**Supplementary Material**

Site Description

The Samoan islands were formed by volcanic activity approximately seven million years ago. The islands are mountainous, with steep slopes; land flat enough for development is limited and concentrated near the coast. As a result, villages and towns all occur in very close proximity to the shoreline which may exacerbate issues with land based sources of pollution to the ocean.

American Samoa exhibits a tropical climate with warm, humid conditions throughout the year. There is a wet season (October to April) and a dry season (May to September), but rainfall is common throughout the year, with annual averages ranging from 320 cm to over 750 cm, depending on topographic location, with mountains receiving more rain (NPS 2015).

Vatia Bay has a diurnal tidal range of 0.85 m (Storlazzi et al 2017). The benthic habitat of the Bay is a mixture of hard bottom (live coral, coral rubble, pavement), crustose coralline algae (CCA), fleshy macroalgae, and turf algae, with small patches of sand (Vargas-Angel and Schumacher 2018). Previous work has quantified a biological gradient, with the inner Bay, which is most likely to be impacted by land based pollution, having worse coral reef conditions than the outer Bay (Vargas-Angel and Schumacher 2018).

 According to U.S. Department of Agriculture National Resource Conservation Service (NRCS), at the time of this study there were ten piggeries and on the order of 70 pigs in Vatia at any given time (Diego Ayala, NRCS, personal communication; USDA-NRCS unpublished data from 2015). As with much of the island, feral or semi-feral dogs are prevalent in the village. An estimate by the island veterinarian places the dog population in Vatia between 60 and 150 individuals (Brenda Smith, veterinarian, 2012, personal communication). While fruit bats can play a large role in the biogeochemistry of ecosystems in American Samoa, at the time of this study, there was not a major roost in the Vatia watershed (Adam Miles, biologist, Division of Marine and Wildlife Resources, 2015, personal communication). Therefore, this has been ruled out as a nutrient source to this system.

Methods

The methodology for sucralose quantification is based on automated online solid-phase extraction (SPE) and high-resolving-power orbitrap mass spectrometer (MS) detection. Operating in full scan (no collision-induced dissociation), detection of the unique isotopic pattern (100:96:31 for [M-H](-), [M-H+2](-), and [M-H+4](-), respectively) was used for ultra-trace quantitation and analyte identification. The method offers fast analysis (14 min per run) and low sample consumption (10 mL per sample).

The caffeine analysis was based on the combined performance of an Equan MAX Plus online Solid Phase Extraction (SPE) preconcentration system coupled to a high pressure liquid chromatography (LC) system equipped with resolution mass spectrometry detection using a QExactive orbitrap-based mass spectrometer (SPE-LC-HRMS). The analytical separation was carried out using a Hypersil Gold aQ column (100×2.1 mm, 1.9 μm) while the SPE pre-concentration column was a Hypersil Gold aQ (0.5×50 mm; Thermo Scientific, West Palm Beach, FL, USA). The automated online SPE clean-up and pre-concentration step was performed using only 10 mL of filtered water samples. The online procedure consisted of a divertion valve on the mass spectrometer which was programmed by the data system to control the loading and elution of the two LC columns. In the load position, 10 mL of sample was injected into a 10-mL loop and then loaded onto a SPE column by the loading LC pump, followed by a wash step with 98:2 0.1% formic acid: acetonitrile to remove interferences (flow rate 2 mL/min). The target compounds were retained in the SPE column and the matrix that is not retained during the extraction process was directed to waste while simultaneously the analytical pump equilibrated the analytical column in the starting gradient conditions. After 5 min, when the valve was switched to inject position, the solvent flow through the SPE column was reversed, and the analytes were then backflushed with a gradient of acetronitrile and 0.1% formic acid onto a Hypersil Gold aQ column for separation and quantitation by heated electrospray ionization source (HESI)-MS/MS. After 7 min, the switching valve was returned to the loading position to allow the extraction column to be re-equilibrated with water. The samples were kept at 10°C in the autosampler. The total run time per sample was 13 min. The analyte was detected on a QExactive Mass spectrometer equipped with an HESI source operated in the positive mode. The capillary temperature was 350 °C with a discharge current of 4 kV and S-lens RF level of 80%. Sheath gas and auxiliary gas (N2) were used at a flow rate of 30 and 20 arbitrary units, respectively. The analysis was performed in Parallel Reaction Monitoring (PRM) (with an inclusion list of the exact mass of the target compounds) at a resolution of 35,000. Quantitation is performed by the internal standard approach (concentrations are calculated based on area ratio between the analyte and labeled internal standard) to correct for matrix effects and any losses in the online extraction step. The monitoring ions for caffeine were 195.0877 and 138.0662 and for the labeled caffeine (13C3 caffeine) was 198.0977.

**References for Supplemental Materials**

National Park Service (NPS). 2015. Weather of American Samoa National Park. <http://www.nps.gov/npsa/planyourvisit/weather.htm>

Storlazzi C, Cheriton O, Rosenberger K, Logan J, Clark T. 2017, Coastal circulation and water-column properties in the National Park of American Samoa, February–July 2015: U.S. Geological Survey Open-File Report 2017–1060, 104 p., <https://doi.org/10.3133/ofr20171060>.

Vargas-Angel, B., Schumacher, B. 2018. Baseline Surveys for Coral Reef Community Structure and Demographics in Vatia and Faga'alu Bay, American Samoa NOAA Pacific Islands Fisheries Science Center, PIFSC Special Publication, SP-18-002, 38 pp.

Wingert, E, Pereira, J. 1981. A coastal zone management atlas of American Samoa. University of Hawaii Cartography Laboratory, GSA Bulletin 55: 13- 17.