

**Introduction:** Natural water treatment systems, including shallow unit process open water treatment wetlands (UPOWs), are a practical, cost-effective, and highly scalable approach to managing environmental water quality.<sup>1</sup> UPOWs utilize microbial growth in the benthic region within a photosynthetic biomat, hosting a stratified population in aerobic, anaerobic, and anoxic zones. Biomat microbe ecosystems have demonstrated treatment of influent water for nutrients, trace organic compounds, and other contaminants at rates that match—and in many cases exceed—those of traditional vegetated or subsurface wetlands.<sup>1</sup> These microbial populations develop independently over multiple months, using algae and other detritus as carbon and electron sources.

The low implementation and maintenance costs of these systems have drawn attention to their use for increasing water availability and decreasing risk in otherwise water-poor or unprotected communities, such as the Arequipa region in Peru. These communities utilize surface water from local rivers such as the Tambo, which contains concentrations of arsenic (As) exceeding Autoridad Nacional de Agua regulations for both domestic and agricultural use.<sup>2</sup> Elevated concentrations are likely a result of high background levels of As in local geology and introduction from mining operations in the area. The surrounding community can no longer safely consume or export important commercial products such as rice or river shrimp because of this threat. The long-term effects of these economic limitations and human health impacts cannot be understated and will continue to persist so long as the region suffers from degraded surface water quality.

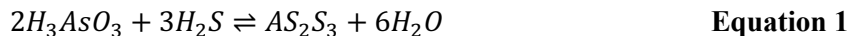
Dr. Josh Sharp, professor of Civil and Environmental Engineering at the Colorado School of Mines, is currently working with the Universidad de San Agustín de Arequipa (UNSA) in Peru to study the potential for UPOWs to treat surface waters for metal and metalloid contaminants. UPOWs with the capability to remove these hazards would provide communities with a first step toward improving environmental water quality.

Challenges of degraded water quality do not adhere to national or state boundaries. Communities all over the world, including here in the United States, contend with a lack of access to safe water sources. My goal is to apply research on UPOWs to ensure no one has to suffer from contaminated water. I will build upon Dr. Sharp's research on UPOWs by determining their capacity for arsenic removal.

**Hypothesis:** UPOWs are able to remove trace organics and nutrients from surface waters and are potentially capable of immobilizing metal and metalloid contaminants.<sup>1</sup> Arsenic (V) is the most prevalent form of As in surface water, and poses a hazard to human and environmental health.<sup>3</sup> I hypothesize that UPOWs incorporating sulfate-reducing bacteria have the capability to remove As (V) from surface water via precipitation with sulfide in a variety of geographic settings.

**Research Plan: Objective 1: Analyze the potential for As (V) precipitation as  $As_2S_3$  in the presence of sulfate-reducing bacteria in UPOWs.**

Arsenic (V) removal by precipitation relies on the transformation of As (V) to As (III), as biological systems have previously been observed to utilize sulfate-reducing bacteria to precipitate As (III) with sulfide.<sup>3</sup>  $H_3AsO_3$ , the naturally occurring form of As (III), reacts with sulfide to produce  $As_2S_3$  (Equation 1) which is insoluble in typical surface water conditions.<sup>4</sup>



Some sulfate-reducing bacteria hold the potential to reduce As (V) to As (III).<sup>5</sup> The presence of these bacteria could allow for the precipitation of As (V), proceeding as in Equation 1. Sulfate-reducing bacteria colonize and function well in biomat ecosystems,<sup>4</sup> but they have yet to be tested for specific removal of As.

**Objective 2: Evaluate As removal efficiency of UPOWs across largely differing geographical areas.**

The formation and function of biomats in UPOWs rely on both biotic and abiotic constituents of surface water. Successful arsenic removal depends on the colonization and function of sulfate reducing bacteria, algae, and other diatoms, all of which could differ by region. I will observe whether biomat ecosystems will support microbe composition necessary to perform key contaminant removal functions regardless of UPOW location.

Differing water chemistry and abiotic constituents could alter the As removal pathway or block As precipitation altogether. In some cases, As may complex with other constituents to produce undesired

byproducts, such as Thioarsenic.<sup>6</sup> A particularly interesting factor in the success of As removal may also be sulfate concentration, though determining direct influence is outside the scope of this project.

**Approach/Methods:** Testing will occur at both the bench and field scales. After the effectiveness of the mesocosm-sized UPOW biomat has been determined, the biomat composition and design will be tested at the field scale at the Prado Wetlands in California and then at the UNSA in Peru.

**Objective 1:** Bench scale biomats will be harvested from existing UPOWs in the Prado Wetlands and deployed in the lab at the Colorado School of Mines to be tested with spiked influent water. Test water will consist of local Colorado water samples spiked with known levels of arsenic. Sulfate will be held constant in a similar concentration to that of the Tambo. Removal efficiency will be calculated using a mass balance on As, with a known influent concentration, precipitation concentration determined using a modified Tessier extraction of the biomat,<sup>7</sup> and effluent concentration determined using ICP-MS chromatography. Selective inhibitors for sulfate reducing bacteria, such as molybdenum<sup>8</sup>, will be used to evaluate arsenic precipitation in response to sulfate reducing capacity.

Testing will move to the field scale as a validation step in large-scale performance after bench-scale testing has been completed. Field testing will first take place at the Prado Wetlands, where a colonized UPOW will be allowed to run for an extended period of time. As concentrations will be measured using the same methods as at the bench scale.

The continual rise of precipitated arsenic in the biomat could lead to concern after long periods of time in field operating conditions. To mitigate potential release of highly concentrated arsenic from a biomat, I recommend an operating system in which sections of biomat could be harvested prior to the accumulation of dangerous levels of As or other harmful constituents. These sections could go on to be used as fertilizer to utilize their elevated levels of nitrogen, resulting from abundant nitrifying bacteria.

**Objective 2:** Successful function of a UPOW system in Peru will first be estimated at the bench-scale using replicated Tambo River water at the Colorado School of Mines. Biomat colonization and As removal will be monitored over the course of several months using these waters, with an emphasis on the perception of sulfate reducing bacteria presence.

Field-scale testing will occur at the UNSA and will mirror procedures in the United States, now using unmodified water from the Tambo River. Biomats will colonize and undergo testing in mesocosm and field-scale UPOWs and arsenic concentrations will be determined using a mass balance approach.

**Intellectual Merit:** Metal and metalloid removal has not yet been tested in UPOW systems, but the successful performance of sulfate-reducing bacteria in previous UPOWs could lead to an innovation in As removal methods. This study would quantify the effectiveness of this mechanism for arsenic removal from surface water via UPOWs.

UPOWs have been tested in the United States but have not been observed abroad. This study will demonstrate the effects of differing surface water characteristics of different regions on arsenic precipitation. Additional application of UPOWs, including biomat harvesting, could have basis for further investigation to increase utility of these already compelling systems.

**Broader Impacts:** The development of this system, and other natural treatment systems, would make progress on the priorities set forth by the UN Sustainable Development Goals and the Grand Challenges of the National Academy of Engineering. My work would directly contribute to these efforts aimed at increasing global sustainability and standards of living. More immediately, an UPOW system has the potential to mitigate the threat of arsenic for the Arequipa community and others like it. Depending on sequestered metal concentrations, the periodic harvesting of UPOW biomats, for fertilizer or otherwise, could also prove UPOW potential to serve a purpose beyond water treatment. Further research on natural treatment systems will continue to drive down cost, increase understanding, and foster education in communities using natural water treatment.

**References:** <sup>1</sup>Jasper, *et al.* (2013). *Environ. Eng. Sci.* 30(8), 421-436. <sup>2</sup>Autoridad Nacional de Agua. (2020) Ministerio de Agricultura y Riego. <sup>3</sup>Lizama, *et al.* (2011). *Chemosphere.* 84(8), 1032-1043. <sup>4</sup>Jones, *et al.* (2017). *Appl. Environ. Microb.* 83:e00782-17. <sup>5</sup>Macy, *et al.* (2000). *Arch. Microbiol.* 179, 49-57. <sup>6</sup>Stucker, *et al.* (2014) *Environ. Sci. Technol.* 48(22), 13367-13375. <sup>7</sup>Tessier, *et al.* (1979). *Anal. Chem.* 51(7), 844-851. <sup>8</sup>Blum, *et al.* (1998). *Arch. Microbiol.* 171, 19-30.