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Approach for On-Site, On-Demand Contaminant-Removal Devices Enabled by Low-Cost 3D Printing

by Mark Ballentine, Alan J. Kennedy, Nicholas Melby, Andrew McQueen, Christopher Griggs, and Ashley Kimble

PURPOSE: The purpose of this technical note is to disseminate methods to design and create a 3D device that could be used to determine relative toxicity potential of existing and emerging contaminants of concern in situ for sediment shoaled in federal navigation channels prior to being dredged. This device has the potential to reduce the cost of conventional sediment evaluations conducted prior to dredging operations.

BACKGROUND: Dredge material (DM) evaluation, conducted under Section 103 of the Marine Protection Research and Sanctuaries Act (MPRSA) and Section 404 of the Clean Water Act (CWA) to determine whether dredged sediment requires special handling, follow decades old guidance (USEPA and USACE 1991, 1998) that is in need of modernization. Evaluating DM currently involves costly and time-consuming processes, encompassing planning, mobilization, extensive field work to collect several hundred liters of sediments, various laboratory testing stages, and analytical hold-time concerns (USEPA 2001; USEPA and USACE 1991, 1998).

3D printing or additive manufacturing (AM) provides an opportunity to update, reduce cost, and speed up the process of DM evaluations, including providing an understanding of what chemical classes and emerging contaminants may be of toxicological concern. 3D printing could be used in several applications alongside the toxicity evaluation method, and potentially during dredging operations, to do quick in situ sediment evaluations to help provide useful insights into toxicological and bioavailability questions and reduce the amount of DM needed to send to the research laboratory.

3D printing is readily available, user-friendly, and relatively low cost (less than $300 for a printer). Material extrusion (MatEx) has specifically gained interest in industrial and academic institutions. Filament-based MatEx or fused filament fabrication (FFF) uses a thermoplastic filament that is heated to semiliquid state and fed through an extrusion nozzle. The nozzle moves along a predefined path, layer-by-layer, depositing the melted material that cools and solidifies and the 3D object gradually builds up. Thermoplastic spools can be purchased from commercial companies in a wide variety of types with polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), and polyethylene terephthalate glycol (PETG) being some of the most popular. With specialty equipment, a user can make thermoplastic filament from beads of thermoplastics and mix in other additives such as metals, activated carbon, zeolite, and titanium dioxide (TiO_2). Each combination of thermoplastics and additives used in FFF printing results in different chemical and physical properties that affect performance and use, and thus, should be considered carefully for each project.

Softer materials that harden over time (clay and ceramics) can also be 3D printed using MatEx methods. MatEx ceramic 3D printers function similarly to FFF printers, depositing one layer at a time building up to a 3D model, but do not necessarily require heating. Ceramic 3D printers use a cylinder that is loaded with a soft clay or ceramic that is then pushed out of a nozzle using compressed air or a mechanical screw drive that acts as a syringe (Figure 1). Much like other types of MatEx, there are different materials that can be utilized such as stoneware clay, porcelain, bentonite, and other clay mixtures. Clay material extrusion allows for greater loading of an additive to give the clay unique properties, such as removal of ammonia or other toxins of emerging concern from water. For example, successful 3D clay prints containing a specific zeolite (Zeolyst, Kansas City, Kansas) in collaboration with the University of Kansas (Dr. Mark Shiflett) has been completed in the laboratory and successfully reduced up to 90% of aqueous PFAS compounds concentrations over just stoneware controls. Clay prints do require a simple postprocessing heating step to be fully cured.

The successful use of 3D printing to monitor dredge sediment plumes in situ could reduce time and cost through reduced transportation feeds of bulk material for DM toxicity evaluations. The 3D prints could be done on-site, even on the vessel. A passive sampler could be 3D printed and designed to be thin (1–2 mm thickness) and small (20 mm^2)* (Figure 2). A passive sampler could be 3D printed along with a chamber to hold an organism and a small-scale toxicity test could be conducted. For this technical note, the design, 3D printing, and testing of a 3D printed chamber and filter is detailed, and guidance for 3D printing to monitor and reduce toxins related to DM is detailed to help future researchers.

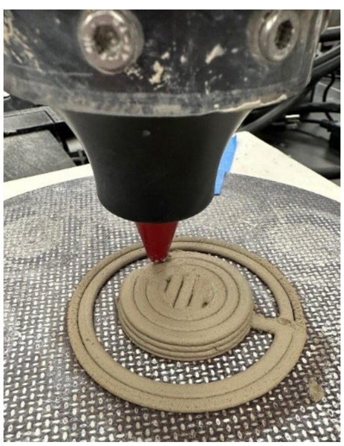

Figure 1. Stoneware being 3D printed using a clay 3D printer (3D Potter).

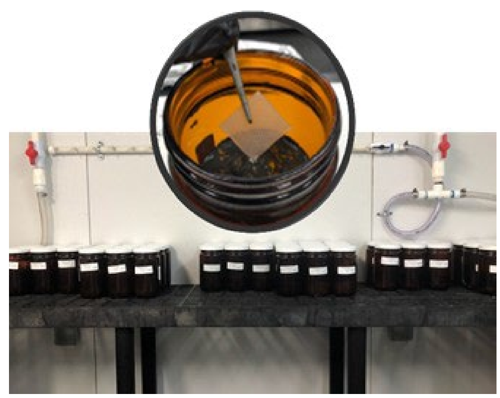

Figure 2. A small 3D-printed passive sampler being placed into dredge material.

APPROACH: To determine the feasibility of removing contaminants sometimes found in dredged sediments, a cylinder-shaped container and clay insert amended with zeolite was designed and 3D printed.

* For a full list of the spelled-out forms of the units of measure used in this document, please refer to *US Government Publishing Office Style Manual*, 31st ed. (Washington, DC: US Government Publishing Office, 2016), 248–52, https://www.govinfo.gov/content/pkg/GPO-STYLEMANUAL-2016/pdf/GPO-STYLEMANUAL-2016.pdf.

FFF printer and thermoplastic filament for cylinder construction: Fused filament fabrication was used for the construction of the cylinders in this design due to its relatively strong structure, ease of printing, and ability to hold water. Clay was used instead of the FFF print mainly due to the ease of combining an additive with the base clay.

Fused filament fabrication works by depositing layers of thermoplastic filament on top of each other to create a 3D object. Prior to selection of an FFF printer for a project, the user should consider printer specifications closely (Table 1). For this project, the Ender-3 printer (Creality, Shenzhen, China) (Figure 3) was chosen based on build volume and ability to handle a wide variety of filaments that could contain a variety of additives that can adsorb or destroy contaminants.

Table 1. Fused filament fabrication printer project considerations.

FFF Printer Parameters	Considerations
Build volume	Determines the maximum size of objects that can be printed.
Printer resolution	Ability to produce fine details, measured in microns or millimeters.
Filament compatibility	Ability to print a wide range of thermoplastic materials.
Filament diameter size	Two standard sizes, 1.75 and 2.85 mm.
Nozzle size	Smaller nozzles offer finer details. Can be switch out.
Heated build plate	Heated build plates allow for wider range of materials to be printed and an easier removal of the print. Heated build plates that can reach 110°C are adequate for most thermoplastic materials.
Connectivity	Primary method of file transfer of print files onto the printer and can be used for printer control. Examples include USB, secure digital (SD) card, Wi-Fi, and/or Ethernet connections.
Software compatibility	Verify that the printer’s software is compatible with your computer and offers user-friendly slicing and printing controls. Occasionally, some printers have proprietary software.
Print speed	Consider the printer’s speed, since faster print times may be essential for larger projects.
Support and community	Important for troubleshooting assistance and printing tips.
Price	Wide range of cost for FFF printers. More expensive may have more options but could also be harder to work with and repair if damaged while using unique filaments.

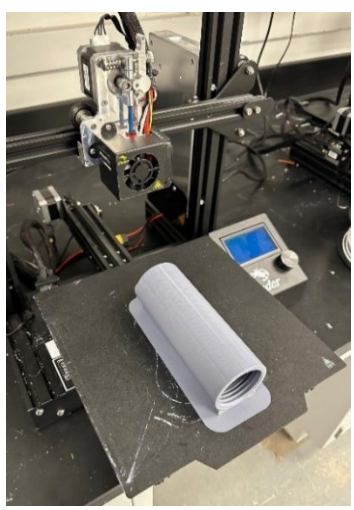

Figure 3. Fused filament fabrication printer
with ERDC-designed cylinder on a build plate.

Several filaments were considered for the printing of the test cylinder including PLA, ABS, PETG, and PLA+. Each type of filament has different physical and chemical properties that should be considered based on experimental parameters such as chemicals to be used, environmental durability needs, and ease of printing. Table 2 lists potential filaments that could be selected and purchased commercially. For example, the PLA filament could be used for environmental experiments because it is derived from materials such as corn starch and sugar cane and can be recycled. Almost all commercially available printers can print PLA and it is both inexpensive and readily available. For the printing of the experimental cylinder, PLA+ was selected. PLA+ is PLA filament with proprietary additives added into the base PLA material. The additives help to improve layer adhesion, surface quality, and durability (Table 2). A higher printing temperature is required to successfully extrude PLA+.

The experimental cylinder (Figure 4) was designed using a commercially available software (AutoDesk Inventor Professional 2020, AutoDesk, San Francisco, California); however, many computer-aided design (CAD) programs could be used, including free online CAD programs (e.g., TinkerCAD by AutoDesk, San Francisco, California; SketchUp by Trimble, Westminster, Colorado).

Figure 4. Two different size 3D printed cylinders:
(*A*) 80 mm long and 50 mm in diameter and
(*B*) 160 mm long and 50 mm in diameter.

The cylinder was designed for reuse, small enough to be easy to transport, and large enough to hold a large enough amount of material to remediate the chemical of concern during testing. The cylinder can be scaled up or down quickly in the CAD program (Figure 4).

The summary of the 3D print parameters for the cylinder are as follows:

- Printer: Ender 3
- Nozzle size: 0.4 mm
- Layer height: 0.2 mm
- Nozzle temperature: 200°C
- Print bed temperature: 60°C
- Print speed: 60 mm/s
- Supports: touching bed
- Bed adhesion: raft
- Infill percent: 20%
- Infill type: Cubic

Table 2. Common commercially available thermoplastic filaments.

Filament	Common Abbreviation	Usage Benefits	Usage Drawbacks	Nozzle Print Temperature (°C)	Heated Bed (°C)
Polylactic Acid	PLA	Low cost, stiff, good dimensional accuracy, filament shelf life, environmentally friendlier option	Low heat resistance, lower toughness (brittle and break), lower environmental resilience	190–220	45–60 recommended, but heated bed is optional
Polylactic Acid +	PLA+	Low cost, tough and better layer adhesion than PLA, high speed printing, environmentally friendlier option	Not as many commercial brands, low heat resistance	210–230	45–60
Acrylonitrile Butadiene Styrene	ABS	Heat and impact resistant, low cost, less stringing	Warping during printing, produces odor while printing, poor dimensional accuracy (print shrinkage), less green	220–250	95–110
Polyethylene terephthalate glycol	PETG	Smooth finish, adheres well to bed, fairly water resistant, chemically resistant, durable	Poor bridging, can produce stringing, PETG is considered a microplastic	230–260	75–90
Thermoplastic polyurethane	TPU	Flexible, elastic, and soft; vibration dampening; long shelf life	Difficult to print, poor bridging, does not work well with Bowden extruders	225–245	45–60 recommended, but heated bed is optional
Polycarbonate	PC	Heat, fatigue, and impact resistant; naturally transparent; bendable without breaking	Very high print temperatures, print warping, absorbs moisture from air while printing, considered microplastic	260–310	80–120
Polyvinyl alcohol	PVA	Dissolvable (water), fatigue resistant, flexible and soft	Very moisture sensitive, airtight storage required, nozzle clogging, expensive	185–200	45–60
High impact polystyrene	HIPS	Dissolvable (d-limonene), water resistant, heat and impact resistant, lightweight	Heated chamber needed, strong odor and ventilation required, considered microplastic	230–245	110–115
Nylon	Nylon	Tough and partially flexible, impact and abrasion resistant	Print warping, air-tight storage, not suitable for humid environments, considered a microplastic	225–265	70–90

Clay 3D printer preparation and cylinder insert printing: The use of 3D-printed clay potentially has many advantages for passive sampling (Kirtane et al. 2020) and toxicity reduction of chemicals (Gupta et al. 2017), especially when combined with an additive. Clay 3D printers act much like FFF printers, building up the model one layer at a time and can be either a direct drive or Bowden style printer. The direct drive is normally a large syringe type cylinder with a motor that pushes the clay out of a nozzle, while a Bowden style printer pushes the clay from a container through a tube to the print nozzle. Consideration of which clay printers to choose are similar to those listed in Table 1. The type of clay to consider for the experiment will primarily come down to two factors: (1) type and chemistry of clay compatible with your additive, and (2) availability to purchase and in what form (powder or moist clay).

For this experiment, a direct style clay printer (3D Potter, Stuart, Florida) was used. Much like the selection of PLA filament, the selection of clay would be determined by the experimental need. In this example, the base clay material was a stoneware clay and was shipped as two 25 lb prewetted clay bricks. While the clay is prewetted, it is not the correct consistency for most 3D clay printers. The percent water content for the clay was determined to be between 29% and 31% water for optimal printing on the 3D Potter. This value might vary depending on the clay being used and the recommendations of the printer manufacturer. Water can be added by different methods. For this method, water was added in approximately 50 mL volumes and kneaded into the stoneware clay until the consistency was correct.

A commercially purchased resin, SIR600 (ResinTech, Camden, New Jersey), was added into the stoneware clay during the kneading process. The SIR600 was 50% loading by volume and 30% loading by mass. To load the SIR600, 50 mL of water was added to the stoneware clay and kneaded, followed by an addition of a small portion of the SIR600. This process was repeated until the measure amount of SIR600 was added. Each additive that is included into the stoneware mix will change the amount of water that is required to obtain the correct clay consistency (approximately 30% water). Resins such as SIR600 absorb water readily and require additional water content to obtain the correct clay consistency. During printing of the clay, the additive will continue to absorb the water from the clay, thus reducing the amount of time that the clay will be at the correct consistency.

Once the clay/additive mixture was prepared, it was added to the 3D printer tube. When loading clay, it is important to remove as much air from the clay prior to loading. Each air pocket in the clay will eventual be pushed out of the printer extruder and will potentially compromise the printed build since the air will be pressurized and come out as a burst.

Postprocessing of printed models: Depending on the 3D printer, there may be some postprocessing that needs to be done to finish the device. The FFF printed devices did not require postprocessing other than removal of supports.

Clay models required postprocessing. After printing, the clay insert needs time to dry before it can be removed from the build platform. The larger the clay insert, the longer this will take. While drying, the clay insert can be modified by hand or with tools to a small degree to remove potential supports or to smooth. Once the clay insert dries enough to be removed from the build platform, it will need to be fired in a kiln. This experiment used a large top-loading kiln (Skutt, Portland, Oregon). The stoneware clay used has a typical firing range of 1,207°C–1,305°C. However, when fired to this temperature, the clay particles are sintered and welded together, making the clay a ceramic and impervious to water, thus locking the additive away from the contaminant.

All clay materials used in 3D printing will need to be postprocessed to retain their structure. Most clays are fired to between 1,100°C and 1,300°C to become completely ceramic. Lower temperatures were tested to balance the need for porosity to allow for the availability of any additive and structural durability in water. The stoneware clay inserts were fired to final temperature of 650°C. Inserts cured to various temperatures, ranging from room temperature to 650°C, were placed into water and tested for durability. Starting at 400°C, the clay inserts held together reasonably well in static water for 24 h. The addition of agitation to the water dramatically reduced the structural durability at 400°C.

Reduction of ammonia case study: Ammonia is a common contaminant that confounds the results of toxicity and bioaccumulation testing conducting in dredging evaluations (Melby et al. 2018; Kennedy et al. 2015). Case study ammonia reduction experiments were conducted using the 3D-printed cylinders and clay/SIR600 inserts; one experiment used the smaller cylinder and inserts and the second experiment used the longer cylinder and inserts (Figure 4). The ammonia reduction experiments consisted of three cylinders with clay/SIR600 3D-printed inserts and an empty cylinder with no insert as a control. The cylinders were suspended in a vertical position (Figure 5) with solution flow from top to bottom. Samples were collected in glass flasks after the ammonia solution passed from the top through the cylinder and clay/SIR600 insert and out the bottom tube.

Figure 5. The 3D-printed cylinders in a vertical position for the ammonia removal experiments.

An ammonia chloride (NH_4Cl) solution was made and pumped through the cylinders using a peristaltic pump (Masterflex L/S, Cole-Parmer, Barrington, Illinois) with a 2 h turnover time in the each of the cylinders. Samples were collected into smaller beakers then measured using an ammonia probe (Orion Dual Star pH/ISE meter, ThermoFisher Scientific, Waltham, Massachusetts) and recorded. Ammonia initial water levels of 30.8 mg/L were reduced 84% in 30 min and 91% over a total of 3 h.

CONCLUSION: The forward thinking MatEx technology concepts and applications presented in this technical note are initial steps to broader goals of transitioning methods for using 3D-printed clay and PLA to use in passive sampling, toxicology, and sequestering of aqueous contaminants commonly found in dredging evaluations. The ability to create 3D-printed cylinders and inserts that can target specific contaminants could cut costs and time for rapid assessments. 3D printing with clay also allows flexibility of design, but with the added benefit of higher additive loadings. However, clay MatEx needs pre- and postprocessing that will need to be considered when selecting materials to use in experiments. The methods developed have shown promise in the ability to reduce ammonia, a common toxicant in shoaled sediments. Future studies will focus on other contaminants of concern for the Dredging Operations and Environmental Research Program.

POINT OF CONTACT: For additional information, contact Mark Ballentine, Research Biologist, Engineering Research and Development Center–Environmental Laboratory, Vicksburg, MS (mark.l.ballentine@usace.army.mil; 601-634-2910).

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