

Hydrothermal Organic Geochemistry (HOG) sampler for deployment on deep-sea submersibles

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1. Abstract

The fate of carbon while passing through the rocky subseafloor of the ocean has direct implications on the global carbon cycle now and over geologic time, as well as the abundance and distribution of subseafloor life. Many organic geochemical studies require larger volumes of fluids than traditional hydrothermal samplers can provide, and also require rigorous steps to be taken to prevent contamination. The Hydrothermal Organic Geochemistry (HOG) sampler is designed to collect large volume (2 – 9 L) fluid samples with minimal introduction of organic or microbial contamination, and to be powered and deployed in real time from a submersible. Additional design constraints include utilizing materials appropriate for sampling fluids with elevated temperatures, fitting the sampler into the space available on the submersible, and minimizing the time needed to remove samples and prepare the sampler for re-deployment between dives. It utilizes two inlets, one devoted to natural abundance geochemistry and one that can be used for samples pre-dosed with isotopic labels or preservatives. Temperature probes providing real-time data are incorporated into each inlet to facilitate positioning the intake in areas of the hottest fluid flow, thereby minimizing entrainment of ambient bottom seawater while sampling. Fluids are shunted through two main conduits by a large volume pump. Smaller ports stemming off the main conduit connect to positive displacement fluid sample chambers and in situ filters. The outlets of these chambers and filter holders are connected to a 24-port valve, which in turn is connected to a small volume pump. The HOG sampler has successfully collected over 100 high purity fluid samples and 50 in situ filters during two expeditions to deep sea hydrothermal fields.

Highlights (3-5 bullet points, maximum 85 characters, including spaces, per bullet point)

- Sampler built for collecting hydrothermal fluid and filter samples
- Designed for collecting large (2-9 L) volumes and be 'clean' for organics
- Successfully deployed at three hydrothermal fields during two ocean cruises

Keywords: hydrothermal, organic geochemistry, microbiology, water sampler

Declaration of Interest: none

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1. Introduction

Seawater circulation through the rocky oceanic crust results in extensive transformations of both inorganic and organic compounds as a result of heating, fluid-rock interactions, microbial activity, and other processes. The fate of carbon while passing through hydrothermal systems has direct implications on the cycling of deep seawater dissolved organic carbon (DOC; Lang et al., 2006; Hawkes et al., 2015; Shah Walter et al., 2018), one of the largest reduced carbon reservoirs in the ocean ($\sim 622 \times 10^{15}$ g C; Williams and Druffel, 1987; Hedges, 1991; Hansell et al., 2009). Organic molecules can complex with dissolved trace metals such as iron to stabilize it in the water column (Toner et al., 2009; Sander et al., 2011; Resing et al., 2015), fueling primary production in the upper ocean thousands of kilometers from hydrothermal vent sites (Tagliabue et al., 2010). Under certain hydrothermal conditions, organic molecules can form in the absence of life, fueling microbial activity and potentially mimicking the earliest steps of pre-biotic chemistry (Lang et al., 2010; 2018; McDermott et al., 2015).

Studies of the organic geochemistry of hydrothermal fluids have lagged behind those of its inorganic chemistry and microbiology in part because of limitations in the ability to acquire samples of sufficient volume without contamination. To date, most reports of organic compounds in hydrothermal fluids focus on methane and other volatile compounds while the composition and even bulk concentration of non-volatile organic carbon are rarely reported due, in part, to lack of appropriate sampling equipment (Lang et al., 2019).

Here we describe a Hydrothermal Organic Geochemistry (HOG) sampler designed with the primary goal of collecting samples for organic geochemistry of hydrothermal fluids. Our goals were to allow (a) collection large volumes (2 – 9 L) of (b) elevated temperature fluids while (c) minimizing the risk of contamination, (d) fitting within the space available on the submersible, and (e) making the re-deployment of the sampler as simple and rapid as possible. Its versatility allows it to also be used for sampling in other environments with high fluid advection rates such as cold seeps, mud volcanos, and instrumented ocean drilling sites.

2. Design Constraints

A primary goal for building the sampler was to allow for the collection of larger fluid volumes than currently possible with most hydrothermal samplers. Many organic geochemical and microbiological analyses require very large volumes. Due to the low concentration of organic compounds in many hydrothermal fluids, organic carbon isotope analysis and isolation by solid phase extraction for Nuclear Magnetic Resonance (NMR) and Fourier Transform Ion Cyclotron Resonance (FT-ICR-MS) analysis requires at least a liter of sample and, ideally, would utilize 10 L or more (Repeta, 2015; Simpson et al., 2011). Isolation of viruses and microbial incubation experiments can often require tens to hundreds of liters (Breitbart et al., 2002; Anderson et al., 2014).

Hydrothermal fluids can reach 400°C (Campbell et al., 1988; Haase et al., 2007), although these fluids are not necessarily the primary target of most organic geochemical or microbiological analyses. Still, the vast majority of fluids of interest are at temperatures well above that of deep seawater. Sampling materials that come into direct contact with such fluids must therefore be capable of withstanding elevated temperatures.

Organic geochemical analyses are notoriously difficult to collect in a clean fashion. Famously, high concentrations of dissolved organic carbon were widely reported in the deep ocean, until it was later determined that these values were erroneously high due to contamination (Benner and Strom, 1993; Hedges, 2002). The ubiquity of organic carbon contaminants and the sensitivity of the analyses require that samples are collected and treated with as much care as those being collected for trace metals.

Since the sampler is designed to be deployed on a submersible such as a Remotely Operated Vehicle (ROV) or Human Occupied Vehicle (HOV), its size is limited by the available space. A modular design allows it to be deployed on different submersibles with different size constraints.

Finally, the time required to remove samples and prepare the sampler for re-deployment should be as short as possible. Some submersibles are now capable of turnaround times as short as 4 hours. To optimize bottom time, the sampler would ideally be able to be re-deployed within a similar time period.

Current sampling devices include titanium hydrothermal Major Samplers, which collect volumes of 750 mL (Von Damm et al., 1985). Samples designed to return fluids at pressure so as to preserve their volatile content are also relatively low volume, including titanium GasTight samplers (150 mL; Edmond et al., 1992), titanium isobaric gas-tight samplers (150 mL; Seewald et al., 2002), and a mechanical gas tight sampler (100 mL; Chen et al., 2007).

An alternative approach to collect fluids is by positive displacement. Flexible sample bags connected to the inlet are housed in water-tight chambers. Sampling commences when the water is pumped out of the chamber, causing a negative pressure gradient that draws fluid into the bag. This design is used by the commercial Remote Access Sampler (McLane Research Labs) as well as the custom-built Hydrothermal Fluid and Particle Sampler (HFPS; Butterfield et al., 2004) and the GeoMICROBE sampler (Cowen et al., 2012). All have been demonstrated to be capable of collecting a flexible range of fluid volumes and filter in situ with minimal contamination (Lang et al., 2006; Lin et al., 2012). The benefits of this approach are that the sample does not come into contact with the pump and that fluid volumes are constrained only by the size of the sample chamber. This approach was therefore chosen for the HOG sampler, with design elements adopted from both the HFPS and the GeoMICROBE sampler. The HOG sampler differs from the HFPS and the GeoMICROBE sampler in that the chambers for biology are separated from those for chemistry so that preservatives and isotopically labeled compounds can be pre-added to bags for microbiological studies without concern about cross-contamination.

3. Overview

The HOG sampler continually flushes fluids through two separate intakes, each with an embedded temperature probe that provides real-time temperature monitoring (Figure 1). These intakes lead to two separate flow paths, with one devoted to natural abundance geochemistry. The second flow path is devoted to microbiology and can accommodate incubation experiments spiked with isotopically labeled compounds or preservative. The separate flow paths ensure there is no cross-contamination between natural abundance and spiked samples.

Up to 24 individual samples can be collected on any individual dive. The main types of samples are 2 L water samples, large volume (9 L) water samples, and in situ filters. Two racks that house up to seven 2 L

sample chambers each (one for geochemistry, one for microbiology) are designed to be easily removed from the sampler frame without needing to offload other sampler components (Figure 2; Figure 3).

The electrically operated components were supplied by McLane Research Laboratories (Figure 4). A 4 L/min variable rate pump draws fluids through the main conduit. A 24-port valve connects to the outlet of all water sample chambers and in situ filters. A 250 mL/min variable rate pump connects to the home port of the 24-port valve so that it can be connected to any of the individual sample chambers or filters.

To collect a water sample, the main conduit is first flushed with sample fluid and the 24-port valve is turned to the appropriate connection. The 250 mL/min pump is then engaged to withdraw fluid from a water-tight sample chamber, causing sample fluid to be drawn into flexible bags. Check valves installed between the main conduit and the sample bags prevent cross-contamination between samples. The volume is monitored and sampling is halted after an appropriate volume has been pumped from the chamber. Filter samples are collected similarly but the volume of water they are capable of collecting is limited only by clogging and available dive time. A custom-built controller supplies the communication and power to the two pumps and the valve (McLane Research Laboratories). It is connected to the junction box of the submersible and controlled by company supplied software in real time. The controller housing was pressure tested to 8,200 PSI (5,500 m) by McLane.

The 2-L and large volume sample chambers take the most time to turnaround between deployments. Therefore, a full second suite of these chambers was manufactured so that they could be prepared for deployment while the first set was deployed. With this approach the HOG sampler could regularly be deployed on back-to-back dives even with 4 h turnaround times.

Specifics of the individual components and design choices are described in the following section (Table 1). A detailed component list including suppliers and part numbers is included as a supplementary table (Table S1).

Table 1. Main attributes of the HOG sampler

Attribute	Details
Pressure tested	8,200 PSI (5,500 m)
Weight in air	98 lbs
Weight in water	30 lbs
Minimum footprint	41" wide x 21.5" high x 28" deep
Intake and tubing material	titanium, PTFE lined braided hose assembly, PTFE connectors and tubing
Temperature probes	NKE Instrumentation, max temperature 450°C
Sample bag material	Kynar
Number of sample ports	24
Bag sample volumes	chamber dependent; currently 2L and 9L

4. Details

4.1. Titanium intake nozzle

The titanium intake nozzles were designed to prevent large solid material from entering the system and to allow a temperature probe to be incorporated into the intake stream (Figure 5). Each intake consists of titanium tubing (0.5" OD, 10.5" length) that has been specially welded with a cap. Six slots (0.125" wide x 0.75" long) were machined in the tube 0.25" in from the cap. A horizontal length of the same tubing (8.5" length) was welded at a right angle 8.0" in from the cap.

4.2. Temperature loggers

Monitoring temperature in real time is essential for the collection of high quality hydrothermal fluid. It is often very difficult to position the intake of a sampler in the hydrothermal fluid even when there is a clear orifice. The entrainment of deep seawater can be minimized by monitoring the temperature and adjusting the intake position into the warmest fluids.

The temperature loggers were purchased from NKE Instrumentation, and consist of a temperature sensor and a data pencil that reads the output from the sensor. The temperature sensor is powered with a lithium battery and can be deployed independently of the data pencil. It outputs a wireless signal that is read by the data pencil via an inductive link. The output of the data pencil is a 5-pin SubConn connector. For the purposes of sampling with a submersible, the data pencil was hardwired into the submersible's RS-232 feed by a 15' SubConn cable. The data is read in real time by PC using the manufacturer's software (WinMemoll), allowing real-time feedback on the positioning of the intake.

The narrow temperature probe is placed into the interior of the larger main titanium horizontal stem such that its tip is aligned with the intake slots at the end of the stem. The connection between the two is sealed with PTFE compression fittings (iPolymer). The probe is bent to reduce the total size of the intake, and allow easier maneuverability. A custom built aluminum housing with a u-handle houses the titanium intake and the temperature loggers, and allows the intake to be picked up by a submersible manipulator. It consists of a ½" diameter u-handle for durability during sampling (Figure 5).

4.3. Connection between titanium intake and main conduit

The tubing connecting the titanium intake to the main fluid conduit is made of inert materials, flexible enough to adjust to the intake being manipulated, and strong enough that the tubing would not kink if it is bent too aggressively. It consists of a PTFE lined braided hose assembly with 3/8" F-NPT connections (Swagelok). The titanium intake is connected to the hose via PTFE connectors (iPolymer).

4.4. Main conduit

Two fluid conduits carry the sample from the front basket of the submersible to the aft sled, where the body of the sampler is housed. The conduit is 3/8" OD tubing composed of either PTFE or PFA (Cole Parmer). Fluids are drawn through it with the 4 L / min variable rate pump (McLane Research Laboratories).

These conduits are each connected to separate titanium stems. The chemistry conduit consists of ½" OD titanium tube with seven ¼" OD stems welded at 5" intervals. The biology conduit is identical, but with a total of twelve stems welded at either 5" or 2.5" intervals (Figure 1).

172 After the titanium tube, the fluids then pass through a large volume strainer to prevent particles from
173 entering and damaging the pump (VacuMotion). They then pass through a visual flow indicator
174 (GemSensors) and, finally, to the 4L/min variable rate pump.

175 *4.5. 2 L chambers for water samples*

176 The design of positive displacement type sampling involves pre-filling sealed chambers with water. An
177 empty bag is housed in the water-filled chamber and connected to the main intake stem. Sampling
178 commences when the water is pumped out of the chamber, causing a negative pressure gradient and
179 drawing the sample fluid into the bag from the inlet side.

180 The 2 L sample chambers consisted of 4" diameter, 18.5" long acrylic tubes that are sealed on the
181 bottom with acrylic discs cut to size (Figure 6). The tops are acrylic lids with a lip to accommodate an o-
182 ring. A hole is drilled at the center to accommodate the bulkhead fitting that connects the Ti-stem to
183 the bag. A smaller tapped hole that can be sealed with a small plug (¼-28, tefzel) is also drilled in the
184 chamber lid so that bubbles could be removed prior to deployment.

185 The sample bags (16.5" length by 5.75" width, 2 L, see below for details) are connected to the main stem
186 through bulkhead fittings that breach the lid of the chamber. Fluids are shunted from the fluid conduit
187 into the titanium stem. Each bag is connected to the main stem with a ¼" check valve to prevent
188 backflow of sample from the bags after collection (Smart Products), a ¼" ball valve, and finally the
189 bulkhead fitting. Tubing (¼" PFA, Cole Parmer) connects the interior bulkhead fitting directly to the ¼"
190 Jaco fitting on each sample bag. The pathway of the sample fluid therefore does not come into contact
191 with the water in the sample chamber nor with the sampling pump.

192 The bottom of each sample chamber is drilled (¼") and tapped to allow water to be pumped out. Each
193 chamber is connected to a different port on the multi-port valve via flexible ¼" tubing. The exhaust of
194 the multi-port valve is connected to a 250 mL/min pump. Samples are collected by turning the valve to
195 the appropriate port number and the small pump was activated to withdraw the fluid from the
196 chamber.

197 The 2 L sample chambers are housed in two removable racks held in place by cotter pins. To remove the
198 racks, the main conduit inlet is disconnected in two places. The 24 outlet lines are each connected to a
199 different port on the valve. Several are shunted through six-tube quick disconnects (Cole Parmer) to
200 facilitate disconnecting and reconnecting the outline lines.

201 *4.6. Large volume chambers*

202 Sample volumes larger than 2 L are required for many applications including the analysis of trace
203 organics and viruses.

204 Large volume boxes are designed such that six could be mounted on the aft sled of ROV JASON II,
205 adjacent to the main frame of the HOG sampler, in a space alternatively occupied by the slurp sampler
206 (Figure 3). They are modular, however, and could be mounted in any location with sufficient space. They
207 house 9-L sample bags (20" length x 11" width).

208 *4.7. In situ filtering*

In some cases it is preferable to filter large volumes of fluid in situ rather than recovering the fluids themselves. Several of the ports are connected to 0.22 μm Sterivex™ filters to trap cells for DNA or RNA analysis, or 47 mm filter holders (Advantec, P/N 501200) to house filters for particulate organic carbon and sulfur analysis. Filter holders that can deliver RNA/ater™ to a filter immediately upon collection (McLane Laboratories; Cowen et al., 2012) are also employed. The volume of water that can be drawn through these filters is limited only by clogging and available dive time. The 250 mL/min pump provides real time feedback on flow rates and automatically halts pumping if flow rates drop below a set point. Therefore the total volume pumped and extent of clogging can be monitored.

4.8. Choice of bag material and design

The sample bag materials and design were chosen to (1) have a very low chemical blank, particularly for organics (2) be chemically inert, i.e. not cause the loss of compounds due to sorption (3) be sufficiently strong to survive handling and manipulation, including freezing and thawing (4) allow for acid cleaning with 10% HCl (v/v).

Sample bags were obtained from Pollution Measurement Corporation (PMC; PMCbags.com) and Keika Ventures (Keikaventures.com). Both companies offer a wide range of custom made bags with options for different materials, intake ports, and sizes. A ¼" Jaco compression fitting inlet was chosen in all cases as it is made from polypropylene and could be acid washed. It is also the same dimension as the titanium stem so would not require a step-down in tubing size. Bags of 10 mil Teflon® and 2 mil Tedlar® were ordered from PMC and bags of 3 mil Aclar®, 4 mil Kynar®, and 2 mil Tedlar® were ordered from Keika.

The bags were filled with Milli-Q water and tested for their ability to withstand regular handling. The 10 mil Teflon® was by far the strongest but was also too thick to manipulate easily. The 4 mil Kynar® was strong and able to withstand a drop from a short height. The 2 mil Tedlar® was reasonably strong but did eventually leak with rougher handling. The 3 mil Aclar® bags were very fragile and quick to leak along the seams.

Table 2. Blank testing of sample bags for dissolved organic carbon. Peak areas are reported since they are smaller than the lowest standard of (6.2 $\mu\text{mol/L}$).

Bag type	Time	Peak Area (mV sec^{-1})
Kynar (4 mil, Keika, 2.1 L)	0	3.0
	2 days	3.3
Teflon (10 mil, PMC)	0	3.2
	2 days	3.7
Aclar (3 mil, Keika)	0	2.3
	2 days	3.8
Tedlar (2 mil, PMC)	0	2.4
	2 days	4.7
Kynar (4 mil, Keika, 1.4L)	0	2.2
	2 days	4.3

Initial blank testing was carried out by first acid washing the bags (see section 4.9) then filling them with Milli-Q water and letting them sit at room temperature. Aliquots were withdrawn immediately after their initial filling and after 48 hours. Samples were analyzed for DOC content by persulfate oxidation on an isotope ratio mass spectrometer (Lang et al., 2012).

All of the aliquots had smaller peak areas than the smallest analyzed standard ($6.2 \mu\text{mol C/L}$, peak area 4.4 mV sec^{-1}), with the exception of the subsample from the Tedlar bag after 2 days (Table 2). One of the Kynar® bags had the smallest increase in peak area after 2 days while the other had the largest, likely due to issues with sample handling. These results indicated that the Kynar® bags were capable of storing samples with as low an extraneous carbon content as Teflon® bags. Since the Kynar® material was also suitably strong and flexible, this material was chosen for the bags.

According to the guidance posted on the Keika Ventures website, Kynar® bags have the potential concern that due to their chemical structure, highly polar compounds such as amines can adhere to the interior surface of the bag. An experiment was therefore carried out with amino acids to determine if any loss occurred with storage. After acid cleaning (see section 4.9), a bag was filled with Milli-Q water spiked with an amino acid standard solution of over 24 individual monomers for a final concentration of 100 nM each. Samples for amino acid analysis were taken after 0 hr, 6 hr, 24 hr, and 48 hr. At all time periods, the concentration of the monomers remained within 2% of the initial concentration (Table 3).

The final bag design for the 2 L chambers was a 4 mil Kynar material (Keika Ventures, 16.5" x 5.75") with a polypropylene JACO ¼" compression fitting centered on the top fold. The final design for large volume sample chambers was identical, except for the size of the bags (20" x 11").

4.9 Cleaning protocols

All non-metal materials such as the tubing and fittings were soaked in 10% HCl (v/v) overnight followed by rinsing with deionized water. They were then soaked in a Milli-Q bath overnight, then rinsed again at least three times with Milli-Q water and dried at 45°C. The bags were filled with 10% HCl (v/v) for 24 h, then rinsed with Milli-Q water, then filled with Milli-Q water for 24 h. They were rinsed with Milli-Q water three more times and stored frozen until use since they could not be easily dried.

Components with both metal and non-metal components such as the check valves were soaked in Milli-Q water for 24 h then rinsed three times with Milli-Q water and dried at 45°C. Metal components such as the titanium intakes and stems were solvent washed with dichloromethane and methanol and dried with a stream of N_2 .

Table 3. Assessment of loss of amino acids due to sorption onto Kynar® bags

AA	t = 0 Conc (nM)	t = 6 hr Conc (nM)	t = 24 hr Conc (nM)	t = 48 hr Conc (nM)	Std Dev	% Std Dev
L-ASP	105.1	104.5	105.2	104.8	0.32	0.08
D-ASP	104.5	103.4	104.7	104.9	0.65	0.15
L-GLU	103.4	103.6	103.6	103.6	0.12	0.03
D-GLU	103.0	102.7	103.2	104.2	0.67	0.16
L-ASN	100.7	100.5	101.1	100.6	0.27	0.07
L-SER	94.5	94.4	94.5	94.6	0.11	0.03
MUR-A	104.0	103.6	106.5	105.7	1.37	0.33
D-SER	98.3	99.9	99.0	99.7	0.73	0.18
L-GLN	100.1	100.9	100.1	100.8	0.41	0.10
L-THR	107.2	105.0	107.3	106.5	1.05	0.25
GLY	94.2	96.2	94.4	94.9	0.92	0.24
L-ARG	90.5	101.4	98.7	91.4	5.38	1.41
B-ALA	107.3	112.6	113.9	112.3	2.90	0.65
L-ALA	96.1	96.7	96.9	96.5	0.35	0.09
GABA	96.9	97.7	96.8	96.6	0.49	0.13
D-ALA	98.8	98.0	98.3	98.2	0.34	0.09
L-TYR	100.1	99.4	99.7	99.2	0.42	0.11
L-VAL	102.7	101.1	101.9	101.6	0.68	0.17
L-MET	79.1	85.6	76.3	78.3	4.05	1.27
L-TRP	101.8	104.0	92.3	97.0	5.19	1.31
L-ILE	92.1	94.3	98.0	91.6	2.93	0.78
L-LEU	105.9	107.1	106.2	106.8	0.55	0.13
L-ORN	100.0	106.6	101.5	99.1	3.32	0.82
L-LYS	96.6	102.1	97.9	95.2	2.98	0.76

5. Deployments

As of 2020, the HOG sampler has been deployed on two oceanographic expeditions. The first expedition was on the R/V *Atlantis* leg AT42-01 at the Lost City hydrothermal field on the Mid-Atlantic Ridge (30°07N, 42°07W, 750 – 800 m water depth), utilizing the ROV *JASON II* from September 8 – October 1, 2018. The HOG sampler was deployed on five dives and collected thirty-four 2 L samples and six 11 L samples for geochemistry, thirty-three 2 L samples for microbiological incubation and RNA analyses, and twenty-five 0.22 µm Sterivex™ filters for DNA analyses (Lang et al., 2020).

The second expedition also utilized the R/V *Atlantis* and ROV *JASON II* to collect samples from vent fields on the Mid-Cayman Rise from January 14 – February 5, 2020. The HOG sampler collected fluids and filters from the Von Damm (18°33N, 81°43W, 2,200 m water depth) and Piccard (18°33N, 81°43W, 5,000 m water depth) vent fields. A total of seventy-nine 2 L and twenty-one 9 L fluid samples for

geochemistry and biology were collected, along with eleven filters that were preserved in situ for RNA and fourteen 47 mm flat filters for sulfur particulate analysis.

The temperature, pH, and Mg concentrations of collected fluids indicate they are of similar quality as those collected in previous expeditions by other samplers (Table 4). The pH and temperature values of Lost City (pH: 9.1 – 10.6; temperature: 22 – 96°C), Von Damm (pH: 5.9 – 7.2; temperature: 37 - 167°C), and local deep seawater (2062 m; pH: 7.7, temperature: 4.4°C) are similar to previously published values (Lang et al., 2010; McDermott et al., 2015; Bennett et al., 2013).

The concentrations of DOC from seawater collected at 2062 m in the Von Damm vent field (47 µmol/L) is comparable to samples collected by CTD at a similar depth range (1970 - 2150 m) directly above the field in 2011 (43.7 – 48.1 µmol/L; Bennett et al., 2013). The concentrations of DOC from Lost City fluids (38 – 73 µmol/L) are similar but somewhat lower than they were in 2003 (46 – 106 µmol/L; Lang et al., 2010). Semi-volatile organic acids constitute a substantial portion of the DOC in these fluids (Lang et al., 2010), and initial indications suggest that the concentrations of these compounds may have decreased from previous years. DOC concentrations have not been previously reported from the Von Damm field so no direct comparison is possible, but lower temperature diffuse fluids have been shown to have DOC concentrations elevated over background seawater in other hydrothermal systems (Lang et al., 2006; Hawkes et al., 2015).

Table 4. Geochemical properties of fluids collected by the HOG sampler. On dive J_1111 communication was lost with the temperature probe in the intake and temperatures are instead reported from the Jason high temperature probe.

Sample ID	Field	Location Name	T _{max} (°C)	T _{avg} (°C)	pH	Mg (mmol L ⁻¹)	DOC (µmol L ⁻¹)
Local seawater, 2062 m							
J_1244_C7	Von Damm	depth	4.1	4.1	7.7	N.D.	47
J_1243_C2	Von Damm	Mustard Stand	100.3	96.3	6.1	N.D.	448
J_1235_C4	Von Damm	X-18	37.0	N.D.	7.2	N.D.	52
J_1235_C2	Von Damm	White Castle	167.2	165.5	5.9	N.D.	143
J_1107_C6	Lost City	Marker 2	63.9	61.2	10.3	3.1	38
J_1108_C1	Lost City	Beehive	95.7	95.0	10.6	1.9	73
J_1110_C2	Lost City	Marker C	80.0	78.4	10.0	11.1	65
J_1110_C4	Lost City	Marker 8	53.8	46.7	10.0	12.0	66
J_1111_C3	Lost City	Sombrero	58.5	46.6	9.3	21.8	62
J_1111_C5	Lost City	Marker 3	85.0	N.D.	9.8	13.4	68
J_1111_C6	Lost City	Vein on wall	22.0	N.D.	9.1	36.6	39

6. Conclusion

The HOG sampler is designed to collect fluids and filters from deep sea hydrothermal fluids on submersibles with real time feedback. It has the benefit of collecting fluids in a manner that is 'clean' for organics and microorganisms, and allows for large sample volumes. The components are largely modular and can be adapted to the platform and to a wide variety of sample collection approaches. Future developments will allow it to be deployed on other submersibles and incorporate additional

sensors into the flow path so that characteristics such as pH and redox can be monitored in real time. Future uses for the sampler will include connecting the intake to an International Ocean Discovery Program (IODP) borehole via a CORK-Lite (Wheat et al., 2011; Fryer et al., 2018), to collect fluids from deep in the seafloor. It can also be utilized for any application where real-time monitoring, large volumes, and low contamination from extraneous organic material is beneficial.

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Figure Captions

Figure 1. Schematic of the HOG sampler in the configuration with six 9 L boxes. Fluid pathways are indicated by the blue (chemistry) and orange (microbiology) arrows. Symbols: check valves indicated by boxes with an interior arrow; ball valves indicated by circles with an interior X; luer lock indicated by bow-tie symbol.

Figure 2. Images of the front (upper), back (middle), and side (lower) of the HOG sampler. The dimensions of the sampler are 41" wide (including tubing that hangs over the frame), 21.5" high, and 28" deep. The upper and lower drawers of bottles are detachable. Once the frame is mounted on the aft sled of the ROV only the front and side are easily accessible.

Figure 3: Upper left: front basket of the ROV *Jason II* with the two HOG sampler intakes mounted on the port side of front basket. Lower left: HOG sampler frame and large volume boxes mounted on the aft sled of the ROV. Right: removing one of the sample chamber trays after a dive

Figure 4. Components supplied by McLane Research laboratories. Clockwise, from upper left: Controller, including aluminum pressure housing; 4L WTS-LV pump; 25-port valve; 250 mL/min micro pump. Figure 5. Intake nozzle as deployed with a u-handle, both disassembled (left) and assembled (right). The arrows in the right-hand panel indicate direction of fluid flow.

Figure 6. Upper left: partially disassembled sample tray including 2-L chambers and filters. Lower left: an individual 2-L chamber prepped for subsampling. Right: fittings leading from the bags to the titanium stem. When deployed, a check valve prevents fluid from exiting the bag. To subsample without exposing the sample to the atmosphere this check valve is replaced with an NPT to luer connector. If minimizing contamination is the primary concern all of the fitting can be removed and fluids can be collected directly from the bag.

Figure 7: Sampling at the Von Damm hydrothermal field. Image courtesy of Jeffrey Seewald, WHOI / NSF / ROV Jason / 2020 © WHOI

Figure 1

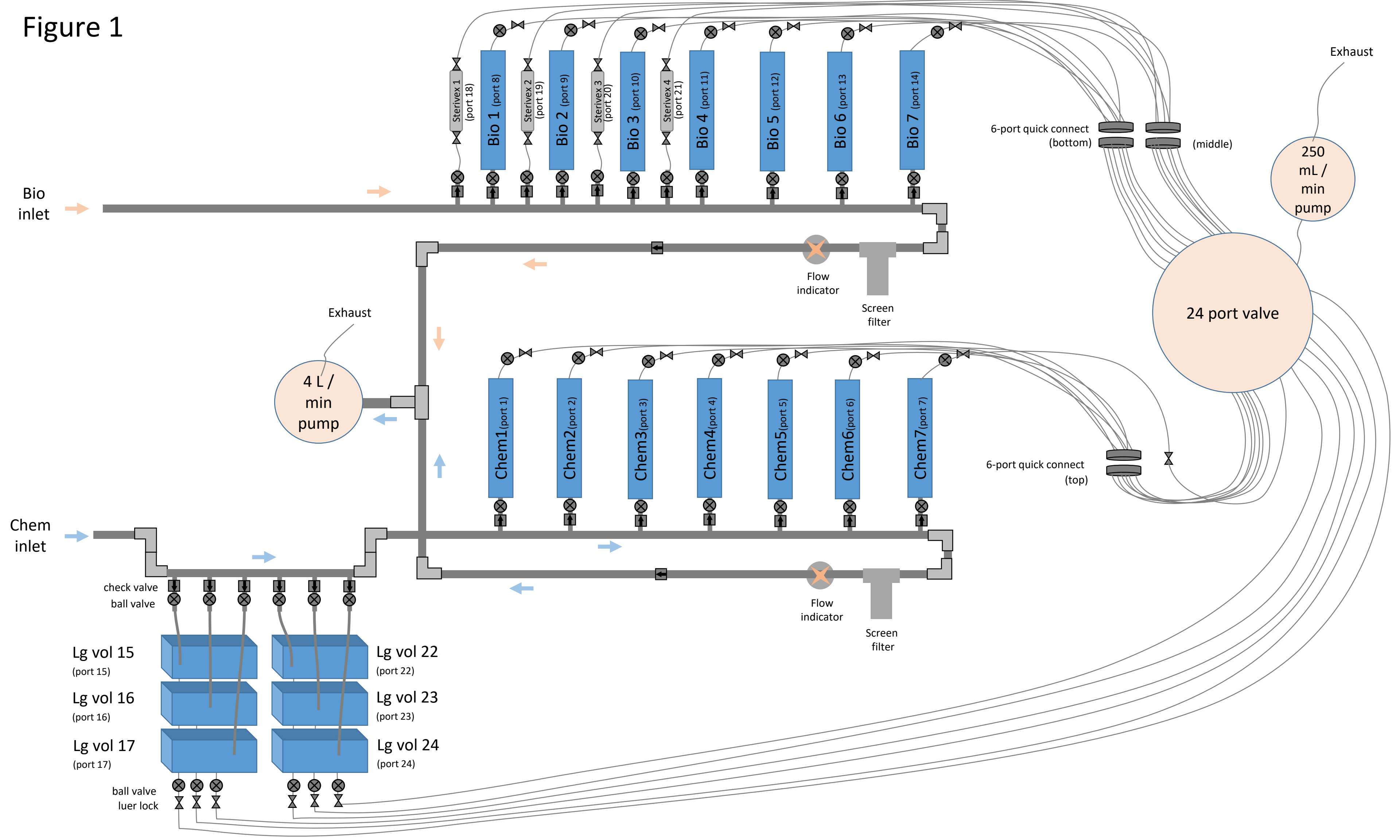


Figure 2

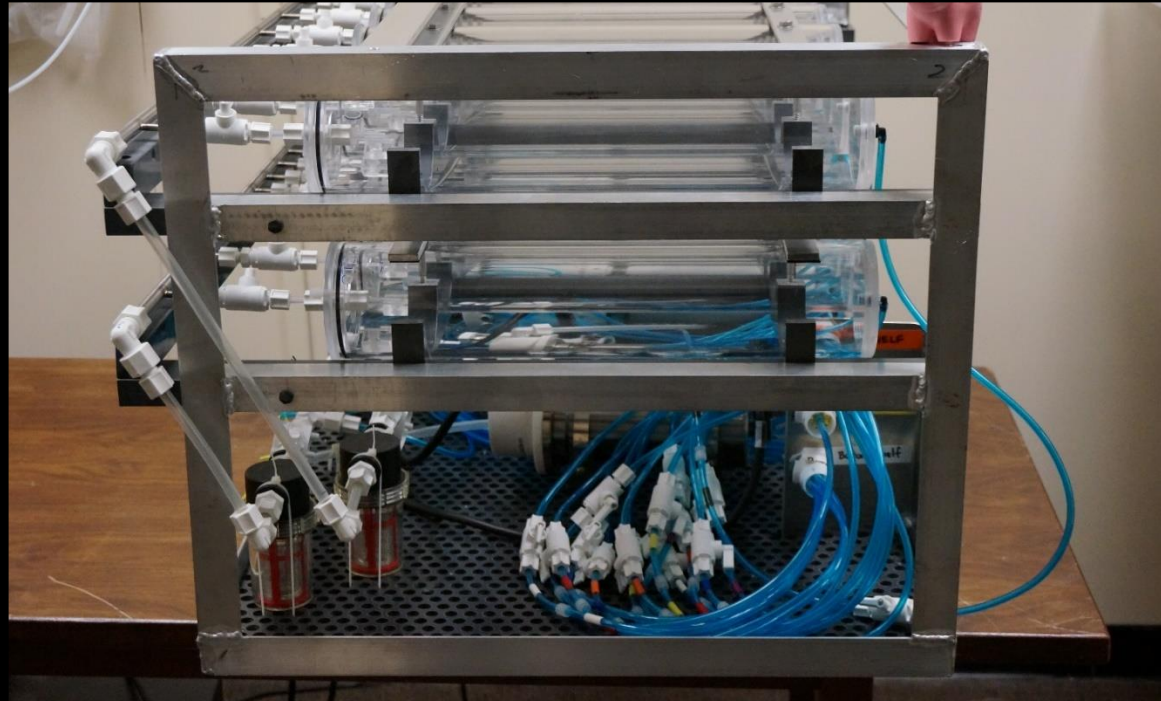
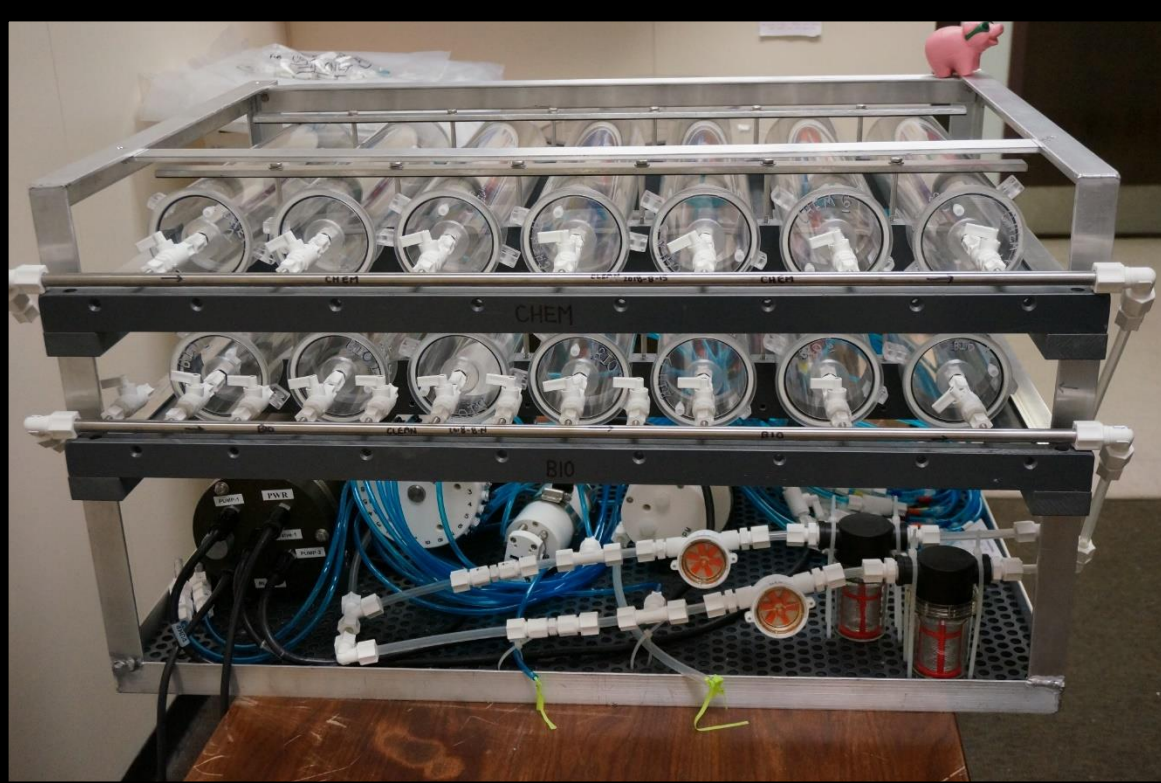


Figure 3



Figure 4

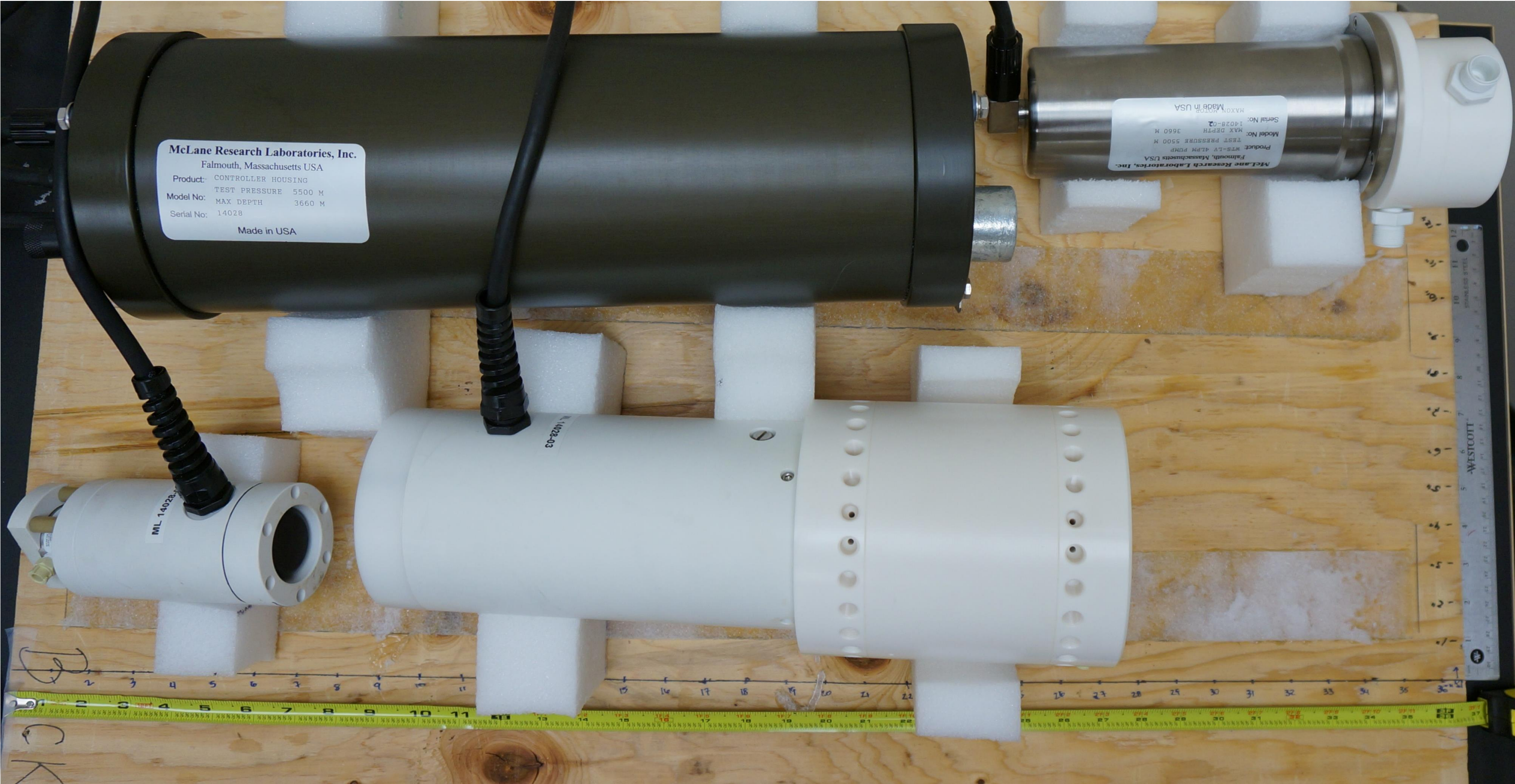


Figure 5

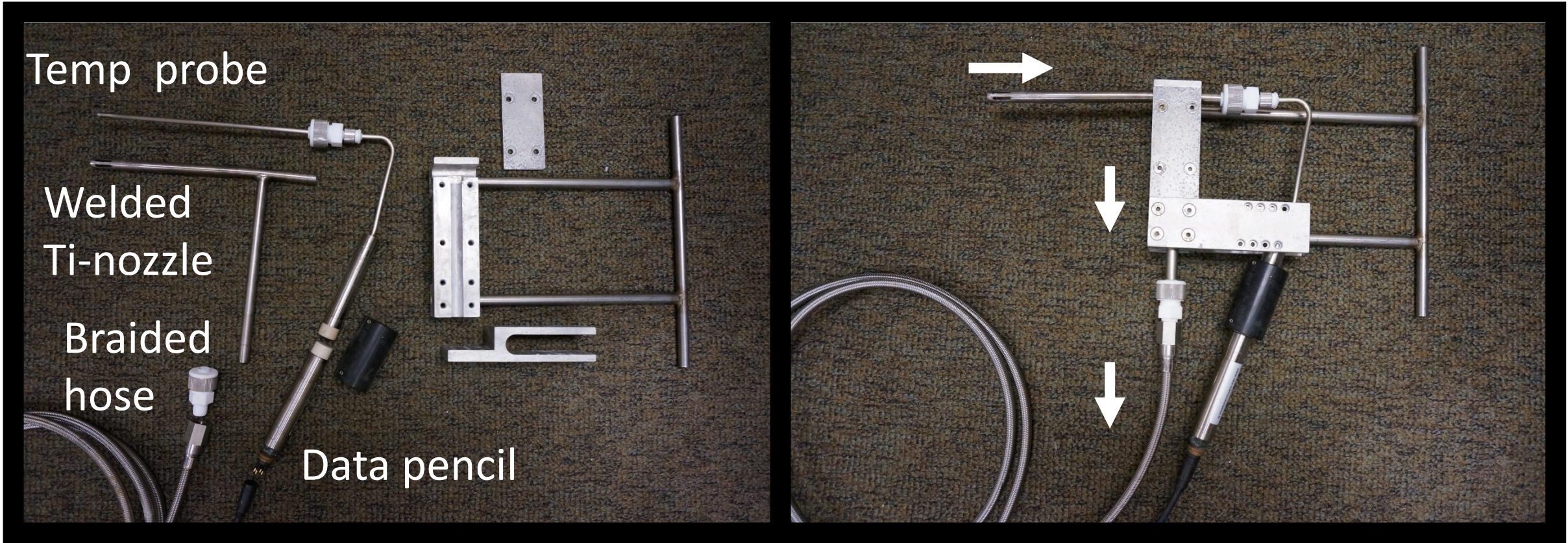


Figure 6

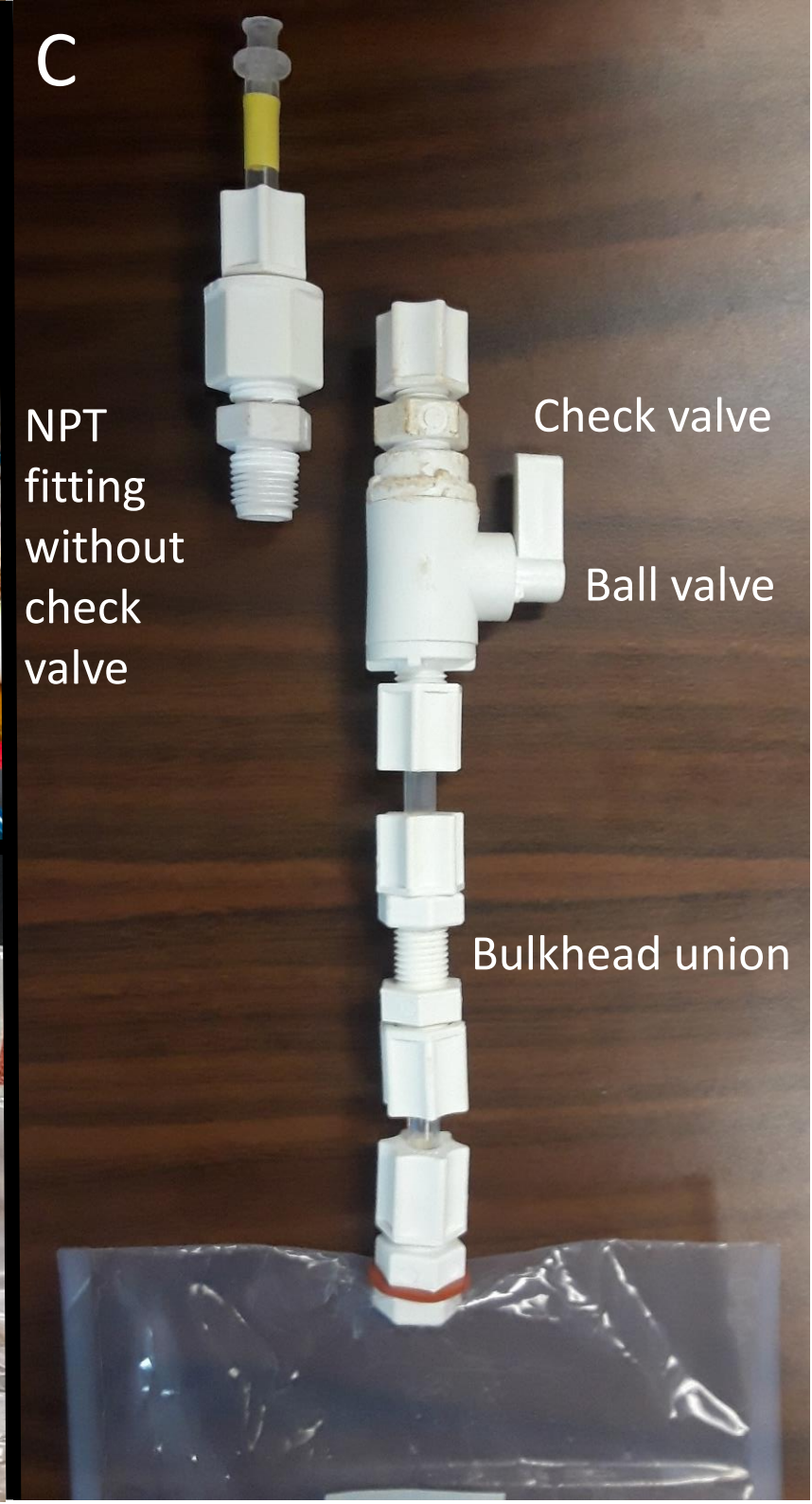
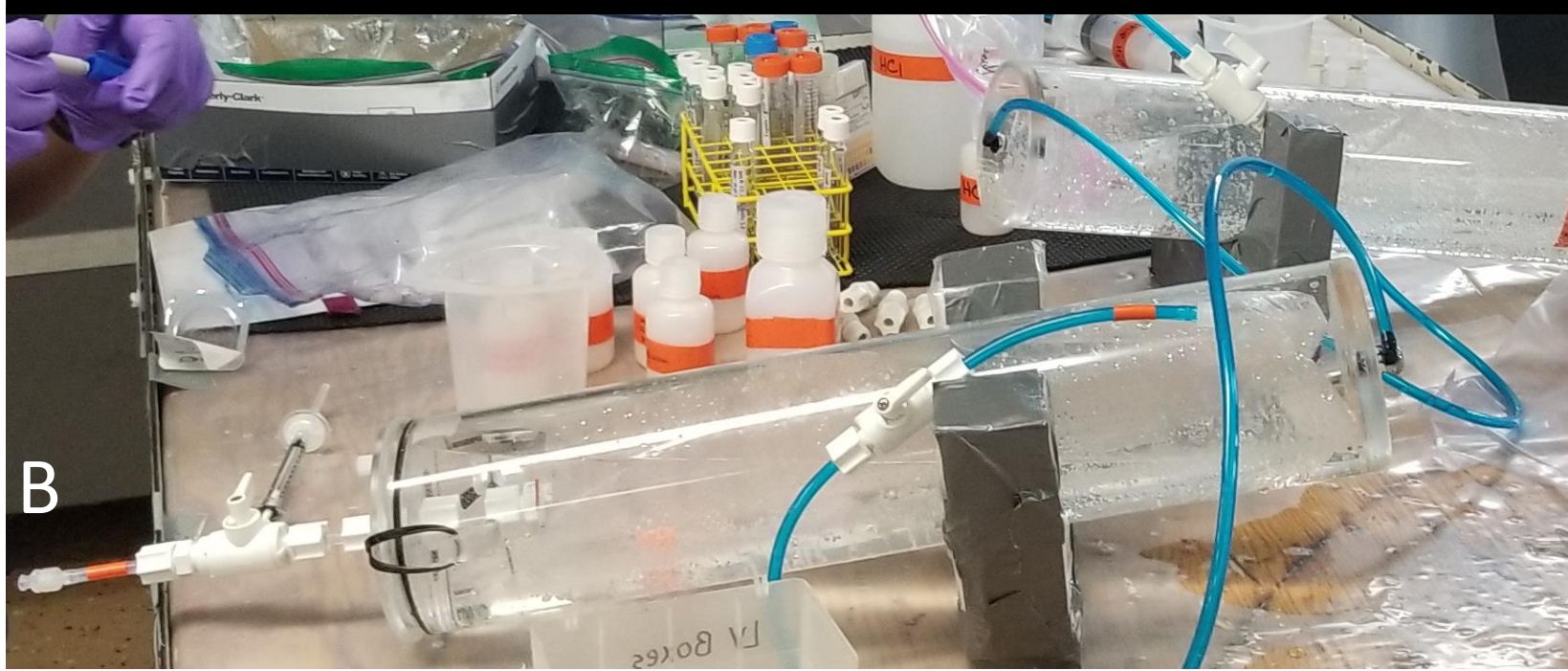
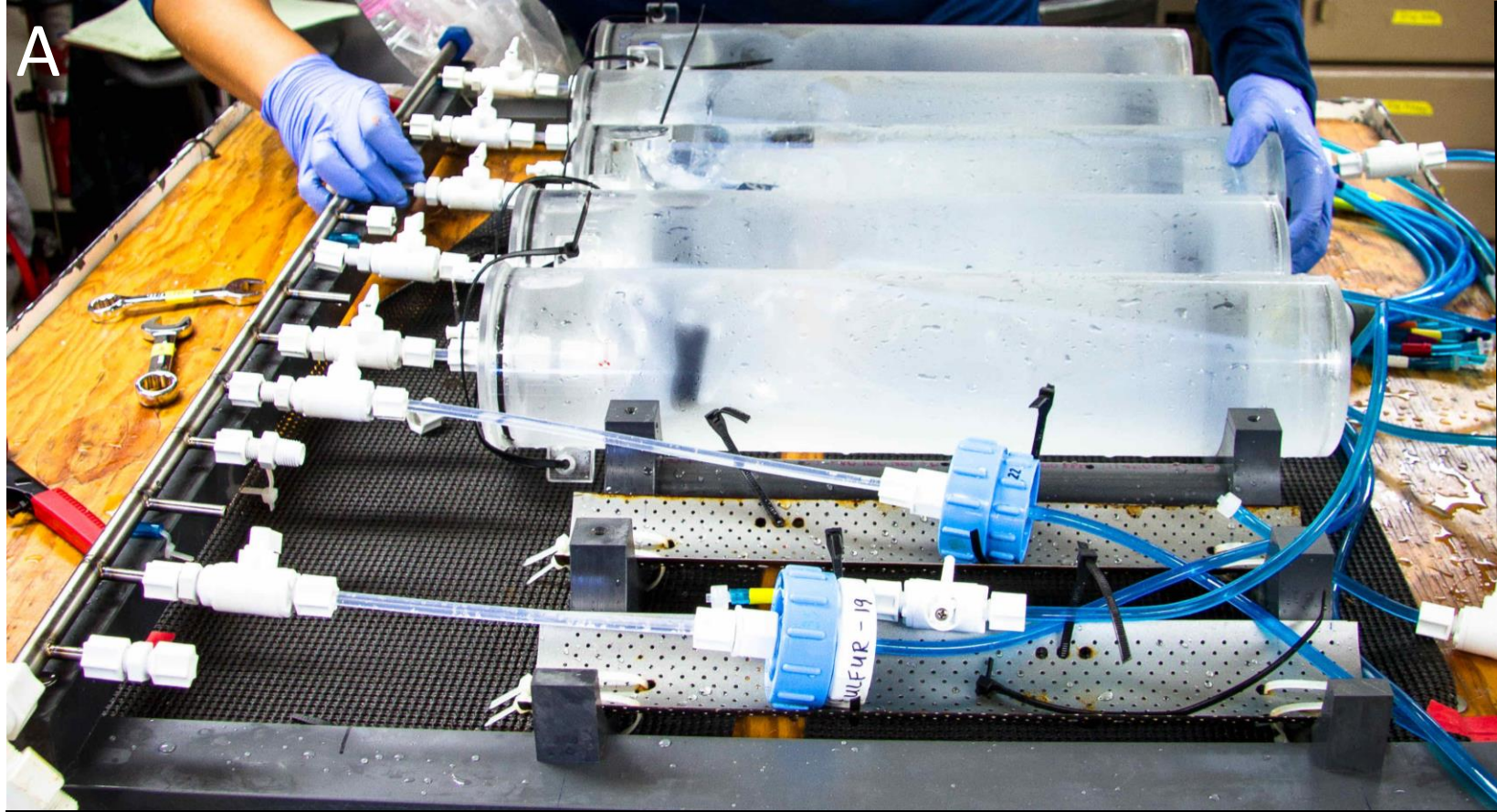


Figure 7

