler at the designated location and depth. This information will be provided in an updated work plan following completion of the Phase 1 sampling program. The profiler's global positioning system coordinates will be documented for its relocating upon retrieval. Data loggers may be used to monitor water quality parameters. The passive profiler devices will be installed by Vibracore or through manually driving from a boat in areas where the water is shallow and the sediments are soft. The profiler will remain at the sampling location for the duration provided in the work plan to collect data.
- **Retrieval and Cell Water Extraction** - After the deployment period, the profiler is retrieved, and samples are extracted from the equilibrium and velocity cells using syringes. If SPME fibers and Bio-Sep beads are involved in sampling, they will be collected from the devices. The samples are then prepared and shipped to the laboratory for analysis listed in the work plan.
- **Demobilization** - The profiler is cleaned, disassembled, and stored for future use. This includes removing sediment, detaching and cleaning components, and securely storing the profiler.

Data Analysis

The bromide solution samples collected during preparation and the water extracted from velocity cells will be analyzed for bromide concentrations following the method listed in the work plan. The post-deployment bromide concentrations will be compared to the pre-deployment concentrations to calculate the ratio of bromide loss using Equation A-1:

Equation A-1:

$$\theta_{Br} = C_{Br,f} / C_{Br,0}$$

Where:

$C_{Br,f}$: Post-deployment bromide concentrations

$C_{Br,0}$: Pre-deployment bromide concentrations

θ_{Br} : Ratio of loss

This ratio, alongside the surface-volume ratios of the cells, is used to calculate the mass transfer coefficient (k_{Br}) for the velocity cells by assuming the release of the bromide to the porewater follows the first-order kinetic model, according to Equation A-2.

Equation A-2:

$$k_{Br} = -\frac{1}{\tau} \frac{V}{A} \ln(\theta_{Br})$$

Where:

- k_{Br} : Mass transfer coefficient
- τ : Sampling duration
- V : Volume of the velocity cell
- A : Area of the velocity cell

An analytical solution for a two-dimensional quasi-steady-state system, described by Equation A-3 and developed by Choy and Reible (2017), is applied to correlate the mass transfer coefficient with the local Darcy velocity at the depth of sampling. Jackson et al. (2022) provides a comprehensive breakdown and derivation of the equation's parameters. By fitting this equation to the mass transfer coefficients (k_{Br}) calculated by Equation A-2 for velocity cells with differing surface-volume ratios, the Darcy velocity at specific depths is estimated.

Equation A-3:

$$k_{Br} = \frac{D_m}{\delta} \exp\left(\frac{D_m^2 L}{\delta^2 U D_z}\right) \operatorname{erfc}\left(\frac{D_m}{\delta} \sqrt{\frac{L}{U D_z}}\right)$$

Where:

- D_m : Diffusivity of bromide in the membrane
- δ : Membrane thickness
- L : Height of the velocity cell
- U : Darcy velocity
- D_z : Effective diffusion coefficient in sediment

Chloride-depth profiles serve two primary purposes: (1) to validate and clarify the Darcy velocity calculations detailed in Equation A-3; and (2) to assess the intensity of mixing within the benthic layer. Adopting the methodologies from Jackson et al. (2022) and Garza-Rubalcava et al. (2023), a one-dimensional (1-D) dynamic transport model, shown as Equation A-4, is employed to analyze the chloride profile in a dynamic sedimentary environment. This model comprehensively accounts for various transport mechanisms, including upward advection attributed to Darcy velocity, hydrodynamic dispersion, molecular diffusion, and the benthic mixing resulting from bioturbation and hyporheic exchange.

Equation A-4:

$$\varphi \frac{\partial C}{\partial t} = \frac{\partial}{\partial z} \left(-UC + (\alpha U + D_e + D_{ben}) \frac{\partial C}{\partial z} \right)$$

Where:

- φ : Porosity of the sediment
- D_e : Effective diffusivity corrected for tortuosity
- α : Hydrodynamic longitudinal dispersivity

D_{ben} : Benthic exchange coefficient

C : Chloride porewater concentration

z : Depth

The model is used to evaluate the benthic exchange coefficient to be depth-dependent variable, which follows a Gaussian intensity with depth (Shen et al. 2018).

Equation A-5:

$$D_{ben} = D_{ben,0} \exp\left(-\frac{z^2}{2\sigma^2}\right)$$

Where:

σ : The characteristic depth where benthic exchange intensity drops ~ 60% of its maximum value (at the sediment-water interface)

$D_{ben,0}$: The maximum intensity of benthic exchange (the intensity at the sediment-water interface)

Integrating Equations A-4 and A-5, a numerical method is employed to resolve the transport model, aiming to simulate the 1-D chloride profile. This simulation introduces two pivotal, yet initially undefined parameters: the maximum intensity of benthic exchange ($D_{ben,0}$) and the characteristic depth (σ). The resultant simulated profile, depicted on Exhibit A-2, undergoes comparison with the chloride profile acquired via the passive profiler for the following objectives:

- **Verification of Darcy Velocity:** This involves aligning the simulated chloride profile with the actual measurements by the passive profiler. Such comparison aims to verify the magnitude of the Darcy velocity estimated. At the bottom of the transient zone, benthic exchange impacts are presumed minimal, allowing the observed profile to predominantly reflect the interplay between Darcy velocity-driven transport, diffusion, and hydrodynamic dispersion.
- **Determination of Benthic Exchange Parameters:** Through model fitting the observed chloride profile in the benthic mixing zone and the upper portion of the transient zone, the benthic exchange parameters, the characteristic depth (σ) and the maximum benthic exchange intensity ($D_{ben,0}$) can be estimated. The measured chloride profile in these two zones reflects the interplay between the Darcy velocity-induced transport and localized benthic mixing dynamics.

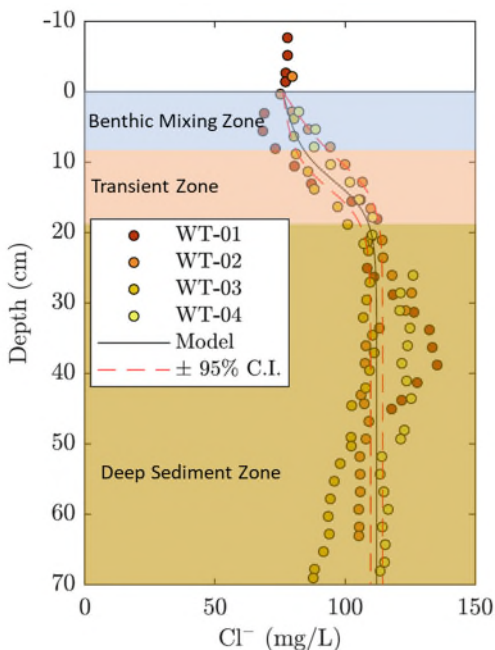


Exhibit A-2. Example of Chloride Profile (Jackson et al. 2022)

Evaluation of the COC Concentrations and Flux

If passive profilers are used in Phase 2, the COC concentrations at the upwelling groundwater/surface water interface (GSI) will be measured. The COC flux from groundwater upwelling to surface water may be calculated to support GSI compliance assessment, if applicable, by multiplying the COC concentrations measured at the GSI and the estimated groundwater upwelling velocity, following the Equation A-6.

Equation A-6:

$$Flux = U * C_{GSI}$$

Where:

Flux: The flux of COCs to the overlying waterbody along with the upwelling groundwater velocity

C_{GSI}: The concentration of COCs at the GSI.

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