LOW-COST FILTERS FOR EMERGENCY TREATMENT OF DRINKING WATER FOR REMOVAL OF EXCESS FLUORIDE IN VOLCANIC AREAS

> *"…research has shown that the semi-continuously degassing of Ambrym volcano is introducing significant levels of fluoride into the drinking water of the local Ni-Vanuatu." - (Crimp, 2006).*

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ABSTRACT

Fluoride toxicity affects millions worldwide and is mainly caused by drinking water with elevated fluoride concentrations. It is particularly prevalent in low socio-economic groups, rural communities and volcanic areas. While defluoridation, with adsorbents such as calcium carbonate, is the most viable solution, the majority of technologies are unsuitable for resource-constrained areas. Coral sand is widely available in the Pacific but yet to be thoroughly investigated as a potential adsorbent. Acid enhances fluoride removal in calcium-systems and citric acid is an accessible, palatable and safe choice.

Using adsorbent doses of 1 g/6 mL, the adsorption capacity of coral sand for fluoride was very low at <0.12 and <0.04 mg/g, with and without the addition of 0.025 M citric acid, respectively. Columns with a sand-fluid ratio of 5:1, 0.025 M acid and a 4-hour residence time, could be used seven times to reduce fluoride from 10 mg/L to below the NZ safe limit of 1.5 mg/L. Coarser Vanuatu sand columns could be used 14 times. Increasing citric acid to 0.05 M reduced removal efficiency, likely due to release of pre-existing fluoride in sands or an increase in volume which drained from columns. Scaled-up prototype treatment devices, developed using 1 L HDPE jerrycans and 1 kg of sand, could only be used successfully three times with 0.025 M citric acid. An increase in extractable volume in the prototypes, likely due to fluid mechanics or physical properties of the larger vessel, is a possible cause. Careful control over grain size, sand-fluid ratio, contact time, and other variables will be required to successfully scale-up the treatment system.

Coral sands contained traces of fluoride and contaminants of concern, including: As (0.244 to 1.45 mg/kg); B (46 to 81 mg/kg); Cr (1.9 to 10.4 mg/kg); Mn (7.7 to 45.4 mg/kg); and Ni (0.275 to 2.55 mg/kg). Use of acid and high sand-fluid ratios to remove fluoride from solution concurrently released contaminants from sand, rendering all extracts analysed unsafe to drink. Chromium was present above NZ drinking water maximum allowable value (MAV) in all sand extracts (Kiribati, Vanuatu, and store-bought) until the end of the experimental trials. Arsenic remained above MAV in fine store-bought sand extracts for 2-3 days, and until the end of the trials in Pacific sand extracts. Kiribati and Vanuatu sand column extracts also contained B, Na, and Ni above the MAV in newer columns. Though sand treatment did neutralise acidic waters, treated samples were unpalatable based on total dissolved solids, hardness and high concentrations of Al, Fe, and Mn. A white precipitate also developed in extracts from newer columns some hours after treatment. A further treatment step with activated charcoal reduced fluoride concentrations but not trace elements of concern. Investigations into methods able to reduce contaminants before or after sand treatment, or limit contaminant leaching, will be essential if coral sand is to be used in fluoride remediation of drinking water.

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DECLARATION

I hereby declare that I have conducted the work reported here, with the exception of specified collection of data sets. The help received with the collection and interpretation of this data is acknowledged at the appropriate points in this thesis.

Signature:

Date: July 19th, 2021

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ABBREVIATIONS, ACRONYMS, AND DEFINITIONS

2SD	2 x Standard Deviation
AC	Activated Charcoal
AELD	Acid-enhanced limestone defluoridation
ASTM	Formerly American Society for Testing and Materials, now the ASTM International
AR	Analytical Reagent
BET	Brunauer-Emmett-Teller, a method to determine specific surface area.
BED-C	Backscatter Electron Detection
CCV	Calibration Curve Verification
CDTA	1,2, cyclohexylenediamine tetraacetic acid
C_i /C_e	Initial concentration / equilibrium (or final) concentration
CRM	Certified Reference Material
dH_2O	Distilled H_2O
DL	Detection Limit
E	Potential
EDS	Energy Dispersive X-Ray Spectroscopy
EDTA	Ethylene diamine tetraacetic acid
EPA	United States Environmental Protection Agency
ESR	The Institute of Environmental Science and Research
FG	Food Grade
F^-	Fluoride ion
FISE	Fluoride Ion Selective Electrode
GC-MS	Gas Chromatography - Mass Spectrometry
GL	Guideline
ICP-MS	Inductively Coupled Plasma - Mass Spectrometry
ICS	Isotherm Calibration Standard
IRM	Independent Reference Material (Fluoride Standard for Ion Chromatography)
ISO	International Organization for Standardization
LCS	Laboratory Control Sample
LOQ	Limit of Quantification
MeV	Milli electron Volts, a measure of potential
MAV	Maximum Acceptable Value
MOH	NZ Ministry of Health
NIST	National Institute of Standards and Technology
ppd	Person per day
PSD	Particle Size Distribution
Purite	Ultrapure water system trade name

QC	Quality Control
q_e	Adsorption capacity (usually in mg/g of adsorbent)
SED	Secondary Electron Detection
SEM	Scanning Electron Microscopy
SRM	Sediment (Certified) Reference Material
SRL	Suggested Release Limit
s/n	Serial number
TDS	Total Dissolved Solids
TL	Trendline
TISAB	Total Ionic Strength Adjustment Buffer
THAM	Tris (hydroxymethyl) aminomethane
UC	University of Canterbury
Ultrapure	Water with a resistivity of 18.2MΩ-cm
UN	United Nations
WHO	The World Health Organization
% w/w	Measure of concentration, in weight by weight
XRD	X-ray Powder Diffraction

TERMINOLOGY

Initial solution: generally 10 mg F^-/L with or without citric acid (0.025 M, 0.05 M, or 0.1 M).

Treatment system: a device containing coral sand which is filled with initial solution for a specified period of time, in an attempt to remove contaminants from the initial solution. Could be a column or prototype jerrycan.

Prototype: treatment system fabricated from 1 L HDPE jerrycan containing 1 kg of coral sand made to approximate 1:20, 20 L drum.

Column: syringe with plunger removed and a stoppered tip, containing a specified amount of coral sand.

Extracts or treated solution: Solution removed from a treatment system which usually contained coral sand.

White powder: white substance collected from the dried sand after AELD treatment.

White precipitate: white substance which developed in extracts, after removal from a treatment system.

% extractable volume: ratio of the volume that can be removed/extracted from a treatment system, to the total volume placed into the treatment system.

Long-term: This term relates to the reuse of a treatment system and implies throughout the entire duration of the experiments, from the first to the last extract collected when the experiment was terminated.

UNITS

cm	centimetre
g	gram
kg	kilogram
hr	hour
L	litre
mL	millilitre
cm^2	centimetre squared
cm^3	centimetre cubed
mg	milligram
min	minute
mS / cm^3	milli Siemens / cm^3
µs / cm^3	micro Siemens / cm^3

1 INTRODUCTION

1.1 PROBLEM STATEMENT

One of the World Health Organization’s (WHO) Sustainable Development Goals is that access to safe and affordable drinking water should be universally and equitably available to all by 2030 (WHO, 2017). One highly recognised pollutant, which significantly threatens the safety of water and human health, is fluoride (Singh et al., 2016; WHO, 2004). Concentrations of fluoride in drinking water should be below the recommended safety guideline of 1.5 mg/L (WHO, 2004).

Fluoride toxicity (i.e. fluorosis), which is mainly caused by the ingestion of drinking water with elevated fluoride concentrations, is a widespread problem (Allibone et al., 2012). Over 200 million people in more than 25 countries are affected, including New Zealand and Australia (Amini et al., 2008; Ayoob & Gupta, 2006; Mameri et al., 1998; Meenakshi & Maheshwari, 2006; WHO, 2004). The issue is particularly prevalent and problematic in low socio-economic groups (Levy, 2005), rural communities lacking central treatment systems (Kimambo et al., 2019) and areas with volcanic activity (D'Alessandro, 2006) such as Vanuatu.

The only viable solution in many instances is defluoridation of drinking water (Keesari et al., 2019; Meenakshi & Maheshwari, 2006), however most techniques are unsuitable for resource poor areas due to costs, complexity, scarcity of materials and trained operators (Cherukumilli et al., 2018; Vijayeeswarri et al., 2019).

Coral sand is generally readily available in the Pacific Region where volcanic and geothermal activity are prevalent and consequentially, elevated fluoride concentrations are common (Allibone et al., 2012; Cronin et al., 2003). In response to this problem, this study proposes to investigate the ability of coral sand to lower fluoride concentrations in drinking water, in particular, by utilising acid enhanced lime defluoridation (AELD) with citric acid, an edible and easily accessible acid. Functional parameters may hopefully be optimised so that a simple and affordable household gravity-fed system could sufficiently lower fluoride concentrations to or below the recommended safe drinking water limit.

1.2 RESEARCH AIMS AND KEY OBJECTIVES

RESEARCH AIMS: This research was conducted to increase the body of knowledge of AELD using coral sand. The penultimate goal was to develop an effective, simple, low-cost, locally-made household coral sand filter for use in emergency filtration of drinking water to reduce fluoride concentrations to below the safe drinking water limit, particularly in the Pacific region such as Vanuatu.

KEY OBJECTIVES:

1. Determine the ability of coral sand to reduce fluoride concentration in water using fixed-bed filtration system with acid enhanced lime defluoridation by optimising conditions such as contact time, adsorbent dose, and acid concentration.

2. Determine whether treatment systems can be reused, and how often, before the filter loses its efficiency.

3. Assess the safety and palatability of the treated water with regards to the presence of other possible contaminants (metals, pH, elevated fluoride) and aesthetic parameters (total dissolved solids/conductivity, colour).

1.3 THESIS OUTLINE

This thesis has been organised into six main chapters, supplemented with an appendix containing a large portion of the raw data, supplementary information as well as methodology development details. A large amount of electronic data files were generated during sand characterisation processes that were too big to include.

A statement of the problem, overarching aim, and objectives of the study are broached in the Introduction (Chapter 1). The literature review is detailed in Chapter 2 and provides an overview of background information on fluoride in drinking water, fluoride detection methods as well as mitigation and remediation options best suited to low-income areas to provide context for this research project. Instruments, equipment, sourcing and preparation of materials and treatment devices are discussed in Chapter 3 along with detailed methodology used for sand characterisation, small-scale batch and column experiments, as well as the final prototype trials.

The experimental portion of the research was divided into two main parts, the first relates to small-scale batch and column experiments and includes characterisation of the sands used. These results and discussion are presented in Chapter 4. The experimental trials were scaled-up to prototype treatment devices, made from 1 L jerrycans and 1 kg of coral sand to approximate a 20 L drum. Chapter 5 details the results and discussion relating to these prototypes as well as a preliminary trial conducted with activated charcoal. The final chapter summarises the key findings of this research and discusses limitations, potential improvements and implications of the findings from this research as well as future recommendations.

2 LITERATURE REVIEW

2.1 FLUORIDE AND HEALTH

With climate change rapidly imposing its effects on the planet, combined with a relentless growth in world population, the demand for safe drinking water is on the rise (Amini et al., 2008; Ray & Brown, 2015). It is argued that fluoride is beneficial for caries prevention (Jayarathne et al., 2015; WHO, 2004), however, elevated consumption is associated with numerous negative health effects (Ayoob & Gupta, 2006; Bhatnagar et al., 2011). Fluoride and arsenic are recognised as the most serious inorganic drinking water contaminants throughout the world (Chouhan & Flora, 2010). The WHO's safety limit for fluoride in drinking water was set to 1.5 mg/L in 1984 but they acknowledge the need to account for fluoride intake from other sources (WHO, 2004). Climate will affect the optimal concentration of fluoride in drinking water (Jayarathne et al., 2015). Lower limits (0.5 - 1.0 mg/L) are warranted for tropical and/or warm countries where water intake is higher or where fluoride consumption from other sources is more elevated (Jayarathne et al., 2015; Meenakshi & Maheshwari, 2006; WHO, 2004). It is also possible that evapotranspiration due to climate change may exacerbate the fluoride problem in the near future (inferred from Bundschuh et al., 2010). Sadly, the lack of adequate water sources and suitable solutions has caused some countries to accept much higher drinking water limits, in some instances up to 8 mg/L (Addison et al., 2019; Water Utilization, Control and Regulation, Amendment Act, 1981 as cited in Kaseva, 2006; Rural Water Supply Health Standard Committee, 1974 as cited in Mjengera et al., 1997).

Near all absorbed fluoride is deposited in bones and teeth (WHO, 2004). Dental fluorosis is the accumulation of fluoride in teeth leading to increased enamel porosity and decreased mineral content (Rajkumar et al., 2015). This 'mottling' of the teeth generally occurs during their development (Allibone et al., 2012) and severe cases may be characterised by tooth loss or fragility (Ayoob & Gupta, 2006). Prolonged exposure to elevated fluoride concentrations increases the risk of skeletal fluorosis, a painful and debilitating condition of "fragile bones having low tensile strength" (Ayoob & Gupta, 2006, p.459). Symptoms may also resemble arthritis with restricted movement of the spine, neck, knee, pelvis or shoulder joints (Ayoob & Gupta, 2006). In addition, elevated fluoride exposure has negative effects on almost every other major bodily area and function including but not limited to: muscles, brain, lungs, bones, kidneys, bladder, reproductive system, red blood cells, gastrointestinal, ligaments, DNA, enzymes, and metabolism (Ayoob & Gupta, 2006; Bhatnagar et al., 2011; Chaudhary & Prasad, 2015; Ghosh et al., 2012; Meenakshi & Maheshwari, 2006). Unfortunately, malnutrition in children exacerbates the ill effects of high fluoride ingestion (Ayoob & Gupta, 2006; Peckham & Awofeso, 2014; Teotia et al., 1998). The damaging effects of fluoride are due to it being the most electronegative and thus reactive element on the planet (Jayarathne et al., 2015), hence why it is rarely found in its elemental state (WHO, 2004). It is also similar in size and charge to the hydroxyl group enabling the chemical exchange between the two possible and making the fluoride anion easily solubilised (Jayarathne et al., 2015).

2.2 SOURCES OF FLUORIDE

2.2.1 DRINKING WATER

Fluoride is abundant in the earths' crust, in the form of minerals or fluorine-containing rocks, soils and clays (Mason & Moore as cited in Allibone et al., 2012; Ayoob & Gupta, 2006; Bhatnagar et al., 2011; WHO, 2004). Dissolution of these materials releases fluoride into groundwater (Bhatnagar et al., 2011) where its concentration is dependent on various geological, chemical, and physical characteristics of the environment (Meenakshi & Maheshwari, 2006).

Elevated fluoride concentrations are prevalent in volcanic areas and geothermal waters (Alarcon-Herrera et al., 2013; Cordeiro et al., 2012). The emission of gas, ash and tephra from volcanoes can have severe impacts on the health of animals, humans, and vegetation (Allibone et al., 2012; Cronin et al., 2003). One particularly toxic volcanic gas is hydrofluoric acid, which is highly soluble, thus enhancing the bioavailability of fluoride (Delmelle et al., 2002). Allibone et al. (2012) noted that dental fluorosis rates and high fluoride water concentration correlated with wind and rainfall patterns, distance from and elevation to an active volcano.

Given almost 10% of the world population lives in volcanic areas, the fact that fluorosis is endemic in over 20 countries is not surprising (Baxter, 2005; Meenakshi & Maheshwari, 2006). Excess fluoride in groundwater is a world-wide problem affecting many large nations such as China, India, Sri Lanka, and Africa (Gogoi & Dutta, 2016). Unfortunately, most high fluoride groundwater sources are located in tropical rural areas which lack central water treatment and in communities with low socioeconomic status (Jayarathne et al., 2015; Levy, 2005).

2.2.2 OTHER FLUORIDE SOURCES

Fluoride may also be ingested through products such as medicines, toothpastes and some foods (especially tea leaves) (Allibone et al., 2012; Chaudhary & Prasad, 2015; Fung et al., 1999; Levy, 2005). Other anthropogenic sources are numerous and include: pesticides and fertilisers (Ayoob & Gupta, 2006); various industries (e.g. glass, ceramic, semiconductor, electroplating, iron, brick, enamel, tile, textile dyes, plastic, aluminium smelters, coal power stations) (Shen et al. as cited in Bhatnagar et al., 2011; WHO, 2004; Vinati et al., 2015); cigarettes and cosmetics (Gogoi et al., 2018); and potentially teflon-lined cookware (Ayoob & Gupta, 2006). These are less likely to be of concern in a Pacific Island context.

2.3 SAFETY OF DRINKING WATER IN VANUATU

Vanuatu is a Pacific Island Country comprised of numerous islands on the Pacific Ring of Fire. There are many active volcanoes throughout the islands including Manaro, which erupted in July 2018 and forced the evacuation of Ambae island inhabitants (Fogarty & Graue, 2018). This volcano has been persistently degassing for years and a volcanic plume is overhead on most days (Allibone et al., 2012). Since communities on the islands make extensive use of rainwater harvesting for drinking purposes (Allibone et al., 2012; Foster & Willetts, 2018), the safety of drinking water near active volcanoes is highly questionable. Testing conducted shortly after the 2018 eruption revealed that a significant proportion of rainwater tanks (approximately 1 in 5) sampled in the study had fluoride concentrations above the recommended safe limit of 1.5 mg/L (J. Gregor, personal communication, April 29, 2019).

2.4 FLUORIDE REMEDIATION, MITIGATION AND SOLUTIONS

Four solutions to mitigate against fluoride toxicity have been put forward (Allibone et al., 2012; Keesari et al., 2019; Kimambo et al., 2019; Meenakshi & Maheshwari, 2006):

1. find an alternate water source
2. dilute high fluoride water with a second low fluoride water
3. improve the nutritional state of the population
4. defluoridation of drinking water.

In some specific situations like rainwater harvesting, protecting the water source by covering tanks, filtering or disconnection during ashfall and off-gassing, can reduce fluoride contamination (Allibone et al., 2012). In general however, the only practical options where an alternate water source is not available is nutritional supplementation (Keesari et al., 2019) and defluoridation (Ghosh et al., 2012; Meenakshi & Maheshwari, 2006).

Water defluoridation methods generally fall into the following categories: precipitation / coagulation, absorption, membrane technologies, and electrochemical techniques (Fan et al., 2003; Ingle et al., 2014; Jayarathne et al., 2015; Kimambo et al., 2019; Loganathan et al., 2013; Mohapatra et al., 2009; Rajkumar et al., 2015; Wong & Stenstrom, 2018; Yadav et al., 2018; Yitbarek et al., 2019). Many of the latter two types of techniques are complex in terms of cleaning and regeneration of membranes, resins or particles; require skilled labour; have high initial and maintenance costs; cause intense secondary pollution; and need reliable power and supplies for operation (Bhatnagar et al., 2011; Fan et al., 2003; Tomar & Kumar, 2013; Vijayeeswarri et al., 2019; Yitbarek et al., 2019). Due to their unsuitability for resource-poor situations and practical limitations, these techniques are not discussed further here (further details can be found in Karunanithi et al. (2019); Kumar et al. (2019); Lacson et al. (2021); Mohapatra et al. (2009); Pillai et al. (2021); Yadav et al. (2019)).

2.4.1 PRECIPITATION

Precipitation techniques are generally used for highly concentrated solutions but can generally only reduce concentrations to about 2 mg/L (Fan et al., 2003; Wang & Reardon, 2001; Yang et al., 1999). Fluoride is precipitated with aluminium or calcium salts as noted in equations (1) and (2) (Karunanithi et al., 2019; Yang et al., 1999):

$$Al\ (\text{from } Al\ salts) + F^- \rightarrow Al\text{-}F\ complex + undefined\ product \qquad (1)$$

$$Ca^{2+}\ (\text{from } CaCO_3) +\ 2\,F^- \ \rightarrow\ CaF_2 \qquad (2)$$

As the pH is lowered, calcium carbonate dissolves, the concentration of calcium increases and precipitates as calcium fluoride following Le Chatelier’s principle. The reaction is dependent on the initial concentration of fluoride and is governed by equation (3), the solubility product (Yang et al.,

1999) where the solubility of CaF_2 in water is 0.015 g/L at 18 °C (National Centre for Biotechnology Information, n.d.).

$$K_{sp} = [F^-][\,Ca^{2+}] = 3.5\ x\ 10^{-11} \qquad (3)$$

This method is low-cost but the precipitated aluminium sludge generated in the process is problematic in terms of waste management (Nath & Dutta, 2010b). As mentioned, it is also impractical and near impossible to reduce the fluoride concentration below 2 mg/L.

2.4.2 ADSORPTION

Adsorption has been extensively used to remove fluoride with promising results (Jagtap et al., 2012; Yadav et al., 2018). Its advantage, over other methods include its effectiveness, convenience, low-cost, simple operation process and design, potential for reuse, and availability of a wide range of adsorbents (Kanaujia et al., 2015a; Kimambo et al., 2019; Mohapatra et al., 2009; Vijayeeswarri et al., 2019; Vinati et al., 2015; Yadav et al., 2018). Earlier studies by Reardon and Wang (2000) found that sorption was more effective than precipitation at reducing fluoride concentrations to below 1 mg/L. Hundreds of adsorbents have been studied, ranging from simple natural materials like clays to fabricated compounds like carbon nanotubes (Bhatnagar et al., 2011; Li et al., 2003; Vinati et al., 2015). In spite of this, research is ongoing as no material has been fully successful for resource constrained rural regions due to barriers including sourcing, costs, processing methods, complexity of operation/maintenance, labour intensity and social acceptability (Cherukumilli et al., 2018). "Characteristics of the adsorbent such as selectivity, regeneration potential, and physical and chemical stability" are drawbacks that require improvement (Yadav et al., 2018, p.102). The mechanism of adsorption of fluoride onto solid membrane, resin or other particles occurs in three essential steps (Fan et al., 2003):

I. external mass transport (the diffusion of fluoride ions to the outer surface of the adsorbent)
II. adsorption of fluoride onto the particle surface
III. intra particle diffusion (the exchange or transfer of the fluoride ion to the inner surfaces of porous materials).

These steps are affected by the properties of the adsorbent such as its adsorption capacity, particle size and surface area, as well as the physico-chemical conditions of the solution (e.g. pH, agitation speed, contact time, initial fluoride concentration, adsorbent dose, temperature, presence and nature of other ions, solvent dose kinetics, equilibrium isotherms) (Camlek, 2017; Kimambo et al., 2019; Loganathan et al., 2013; Tomar & Kumar, 2013; Yadav et al., 2018).

2.5 ADSORBENTS

Categories of adsorbents include aluminium-based; carbon-based; calcium-based; oxides/hydroxides; nanoparticles; natural materials; building materials/industrial wastes; agricultural and biomass-based which are well described in Yadav et al. (2018). An ideal adsorbent would be low-cost, easily regenerated, have good physical characteristics with regards to water flow, and rapid and high fluoride adsorption (Loganathan et al., 2013). To be effective, many studied adsorbents require high energy inputs (e.g. boiling, heating) (Larsen & Pearce, 2002; Mjengera et al., 1997) and low pH (Chaudhary & Prasad, 2015). Low-cost adsorbents are often limited in their effectiveness due to low removal capability and lack of cultural acceptance (Kimambo et al., 2019).

Carbon-based adsorbents: Activated carbons are adsorbent materials traditionally used for wastewater treatment (dos Santos et al., 2021; Fundneider, Acevedo Alonso, Wick, et al., 2021). Powdered Activated Carbon (AC) from coconut shells has been used to improve the water quality index in China (Chan et al., 2021) and is currently used in household water filters such as Brita (Brita®, n.d.). Various biomaterials including tobacco, coconut shells, olive stones, bamboo, and durian have been converted to activated carbon/charcoal or biochar. These products offer a potential solution to the remediation of different contaminants from water (Manfrin et al., 2021) as they have been used to remove Pb (Manfrin et al., 2021), Fe (Baharudin et al., 2021; Corral-Bobadilla et al., 2021), Mn (Baharudin et al., 2021), As (Alchouron et al., 2021), micropollutants (Fundneider, Acevedo Alonso, Abbt-Braun, et al., 2021); and fluoride (Choong et al., 2020). Recently, Alhendal et al. (2020) used a limestone and AC filter with a short reaction period and no agitation to reduce fluoride concentrations below 1.5 mg/L, however generation of AC is energy intensive.

Calcium-based adsorbents: Several studies have shown that calcium carbonate materials (e.g. lime, hydroxyapatite), which are abundantly available in various forms, are effective in fluoride removal (Vijayeeswarri et al., 2019). Coral sand, which is mostly comprised of skeletal remains of coral reefs and aquatic species, is mainly calcium carbonate and conveniently widespread in the Pacific Islands (Camlek, 2017; Mallik, 1999).

2.6 PRIOR RESEARCH ON LIME DEFLUORIDATION

After much debate, researchers have determined that in calcite systems, fluoride is removed by both adsorption and precipitation (Turner et al, 2005; Nath & Dutta, 2010a; Nath & Dutta 2012; Camlek 2017) and is heavily influenced by pH (Chaudhary & Prasad, 2015; Turner et al., 2005; Yadav et al., 2018). Adsorption occurs onto the entire calcite surface whereas fluoride precipitates at kinks and step edges where a higher concentration of dissolved calcium ion is present (Turner et al., 2005). In acid enhanced lime defluoridation (AELD), acidification both improves the availability of Ca^{2+} ions for the precipitation reaction (Gogoi et al., 2015; Nath & Dutta, 2010a & b) and protonates the adsorbent surface to increase the attractive forces between fluoride and the adsorbent (Yadav et al., 2018). Both adsorption and precipitation occurring simultaneously enables the removal of fluoride in lower concentrated solutions (Nath & Dutta, 2012) which is essential for remediating fluoride issues in safe drinking water.

Numerous studies have been conducted into the lime defluoridation process and a summary of the general findings, which have shaped this current research project, include:

- The main mechanism of precipitation is fast, whereas adsorption is slower and continues beyond 6 hours (Nath & Dutta, 2012).
- Fluoride removal decreased if the pH is increased (Turner et al., 2005).
- Adsorbed fluoride begins to desorb as the pH increases towards the alkaline region (Yadav et al., 2018).
- Stirring has a big effect on removal (Chaudhary & Prasad, 2015; Mondal et al., 2016) as this speeds up the external mass transport of fluoride to the absorbent surface.
- There is an increase in fluoride removal with an increased adsorbent dose, or solid-to-liquid ratio (Turner et al., 2005).
- Repeated use of the adsorbent decreases fluoride removal (Nath & Dutta, 2012), which could be caused by a loss of smaller particles upon reuse of material (Camlek, 2017).
- The amount of precipitation is the same when material is reused but adsorption is reduced therefore, the adsorbent eventually requires replacement (Nath & Dutta, 2012).
- A lower initial concentration of fluoride extends filter life (Nath & Dutta, 2012).

- Fluoride removal is dependent on particle surface area (Camlek, 2017; Tomar & Kumar, 2013; Turner et al., 2005).

- A smaller particle size is more effective (Camlek, 2017; Nath & Dutta, 2010a; Wong & Stenstrom, 2018).

- The fluoride removal performance of Port Villa (Vanuatu) coral sand was comparable to store-bought coral sand (from the Institute of Environmental Science and Research Pioneer Fund Final Internal Report - Low-Cost Fluoride Removal [*Pioneer*] - M. Ashworth, personal communication, 2021).

- The presence of other anions decreased fluoride removal (Nath & Dutta, 2012).

- The porous structure of the adsorbent is essential for effective adsorption (Dubey et al., 2009).

- The kinetics of AELD are believed to be pseudo-second order where precipitation and adsorption occur concurrently (Camlek, 2017).

- Fixed bed columns are affected by bed height, flow rate, and initial adsorbent concentration (Murutu et al., 2012).

2.6.1 SELECTION OF ACID FOR ACID ENHANCED LIME DEFLUORIDATION (AELD)

Various acids can and have been used for AELD including citric, phosphoric, oxalic and acetic acids (Gogoi & Dutta, 2015; Nath & Dutta, 2010a, 2012). The edible acids such as phosphoric, citric and acetic are preferred given they are safe for consumption and common in food products (e.g. soft drinks, fruits, and vinegar, respectively). Though acetic acid is edible and safe in diluted form, it is highly corrosive in its concentrated and liquid state. Both phosphoric and acetic acids are listed as dangerous goods under the United Nations (UN) classification and thus transport is highly regulated (Chemwatch, 2019a, 2019b). As citric acid is unregulated, transportation, importation and access is simplified. Citric acid is not only commonly used as a food additive, but it is also easily obtainable in supermarkets and found naturally in fruits, more notably citrus (Penniston et al., 2008). Its use in AELD does not add harmful contaminants or unpleasant taste to treated water (Osada as cited in Nath & Dutta, 2010b). In addition, it is classified as a weaker acid and generally does not cause heart burn (Osada as cited in Nath & Dutta, 2010b). For these reasons, citric acid was selected for use in this current research.

2.7 RESEARCH GAPS

In spite of the abundance of adsorptive materials and their advantages, there is still an urgent need for simple defluoridation techniques (Gogoi et al., 2018; Gogoi et al., 2015; Jayarathne et al., 2015; Larsen & Pearce, 2002; Mondal et al., 2016). No material has been successful for rural and resource-constrained regions due to barriers such as sourcing, costs, processing methods, complexity of operation/maintenance, labour intensity and social acceptability (Cherukumilli et al., 2018; Mahlangu et al., 2012; Yadav et al., 2018). Sadly, lack of funding and technical assistance has slowed down development of small-scale, low-cost remediation methods in spite of various sustainable solutions (Bundschuh et al., 2010, discussing low-cost arsenic filters).

Batch adsorption studies of calcite materials have shown potential for remediation of contaminated water but additional column studies are required to assess the feasibility of the adsorbent in the field, as a fixed-bed filtering medium (Camlek, 2017; Yadav et al., 2018). Though fluoride removal with calcium-based materials has been successful in laboratory experiments, these methods need field testing with real water samples (Yadav et al., 2018).

Recent experiments conducted by the University of Canterbury and the Institute of Environmental Science and Research (ESR) had promising results for the ability of coral sand to reduce fluoride concentrations in water by batch treatment (M. Ashworth, personal communication [Pioneer], 2021; Camlek, 2017). Additional research is required to determine the efficacy of removal in column format and whether treated water meets WHO drinking water standards. More specifically, verifying post-treatment water quality in terms of fluoride, metal ions, microbes and other physico-chemical properties like pH is of great importance (Mavura et al., 2004). Aesthetic attributes (taste, odour, colour) also deserve attention as these influence drinking water choices (WHO, 2017).

It is well documented (Bhatnagar et al., 2011; Kanaujia et al., 2015a; Meenakshi & Maheshwari, 2006; Mwabi et al., 2011) that site-specific conditions like competing or interfering substances such as organic matter or ions, effects fluoride removal and that the adsorptive capacity of an adsorbent is expected to decrease in a field setting (Mlilo et al., 2009; Mwabi et al., 2011). Therefore, field testing of new technologies is imperative before implementation (Meenakshi & Maheshwari, 2006).

2.8 CHARACTERISTICS OF AN IDEAL HOUSEHOLD FILTER

Any technique for use in rural areas without central water supply needs to be effective, small scale, affordable, made from local materials and energy sources, simple and low maintenance (i.e. ability to be reused or regenerated) (Bundschuh et al., 2010; Wong & Stenstrom, 2018). The adsorption technique is possibly the most suitable in these circumstances and may require only a filter (Li et al., 2011). Design should take into account the safe storage of water after treatment as water can be re-contaminated (Mahlangu et al., 2012) as well as cultural and local water collection practices as understanding of cultural and social facts are important to project success (Schoeffel, 1995).

2.9 FLUORIDE DETECTION METHODS

The most satisfactory methods for fluoride ion determination in water are potentiometry and colorimetric methods (Baird & Bridgewater, 2017) however interfering ions may cause errors in both. Distilling samples circumvents these errors when the ions are present in excess of tolerated limits (Baird & Bridgewater, 2017). Colorimetric procedures are particularly affected by ionic interferences whereas some electrode procedures can eliminate the need for distillation altogether (ASTM International [ASTM], 2016). The ASTM discontinued the SPADNS colorimetric procedure in favour of an ion selective electrode (ISE) method, due to a lack of interest from laboratories (ASTM, 2016). The method has a limited analytical range (up to 3.5 mg/L) and requires a filter or spectrophotometer for analysis (Baird & Bridgewater, 2017), which are not particularly portable. The complexone method, another colorimetric method detailed in Baird and Bridgewater (2017), requires distillation, a continuous-flow analytical instrument and also has a limited range of 0.1 to 2 mg/L. Ion chromatography and capillary ion electrophoresis are other options, but again, require bulky and sophisticated instrumentation.

A large portion of studies measuring fluoride in water are conducted using an ISE and total ionic strength adjustment buffer (TISAB) as it is the most reliable detection method (Baird & Bridgewater, 2017; Camlek, 2017; Shen et al., 2016). The analytical range for fluoride ion selective electrode (FISE) is quite large, spanning anywhere from 0.1 mg/L to 2 g/L (Baird & Bridgewater, 2017) and the instrumentation is field-capable (EDT directION, n.d.-a).

2.9.1 PRINCIPLE OF ION SELECTIVE ELETRODE (ISE)

The key component of the FISE is the laser-type doped lanthanum fluoride crystal (Baird & Bridgewater, 2017; International Organization for Standardization [ISO], 2018). When a reference and a fluoride measuring electrode are placed into waters containing fluoride, a potential difference develops between the two, which is proportional to the logarithm of fluoride ion activity based on the Nernst equation (ISO, 1992), detailed in equation (4).

$$E = E_0 + S*\log (F^-) \tag{4}$$

Where,

(F^-) is the fluoride ion activity in solution (approximated by $[F^-]$ if using TISAB),

E_0 is the reference potential (a constant) - intercept of the linear calibration curve,

E is the measured electrode potential (usually in MeV),

S is the electrode slope.

This potential (E) shows a linear relation with the log of fluoride activity or ‘effective’ fluoride ion concentration. When using TISAB with samples and standards, the fluoride activity can be approximated by the fluoride ion concentration. Both temperature and ionic strength of the solution influences the potential difference at the electrodes (ISO, 1992). The pH and the presence of complexing ions also affects the activity of the fluoride ion. In addition, the degree of complexation is influenced by the pH, fluoride and complexing ion concentration. Aluminium and iron, if present at 3 mg/L and 200 mg/L respectively, are the most problematic interferants as they cause a 10 % measurement reduction in solutions containing 1 mg of fluoride/L (Baird & Bridgewater, 2017, Section 4500F p.1).

2.9.2 TOTAL IONIC STRENGTH ADJUSTING BUFFER (TISAB)

To remedy the limitations of the ISE, a total ionic strength adjusting buffer is added to samples, controls, and standards. The functions of the buffer are as follows (Camlek, 2017; Agarwal et al., 2002):

I. a decomplexing agent present, such as EDTA or CDTA, releases any complexed fluoride by chelating metallic ions;

II. the high total salt concentration ensures the ionic strength of the standards and samples is comparable; and

III. the acetate / acetic acid (or other chemical pair) buffers the samples to an appropriate pH range.

The solution pH is crucial as the hydroxide ion is another known problematic ion which interferes with the electrode if its concentration is more than a tenth that of fluoride (EDT directION, n.d.-b; United States Environmental Protection Agency [EPA], 1996). At low pH, fluoride forms HF-HF complexes which is undetected by the FISE (EPA, 1996). Buffering at pH between 5 to 5.5 resolves these issues (EPA, 1996).

Consultation of literature revealed several TISAB formulations as well as some commercially available options which are used with the FISE. Selection of an appropriate TISAB is critical in the analysis of fluoride in water as the presence of ionic or non-ionic species can greatly influence ISE measurements (Agarwal et al., 2002). As mentioned, polyvalent cations such as Fe^{3+} and Al^{3+} form complexes with fluoride and interfere with FISE measurements as the electrode only measures free fluoride ion (EPA, 1996). Aluminium is particularly problematic as it forms fluoride complexes about 10 times more stable than fluoride-iron complexes (EPA, 1996). The boron tetrafluoride anion is not decomplexed by TISAB (ISO, 1992) and, if boron or select substances from industrial waste are present, distillation is necessary (Baird & Bridgewater, 2017).

Though low concentrations of aluminium and iron are counteracted with the addition of TISAB (ASTM, 2016), two other buffers are recommended for use when waters contain aluminium due to their increased effectiveness at greater aluminium concentration ranges (ASTM, 2016). Buffer A contains the tris-hydroxymethyl aminomethane hydrochloride (THAM) complexing agent. One study, which examined the efficacy of several TISAB formulations in fluoride removal from iron and aluminium contaminated waters, found that only TISAB formulations with THAM could effectively release fluoride from aluminium complexes at aluminium concentrations of 1-2 g/L (Agarwal et al., 2002). The second buffer, Buffer B, is composed of a mixture of citric acid, sodium citrate dihydrate, ammonium chloride and ammonium hydroxide, a formulation which was not evaluated by Agarwal et al. (2002). Another complexing component which was not evaluated is CDTA, which can preferentially complex aluminium in solutions containing up to 3 mg/L (Baird & Bridgewater, 2017). Another source (ASTM, 2009), states that aluminium ion concentrations up to 5 mg/L can be tolerated in a 1.5 mg/L fluoride solution. It is important to note that standard methods were validated in reagent waters, therefore the procedure must be validated with untested matrices to confirm appropriateness of the buffer and analytical method (ASTM, 2016). Additional testing with synthetic or artificial rainwater (with or without an aluminium spike) could be used to approximate field conditions encountered in volcanic regions.

Given the aim of this research was to develop a prototype filtration device to be field-tested in developing communities, a few other aspects were taken into account when designing the experiments and selecting the TISAB formulation. A formulation using the least problematic chemicals with regards to travel and/or importation was preferred. This aspect is largely influenced by a compounds' UN dangerous goods classification which will dictate appropriate storage and transport conditions. A second consideration is cost of chemicals, shipping and importation fees, to render the field-component more attractive to potential research funding entities. Sigma-Aldrich, one of the University's chemical suppliers, was approached to assess the feasibility and cost of shipping the required chemicals to Vanuatu, as well as any potential problems regarding importation. The logistical complexity and thus lag in response regarding shipping and importation to Vanuatu did not assist in selecting a TISAB recipe. In addition, the COVID pandemic halted thoughts of field-testing any successful filter overseas in 2020-21.

2.9.3 ANALYTICAL FLUORIDE ION SELECTIVE ELECTRODE (FISE) METHOD SELECTION

Direct measurement (or potentiometry) is the easiest and most common analytical method which involves comparing the potential (E) of an unknown to a standard calibration curve (or a direct reading can be obtained from an internally calibrated ion meter).

In the known or standard additions method, the potential of an unknown sample is measured. A small but very concentrated standard solution is added and the potential is remeasured. This addition is usually repeated a number of times (EDT directION, n.d.-b). It is a useful method when fluoride in solution may be bound or if the matrix contains substances that interfere with the analytical method (ISO, 2018). The sample addition technique (also known as the dilution analysis method) may be used if samples are highly concentrated or if the sample matrix is complex and the available sample volume is small (ISO, 2018). The procedure involves the incremental addition of small amounts of sample into a large amount of TISAB. The latter two analytical methods may be required if direct potentiometry is over or underestimating fluoride concentrations outside of the range of acceptability as defined by quality control measures. Complex matrices such as natural groundwater, rainwater or contaminated waters which would be encountered in field samples may require such analysis.

Several published and standard methods were consulted during the method development phase of this study, including but not limited to: D1179 - Standard Test Methods for Fluoride Ion in Water (ASTM, 2016); Standard Methods for the Examination of Water and Wastewater (Baird & Bridgewater, 2017) ; ISO 10359 - Water Quality - Determination of Fluoride Part I and II (ISO, 1992; ISO, 1994); ISO 19448 - Dentistry - Analysis of Fluoride Concentration in Aqueous Solutions by Use of Fluoride Ion-Selective Electrode (ISO, 2018); D3868 - Standard Test Method for Fluoride Ions in Brackish Water, Seawater, and Brines (ASTM, 2009); 9214 - Potentiometric Determination of Fluoride in Aqueous Samples with Ion-Selective Electrode (EPA, 1996).

The following recommendations and instructions were noted:

- Calibration standards should be stored in borosilicate glass, polyethylene (ASTM, 2016) or plastic bottles and used within a month (ISO, 1992).
- Fluoride measurement with ISE should be measured at a pH of 5.2 ± 0.2 (ISO, 1992).
- Samples should be stored into polyethylene bottles. Though no preservatives are necessary, analysis should be completed as soon as possible and within 3 days (ISO, 1992).
- Colloidal substances, which interfere with analysis, can be removed with filtration (EPA, 1996). ISO recommend filtering samples with a 0.45 µm filter (ISO, 1992).
- Samples and standards should be analysed at the same temperature, given temperature affects electrode potentials. A range of ± 0.5 °C (ISO, 1992) to ± 1 °C (EPA, 1996) is recommended.
- It can take two minutes for a potential reading to stabilise, though it should not take more than five (ISO, 2018).

<u>Interference of Humic Substances:</u> Natural waters often contain both a high fluoride concentration and high levels of natural organic matter (Shen & Schäfer, 2015). Humic substances are somewhat ill-defined and are partly made up of organic matter from decaying animals and plants. They act as complexing agents in aquatic system and may trap fluoride ion, thus affecting fluoride measurements (Shen et al., 2016). Sample pre-treatment with centrifugation shows 100% fluoride recovery as the humic substances aggregate in the sediment and the fluoride is released into solution (Shen et al., 2016). This aspect would be important to consider if natural water samples, particularly ground or surface waters, were collected and analysed.

2.10 CHAPTER SUMMARY

In summary, fluoride is a drinking water contaminant of major worldwide concern, and is particularly prevalent in volcanic, rural and/or lower socio-economic regions, including some Pacific Island communities. Of the various techniques available for fluoride remediation, adsorption has been extensively studied and appears to be the method of choice for simple, low-cost fluoride removal from water. Adsorbents such as calcium carbonate or activated charcoal created from locally-sourced natural materials may be readily available. Fluoride removal in calcium-based systems occurs from both precipitation and adsorption mechanisms and is greatly enhanced in acidic environments. Excellent fluoride removal has been obtained following multiple reuses of a treatment system which used AELD and limestone, a calcium carbonate material (Nath & Dutta, 2010a). Numerous studies on AELD have elucidated several variables and findings which can be used to optimise the defluoridation process and further research. Citric acid is unregulated, easily obtainable and present naturally in fruits, thus an obvious choice in a tropical setting. In spite of the abundance of research conducted into defluoridation, no single material or method has been successful in all settings and further study is required.

Coral sand is another calcium carbonate containing material and its use as a fluoride adsorbent in batch studies conducted at the University of Canterbury gave encouraging results. Additional preliminary batch trials conducted at ESR using adsorbent dose of 1 g to 1 mL indicated that the adsorbent could *not* be successfully reused to reduce fluoride from 10 mg/L to below the NZ drinking water limit of 1.5 mg/L (M. Ashworth, personal communication [*Pioneer*], 2021). Very limited published research has been conducted on the use of coral sand for fluoride remediation and exploration of this adsorbent, particularly for use in Pacific regions, may prove beneficial to our resource-constrained neighbours.

Design of a treatment system should take heed of cultural practices and locally available resources. FISE using a buffer solution (TISAB) is the analytical method of choice. Careful selection of the buffer formulation may be helpful in complicated matrices, such as those which may be encountered in local ground, surface or rainwaters. Consideration should also be given to the ease of obtaining and importing instrumentation, materials and chemicals if field trials are to be conducted in overseas or rural settings.

3 MATERIALS, EQUIPMENT AND METHODS

3.1 SOURCING AND PREPARATION OF MATERIALS

The fine and coarse store-bought coral sands utilised in this research were purchased from Living Reef (livingreef.co.nz). Pacific coral sands (from Kiribati and Vanuatu) were graciously obtained from colleagues B. Humphries and M. Ashworth at the Institute of Environmental Science and Research (ESR).

All chemicals used were analytical grade unless stated otherwise. Most materials and reagents were sourced from the University of Canterbury Chemistry Department unless stated. Plasticware used in the 1 kg jerrycan experiments was obtained from Stowers Containment Solutions (www.plastic.co.nz). A list of reagent details, UC tracking numbers, and uses throughout this research is provided in Appendix A.

The food-grade citric acid used in the 1 kg prototype experiments was purchased in two 50 g tubs from New World, St Martins in January 2021. The tubs were labelled “VALUE…Citric Acid 100%. Store in cool, dry place.” And with a sticker label “#7300… Best before 03.12.22”.

Buffers, solutions and dilutions were made using ultrapure water with a resistivity of 18.2 MΩ.cm, obtained from a Select Fusion water purification system by Purite. Deionised (DI) water was obtained from the DI water taps at the University of Canterbury Geology laboratory, Ernest Rutherford Room 205.

Extracts collected from sand filters (columns and prototypes) were filtered using Ahlstrom 0.2 µm Reliaprep™ cellulose acetate sterile syringe filters, unless otherwise stated.

Samples treated with activated charcoal (purchased from Piko Wholefoods, in late 2020) were filtered with 125 mm diameter, Whatman paper grade “5”, for about 20 minutes until the fluid had drained by gravity.

3.2 EQUIPMENT USED

Acid Digester: Milestone Single Reaction Chamber Microwave Digestion System.

Balances:

a) Mettler-Toledo Delta Range Type PJ360 (60 g – 310 g); s/n N63400, GEOL# 1212.
b) Sartorius analytical balance Secura224-1S (220 g / 0.1 mg); UC# 9868
c) AND HR-250AZ compact analytical balance (252 g / 0.1 mg); UC# 9203
d) AND EJ-6100 (6100 g / 0.1 g); s/n 2863404 UC# 9230

BET: Micrometrics Gemini VI 2385 Analyser with Vacprep 061 de-gassing unit and Gemini VI 2385 v1.03 Software.

Chute splitters: Several chute splitters were obtained from the UC Geology Department: a large SOILTEST MODEL CL-280A chute splitter (instrument 'GEOL 290'); a smaller SOILTEST splitter (no serial number); and a GREEN GEOLOGICAL mini splitter (no serial number). Chute splitters were washed or wiped clean prior to being used to divide store-bought coral sand.

Conductivity meter: A HACH HQ440d multimeter (s/n 180700000989, UC# 9288) was used with a CDC401 conductivity probe (s/n 181562587009). The following method settings were applied:

- Parameter = conductivity
- Measurement options: units: auto
- Temp correction. None
- Measurement limits. 0.01 µS/cm to 400000.0 µS/cm
- Calibration options: 0.01 M. KCL. 1413 µS/cm.
- Acceptance limits. ± 8 %

EDS/Scanning Electron Microscope: Samples were carbon-coated with an "EMS150T ES Quorum" carbon coater and imaged with a "JEOL JSM-IT300" EMS-Scanning Electron Microscope.

Endecott sieves: A nest of Endecott sieves was constructed using 4 mm, 2 mm, 1 mm, 0.5 mm, 0.250 mm, 0.125 mm, and 0.063 mm mesh as well as a lid and pan. The sieves were cleaned as best as possible, either mechanically using tapping, brushing, and compressed air application or water washed, treated with compressed air and allowed to dry overnight.

FISE: An EDT instruments DR359Tx Ion concentration pH meter (s/n 33197, UC# 9262) with a fluoride electrode EDT DIRECTion 3221F (UC no. 91249 ''probe 2'' 30H10) was used for fluoride measurements.

Fridge: The Geology department 'SKOPE' fridge located in room 206 (no obvious serial number) was used for the occasional storage of samples where immediate FISE analysis (i.e. within 24 hours) could not be undertaken. Acidified ICP-MS samples stored long-term were also stored in this fridge.

Heating Magnetic Stirrer: a Velp Scientifica HSC ceramic hot plate stirrer (no noted serial number or UC#) was used for particle density determination.

ICP-MS: An Agilent Model 8900 triple quadrupole with a standard aqueous configuration.

Magnetic stirrer: a Kika-Mini-MR magnetic stirrer (UC Chem #5239) was used to stir samples during FISE analysis.

Mechanical shaker: a GFL head-over agitator model 3040, serial number 10189518A (UC #9269) was used for gentle agitation of samples for absorption isotherm experiments.

Oven: A Sanyo convection oven model MOV102F serial number 01201922 (instrument 'GEOL 1108'), was utilised to dry sand, samples and chemicals when required.

pH (and temperature) meter: A Mettler Toledo FiveGo pH meter (UC# 9150 and/or 9149) with a pH and integrated temperature sensor probe, model LE438 (UC# 9160) was used for pH measurement.

Pycnometers: two pycnometers were used for particle density determination: a 50 mL unit labelled "Czechoslovakia" "IN + 20°C" and a 25 mL unit labelled "GRIFFIN NOM C20°C".

Sieve shaker: An Endecotts Geotech EF2 2000/2 (instrument 'L2-206C-EQ02') was used to agitate the nest of Endecott sieves.

XRD: A Rigaku Smart Lab X-Ray diffractometer 3kW instrument was used with a copper K-α wavelength source.

3.2.1 QUALITY CONTROL OF PIPETTES, BALANCES, AND PH / CONDUCTIVITY METERS

The accuracy of pipettes was verified daily using the gravimetric method and calculated using the average and standard deviation of 4 to 10 readings. An error of no more than 2 % was noted on the 5 mL pipette and 3 % on the lower ranges of the 1 mL and 0.1 mL pipettes. The 0.1 mL pipette was used to measure volumes of less than 10 µl (i.e. below its operational range) for the acidification of select low volume ICP-MS samples only (<2 mL). Errors up to 15 % for these minute volumes were noted and tolerated.

Balances were levelled prior to use and, on applicable balances (i.e. Sartorius), an internal balance calibration was performed every other month or when measurement drift was noted.

The pH meter was calibrated monthly using three-point calibration and LabServ Solutions of pH 4, 7 and 10, resulting with a slope between 96 to 99 % and an offset of no more than -35 mV.

The conductivity meter was calibrated at least every second month using Hanna Instrument 1413 µS/cm conductivity solution sachets. Calibration checks were within the 8 % acceptance limit.

3.3 PREPARATION OF ACID, FLUORIDE SOLUTIONS AND TISAB

Sodium fluoride (NaF) used in this study was oven dried at 60 ± 2 °C for a minimum of 8 hours and used directly or stored in a dessicator until use.

3.3.1 STOCK FLUORIDE SOLUTION AND CALIBRATION STANDARD (CS) PREPARATION

A 200 ± 2 mg/L fluoride stock solution was prepared by dissolving a target amount of 0.4421 g NaF in 1000 mL of ultrapure water using a glass volumetric flask. 100 mL of this stock solution was diluted in a 1000 mL flask to create a stock 20.0 ± 0.2 mg/L fluoride solution. These solutions were further diluted to create calibration standards (Table 3.1).

Exact concentrations were calculated assuming 100 % purity (reagents used were noted to be at least 99% pure) and using gravimetric method assuming 1 mL of solution weighed 1 g. Volumetric methods was generally not used as the variation in volume and/or weight of volumetric flasks appeared to be larger than the error stated on the glassware and also, the ambient laboratory temperature varied significantly throughout the duration of this research (from approximately 14°C to 25°C).

Table 3.1

Preparation of FISE Calibration Standards

Calibration Standard Concentration (mg/L)	Volume of Fluoride Solution Used (mL)	Concentration of Fluoride Solution Used (mg/L)	Final Volume of Water (mL)
25	12.5	200	100
15	75	20	100
10	50	20	100
5	25	20	100
2	10	20	100
0.5	2.5	20	100
0.25	12.5	2	100
0.1	5	2	100

Note. Volumes and concentrations of stock fluoride solutions used to prepare calibration standards

Calibration Standards for Triplicate Isotherm Experiment

A 250 ± 5 mg/L fluoride stock solution was prepared by dissolving 0.1407 g of >99 % pure NaF in 250 mL ultrapure water using a volumetric flask. This solution was further diluted in volumetric flasks to create isotherm calibration standards (ICS) according to Table 3.2.

Table 3.2

Preparation of FISE Calibration Standards for the Isotherm Experiment

Isotherm Calibration Standard (ICS) Concentration (mg/L)	Volume of Fluoride Solution Used (mL)	Concentration of Fluoride Solution Used (mg/L ± 2 %)	Final Volume (mL)
125	50	250	100
75	30	250	100
25	10	250	100
10	4	250	100
5	2	250	100
2	8	25	100
0.5	2	25	100
0.25	50	0.5	100

Note. Volumes and concentrations of fluoride solutions used to prepare calibration standards for the isotherm experiment.

3.3.2 CALIBRATION CURVE VERIFICATION SAMPLES & LABORATORY CONTROL SAMPLES

Laboratory control samples (LCS) and calibration curve verification (CCV) samples were prepared by using a different batch of oven-dried sodium fluoride. A target amount of 0.1105 g of NaF was dissolved in 250 mL of ultrapure water using a glass volumetric flask, producing a solution of 200 ± 2 mg/L of fluoride (LCS200) or a final volume of 1 L for a final concentration of 50 mg/L (LCS50). Otherwise, a target weight of 0.2210 g of NaF was dissolved in 1 L for a final concentration of 100 mg/L (LCS100). These solutions were further diluted to generate several laboratory control samples according to Table 3.3.

Table 3.3

Preparation of Laboratory Control Samples (LCS)

Laboratory Control Sample Concentration (mg/L)	Volume of Fluoride Solution Used (mL)	Concentration of Fluoride Solution Used (mg/L)	Final Volume (mL)	Laboratory Control Sample Abbreviation
20	10	200	100	LCS20
	40	50	100	
	20	100	100	
4	20	20	100	LCS4
5	25	20	100	LCS5
	10	50	100	
2.5	5	50	100	LCS2.5
	1-in-2 dilution of 5 mg/L fluoride solution			

Note. Volumes and concentrations of fluoride solutions used to prepare LCS/CCV solutions.

3.3.3 CITRIC ACID SOLUTION PREPARATION

<u>Column and Isotherm (Batch Adsorption) Experiments</u>: A 0.2 M citric acid solution was prepared by dissolving a target amount of 84.056 g citric acid monohydrate in a total volume of 2000 mL using a glass volumetric flask (or alternatively, 42.028 g in 1000 mL). The 0.2 M citric acid solution was diluted two-fold for a 0.1 M citric acid solution. 0.05 M solution was made from a 1:2 dilution of 0.1 M citric acid or a 1:4 dilution of 0.2 M citric acid. When required, a 0.025 M solution was produced from a 1:2 dilution of 0.05 M solution or a 1:4 dilution of 0.1 M. Solutions were stored in Schott bottles unless otherwise indicated.

3.3.4 INITIAL ACIDIFIED OR NON-ACIDIFIED 10 MG F^-/L SOLUTION PREPARATION

<u>Column and Batch Sorption Experiments</u>: The preparation of initial solutions is described in the appropriate experimental sections below. All initial fluoride solutions used were 10 mg F^-/L ± 2% (or less).

<u>1 kg Prototype Experiments</u>: Initial non-acidified solutions were made by diluting 50, 25, or 12.5 mL of stock 200 ± 2 mg/L fluoride solution (refer above) into a 1000 mL, 500 mL, or 250 mL glass volumetric flasks, respectively. Solutions were used within the day or stored in acid-washed plastic bottles. The initial solutions with 0.025 M citric acid were made as above, with the addition of a target amount of 5.255 g, 2.6275 g, or 1.3138 g of store-bought citric acid respectively, and used within the day.

The acidified prototype experiments required larger volumes on first use, thus 1 L of 0.05 M citric acid solution (made by diluting a target amount of 10.507 g citric acid in a 1000 mL volumetric flask) and 1 L of 20.0 ± 0.1 mg/L stock fluoride solution were mixed together into a 2 L Schott bottle and use within the day.

3.3.5 SPIKE SOLUTIONS

Spike solutions of 50 mg/L; 100 mg/L; 200 mg/L; and 250 mg/L were prepared as described in Table 3.4 using gravimetric means, by diluting a 1 g/L Fluoride Standard for Ion Chromatography, an independent reference material as recommended in Baird and Bridgewater (2017). Additional details regarding which spike concentration to use based on final fluoride concentration of extracts measured is detailed in Appendix B.

Table 3.4

Preparation of Spike Solutions

Concentration of Spike Solution (mg/L)	Dilution Ratio	Concentration of Reference Standard or Spike Solution Used
250 mg/L	1 in 4 dilution	1 g/L reference standard material
200 mg/L	1 in 5 dilution	1 g/L reference standard material
100 mg/L	1 in 10 dilution	1 g/L reference standard material
	2 in 5 dilution	250 mg/L spike solution
50 mg/L	1 in 4 dilution	200 mg/L spike solution
	1 in 20 dilution	1 g/L reference standard material

Note. Volumes and concentrations of independent reference standard solution (1 g/L) used to prepare spike solutions.

3.3.6 TISAB PREPARATION

The TISAB formulation used in the majority of this study was a slightly modified version of the formulation used in the UC Undergraduate Chemistry Laboratory and obtained from N. Alexander (personal communication, March 2, 2020). Refer Appendix C for original formulation and communication. The only modification was the use of NaOH pellets directly as opposed to using a 10 M NaOH solution, in some instances.

The TISAB solution was made of 0.05 M disodium EDTA dihydrate, 1 M sodium chloride and 0.5 M glacial acetic acid by dissolving 13.6086 to 13.6222 g of $Na_2H_2EDTA\text{-}2H_2O$; 58.4822 to 58.6036 g of NaCl and 30.035 to 30.2 g of glacial acetic acid in approximately 900 mL of ultrapure water. The pH was adjusted to slightly above 5 (between 5 – 5.5) with either 10 M NaOH solution and/or NaOH pellets and topped up to a final volume of 1000 mL. The final pH was between 5.04 to 5.19, at a temperature of 22 to 26 °C.

The 10 M solution of NaOH was made using 99.9 g of NaOH pellets dissolved in 250 mL of ultrapure water using a glass volumetric flask.

3.4 CORAL SAND

3.4.1 ORIGIN, TREATMENT AND PARTICLE SIZE OF CORAL SAND

Fine store-bought sand: Three 20 kg bags of 'Natural Colour' coral sand were purchased from Living Reef (www.livingreef.co.nz), which are supplied by Brooklands Pet Supplies (www.brooklands.co.nz). According to the manager at Brooklands (personal communication, 2019), the 'Natural Colour' coral sand is obtained from a Chinese importer. No additional information is known regarding the geographical origin of the product or what treatment processes, if any, are applied to the sand.

The sand was minimally treated prior to conducting experiments to more accurately simulate field conditions but more importantly, to avoid altering its geochemical composition which could bias or skew experimental outcomes. To more accurately calculate particle density, the sand was oven dried at 60-65 °C for at least 24 hours prior to use, unless otherwise stated.

Coarse store-bought sand: A 5 kg bag of coarse (1-2 mm) coral sand, branded "Natural Color Aquarium Marine Sand" from "XIONGFA GARDEN Co. LTD Aquarium Products" was purchased from Living Reef. The product is packaged and labelled as "collected from non-polluted pure natural environment… free from harmful chemicals, ash and unwanted impurities… passed high technology treatment". This sand was thoroughly agitated in its bag and emptied into three cleaned glass containers to oven dry for two days (60-65 °C) prior to use in the final experimental prototypes.

Kiribati Sand: Approximately 1.5 kg of untreated coral sand collected in September 2017 from Kiribati (Bikenibeu Beach) was obtained from Bronwyn Humphries (ESR). Very large coral clasts had previously been removed and the sand had been dried for 48 hours at 60-65 ℃ in 2017.

The sand received was dried overnight (~65 ℃), mixed, and a subsample of ~100 mL was removed for Particle Size Distribution (PSD). Particles larger than 2 mm were removed using a hand-sieve and the remainder was dried (~65 ℃) for a total of 24 hours prior to being used in columns experiments.

Vanuatu Sand: An unused portion of sand collected from Vanuatu in February 2018 was obtained from Bronwyn Humphries (ESR). The sand had already been sieved into fractions and particles larger than 2 mm were not used in this present study. Fractions labelled as 250 µm (~10 g), 500 µm (~160 g) and >1 mm (~578.2 g) were obtained in separate labelled plastic containers and oven dried (~60 ℃) for at least 48 hours upon receipt. These were then re-weighed and combined as one fraction, mixed inside the tub and used in column experiments.

3.4.2 MIXING & SUBSAMPLING OF CORAL SAND

Store-bought fine coral sand: After thorough agitation of one of three 20 kg sand bags, a small portion of sand (<1 kg, a gross approximate volume of 300-400 mL) was removed from one bag and used for method development. Preliminary testing of column set-up and fluid extraction was done on this portion to provide an idea of sand amounts, sample volumes, and column sizes required for further experiment (detailed in Experiment A & B – Appendix D).

To avoid the challenge of bulk sampling 20 kg bags of sand, representative samples were then obtained by splitting the entire volume of sand as recommended by NIST (Jillavenkatesa et al., 2001) using large and small chute splitters. The sand was thoroughly agitated while still inside the three bags. Extra effort was applied to the corners as they tend to trap powder particles disproportionately

(Jillavenkatesa et al., 2001). The bags were mixed randomly and haphazardly several times by splitting and recombining fractions using the large Soiltest™ splitter. The entire volume of the remainder of the three bags was split into two halves, each half was mixed randomly and haphazardly several times, and split again to create four mixed portions of about 15 kg. A visual representation of the splitting and subsampling of the fine store-bought coral sand done in this study as well as which portions were used for various analyses, can be found in Figure 3.1. Each quarter was stored in a new and cleaned white plastic 20 L paint tub and designated lots A through D. The sand used for this study was obtained almost entirely from tub A, with the exception of the activated charcoal experiment (refer Experiment M) which utilised sand from Tub B, following thorough agitation by shaking and rolling of the tubs.

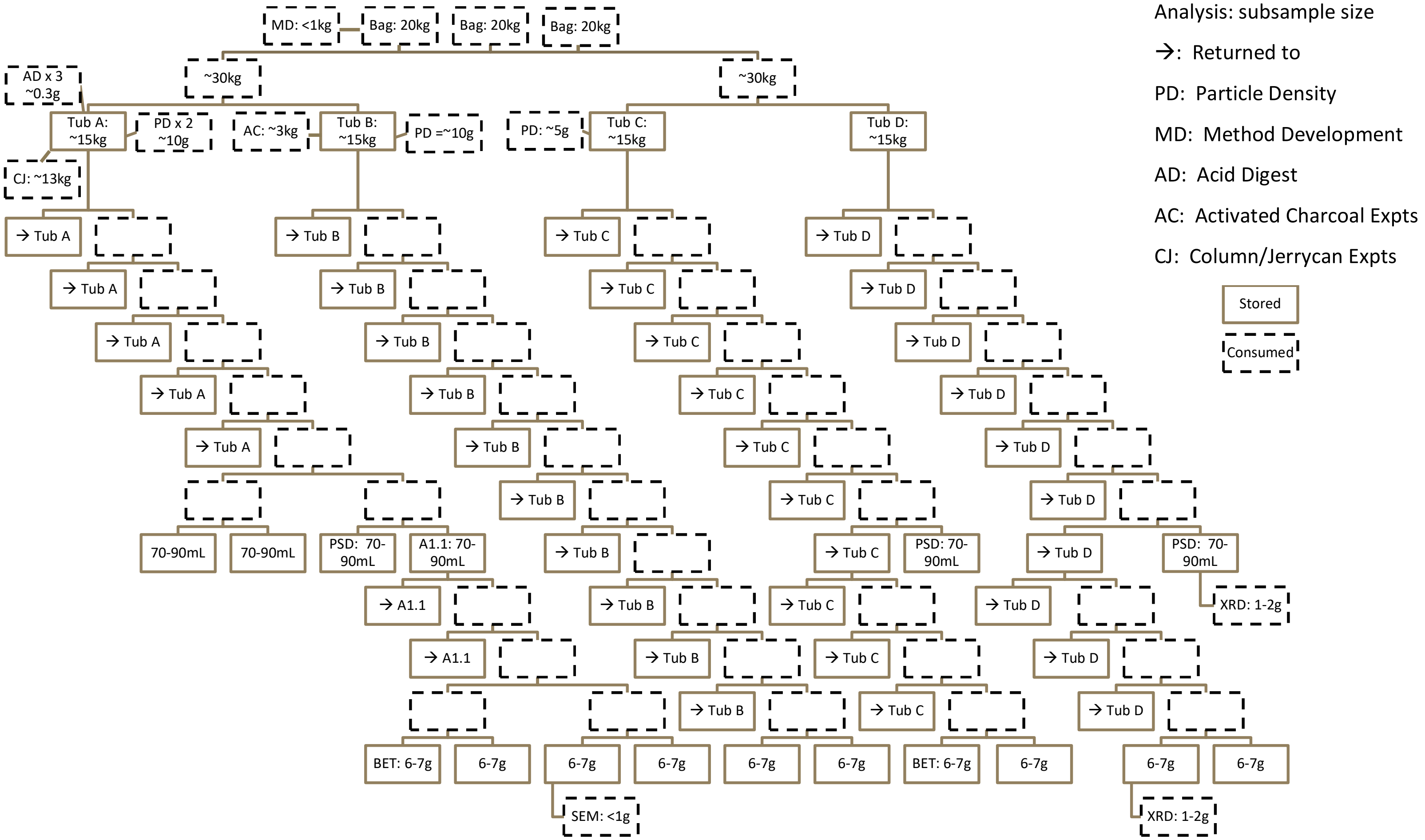
Three samples of about 75-90 mL were obtained by splitting the sand (with chute splitters) from tubs A, C and D seven times and used for PSD. Smaller ~6-7 g samples were obtained from an additional four splits and used for sand characterisation: one sample from tub A for SEM; and two portions of 1-2 g were removed from subsamples of tub D for XRD.

A sample of about 5 or 10 g was removed from three tubs after thorough mixing, for particle density determination. Following all adsorption experiments, three ~0.3 g samples of the remaining coral sand from tub A was used for acid digestion and subsequent ICP-MS analysis.

Kiribati sand: The ~1.5 kg of sand was mixed in its original plastic container and a scoop of ~100 mL was removed and stored in a clean Schott bottle (designated BB1) for PSD. The sand, without sample BB1, was hand sieved and particles larger than 2 mm were removed and stored. The remaining sand was then used in column experiments and sand characterisation analysis. Portions of ~3.5 g and ~2 g were scooped out from the mixed sand remaining and ground for XRD analysis. It was noted that sample BB1 gave moderately different PSD results from that obtained from similar sands (Burbery et al., 2015; Humphries et al., 2019), thus the entire volume of sand remaining after column experiments were completed was analysed for PSD. A portion of ~30 g was then collected for particle density measurements, a few grams for SEM analysis and three samples of ~0.3 g for acid digestion.

Figure 3.1

Splitting and Subsampling of 3 X 20 kg Sand Bags



Note. Splitting and subsampling of fine store-bought coral sand for various analyses.

Vanuatu sand: The three sand fractions received were dried, combined, and thoroughly mixed by agitation in one plastic container. Six ~75 g samples were removed for column experiments and a small subsample of about 4.2 g was stored for SEM and XRD analysis. The remainder of the sand was used for PSD determination. Approximately 1 g was then collected and ground as a second XRD sample and a portion of about 30 g was used to determine particle density. Two additional ~1-2 g samples were also ground for XRD.

Coarse store-bought coral sand: The sand was oven-dried then thoroughly mixed in a 15 L plastic tub. Three samples of approximately 85-95 g were removed for PSD determination. Two samples of about 5 g and 10 g each (four in total) were removed to perform particle density determination. Four portions of 1000 ± 0.2 g of sand were removed for the 1 kg prototype experiments, two samples of 1 to 2 g for XRD analysis, and three samples of ~0.3 g for acid digestion. No SEM analysis was undertaken on this sand.

3.4.3 PARTICLE DENSITY

The particle density of the coral sands was determined using pycnometers as described in Section 2.3 of Sarkar (2005). Four samples of approximately 5 or 10 g were analysed with 25 mL and 50 mL pycnometers respectively, and the mean and standard deviation calculated.

3.4.4 PARTICLE SIZE DISTRIBUTION

The particle size distribution was measured by sieving. A nest of sieves was constructed from the following aperture sizes based on the Wentworth Scale classification: >2 mm; 1 mm; 0.5 mm; 0.250 mm, 0.125 mm, 0.063 mm, and <0.063 mm (Wentworth, 1922). A lid and pan for collection of sub-0.063 mm particles were added. Each sample was dry-sieved and mechanically shaken for a minimum of 5 minutes to no more than 10 minutes, using an 'Endrock Endecotts Sieve Shaker'. The material from each sieve and bottom pan was weighed on an analytical balance and the mass fraction for each size interval was calculated according to equation (5):

$$\text{Mass fraction } (\mu_{3,i}) = 100 \times \frac{\text{Mass of size interval}}{\text{Total mass of sample}} \tag{5}$$

Where applicable, the mean and standard deviation of each fraction was calculated using Microsoft Excel. In addition, the fractional weights of subsamples and the averages calculated were entered into GRADISTAT version 8.0 (Blott & Pye, 2001) for particle size determination. Result print-outs are included in Appendix E.

The mean interval diameter ($d_{m,i}$) of the particles on each sieve was calculated from equation (6) in order to calculate the mean particle size ($d_{m,3}$) from equation (7) (Hintz, n.d.).

$$\text{Mean Interval diameter } (d_{m,i}) = \frac{(d_{i+1} + d_i)}{2} \tag{6}$$

$$\text{Mean Particle size } \left(d_{m,3}\right) = \sum_{i=1}^{N} \left(d_{m,i}\ x\ \mu_{3,i}\right) \tag{7}$$

Store-bought sands: Three samples of dried store-bought sand of about 80 mL (fine) or 85-95 g (coarse) were separately analysed as above.

Vanuatu sand: The sand fractions received were dried, weighed, combined and thoroughly mixed. Just over 450 g was used for experiments and sand characterisation, and PSD was conducted on the remaining sand (286.6 g) as described above.

Kiribati sand: The ~100 mL subsample of Kiribati sand (BB1) weighing 171.59 g was processed as above with an additional 4 mm sieve. Given results were fairly different from sands of similar location (Burbery et al., 2015; Humphries et al., 2019), PSD was conducted on the remaining unused 'large' portion (851.7 g). The sand, without sample BB1, had been sieved, particles larger than 2 mm were removed, and about 450 – 470 g used for column experiments or sand characterisation. PSD was conducted on the 2 mm+ fraction of 22.2 g and results were proportionally adjusted to back-calculate the PSD of the original sand received (details in Appendix E, Table E 1).

3.4.5 BRUNAUER-EMMETT-TELLER – SPECIFIC SURFACE AREA

Attempts to determine the surface area of three ~7 g samples of fine store-bought coral sand were made by using a Micrometrics Gemini VI 2385 Analyser with Vacprep 061 De-Gassing Unit in the Chemical and Processing Engineering department at UC. Various analytical settings and run programs using the Gemini VI 2385 v1.03 Software with the assistance of several staff and engineering students

(Michael Sandridge, Jason Li, Dr Alex Yip, Wasim Khan) were attempted but failed, and the instrument stalled at the ‘measuring free space’ stage. A carbon black reference sample (# 004-168 33-00; Lot # 160202; 0.511 g) was run and results were as expected, therefore the BET analysis was abandoned.

3.4.6 SCANNING ELECTRON MICROSCOPY – ENERGY DISPERSIVE X-RAY SPECTROSCOPY

Energy Dispersive X-Ray Spectroscopy-Scanning Electron Microscopy (SEM-EDS) was conducted by Shaun Mucalo of the Mechanical Engineering department at UC. Samples of unused fine store-bought, Vanuatu and Kiribati coral sand as well as oven-dried sand samples used in the 0.05 M citric acid column experiments (refer Experiment K) were analysed.

Samples were prepared with carbon-coating using an “EMS150T ES Quorum” Carbon Coater and imaged (three sites per sample) with backscatter electron detection (BED-C) as well as secondary electron detection (SED) using an EMS-SEM “JEOL JSM-IT300” instrument. Three sites per sample were also analysed using EDS for major elemental composition. Smaller specific sites were also targeted for possible visual contaminants.

3.4.7 ACID DIGESTION AND ICP-MS ANALYSIS OF UNTREATED CORAL SANDS

Triplicate samples of four types of sands (Kiribati, Vanuatu, fine and coarse store-bought coral sands) were digested according to EPA Method 3051A – Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils (EPA, 2007) by Hadee Thomson-Morrison. 0.30 g (± 0.02 g) of sand was pre-digested overnight in 5.00 mL of concentrated HNO_3. This acid was added 0.25 mL at a time until the exothermic reaction subsided, and the volume made up to 5.00 mL (H. Thomson-Morrison, personal communication, April 18, 2021). Two reagent blanks and one NIST Certified Marine Sediment 2702 reference material (NIST, 2019) were processed with the twelve coral sand samples. Samples were digested in a Milestone Single Reaction Chamber Microwave Digestion System using the General Method for Environmental Samples (Milestone, n.d., p. 8).

After digestion, samples were diluted in ultrapure water to a dilution of 1:21 (0.500 mL sample and 10.00 mL water). 0.100 mL of this 1:21 dilution was added to 10 mL of 2% HNO_3 for a final dilution of 1:2121. Diluted digests (1:21) were analysed by Rob Stainthorpe using ICP-MS for: Al^{27}, $As^{75\ \&\ 75\text{-}91}$,

Ca^{44}, Cd^{111}, Co^{59}, Cr^{52}, Cu^{63}, Fe^{56-72}, K^{39}, Mg^{24}, Mn^{55}, Na^{23}, Ni^{60}, P^{31}, Pb^{208}, Zn^{66}, Zr^{90}, B^{11}, Ge^{72}, Mo^{95}, Nb^{93}, Re^{185}, S^{32-48}, Si^{28}, Ta^{181}, Ti^{48-64}, W^{182}, Zr^{90} and the 1:2121 dilutions for Ca^{44}, K^{39}, Mg^{24}, Na^{23}, B^{11}, Ge^{72}, Mo^{95}, Nb^{93}, P^{31-47}, Re^{185}, S^{32-48}, Si^{28}, Ta^{181}, Ti^{48-64}, W^{182}, Zr^{90}.

Data was provided and processed in Excel. The LOQ was established by multiplying the dilution factor with the lowest reliably detected standard (± 15 % of its value). Values below the LOQ were reported as such and the elemental weight per unit of sand was calculated according to equation (8):

$$E = F * 0.005 \text{ x} \frac{(Cs - Cab)}{W} \tag{8}$$

Where,

E = amount of element per unit of sand in µg /g or mg/kg,
W = precise weight of sand digested (in g),
Cs = concentration of sample readout in µg /L,
Cab = average of two blanks,
F = dilution factor of 21 or 2121,
(0.005) = total volume of concentrated acid in the digest (5.00 mL).

The maximum and minimum values as well as the average ± 2SD of triplicates were determined. Elemental weights for the NIST Certified Marine Sediment 2702 Reference Material (SRM) were compared to values in the Certificate of Analysis (NIST, 2019) and percent recoveries calculated. These are reported in the relevant results section below. Percent recoveries for relevant elements from the NIST Trace Elements in Water CRM, measured between 85 – 115% of the reported value in the Certificate of Analysis (NIST, 2015).

3.4.8 X-RAY POWDER DIFFRACTION (XRD) OF CORAL SANDS

Duplicate portions of dried untreated sands weighing about 1-2 g each were ground using a mortar and pestle until the texture of the material felt smooth:

- Untreated fine oven-dried store-bought sand
- Untreated oven-dried Kiribati sand
- Untreated coarse store-bought coral sand
- Untreated Vanuatu sand

Sands used in select AELD experiments were removed from columns or prototypes and dried for at least a day at 60-65 ℃. Duplicate subsamples were collected and prepared as above, following mixing and breaking-up of dried clumps.

- Fine store-bought sand – 0.05 M; sand-fluid ratio of 5:1 – (Experiment K)
- Kiribati sand – 0.05 M and 0.025 M; sand-fluid ratio of 5:1 – (Experiment K)
- Vanuatu sand – 0.05 M; sand-fluid ratio of 5:1 – (Experiment K)
- Coarse store-bought sand – 0.025 M; sand-fluid ratio of 5:1 – (Experiment L2)

All ground sands and white powders were provided to Dr Matthew Polson for processing and analysis as described here (personal communication, April 28, 2021). Samples were mounted as a 0.5 mm layer on glass slides. Scans were made in 1D mode using a D-Tex detector from 5 – 65 ° at 5 °/min using a Cu Kβ filter and 5 ° Soller slits. Data were processed on the Rigaku PDXL2 software, subtracting a polynomial background and calculating the relative amounts of phases using the RIR method. The library used for compound search was ICDD (PDF4+ 2021).

Resulting data was provided on .csv files. The XRD spectrum was created by subtracting the background from the relative intensity (y observed) which was plotted as a function of the diffraction angle (2θ) in Excel. Literature spectra for calcite and aragonite was obtained from the RRUFF project database (RRUFF, n.d.) and used for comparison.

3.5 XRD OF WHITE POWDERS AND PRECIPITATES COLLECTED AFTER AELD

A selection of dried white substances, which developed on top of the sand columns or in the sample extracts overnight, were also analysed with XRD. Excess fluid was decanted from the extracts or a Whatman filter paper ‘5’ was used to capture the precipitate which was then air-dried. Powders collected from sand columns themselves were scraped off the top of the sand. Alternatively, remnants were collected from the glass beakers used to oven-dry the treated sands. The selection of white substances, provided to Dr Matthew Polson for analysis as described in Section 3.4.8, included:

- Powder from used fine store-bought sand column – 0.05 M acid (Experiment K).
- Powder from Vanuatu sand columns with 0.025 and 0.05 M acid (Experiment K).
- Duplicate precipitate samples from isotherm extracts using 200 mg F^-/L and 0.025 M citric acid (Experiment D).

- Precipitate from extracts of coarse sand prototypes I, II, III on day 1 use 2; day 2 use 1, and day 2 use 2 (Experiment L2).

The spectrum for fluorite (CaF_2) was obtained from the RRUFF project database (RRUFF, n.d.) and used for comparison.

3.6 OVERALL FISE EXPERIMENTAL DESIGN

The acid-enhanced lime defluoridation experiments conducted here using coral sand were broadly based and influenced by the original works of Nath and Dutta (2010a, 2010b, 2012), Gogoi et al. (2015), Gogoi and Dutta (2015), Camlek (2017) and research completed at ESR through Pioneer funding (M. Ashworth, personal communication, 2021).

The end objective was to devise a system which could provide 8 L of treated water daily (2 L for four people) from an initial 10 mg/L of fluoride down to below the drinking water limit of 1.5 mg/L, using the least amount of acid and sand, for a maximal number of days.

3.7 QUALITY CONTROL – FISE

The quality controls were guided by those recommended in the Standard Methods for the Examination of Water and Wastewater (Baird & Bridgewater, 2017) and the ASTM D1179 – Standard test methods for fluoride ion in water (ASTM, 2016).

A minimum of three calibrations standards and one blank is recommended for linear curves (Baird & Bridgewater, 2017). The calibration should be verified by using a different source of fluoride at or near the mid-point of the curve, and must be within 10 % of its value (Baird & Bridgewater, 2017, Section 4020, p. 2) or 15 % as recommended by ASTM International (2016).

The recommended minimum quality control checks include a reagent or method blank, a laboratory fortified blank (or a laboratory control sample), a matrix spike (or laboratory fortified matrix) as well as a duplicate matrix spike (Baird & Bridgewater, 2017). The duplicate matrix spike was replaced here with a comparative standard and a duplicate sample.

3.7.1 STANDARD CALIBRATION CURVE

Calibration standards were prepared monthly (or more frequently) and stored in plasticware which had been cleaned through an acid bath process involving one week at 10 % nitric acid, one week at 1 % nitric acid, triple rinsed in ultra-pure water and dried prior to use (R. Stainthorpe, personal communication, February 22, 2021).

Standard calibration curves were prepared daily using the following known concentrations, which were subsequently diluted 1:1 with TISAB as done will all samples, controls, and blanks: 0.25, 0.50, 2.0, 5.0, 10, and 15 mg/L. An additional standard of 25 mg/L was included when necessary, particularly when spiking was incorporated into the quality control measures. The calibration standards used for the isotherm experiments were: 0.5, 2, 5, 10, 25, 75, 125 and 250 mg/L.

Potential (in MeV) instrument readout and calculated fluoride values for the calibration standards were entered into Microsoft Excel to calculate the R value and slope of the linear regression of the calibration data. Curves with an R value of less than 0.999 or where the slope of the calibration data fell outside of the manufacturer's required range of -54 to -59 mV/decade, were discarded and the calibration repeated.

3.7.2 CALIBRATION CURVE VERIFICATION

Control samples with a known concentration of 2.5 mg/L, 4 mg/L, 5 mg/L, 20 mg/L and 50 mg/L were prepared as described above. The calibration curve was verified by measuring an unfiltered laboratory control sample, mixed 1:1 with TISAB. All measured calibration curve standards were within ± 10 % of their calculated values as recommended by Baird and Bridgewater (2017) and ASTM (2016).

3.7.3 REAGENT AND METHOD BLANKS

Ultrapure water mixed 1:1 with TISAB was used as the reagent blank. As recommended by Baird and Bridgewater (2017 section 4020B, p.2), the reagent blank should have no more than half the amount of analyte in the lowest calibration point. A value of 0.125 mg/L (or 0.25mg/L, when the 0.25 mg/L calibration standard was omitted from the curve) was used as a limit of quantification (LOQ) in this research. Other methods recommend a limit of <0.1 mg fluoride / L (EPA, 1996). To speed up the analytical process, once samples or blanks fell below the LOQ, fluoride analyse was at times halted early given concentrations below 0.5 mg/L can take 5 minutes or more to equilibrate (ASTM, 2016) and have a % bias up to 150 % if using linear calibration (EPA, 1996).

Method blanks varied depending on the experiment and are detailed in the appropriate sections. In general, initial solutions were added to empty columns or prototypes to ascertain if the method affected fluoride measurements.

3.7.4 LABORATORY CONTROL SAMPLE (LCS) CHECKS

At least one laboratory control sample of 2.5 mg/L, 4 mg/L, 5 mg/L or 20 mg/L was analysed with each batch of samples. This control was filtered and mixed 1:1 with TISAB as with other unknown samples. These were prepared from a second source of sodium fluoride as recommended by Baird and Bridgewater (2017).

For experiments where diluted FISE samples were prepared using a ratio of 1:1:2 of extract-to-water-to-TISAB, the laboratory control sample was diluted in the same manner and analysed (refer Section 3.8.5). Control samples were within the recommended error of ± 10 % and ± 15 % by Baird and Bridgewater (2017) and ASTM (2016), respectively, except where indicated. The % error is calculated according to equation (9):

$$\%\ \mathrm{Error} = 100\ \mathrm{x}\ \frac{([\mathrm{k}]-[\mathrm{m}])}{[\mathrm{k}]} \tag{9}$$

Where,

[k] = known/calculated fluoride concentration of the control sample,

[m] = measured fluoride concentration of the control sample.

3.7.5 DUPLICATES

Wherever possible and sample size permitting, at least one unknown sample extract per batch (20-25 samples) was run in duplicate. Generally, when the initial fluoride solution was acidified, one duplicate sample per triplicate of each treatment was analysed.

The % difference (%D) between the original and duplicate sample was calculated according to equation (10):

$$\%D = 100\ x\ \frac{(V1 - V2)}{(V1 + V2)/2} \tag{10}$$

Where,

V1 = measured fluoride of original sample,

V2 = measured fluoride of duplicate sample.

Duplicate analysis was deemed acceptable if the % difference was below 5 % for fluoride measurements above 0.5 mg/L. For concentrations below 0.5 mg/L, a difference of 15 % was tolerated given the larger % bias in these low values (EPA, 1996). Any values exceeding these limits are reported in appropriate sections.

3.7.6 MATRIX SPIKES AND COMPARATIVE STANDARDS

A matrix spike was performed on at least one sample per FISE batch, but usually on one of three replicates per treatment, as each treatment may affect the resulting matrix differently. 4 mL of a previously analysed FISE sample was transferred to a new vial and 0.08 mL of spike solution added, mixed and allowed to decomplex at room temperature for a minimum of 30 minutes prior to measurement. A comparative standard was prepared alongside, by spiking a reagent blank. pH of the spiked sample/blank was checked and adjusted, if necessary. Refer Appendix B for spike solution concentration used according to measured fluoride concentration of samples. If less than 4 mL of sample was available, the spike was created using the same sample-to-spike ratio of 50:1 to adhere to the value of <2 % total volume as recommended (ASTM, 2016). Larger ratios can alter matrix composition and introduce error in the method and fluoride recoveries.

The percent recovery (P) of the spiked samples was calculated according to equation (11) (ASTM, 2016):

$$\mathrm{P} = 100\ \mathrm{x}\ \frac{[A(V_S+V)-BV_S]}{2CV} \tag{11}$$

Where,

A = analyte concentration (mg/L) in spiked sample,
B = analyte concentration (mg/L) in unspiked sample,
C = concentration (mg/L) of analyte in spiking solution,
Vs = volume (mL) of sample used,
V = volume (mL) of spiking solution added, and
2 = factor, given spike solution itself was not diluted 1:1 with TISAB.

Given the spike-to-sample ratio used in this study, percent recoveries should fall somewhere between 55 to 76 % and 124 to 145 % (ASTM, 1996). The 95 % tolerance interval for percent recoveries of much smaller spike-to-sample ratios is between 80 to 120 % (ASTM, 1996). Also, the EPA method, which uses spike volumes less than one-thousandth the sample volume, must have recoveries between 75 to 125 % to satisfy quality requirements (EPA, 1996). The narrower range of 80 to 120 % was used herein for quality control and values outside this range are highlighted in the appropriate results section. If the percent recovery is not within control limits, Baird and Bridgewater (2017) recommend using another analytical method, using the method of standard addition, or flagging the data during reporting.

A comparative standard was analysed each day where spiking of unknown samples occurred and was prepared by spiking a reagent blank sample (i.e. unfiltered ultrapure water mixed 1:1 with TISAB) as done with unknown samples. The % recovery of the comparative standard was calculated from equation (11), using a value of 0 for the analyte concentration in unspiked sample (B). The standardised percent recovery of spiked samples was calculated as follows:

$$P' = 100\ x\ \frac{Psp}{Pstn} \tag{12}$$

Where,

Pstn = Percent recovery of the comparative standard,
Psp = Percent recovery of the spiked sample,
P’ = standardised percent recovery of spiked sample.

3.8 EXPERIMENTAL SET-UP, SAMPLE COLLECTION AND PROCESSING

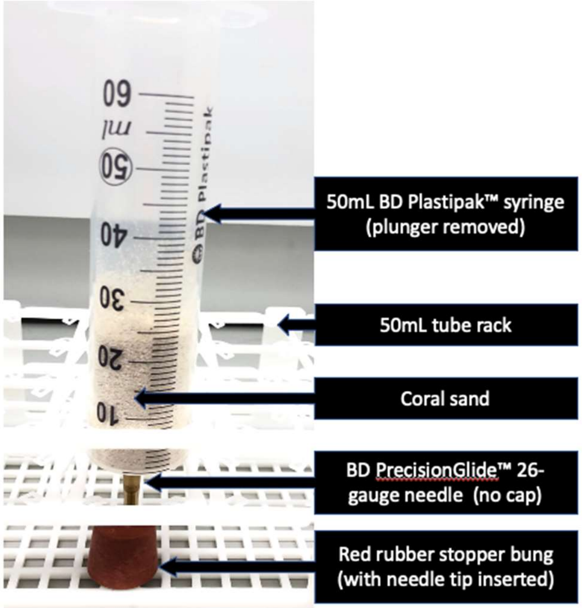
This methodology was established after some trial and error iterations as detailed in the Methodology Development section in Appendix D. A few single-column preliminary trials were also completed throughout the process of this study, to help inform the selection of variables for in-depth, triplicate experiments. Any improvements or learnings were incorporated into the methodology of further experiments.

3.8.1 COLUMN SET-UP

Columns were created from a 50 mL BD Plastipak™ syringe with the plunger removed. The total volume indicated on the 50 mL syringes is actually 60 mL. These columns have an outer diameter of 29.4 mm and a length of 133 mm (Thermo FisherThermo Fisher Scientific, 2020). The syringe body was combined with a BD PrecisionGlide™ 26-gauge needle and the needle tip was inserted into a rubber bung to impede fluid loss – Refer Figure 3.2.

Figure 3.2

Column Experimental Set-Up



Note. Columns made of 50 mL syringe with plunger removed.

‘Packed’ sand columns were packed by spoon-sized increments (up to about 10 mL) and tapped several times on the syringe walls (5-10 times) with a metal implement to enable compaction and settling of the particles. For the majority of experiments however, columns were simply filled because the presence of acid in the initial solution generated carbon dioxide gas which disrupted column packing.

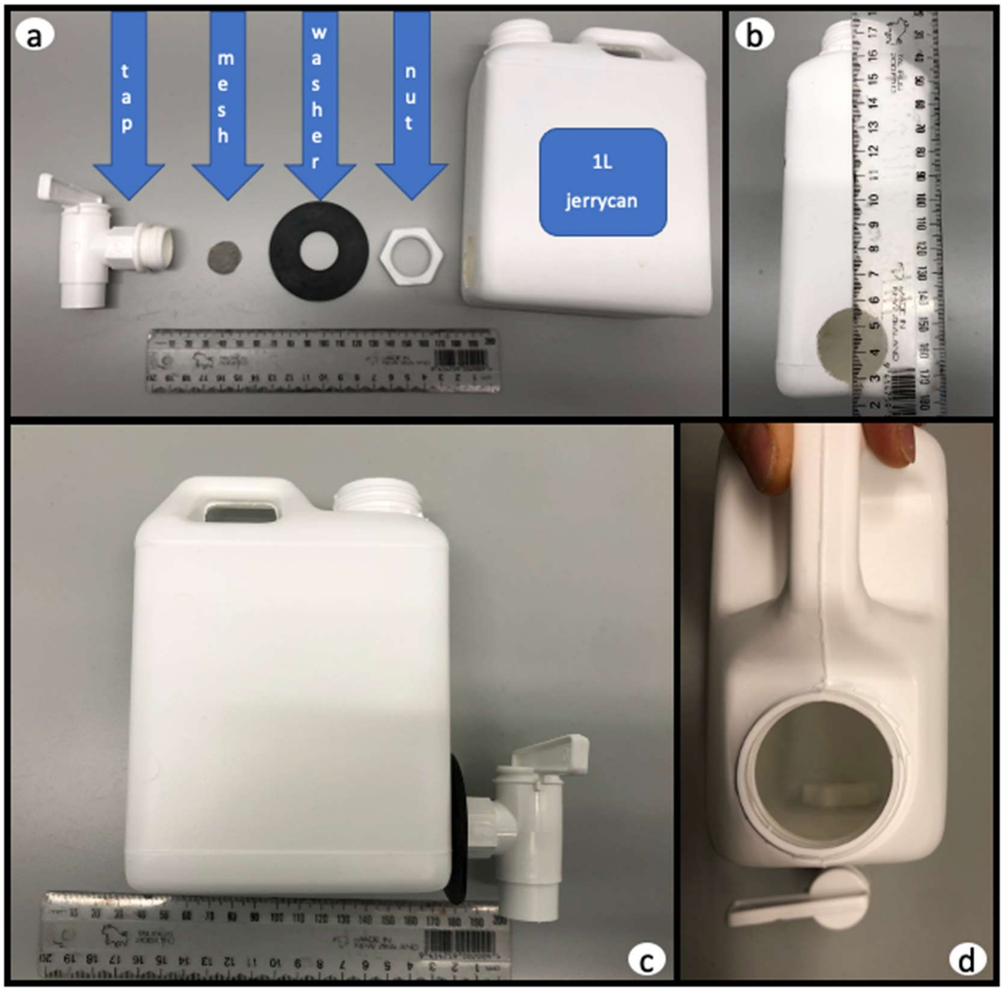
3.8.2 PROTOTYPE SET-UP: 1 L JERRYCANS WITH 1 KG CORAL SAND

A 1 L small-scale pilot treatment device was made to approximate a miniature (1:20) version of a 20 L drum, a likely suitable container for rural, low-cost household water retrieval and storage. Refer Figure 3.3 for detailed photos of assembly of the pilot treatment system. One litre high density polyethylene (HDPE) jerrycans, with outer measurements of 123 mm deep x 67 mm wide x 168 mm high, were fitted with ¾ inch BSP tap assembly with back nut, purchased from Stowers Containment Solutions (parts 2107375, 3134825, & 3079467, respectively). A hole was made approximately 0.7 to 1.0 cm from the bottom of the jerrycan and a ‘Fix-a-loo’ seating washer (www.fixatap.com.au - purchased from Mitre 10) was fitted onto the exterior of the prototype to prevent leaks. Prior to fitting the tap assembly, metal mesh of approximately 150-200 µm in size (obtained from N. Oliver and measured by C. Grimshaw using a calibrated microscope at UC) was hand cut into a circle slightly bigger than the tap hole to ensure a snug fit. This mesh was inserted into the inner portion of the tap and successfully prevented the coral sand from escaping the jerrycan when draining the treated water. The 1 L prototypes were made and assembled by Nick Oliver at UC.

The newly assembled prototypes were rinsed twice with distilled H_2O, filled with ultrapure water (18.2 MΩ-cm) for a minimum of 16 hours, emptied and air dried. Four prototypes were filled with 1000.0 ± 0.3 g of store-bought fine coral sand which had been oven dried (60-65 °C for at least 4 days). Triplicate prototypes were used for acidified 10 mg F^-/L solution and a single prototype for non-acidified fluoride solution. One fully-assembled prototype was left empty (no sand) to be used as a method blank and blank correcting as appropriate.

Figure 3.3

Prototype Assembly of 1 Litre Jerrycan with 1 kg Sand



Note. a) parts disassembled, b) location and size of hand-made hole for tap, c) jerrycan assembled (side view), and d) jerrycan assembled with no sand (top view).

3.8.3 SAMPLE COLLECTION FROM COLUMNS AND PROTOTYPES

Columns: Extracts were collected by twisting off the needle/rubber bung assembly and collecting the fluid directly from the tip of the syringe body. Due to the column size, and thus low extractable volumes for many experiments, the rubber plunger needed to be reinserted into the top of the syringe to apply pressure, sometimes repeatedly, to expel the volume required for sample analysis. For very low sample volumes, some extracts were expelled directly into the 10 mL syringe body used for filtration. For the experiments using 2:1 and 5:1 sand-to-fluid ratios (refer Experiment J & K), the extract was allowed to 'drain' into 25 mL vials by gravity only, as the extractable volume was sufficient for sample processing and analysis. Note that a small amount of sand was often expelled alongside fluid removal from syringes but not when using prototypes.

Prototypes: The tap was opened and the prototype tilted forward with its tap into a 250 mL jar at an angle of roughly 30 degrees, in order to extract the maximum volume per load.

3.8.4 SAMPLE PROCESSING, TEMPERATURE, PH, CONDUCTIVITY MEASUREMENTS

Sample extracts were mixed and a portion of at least 3 mL up to approximately 13 mL was decanted into a 10 mL syringe. Samples were filtered with a 0.2 µm Ahlstrom Reliaprep™ filter into a plastic vial unless stated otherwise. Chirana rubber-free syringes were used with Pacific sand extracts, as well as with the 1 L prototype extracts to reduce potential contamination from the rubber plunger. The pH, temperature and conductivity (select experiments only) were measured from any remaining extract after FISE and/or ICP-MS sampling was completed to avoid unnecessary contamination from electrode carry-over.

3.8.5 FLUORIDE ANALYSIS – FISE

For each FISE sample, 2.5 mL of filtered extract was mixed with an equal volume of TISAB (lower and equal volumes used if limited extract available). The FISE samples were left to decomplex a minimum of 30 minutes to overnight in plastic 'LabServ' 25 mL containers at room temperature, unless otherwise stated. When FISE sample volumes were too low for electrode and magnetic flea immersion, a 5 mL vial was used.

A plastic-coated magnetic flea was added to the sample vial and the vial placed on a magnetic stirring plate with the FISE immersed. Stirring was done at a relatively slow rate to avoid the creation of vortex or air bubbles. Samples were stirred for about 2 to 3 minutes, allowing the electrode to equilibrate and the potential measurement recorded. Some low concentrated samples (i.e. 0.5 mg/L or below) or samples with heavy matrix interference required more time to reach equilibrium and were left up to approximately 5 minutes. Blanks and very low concentrated samples equilibrated faster when the electrode was conditioned, by immersing it in water or low concentrated standards for a few minutes before sample analysis.

pH adjustment: Samples which were not within the adequate pH range of 5 to 5.5 following TISAB addition were adjusted with 10 M NaOH (or rarely, with 5 M HCl). This required 1 to 4 small drops from a 100 µL pipette tip which equated to an average of 0.0105 ± 0.0004 g per drop. Assuming 1 g equates to 1 mL, 5 drops would alter the typical FISE sample of 5 mL by about 1 %.

Dilute FISE samples – preparation of extracts with potentially significant matrix interference (P' < 80 %): For many acidified extracts, particularly during experiments using a high 5:1 sand-to-fluid ratio, an overwhelming matrix effect was noted. In an attempt to improve analytical results, a 'dilute' FISE sample was also prepared and analysed. These were prepared by combining 1.25 mL of extract, with 1.25 mL of ultrapure water, and 2.5 mL of TISAB (or lower volumes in the same ratio, if extract was limited). Measured fluoride concentrations were doubled to account for the dilution. A LCS was analysed in the same fashion and results were no more than 5.02 % different from the calculated/known value.

3.8.6 ICP-MS ANALYSIS OF TREATED EXTRACTS

When ICP-MS samples were collected, an aliquot of the filtered extract (up to 5 mL) was stored in a Sarstedt tube, acidified with concentrated HNO_3 (~5 µL per mL) and refrigerated, unless otherwise stated. Select acidified extracts were diluted in 2% HNO_3 in ratios of 1:21, 1:29, 1:51, or 1:101 based on amount of extract available. The 1:21 dilution was often used to create very dilute samples of 1:2121 (for macro element analysis, i.e. Ca, K, Mg, Na), by diluting 0.1 mL into 10 mL of 2% HNO_3 acid.

Samples were delivered to Rob Stainthorpe and analysed for a combination of macro (Ca^{44}, K^{39}, Mg^{24}, Na^{23}) and trace elements (Al^{27}, $As^{75\ \&\ 75\text{-}91}$, Cd^{111}, Co^{59}, Cr^{52}, Cu^{63}, $Fe^{56/57\ \&\ 56\text{-}72}$, Mn^{55}, Ni^{60}, $P^{31\ \&\ 31\text{-}47}$, Pb^{208}, Zn^{66}, Zr^{90}, B^{11}, Ge^{72}, Mo^{95}, Nb^{93}, Re^{185}, $S^{32\text{-}48}$, Si^{28}, Ta^{181}, $Ti^{48\text{-}64}$, W^{182}, Zr^{90}).

NIST Certified Reference Material (CRM) – Trace Elements in Water was included as standard in ICP-MS runs and percent recoveries for relevant elements calculated from data in the Certificate of Analysis (NIST, 2015). Recoveries for elements reported were within acceptable range (85 – 115% of published value).

3.8.7 DATA ANALYSIS

Conductivity, pH, and temperature values were entered into Microsoft Excel to calculate the average and 2 x standard deviation (2SD) of duplicate or triplicate measurements.

Measured potential (in MeV) of calibration standards for the FISE were entered into Excel and the slope, intercept and R value calculated to ensure the calibration was of adequate quality (refer Section 3.7.1). The potential (in MeV) of samples and controls were converted to fluoride concentration in mg/L by reorganising equation (4) above into equation (13):

$$[\mathrm{F}^-] = 0.18998 * 10^{\frac{(E-E_0)}{S}} \tag{13}$$

Where,

$[\mathrm{F}^-]$ is the fluoride concentration in mg/L,

E_0 is the reference potential – the intercept of the linear calibration curve,

E is the measured electrode potential (in MeV),

S is the electrode slope,

0.18998 is a conversion factor for M to mg/L of fluoride.

Measured fluoride concentrations for controls (LCS; CCV), blanks, duplicates, spikes and comparative standards were compared against the calculated values and/or the quality requirements detailed in Section 3.7. Average and 2SD of the measured fluoride concentrations of samples were calculated with Excel. (Where dilute FISE samples were used, the fluoride concentration was doubled accordingly.)

The fluoride removal rate was calculated from equation (14) and was based on the calculated/prepared concentration of fluoride (as opposed to the measured fluoride concentration of the initial solution):

$$\%\, fluoride\ removal = 100 * \frac{(C_o - C_e)}{C_o} \tag{14}$$

Where,

C_o = concentration of fluoride in the initial solution (prior to treatment),

C_e = concentration of fluoride in the extracted solution (after treatment).

ICP-MS data were obtained in Excel format and corrected for dilution. The limit of quantification (LOQ) was determined from the lowest calibration standard within 15 % error from its intended value. Values below the LOQ were reported as '<LOQ'. The average and 2SD was calculated for triplicate or duplicate samples.

Electrical conductivity / TDS:

Electrical conductivity readings were converted to estimated total dissolved solids (TDS) by using the common conversion factor for high salinity samples of 0.64 (HACH, n.d., p. 9), according to equation (15) (Taylor et al., 2018).

$$TDS = CF * EC \tag{15}$$

Where,

EC = Electrical conductivity readings (µS/cm),

TDS = Total dissolved solids in mg/L,

CF = conversion factor (0.64).

Water Hardness:

Total hardness (expressed in mg/L of $CaCO_3$) was calculated from equation (16) (Boyd, 2000):

$$Total\ hardness = 2.5 *[Ca^{2+}] + 4.12 * [Mg^{2+}] \tag{16}$$

Where,

$[Mg^{2+}]$ = concentration of Mg ion in solution,

$[Ca^{2+}]$ = concentration of Ca ion in solution.

3.9 EXPERIMENTAL TRIALS WITH COLUMNS

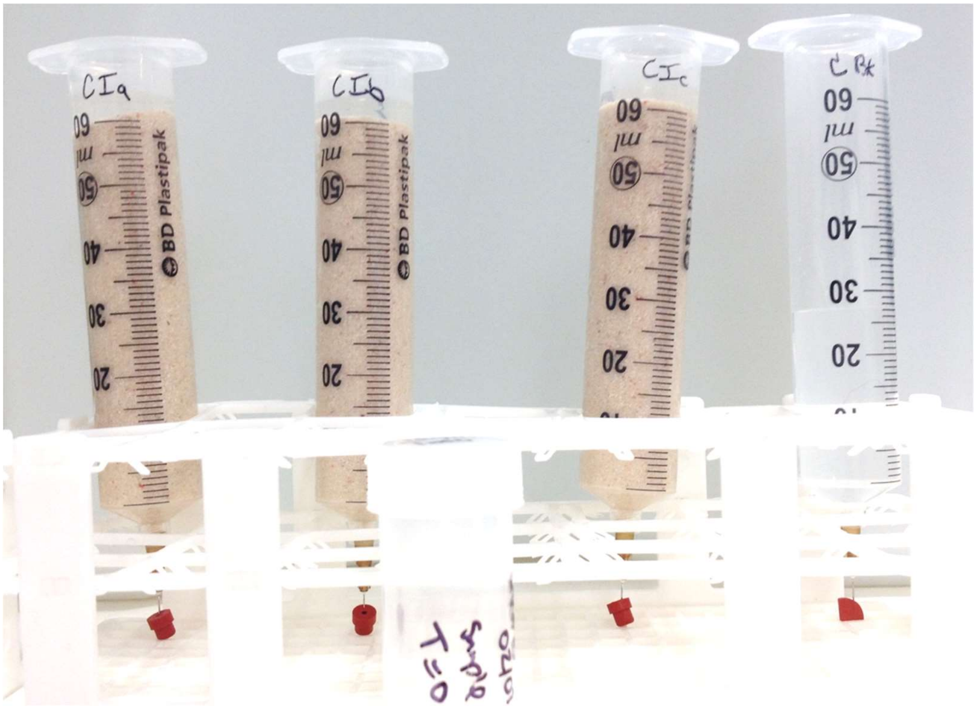
3.9.1 EXPERIMENT C – NO ACID; 10 MG/L FLUORIDE; COLUMN REUSE

Initial solution of 10.0 ± 0.1 mg/L fluoride was made from a 1 in 2 dilution of fluoride stock solution of 20 mg/L or a 1 in 20 dilution of 200 mg/L with ultrapure water. A spike solution of 51.0 mg F^-/L was made using the same source of NaF as the calibration standards, by serial 1 in 2 dilutions of the stock 200 mg/L solution. A method blank was created by placing 30 mL of initial solution into an empty column. A sample was collected after 24 hours through the syringe tip and filtered with a Reliaprep™ filter. A second sample was also collected from the top opening of the column but not filtered.

95.0 ± 0.3 g of sand from tub 'A' was packed into triplicate columns, equating to a volume of approximately 61-62 mL. 30 mL of initial solution was added to the columns and approximately 3-4 mL of fluid was noted above the sand level (refer Figure 3.4). This represented a sand (g) to fluid (mL) ratio of approximately 3.17 to 1.

Figure 3.4

Column Set-up of Experiment C.



Note. Experiment C set-up with 30 mL of initial solution, with 2-3 mL of fluid remaining above the sand line (difficult to see).

Small extracts (~3-4 mL) were expelled from each column after four hours (Time = 250 mins) and eight hours of contact. The columns were force emptied as best as possible and refilled with 10.0 mL of initial solution, a sand-to fluid ratio of 9.5 to 1. The ~2-3 mL of solution which was initially present above the sand level eventually integrated into the sand. Sample extracts were collected 4 hours (T = R4) and 14 hours (850 minutes, T = R14) after reuse. Columns were force emptied and refilled a third time, with 15 mL of initial solution giving a sand-to-fluid ratio of 5.66 to 1. About ~10 mL of fluid was noted above the sand line. Final extracts were collected after 4 and 8 hours of contact (2R4 and 2R8 respectively). With high sand-to-fluid ratios, obtaining two samples per loading (at 4 and 8 hours) was difficult. Using two separate sets of columns for studying the effect of different contact times would be easier.

Sample preparation:

Extracts were mixed, filtered and the pH and temperature measured. 2.8 to 3.0 mL was mixed 1:1 with TISAB and decomplexed overnight (samples T = 4, T = 8, T = R4, T = 0) or for a week (samples T = R14, T = 2R4 and T = 2R8) prior to fluoride analysis. An unfiltered sample of initial solution was collected and analysed (5 mL stored in a 25 mL plastic vial). Spikes were created by adding 0.5 mL of spike solution to 5 mL samples which had been analysed using the FISE. Insufficient volumes were available for duplicate sample analysis. Calibration curves were created from 0.5, 2, 5, 10 and 15 mg/L and the experiment was conducted at an ambient temperature of 20 ± 2 °C.

3.9.2 EXPERIMENT D – ADSORPTION ISOTHERM

A single preliminary isotherm trial with no acid was initially conducted and is detailed in Appendix F. The adsorption isotherm was further studied in triplicate using oven-dried fine store-bought coral sand with an adsorbent dose of 1 g/6 mL, with and without 0.025 M citric acid in 15 mL volume. A wide range of initial fluoride concentrations was used (0, 1, 5, 10, 50, 100, and 200 mg/L), including highly concentrated solutions relative to the drinking water standard of 1.5 mg/L, to ascertain how much fluoride could be adsorbed before the sand reached maximum capacity (and needs regeneration or replacement).

Initial solutions were made as follows: 200 mg/L* and 400 mg/L* stock fluoride solutions were prepared by diluting 0.1103 g and 0.0889 g of >99 % pure NaF in 250 mL and 100 mL volumetric flasks, respectively. Final concentrations were calculated gravimetrically. These stock solutions were further diluted as detailed in Table 3.5.

Table 3.5

Preparation of Initial Fluoride Solutions Used in the Isotherm Experiment

Fluoride Solution Concentration (g/L)	Volume of Solution Used (mL)	Concentration of Solution (g/L)	Final Volume (mL)
0.1	50	0.2	100
0.05	25	0.2	100
0.01 *	5	0.2	100
0.005	2.5	0.2	100
0.001	1	0.1	100
0.02 *	40	0.05	100
0.002 *	40	0.005	100

Note. Details of volumes and concentrations of fluoride solutions used to prepare initial fluoride solutions for the isotherm experiment.

* These solutions were also mixed 1:1 with 0.05 M citric acid to make 0.025 M acid initial isotherm solutions.

The 0.001; 0.005; 0.010; 0.050; 0.100; and 0.200 g/L fluoride solutions were used directly in the 0 M (no acid) isotherm experiment. The 0.025 M citric acid solutions containing the same fluoride concentrations were prepared by mixing a 1:1 ratio of 0.05 M citric acid solution and 0.002; 0.010; 0.020; 0.100; 0.200; and 0.400 g/L fluoride solutions*, respectively.

Oven-dried fine store-bought coral sand (2.5 g ± 1 %) and 15 mL of initial fluoride solution, with or without acid, were placed in 50 mL falcon tubes. These were agitated at a moderate speed on a head-over shaker for five hours at room temperature (setting of '8'; 21 ± 2 °C respectively) and the carbon dioxide was released hourly. Duplicate 'no sand' blanks were prepared by adding 5 mg/L LCS into empty falcon tubes. At 5 hours, aliquots were tipped into a 10 mL syringe and extracts analysed for pH, temperature and fluoride as detailed in Section 3.8.4.

For the non-acidified isotherm experiment, spiked samples and comparative standards were prepared as detailed in Section 3.7.6, using a spike-to-sample ratio of 2 % (0.09 mL spiked solution to 4.5 mL of analysed extract). Unfiltered initial solutions were prepared and analysed in single replicate. FISE samples were decomplexed overnight and analysed. Due to quality issues, the 0 mg/L, 1 mg/L and 5 mg/L initial fluoride solutions were not available for analysis and new duplicate samples of the 1 mg/L and 5 mg/L initial solutions were prepared and analysed a few days later. For the 0.025M citric acid isotherm experiment, duplicate samples of unfiltered initial solutions were prepared and all FISE samples were analysed the day after preparation. Spiked samples for the reanalysed 0 M initial solution samples and all 0.025 M samples were created using the same 2 % spike-to-sample ratio (0.08 mL spike solution to 4 mL of analysed extract).

Quality controls used included at least two LCS and/or CCV of 2.5, 5.0, 20 and 50 mg/L; a reagent blank, at least two duplicates and two spiked samples, as well as comparative standards. Two linear calibration curves were used: one for samples below 25 mg/L and one for samples above 10 mg/L. The curves were created from calibration standards of 0.5; 2; 5; 10; 25 mg/L and 10; 25; 75; 125; 250 mg/L respectively, and prepared as detailed Section 3.3.1 – isotherm calibration standards.

The equilibrium concentration (C_e) was measured with the FISE and the adsorption capacity q_e (in mg of fluoride per gram of sand) was calculate according to equation (17) (Jain & Jayaram, 2009):

$$q_e = \frac{(C_o - C_e)V}{W} \tag{17}$$

Where,

C_o = initial fluoride concentration (mg/L),
C_e = equilibrium fluoride concentration in solution (mg/L),
W = mass of the adsorbent/sand (g), and
V = volume (L) of the solution added (15 mL).

The q_e was determined by using the gravimetrically calculated initial fluoride concentration (C_o), the precise weight of sand used and a volume of 15.00 mL of solution.

Final fluoride measurements (C_e) as well as pH for both acidified and non-acidified samples were entered into Excel. The average and 2SD of triplicates was calculated for the final fluoride concentration (C_e) as well as the absorbent capacity (q_e). The adsorbent capacity was plotted in Excel against the final fluoride concentrations and trendlines fit to the data.

Experimental isotherm data can often be described by the Freundlich and Langmuir models that account for a soluble moiety binding to a limited number of sites on the substrate. The Freundlich model in logarithmic form is expressed according to equation (18) (Choong et al., 2020):

$$\log q_e = \log K_f + \frac{1}{n} \log C_e \tag{18}$$

Where,

q_e = adsorption capacity of adsorbent (mg/g),
C_e = equilibrium fluoride concentration in solution (mg/L),
K_f = Freundlich constant related to adsorption capacity (mg/g), calculated from the intercept,
n = Freundlich constant related to adsorption intensity, calculated from the slope.

The Langmuir isotherm is expressed in linear form as noted in equation (19) (Gogoi & Dutta, 2016):

$$\frac{C_e}{q_e} = \frac{C_e}{Q_0} + \frac{1}{bQ_0} \tag{19}$$

Where,

Q_0 = is the Langmuir adsorption capacity (mg/g),
b = is the Langmuir isotherm constant (L/mg) related to the affinity of the binding sites,
C_e = equilibrium fluoride concentration in solution (mg/L), and

Q_0 and b can be calculated from the plots of C_e/q_e vs.C_e.

3.9.3 EXPERIMENT E – MATRIX RECOVERY (WITH COLUMN REUSE)

This experiment was run to determine if any fluoride was present in the coral sand and whether it can be extracted with contact with ultrapure water.

Three syringe-columns packed with 95 g of coral sand to a level of about 60 mL were topped up with 30 mL of ultrapure water. Approximately 3 to 5 mL of fluid remained above the sand layer. _All fluid was expelled after 4 hours, mixed and pH obtained from a small aliquot. Two FISE samples were prepared from each replicate extract and decomplexed at least 30 minutes: a spiked sample (according to method in Appendix D) and a standard FISE sample made of 3 mL of filtered extract with 3 mL of TISAB. Insufficient volume remained for duplicate samples thus only spike samples were prepared.

Blanks/initial solution (in duplicate): Ultrapure water was collected, the pH measured and two FISE samples (spiked and unspiked) were prepared as above.

Decomplexed samples were analysed between 30 minutes to 3 hours following preparation. The samples were also rerun one and two days later to assess the difference in measured fluoride concentrations with extended decomplexation time (results in Appendix D).

Reuse of matrix recovery columns: To determine if additional fluoride can still be extracted from used sand with ultrapure water, the columns were reused. The three emptied columns were refilled the following day with 10 mL of ultrapure water. Extracts were expelled after 4 hours. One FISE sample (per column) was prepared along with two blanks (i.e. initial solution), one duplicate and one spiked sample. This was repeated on a third consecutive day, with one blank.

3.9.4 EXPERIMENT F – AELD: 2:1 SAND-FLUID RATIO; 0.05 & 0.1 M ACID; 4 & 8 HOUR CONTACT TIME

20 mg/L stock fluoride solution and 0.2 M or 0.1 M stock citric acid solution were mixed together in a 1:1 ratio, providing final concentrations of 10 mg F^-/L and 0.1 M or 0.05 M citric acid, respectively. 28.5 mL of these solutions were loaded into six columns filled with 95 g of oven-dried coral sand. Due to significant carbon dioxide generation in the 0.1 M columns, only 28.5 mL could be loaded not 30 mL, as done in the matrix recovery experiments above. This represents a sand-to-water ratio of about 3.33:1.

Three columns were allowed to react for 4 hours and three columns for 8 hours. All fluid was then extracted and the extracts processed as per Section 3.8.4 and 3.8.5 with Terumo syringes. Duplicate and matrix spike (as described in Appendix D) samples were prepared and analysed for select triplicate sets.

3.9.5 EXPERIMENT G & I – PRELIMINARY AELD TRIAL: VARIED ACID CONCENTRATION & SAND-FLUID RATIOS

In an attempt to counter the matrix effect noted prior as well as economise chemicals and materials used, a preliminary single replicate trial using lowered citric acid concentration and/or sand-to-fluid ratios was conducted.

Two columns with either 50 g or 40 g of oven-dried coral sand were filled with 20 mL of one of the following solutions, creating a 2:1 or 2.5:1 sand-to-fluid ratio, respectively.

10 mg F$^-$/L & 0.05 M: 1:1 ratio of 20 mg/L F$^-$ solution and 0.1 M citric acid.
10 mg F$^-$/L & 0.025 M: 1:1 ratio of 20 mg/L F$^-$ solution and 0.05 M citric acid.

Three columns with 95 g of coral sand were filled with 28.5 mL of the following solutions, providing a sand-to-fluid ratio of 3.33:1.

0.025 M & 10 mg F$^-$/L: 20 mL of 20 mg F$^-$/L; 5 mL of 0.2 M citric acid; 15 mL ultrapure water.
0.025 M citric acid only: 5 mL of 0.2 M citric acid; 35 mL of ultrapure water.
10 mg F$^-$/L only: 10 mg/L calibration standard solution.

The entire volume was expelled after 4 hours and processed as per Section 3.8.4. Samples were decomplex for a minimum of 30 minutes (3.33:1 ratio) to overnight (2 and 2.5:1 ratio samples). Matrix spikes for the 3.33:1 ratio samples were prepared with 100 mg/L spike solution as described in the Method Development (Appendix D). Duplicates were prepared for the 2:1 and 2.5:1 samples (no duplicate for 0.025 M, 2:1 ratio). Matrix spikes for these samples were prepared as described in Section 3.7.6. Initial solutions were also analysed (filtered for 3.33:1 and unfiltered for 2.5:1 and 2:1 ratios) to confirm calculated concentrations match measured fluoride concentrations and that filtration does not alter the fluoride concentration.

3.9.6 EXPERIMENT H – PRELIMINARY TRIAL: SAFETY OF AELD EXTRACTS USING 0.025, 0.05 & 0.1 M ACID

Four columns were filled with 95 g of coral sand. Solutions were made and 28.5 mL was added to each column, representing a sand-to-fluid ratio of 3.33:1. The entire volume of solution was expelled from the columns after 4 hours, mixed, and visual observations made. Filtered samples (7 mL filtered with Reliaprep™ 0.2 µm filter and Chirana rubber-free syringe) were delivered to Robert Stainthorpe, acidified and diluted 1:21 in HNO$_3$ for ICP-MS analysis (personal communication, August 18, 2020). Three solutions contained 10 mg F$^-$/L and:

0.1 M citric acid: 20 mL stock 20 mg F^-/L solution mixed with 20 mL of 0.2 M citric acid.
0.05 M citric acid: 20 mL stock 20 mg F^-/L solution mixed with 20 mL of 0.1 M citric acid.
0.025 M citric acid: 20 mL stock 20 mg F^-/L solution, 5 mL of 0.2 M citric acid and 15 mL of ultrapure water.
Ultrapure water: no fluoride.

Note: Stock citric acid solutions were stored for extended time in glass Schott bottle.

3.9.7 EXPERIMENT J – AELD: 2:1 SAND-FLUID RATIO; 0.025 M ACID; 4 & 8 HR CONTACT

Using a sand-to-fluid ratio of 2:1 and the outer dimensions of the 60 mL syringes, the volumes and weights of sand and fluid were scaled down to roughly approximates a miniaturised 20 L drum which, when partly filled with sand, could provide enough drinking water for four people, that is 2 L / person per day (ppd). 20 g of sand and 10 mL of solution (0.025 M citric acid; 10 mg/L fluoride made from equal volumes of stock 20 mg F^-/L and 0.05M citric acid) were added to six columns in the early morning. This represented about 12.5 mL of sand and 16 mL in total, following fluid addition. Triplicate columns were drained (by gravity via the syringe tip) after 4 hours and triplicate columns after 8 hours. This set-up approximates a practical water treatment system where water is in direct contact with sand and is extracted via a spout at the bottom of a drum. The volume of this first extract was about 3-4 mL (thus insufficient for duplicate analysis).

Extracts were mixed, filtered, an FISE sample prepared, and the pH measured. For the next three mornings, columns were refilled (10 mL) and extracts collected and processed as above. Sand levels reached about 12 mL and the total volume with fluid was about 21-22 mL on subsequent days, meaning that most of the fluid added was above the sand level. Volume of extracts from day 2 onwards were about 10 mL (duplicates analysed). Samples of the initial solution were collected daily and analysed.

Visual examination of samples was conducted following extraction to see whether white precipitate formed. Note that clogging occurred in some syringes after day 2 and a 12-gauge needle was inserted into the syringe tip to facilitate the draining process.

3.9.8 EXPERIMENT K – AELD: 5:1 SAND-FLUID RATIO; 0.025 & 0.05 M ACID; THREE TYPES OF SAND

In an attempt to increase the number of times the columns could be used before losing their efficiency, the sand-to-fluid ratio was increased. In addition, an initial 'clean-up' step using a slightly larger volume of fluid was conducted in an attempt to remove contaminants in the sand and hopefully simplify the FISE analysis by decreasing matrix interference.

Initial solutions of 10 mg/L fluoride with 0.05 M or 0.025 M citric acid were made daily, from 1:1 dilutions of stock 20 mg F^-/L solution and 0.1 M or 0.05 M citric acid, respectively.

Triplicate columns were filled with 75 g of sand and 25 mL of initial solution was first loaded into the columns (sand-to-fluid ratio of 3:1) whereas 15 mL was used on subsequent refills (sand-to-fluid ratio of 5:1). Columns were filled and emptied twice daily (morning and midday), 4-hours after each filling. Extracts were mixed, filtered, an FISE sample prepared, and the pH measured as detailed in 3.8.4. These ratios approximate a water treatment system which could be created from a 20 L drum containing 22 kg of sand (about 14 L based on the sand used here), which, when filled with 4 L of fluid, leaves at least 2 L of space for carbon dioxide generation. Such a system could produce a total of 8 L of treated water daily (2 L for four ppd), using two filling/emptying cycles with a 4-hour contact period.

Samples from day 5 onwards were decomplexed and analysed on the same day. For the first few days, diluted FISE samples were prepared to reduce matrix interference. Both samples (dilute and non-dilute) were analysed for fluoride until standardised percent recoveries (P') of non-dilute samples were over 85 % at which point processing of dilute FISE samples ceased. Duplicate and spike samples were prepared for each triplicate set after first use (insufficient volume prior). The initial fluoride solutions were also analysed.

A sample from each of 0.05 M and 0.025 M acid columns were collected for ICP-MS analysis, filtered using Terumo syringes and acidified with concentrated HNO_3 in 5 mL plastic vials. 0.5 mL was transferred and diluted with 10 mL of 2 % HNO_3 into Sarstedt tubes. A control sample was created from adding 15 mL of initial 10 mg F^-/L and 0.05 M citric acid solution to an empty column for an overnight period and processed as above.

This experiment was repeated on sands from Kiribati and Vanuatu. Duplicate ICP-MS samples were collected, filtered using Chirana® syringes, acidified in the Sarstedt tubes and analysed. A control (no sand) column for 0.025 and 0.05 M citric acid was also prepared and extracted after 48 hrs.

3.10 EXPERIMENT L – SCALED-UP 1 L PROTOTYPES WITH 1 KG CORAL SAND

The same sand-fluid ratio used in Experiment K, was scaled-up into larger prototype treatment devices containing 1 kg of coral sand. These approximate a small version of a 20 L drum as described in Section 3.9.8. Details of the assembly of the prototype treatment system are in Figure 3.3.

3.10.1 EXPERIMENT L1 – FINE SAND PROTOTYPES: 0.025 M ACID; 5:1 SAND-FLUID RATIO

Food grade 0.025 M citric acid (triplicate): 333.3 g ± 1 % of initial solution (0.025 M acid and 10 mg F^-/L) was loaded into triplicate sand-filled prototypes on their first use as well as into a blank (no sand) prototype. Prototypes were extracted after four hours, refilled a second time daily, and extracted again four hours later. Subsequent reloads of initial solution weighed 200.0 ± 0.6 g. A non-acidified 10 mg/L fluoride solution was used in a single 'no acid' sand-filled prototype and processed in the same fashion. The experiments were terminated once the measured fluoride concentration exceeded 1.5 mg/L. The blank prototype was processed on day 1 only. Initial solutions were measured for pH, temperature, and conductivity; select samples prepared for FISE analysis (dilute FISE samples) and ICP-MS to ensure initial fluoride concentration is accurate and to act as control samples for ICP-MS analysis.

Extraction of treated fluid and sample preparation: Extracts were mixed, weighed, and a small portion (<20 mL) used for pH, temperature, and conductivity measurements. A ~10-12 mL portion was filtered, a dilute FISE sample prepared and 2-5 mL acidified for ICP-MS analysis.

Analytical Grade 0.025 M citric acid (single replicate): After completion of the above experiment, the blank prototype was rinsed with dH_2O and ultrapure water, dried and reused to repeat the experiment in single replicate, with the same analytical grade citric acid as used in all column/batch experiments. The sand had been oven dried for 16 hrs at 60-65 °C and no ICP-MS samples were collected. A difference was noted in the visual appearance of the citric acids. The store-bought acid was shiny, crystalline-looking and appeared similar to sugar whereas the AR acid had more rounded granules and a mat white appearance.

3.10.2 EXPERIMENT L2 – COARSE SAND PROTOTYPES: 0.025 M ACID; 5:1 SAND-FLUID RATIO

0.025M food grade citric acid (triplicate): Previously used prototypes were emptied, rinsed twice with dH_2O then soaked with ultrapure water for two days (water changed daily) prior to air drying. The cleaned prototypes were used to repeat the above-detailed food grade citric acid experiment, however with coarse coral sand.

XRD sampling: After completion, the coarse sand from one of the prototypes was dried and two portions prepared for XRD analysis. White precipitate formed in most acid-treated extracts the day following removal and a selection of four was collected and submitted for XRD.

3.10.3 EXPERIMENT M – ACTIVATED CHARCOAL CLEAN-UP OF SAND EXTRACTS

A used prototype was emptied, rinsed and soaked for over 24 hours in ultrapure water. 1000.0 g of fine store-bought sand (dried as received) was added and the prototype used as per experiment L1. Initial solutions were made and kept in a glass volumetric flask for no more than 5 hours prior to use. The first extract of day 2 (weighing ~192.8 g) was mixed and used here.

Three aliquots (~10-15 ml, T = 0) of the extract were filtered (Reliaprep™) and prepared for:

- ICP-MS: 5 mL acidified with 25 µL of concentrated HNO_3
- FISE: 1.25 mL extract; 1.25 mL ultrapure water; 2.5 mL of TISAB.

Activated charcoal 4-hour treatment:

A 15.00 mL aliquot of extract was added to triplicate vials containing:

- 10 g/L activated charcoal (0.15 g);
- 30 g/L activated charcoal (0.45 g);
- 0 g/L activated charcoal – empty vial (blank / control).

Control samples were filtered with Whatman paper and allowed to stand for 4 hours. These were taken as ‘time’ controls, to assess if any changes occurred due to the 4-hr incubation period, without charcoal. Vials containing charcoal were agitated 20 times, allowed to stand for 4 hours and the charcoal removed by filtration using Whatman paper. All nine samples were filtered (Reliaprep™ with Chirana syringes) and prepared for FISE and ICP-MS as described for extracts T = 0 above.

4 RESULTS & DISCUSSION – SAND CHARACTERISATION, BATCH & COLUMN EXPERIMENTS

4.1 SAND CHARACTERISATION

4.1.1 PARTICLE DENSITY

The average particle density of the four coral sands used in this study were comparable and are presented in Table 4.1.

Table 4.1

Particle Density of Coral Sands

Sand Type	Particle Density (g/cm^3)	Measurement of Error (2SD)
Coarse store-bought	2.81	0.02
Fine store-bought	2.82	0.06
Kiribati	2.78	0.01
Vanuatu	2.81	0.03

Note. Values are average of four replicates.

The dry bulk density and total porosity was initially measured but carbon dioxide generation and disruption of the sand pack during the AELD process made column packing irrelevant.

4.1.2 PARTICLE SIZE DISTRIBUTION (PSD)

Print outs from the particle size distribution analysis generated using GRADISTAT version 8.0 (Blott & Pye, 2001) are presented in Appendix E. GRADISTAT classified the coarse store-bought sand as ‘moderately well sorted, coarse sand’; the fine store-bought sand as ‘moderately well sorted, slightly very fine gravelly medium to coarse sand’; the Vanuatu sand as ‘well sorted, slightly very fine gravelly very coarse sand’; and the Kiribati sand as ‘moderately sorted, slightly very fine gravelly medium to coarse sand’. The sieving error, or loss/gain incurred during processing, was calculated at ± 0.1 % for all samples. Some sieves, particularly sizes 250 µm, 125 µm and 62.5 µm, could not be fully cleared from all particles prior to and after the PSD, which can account for error.

The PSD and mean particle size of the store-bought and Pacific Island sands used in this study are compared with published data in Table 4.2. Over 85 % of the purchased fine coral sand was sized between 0.25 mm and 1 mm whereas the coarse sand was sized between 0.50 mm to 2 mm, which is consistent with the products being marketed as 0.8 to 1 mm and 1 to 2 mm, respectively. The 2SD of the more abundant sand fractions were quite small, indicating that the sand was either quite homogenous or the sub-sampling techniques used here produced representative samples.

Some PSD values in Table 4.2 were adjusted to exclude particles 2 mm and larger, to enable like-to-like comparison. The Vanuatu sand had been sorted and the 2 mm + fraction separated out prior to receipt, thus not used during this study. The resulting adjusted % w/w fractions were almost identical to the data provided (B Humphries, personal communication, October 20, 2020 – refer data in green in Table 4.2). Small subsamples were not analysed for this sand type, thus sampling variability is unknown. The PSD of the Kiribati sand seemed quite variable (refer data in blue in Table 4.2). The composition of a small subsample collected after mixing on receipt had a markedly different PSD to published data from Bikenibeu Beach and Bonriki Reserve, Kiribati (Burbery et al., 2015; Humphries, 2018). PSD was therefore conducted on the remaining sand *after* the 2 mm+ particles were removed and column experiments conducted (referred to as 'large' in Table 4.2). The difference in % weight between the subsample and the 'large' portion of remaining Kiribati sand was much bigger than the 2SD of the store bought sands (< 5 %), indicating that even after thorough agitation, large sampling variability is still possible.

Data from Table 4.2 are presented in Figure 4.1 to accentuate the variation in particle sizes between sand types, as particle size is a factor known to affect fluoride removal (Camlek, 2017; Nath & Dutta, 2010a; Wong & Stenstrom, 2018). The Kiribati sand used in this study was quite similar in particle size to the fine store-bought sand, though Kiribati sand had higher proportions of finer and larger particles. The coarse store-bought sand had larger particle sizes, whereas the Vanuatu sand had the largest of particles. This trend can also be noted in the mean particle sizes included in Table 4.2 where size order is 0.55 mm; 0.615 mm; 0.90 mm; and 1.327 mm for fine store-bought < Kiribati < coarse store-bought < Vanuatu sands, respectively.

Table 4.2

Particle Size Distribution and Mean Particle Size of Sands Used in this Study Compared to Published / Available Data

Sieve Diameter (mm)	Aggregate Class	Wentworth[1] scale (% w/w) Store-Bought Coarse	 Store-Bought Fine	 Vanuatu (large)	 Kiribati subsample	 Kiribati Adj'd*	 Kiribati (large)	Sieve Diameter (mm)	*Published / Available* *Bikenibeu*[2]	 *Bikenibeu*[2] *Adj'd**	 *Bonriki*[3]	 *Bonriki*[3] *Adj'd**	 *Vanuatu*[4]	 *Vanuatu*[4] *Adj'd**
4+	fine gravel	---	---	*removed	1.2	excl.	*removed	5+	*0.15*	*excl.*	*7*	*excl.*	*0*	--
2	very fine gravel	0 ± 0	0.04 ± 0.1	0.105	1.5	excl.	*removed	2	*0.2*	*excl.*	*6*	*excl.*	*21*	*excl.*
1	very coarse sand	25 ± 5	0.6 ± 0.2	76.9	3.8	3.89	7.53	1	*9.3*	*9.3*	*9*	*10*	*60*	*76.9*
0.5	coarse sand	64 ± 2	47 ± 2	22.5	32.5	33.5	46.7	0.5	*61.2*	*61.5*	*31*	*36*	*17*	*21.8*
0.25	medium sand	10 ± 5	48 ± 2	0.488	42.2	43.4	35.1	0.25	*25.3*	*25.4*	*26*	*30*	*1*	*1.3*
0.125	fine sand	0.4 ± 0.3	4.1 ± 0.2	0.035	18.6	19.1	10.6	0.125	*3.7*	*3.7*	*14*	*16*		--
0.063	very fine sand	0.07 ± 0.1	0.18 ± 0.03	0	0.12	0.12	0.059	0.063	*0.04*	*0.04*	*5*	*6*		--
<0.063	silt	0.02 ± 0.04	0.058 ± 0.003	0	0.02	0.024	0	<0.063	*0.02*	*0.02*	*2*	*2*		--
Mean particle size ($d_{m,3}$)		0.90 ± 0.03	0.55 ± 0.01	1.327	0.54	0.508	0.615	$d_{m,i}$	*0.719*	*0.703*	*1.23*	*0.571*	*1.66*	*1.32*

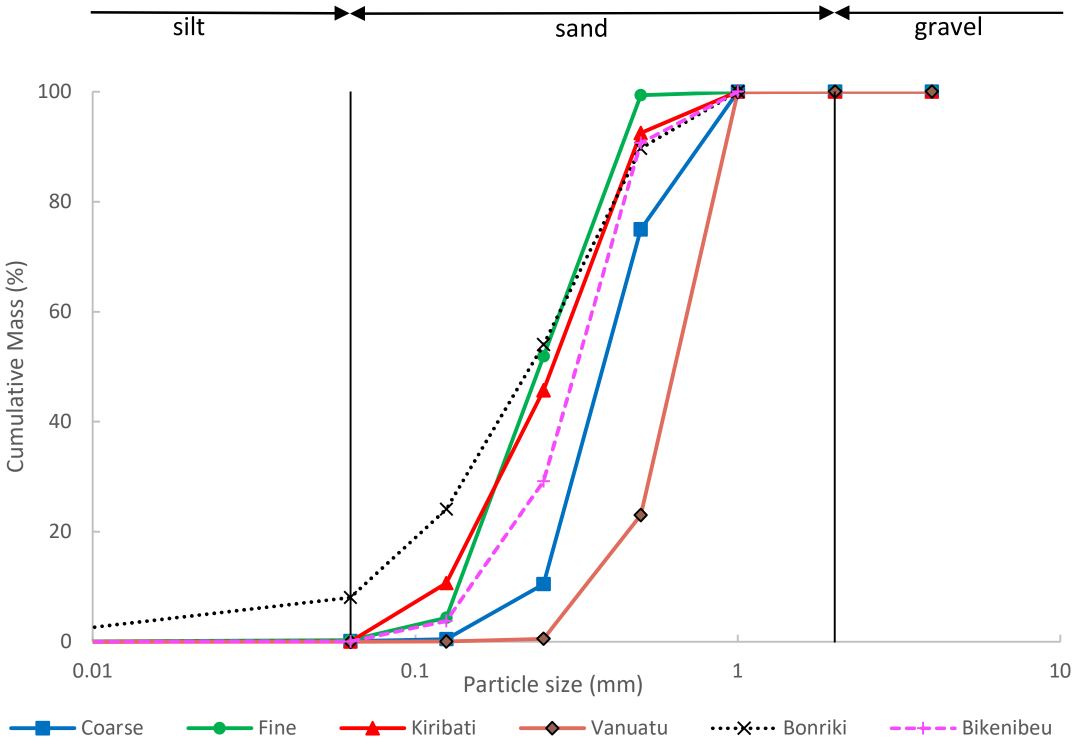
Note. PSD of purchased sands (average ± 2SD, n = 3) and Pacific Island sands (n=1) used in this study compared to three Pacific Island sand sources.

[1]Wentworth (1922); [2]Humphries (2018); [3]Burbery et al. (2015); [4]B. Humphries (personal communication, October 20, 2020).

*Adjusted values are the PSD with 2 mm+ particles excluded to simplify comparison, as 2 mm+ particles were removed from Pacific Island sands prior to conducting trials. Data in green is a comparison of PSD obtained here with data from B. Humphries (personal communication, 2020)[4]. Data in blue is a comparison of PSD from the small subsample vs. large remaining portion of Kiribati sand, as calculated herein.

Figure 4.1

Graphical Representation of PSD of Coral Sands Used in this Study Compared to Published Values



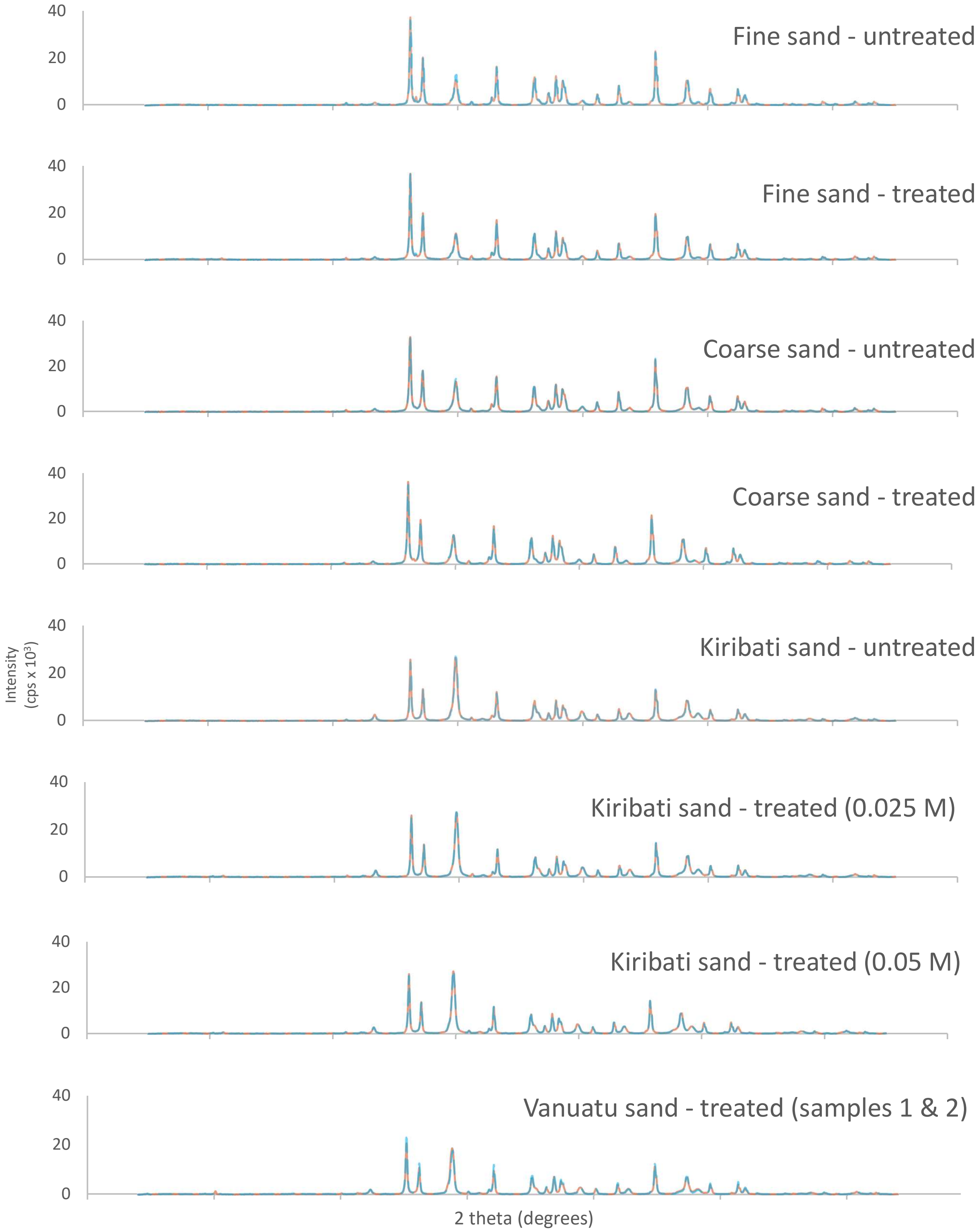
Note. PSD of coral sands compared to sands from two Kiribati locations: Bikenibeu Beach (Humphries, 2018) and Bonriki Reserve (Burbery et al., 2015). Note the cumulative mass of published data excluded particles above 2 mm for comparative purposes.

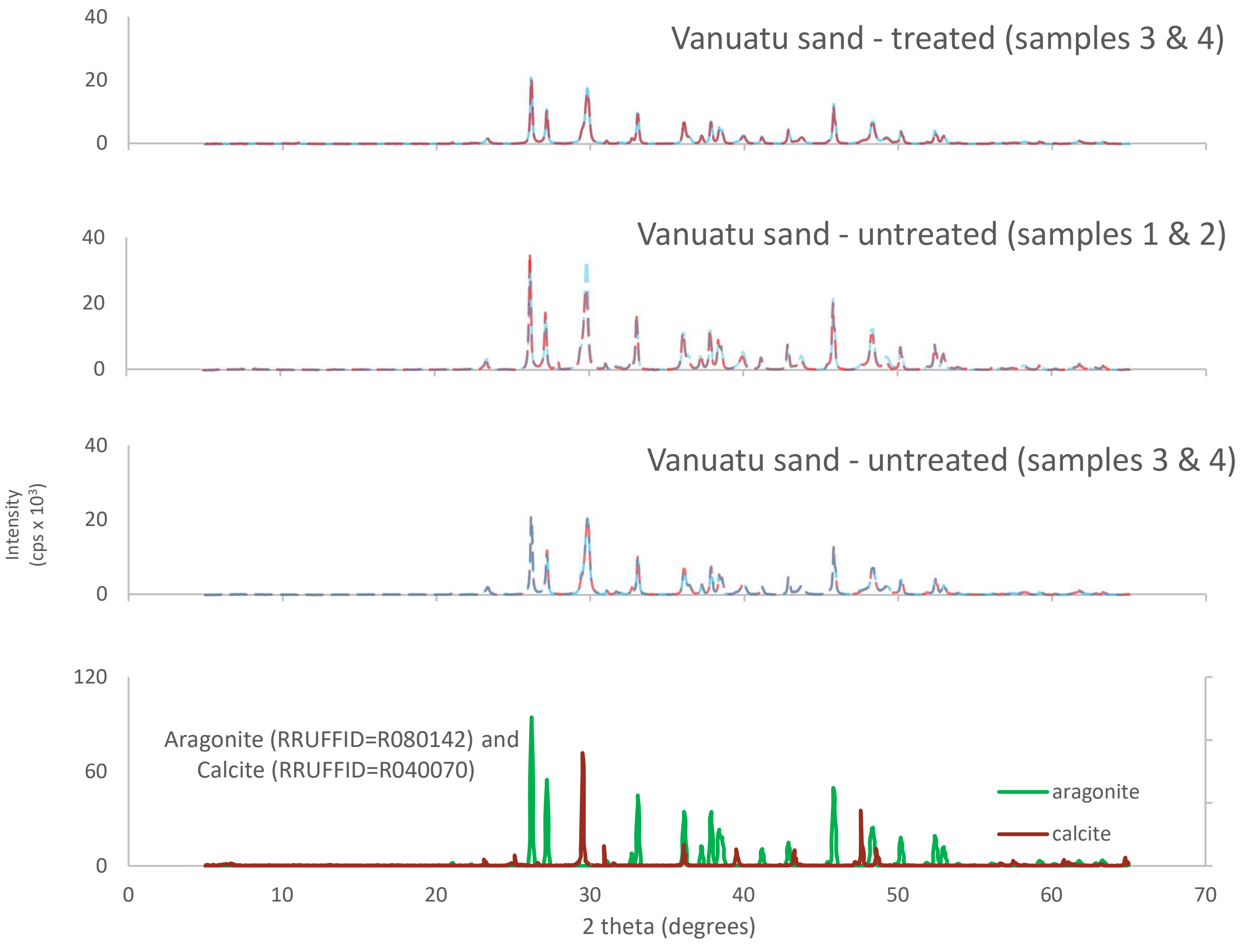
4.1.3 XRD OF CORAL SAND

XRD analysis was conducted on duplicate sand samples, prior to and after treating acidified fluoride solution (10 mg/L). Resulting diffractograms are presented in Figure 4.2 with reference spectra to illustrate that all samples, before and after treatment, are mixtures of calcite and aragonite in different proportions as indicated by peak height differences.

Figure 4.2

XRD Spectra of Untreated and Treated Coral Sands Compared to Reference Data



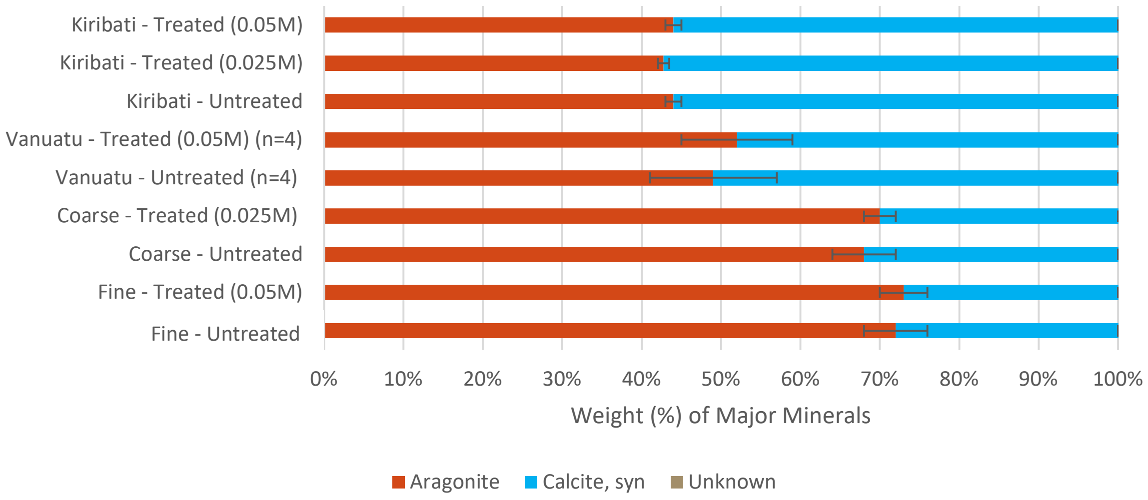


Note. XRD spectra from duplicate sand samples (blue and orange overlaid in each graph) of untreated and treated coral sands from this study. The last spectrum is combined aragonite and calcite references for comparison (RRUFF, n.d.).

The mineral composition (average ± 2SD) determined by XRD is presented in Figure 4.3. The % weights of each component before and after treatment differed very little and were within the 2SD of the samples. The aragonite content of store-bought sands was markedly higher than the two Pacific Island sands and Vanuatu samples had comparatively larger error (2SD). The sample variability of the Vanuatu sands was originally much larger than the other sands (by a factor of 2.5 to 14) therefore two additional samples were analysed. These results confirmed the large difference was due to sample variability and not mix-up.

Figure 4.3

Mineral Composition of Pre- and Post-AELD Coral Sands



Note. Mineral composition as determined by XRD of pre- and post-AELD coral sands from this study. The citric acid concentration used is in brackets. Average ± 2SD (n=2; n=4 for Vanuatu samples).

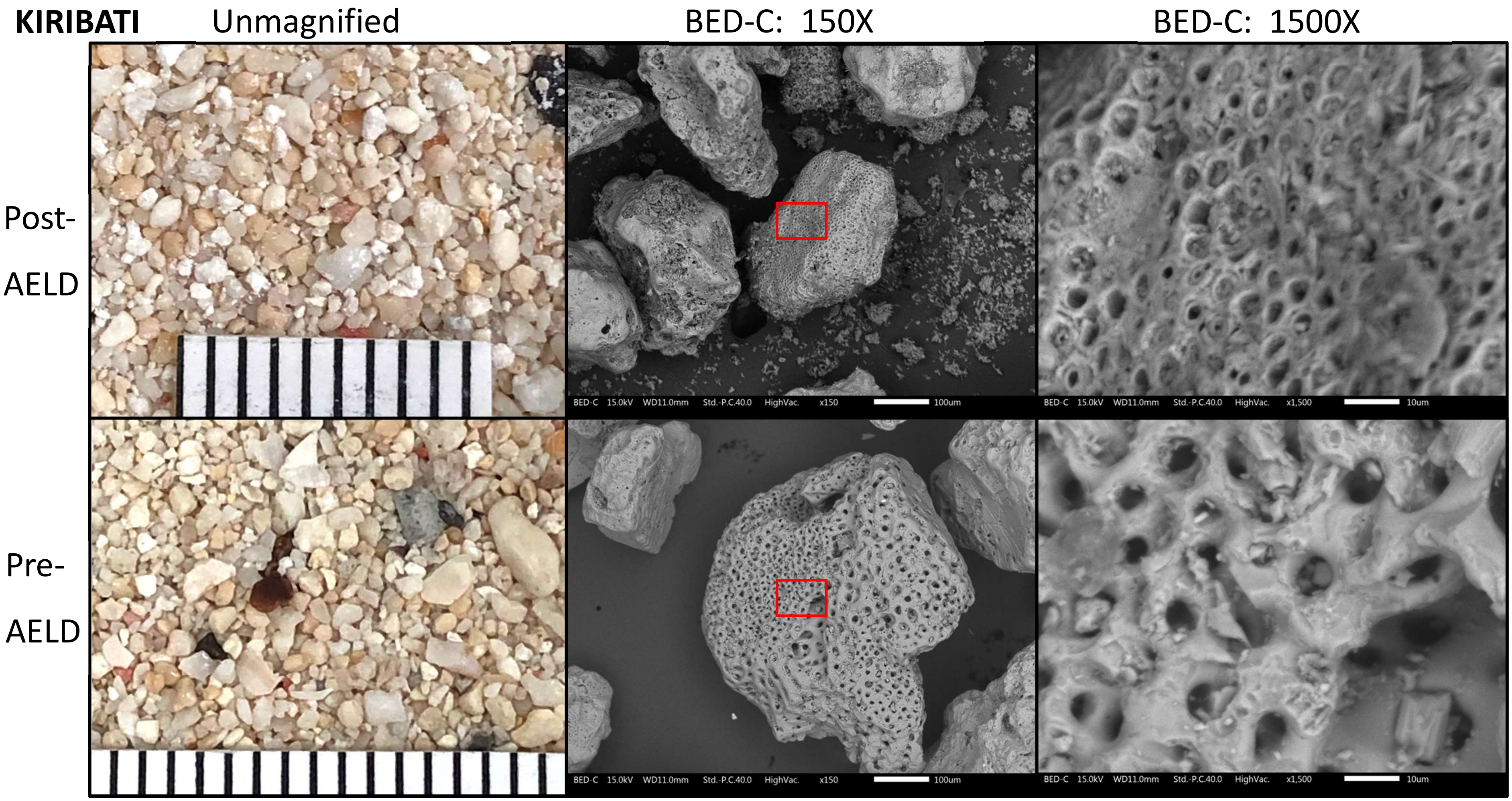
4.1.4 SEM-EDS (IMAGING AND ELEMENTAL ANALYSIS)

SEM micrograms were taken of three sand types before AELD-treatment to identify potential differences in surface features which could affect defluoridation. These were also compared to micrograms post-AELD to assess whether visible changes occurred during treatment. As it is not possible to re-image the same particles before and after treatment, three separate particles (also referred to as sites) were imaged as a general overview of surface morphology. The raw SEM-EDS images and elemental data were too voluminous for inclusion therefore select images are presented in Figure 4.4 The elemental data is reproduced in Appendix G – Table G 1 and has been condensed into Table 4.3.

There were no observable differences in surface morphology between the different sands nor the sands pre- and post-AELD. The larger particle size for Vanuatu sands was noticeable and consistent with the PSD results (refer Section 4.1.2). The unmagnified images illustrate the homogenous appearance and colour of store-bought fine coral sand compared to Pacific Island sands.

Figure 4.4

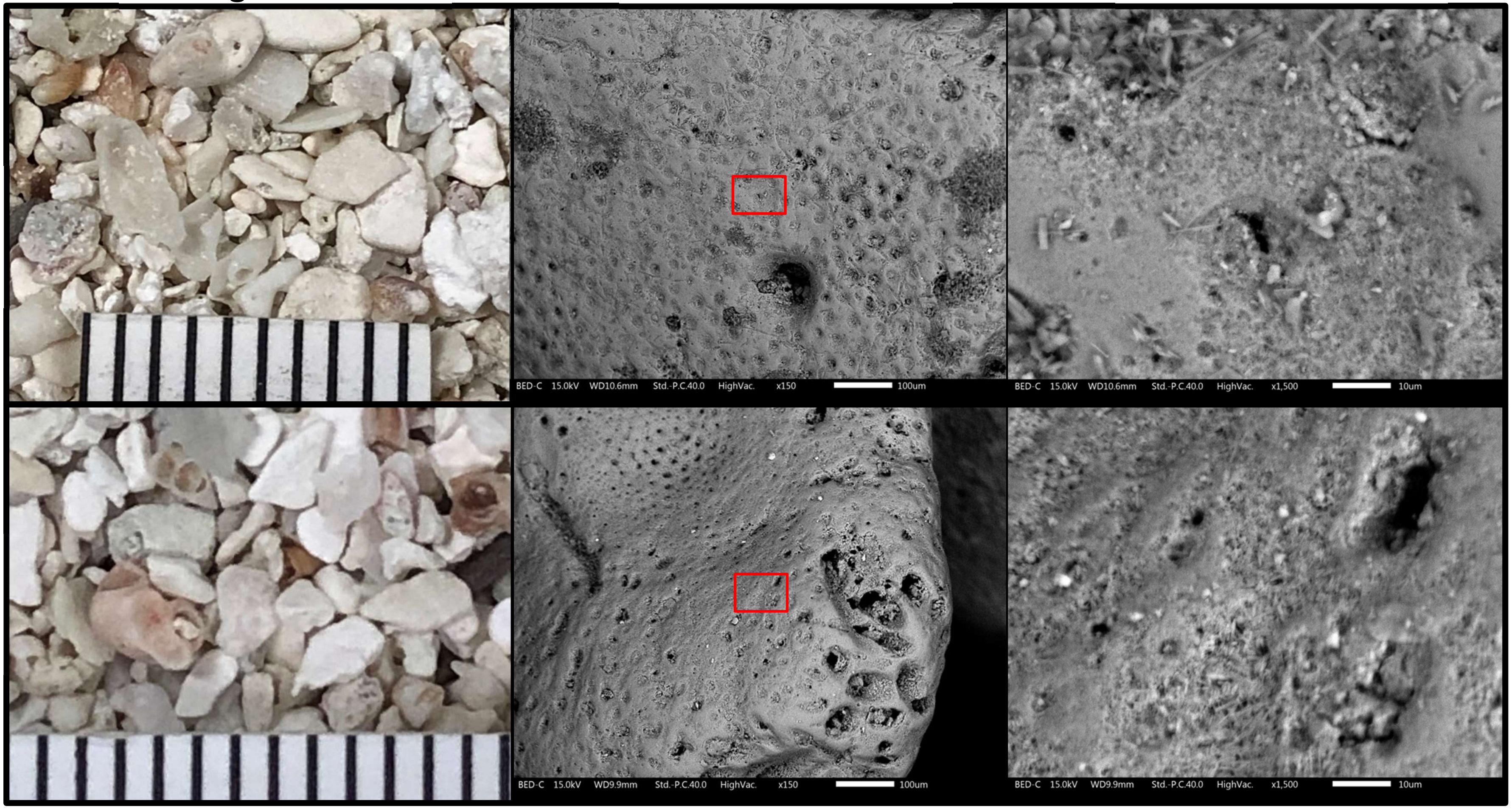
General and SEM Imaging of Three Coral Sand Types, Pre- and Post- AELD

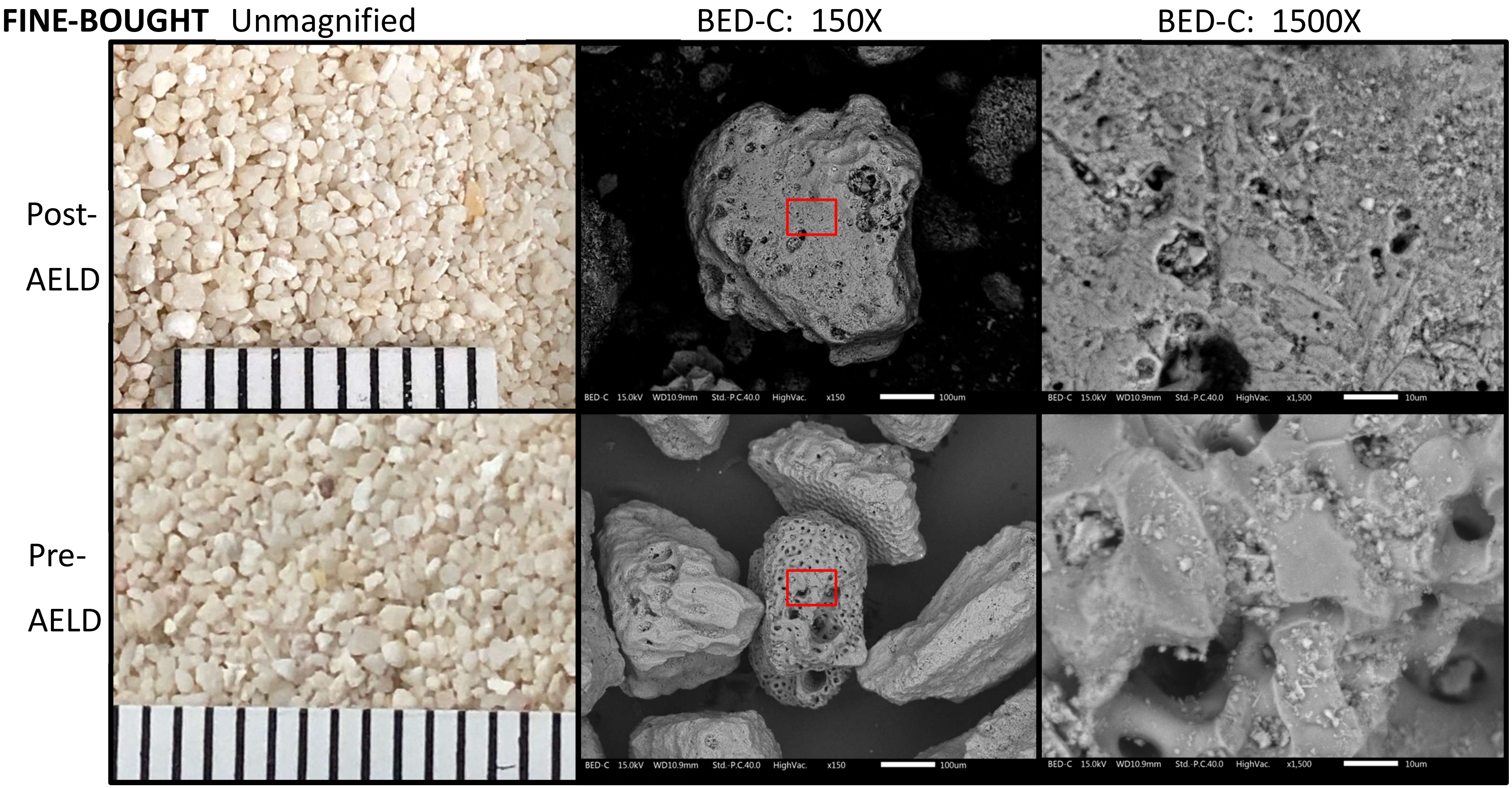


VANUATU Unmagnified BED-C: 150X BED-C: 1500X

Post-AELD

Pre-AELD





Note. General photographs & SEM micrograms using Backscatter Electron Detector (BED-C) at 150X and 1500X magnification. White bars = 100 µm and 10 µm, respectively. Red box indicates area of close up in 1500X image.

Table 4.3

Elemental Composition of Coral Sands Pre- and Post-AELD as Determined by SEM-EDS

Sand	Element % weight												
	O	Ca	C	Mg	Sr	S	Fe	Si	Al	W	P	Na	Cl
Store	45 ± 2	32 ± 3	20 ± 1	1 ± 3	0.5 ± 0.4	0.2 ± 0.2	0.2** ± 0.1	0.2 ± 0.2	0.1 ± 0.1	ND	ND	0.2 ± 0.1	ND
Kiribati	46 ± 1	29 ± 2	22 ± 3	2 ± 3	ND	0.2 ± 0.2	ND	0.3* ± 0	ND	0.5* ± 0.1	0.1* ± 0	0.6 ± 0.4	0.4 ± 0.1
Vanuatu	44 ± 10	26 ± 13	25 ± 10	1 ± 1	0.5**± 0.3	0.2 ± 0.1	ND	0.8* ± 0	ND	ND	ND	2 ± 2	2 ± 4
Store – Used	46 ± 2	25 ± 12	28 ± 13	0.2 ± 0.1	0.5 ± 0.3	0.1* ± 0	ND	0.1* ± 0	ND	ND	ND	0.2** ± 0.1	ND
Kiribati – Used	42 ± 7	35 ± 15	21 ± 9	2 ± 3	0.3* ± 0.1	0.2** ± 0	ND	0.1* ± 0	ND	ND	ND	0.2 ± 0.1	ND
Vanuatu – Used	41 ± 9	35 ± 13	22 ± 2	2 ± 3	0.8* ± 0.1	0.3** ± 0.1	ND	ND	ND	0.4* ± 0.1	ND	0.2** ± 0	ND

Note. Composition in % weight (average ± 2SD; n=3, unless indicated). Values in red are near the DL of the instrument and uncertain. Raw data in Appendix G – Table G 1. ND = not detected.

* One of three samples contained the element – instrument error indicated.

** Two of three samples contained the element.

The major components detected were O, Ca, and C with small amounts of Mg in all samples (lower weighted elements in the periodic table are not detected by the instrument (Wolfgong, 2016)). The % weight ranged between 41-46 %, 25-35 %, and 20-28 %, respectively with Mg below 3 % in all samples. Assuming all sands were 100 % $CaCO_3$, weights of 48, 40 and 12 % respectively, would be expected. The SEM-EDS results supports XRD analysis, being that most of the sand is $CaCO_3$ with little Mg present.

Trace contaminants were also detected in some samples including Al, Fe, S, Si, Sr and possibly P and W. The store-bought sand more consistently contained traces of Al, Fe, and Si. Untreated Pacific sand had low concentrations of sodium and chloride (i.e. salt) present whereas sodium was potentially detected in store-bought sand, which is consistent with contact with seawater. A salt deposit was also detected in one of the untreated Vanuatu samples (refer Appendix G – Table G 1 – site 4*). Broadly speaking, low level contaminants were more common in untreated samples, which is logical given repeated use of the sand with acidic solution would remove contaminants.

4.1.5 TRACE ELEMENT ANALYSIS OF SANDS VIA ACID DIGESTION & ICP-MS

To confirm whether elements of health and aesthetic significance originate from the coral sand itself, an acid digestion of triplicate samples was conducted on all four sand types. Average values of select elements are tabulated in Table 4.4 and juxtaposed to suggested release limits (SRL), measured in mg of metal per kg of food. These are guidelines values for the release of contaminants into food from contact materials as developed by the Nordic Council of Ministers (Cederberg et al., 2015). Some abnormally high individual measurements were obtained for some metals in the Kiribati sands (Fe; Mn; Ni; Pb) and the Vanuatu sands (Al and Fe) (refer values underlined in Table 4.4). This caused the sampling variability (2SD) to be quite high, thus minimum and maximum values are presented in Appendix G – Table G 2. Note the problematic ions for FISE (Al and Fe) which were detected with SEM-EDS in untreated store-bought sand, were also detected in considerable amounts here.

Table 4.4

Elemental Composition of Coral Sands Pre-AELD as Determined by Acid Digestion & ICP-MS Analysis

Element	Elemental Composition (in mg/kg)								LOQ	SRM %	CRM %	SRL
	Vanuatu		Kiribati		Fine – Bought		Coarse – Bought			Recovery		(ug/g)
Al	***800***	***± 1300***	**60**	**± 20**	**150**	**± 10**	**100**	**± 20**	3.5	88	111	5
As $^{75 -> 75}$	**2.5**	**± 0.7**	**3**	**± 1**	**1.6**	**± 0.2**	**1.9**	**± 0.2**	0.35	77	108	0.002
B	50	± 8	76	± 8	71	± 9	58	± 6	3.5	n/a	98	n/a
Cd		<LOQ	**0.084**	**0.008**		<LOQ	**0.05**	**± 0.01**	0.035	93	106	0.005
Co	0.1	± 0.1	**0.2**	**± 0.4**	0.044	± 0.008		<LOQ	0.035	87	99	0.02
Cr	**8**	**± 5**	**3**	**± 3**	2.1	± 0.3	2.3	± 0.4	0.035	80	101	0.25
Cu	0.67	± 0.07	3	± 5	0.21	± 0.07	0.14	± 0.01	0.035	87	106	4
Fe $^{56 -> 72}$	200	± 300	**6000**	**± 12000**	120	± 80	30	± 10	0.35	68	101	40
Mn	10	± 4	30	± 30	9	± 2	11	± 4	3.5	96	99	1.8
Ni	0.4	± 0.2	**1**	**± 2**	0.38	± 0.04	0.29	± 0.04	0.035	84	103	0.08
Pb	**1.9**	**± 0.3**	**40**	**± 110**	**0.40**	**± 0.07**	**0.40**	**± 0.06**	0.035	85	113	0.01
Zn	1.3	± 0.9	7.2	± 2.	1.4	± 0.4	1.5	± 0.4	0.35	120	103	5
Ca (g/kg)	340	± 20	330	± 40	330	± 40	330	± 20	0.035	73	104	n/a
Mg (g/kg)	14	± 4	17	± 2	6.3	± 0.6	9	± 4	0.0035	88	92	n/a
Na (g/kg)	4.4	± 0.5	4.3	± 0.2	3.4	± 0.1	3.1	± 0.2	0.00035	72	106	n/a
S (g/kg)	1.6	± 0.3	1.7	± 0.3	1.4	± 0.1	1.4	± 0.3	0.035	62	n/a	n/a

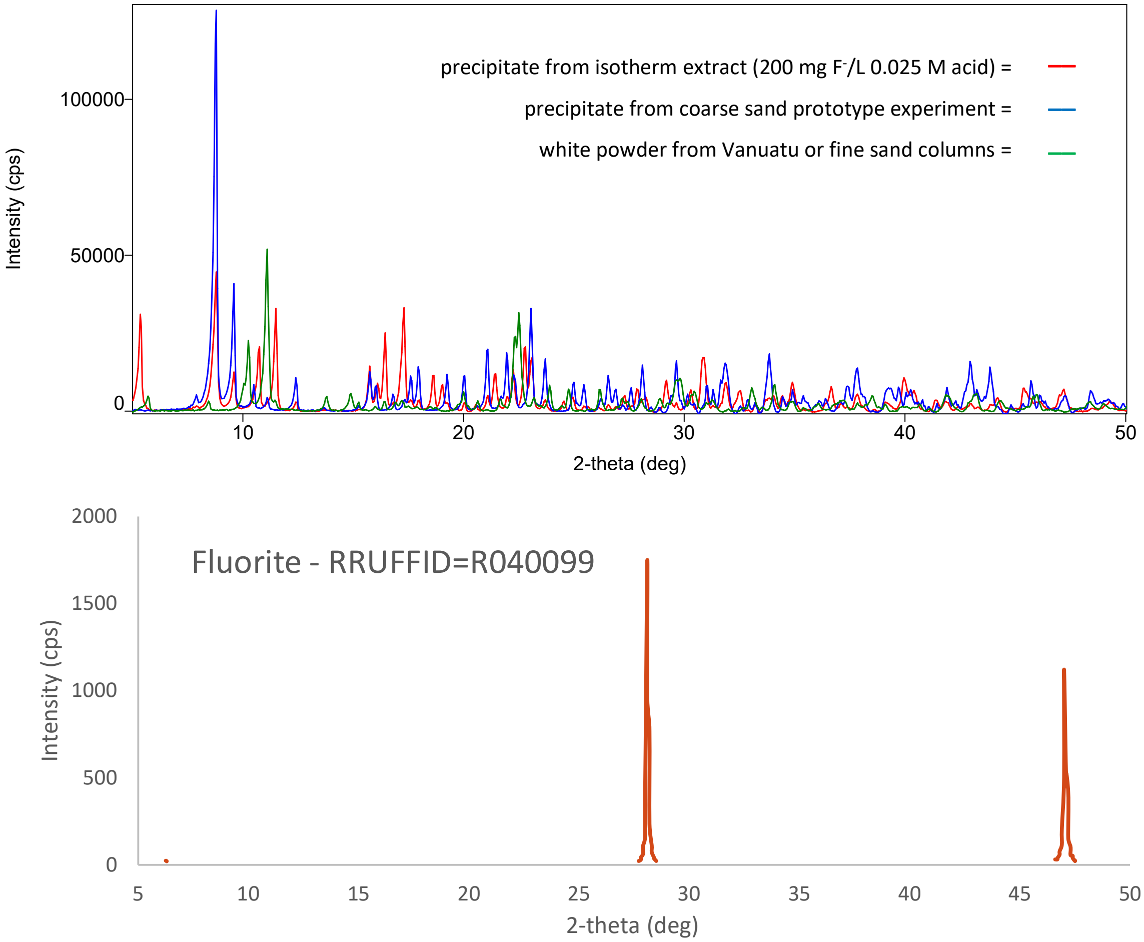
Note. Composition in mg/kg (unless indicated). Average ± 2SD (n=3) with average of two blanks deducted. (Maximum and minimum values presented in Appendix G – Table G 2). Values in blue and red are 10-99X or 100X and higher, respectively, than the Suggested Release Limit (SRL) as developed by the Nordic Council of Ministers (Cederberg et al., 2015). Underlined values have large 2SDs.

4.2 XRD OF WHITE POWDERS AND PRECIPITATES COLLECTED AFTER AELD

The white powders obtained from sand columns and the precipitates isolated from treated extracts were complex mixtures which could not be deciphered with the current spectral library available at UC, as analysed by M Polson (personal communication, February 22, 2021 & April 28, 2021). Samples analysed fell into one of three groups and a representative diffractogram is depicted in Figure 4.5: the precipitates from the isotherm experiment were possibly different calcium citrate hydrates mixed with other compounds; white powders obtained from the Vanuatu and fine sand columns may contain the calcium citrate 6-hydrate as a minor constituent; and the precipitate from the coarse sand prototype extracts may have contained the tetrahydrate form. Powders from sand columns and precipitates from the prototype extracts did not appear to have any compounds in common, which indicate that what precipitates inside the column is different to what precipitates in the fluid, a few hours after extraction. Reference samples of potential contributing compounds may have assisted in deciphering the mixtures, but this investigative effort was not undertaken. A visual comparison with a reference diffractogram of CaF_2 obtained from the RRUFF project database did not seem to indicate that fluorite, the expected precipitation product from AELD using calcium-based adsorbent (refer equation (2)) was a major contributor to the mixtures.

Figure 4.5

Diffractograms of Select White Powders and Precipitates Formed During AELD Compared to Fluorite (CaF_2)



Note. Representative diffractograms of select white substances from sand treatment devices and precipitates formed in select extracts throughout this study (top figure) compared to fluorite, the expected precipitation product from AELD using calcium-based adsorbent (bottom figure - reference obtained from RRUFF (n.d.)). Top image is a modified instrument screenshot obtained from M. Polson (personal communication, April 28, 2021).

4.3 RESULTS – BATCH AND SAND COLUMN EXPERIMENTS

4.3.1 EXPERIMENT C – NO ACID; 10 MG/L FLUORIDE; COLUMN REUSE

Columns were sampled twice daily, at 4-hours and then either 8 or 14 hours (i.e. overnight). Aesthetically, sand extracts from day 1 appeared dirty-yellow and had a quintessential beach smell whereas samples collected afterwards seemed less unappealing.

Some FISE samples were refrigerated and analysed a week after preparation, which is longer than the recommended three days (ISO, 1992). Three 1-week old samples stored at room temperature which had previously been analysed were remeasured and the fluoride concentration was less than ± 3 % different from their original values. This provided confidence that concentrations from the one-week old samples were valid. All quality control measures were adequate with P’ = 102 %, however no duplicates were processed.

Coral sand columns without the addition of acid achieved fluoride removal rates of 59 to 64 % (± 2 %) from initial 10 mg/L fluoride solution, over three consecutive days using variable sand-fluid ratios (refer Table 4.5).

Table 4.5

Final pH and Fluoride Concentrations of Extracts After Sand Column Treatment (No Acid) Over Three Days with Various Contact Times (Experiment C)

Sample and Contact Time	pH After Treatment	Fluoride Concentration (mg/L)	Fluoride Removal (%)	Sand-Fluid Ratio
Day 1 – 4 hours	9.3 ± 0.1	3.6 ± 0.4	64 ± 4	3.17 : 1
Day 1 – 8 hours	9.4 ± 0.3	4.0 ± 0.4**	61 ± 4	3.17 : 1
Day 2 – 4 hours	9.49 ± 0.06	4.3 ± 0.3	59 ± 3	9.5 : 1
Day 2 – 14 hours (o/n)*	9.26 ± 0.06	3.9 ± 0.2**	62 ± 2	9.5 : 1
Day 3 – 4 hours *	9.38 ± 0.05	4.0 ± 0.2	61 ± 2	5.66 : 1
Day 3 – 8 hours *	9.0 ± 0.3	4.1 ± 0.2	60 ± 2	5.66 : 1
Column blanks (x2)	4.64	10.5 ± 0.2	n/a	n/a
Initial solution (C_o) (Ave. of 2 *readings*)		10.4 ± 0.1		n/a

Note. Initial solution of 10.0 mg F^-/L. Average ± 2SD (n=3). Blanks (n=2) extracted after 24 hrs. Overnight (o/n) contact time of 14 hours. Measured initial fluoride concentration (C_o) 2.4-4.0 % different to the calculated value and within quality guideline.

* refrigerated FISE samples analysed a week later. ** P ‘ = 101-102%

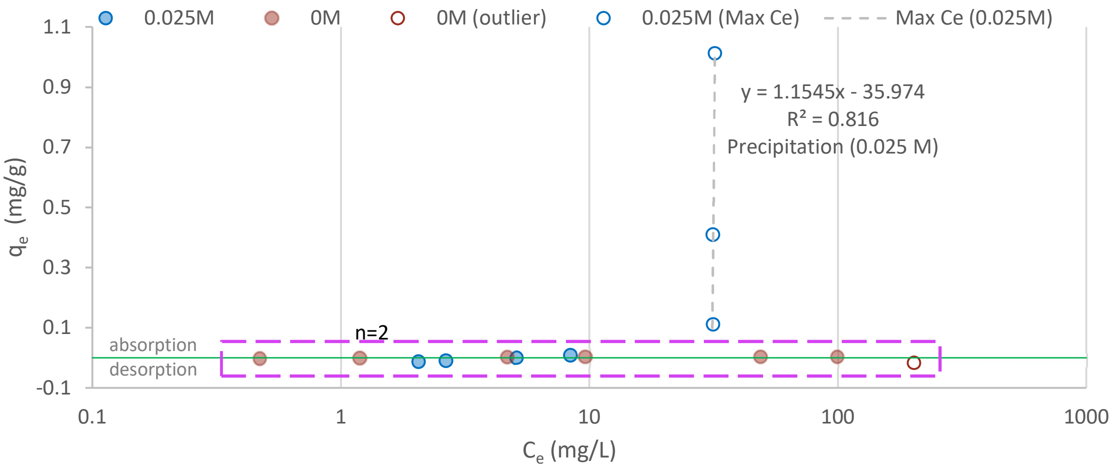
4.3.2 EXPERIMENT D – ADSORPTION ISOTHERM

Batch sorption experiments using an adsorbent dose of 1 g/6 mL were completed to determine the capacity of sand to sorb fluoride, with and without 0.025 M citric acid. Duplicate 'no sand' blanks produced extracts with fluoride concentrations less than 2 % different from the initial solution of 5 mg F^-/L, indicating that the falcon tube itself did not significantly alter fluoride concentrations. Concentration of initial fluoride solutions was calculated gravimetrically (C_o (Calc)) and the adsorbent capacity (q_e) was calculated using these values, as opposed to the measured initial fluoride concentration (C_o(meas)).

Under the conditions tested, the oven-dried coral sand is fairly ineffective as a fluoride sorbent with a q_e value (i.e. the amount of fluoride sorbed per g of sand) below 0.11 mg/g. Adsorption capacity (q_e) as a function of the final fluoride equilibrium concentration (C_e) in ambient solution is plotted in Figure 4.6 (data in Table 4.6).

Figure 4.6

Adsorption Isotherm of Fluoride onto Fine Store-Bought Sand with and without 0.025 M Citric Acid



Note. Adsorption isotherm (T= 22-26 °C) of fluoride onto fine store-bought coral sand with 0.025 M citric acid or without, adsorbent dose of 1 g / 6 mL. Average (n=3), except where indicated (errors omitted for clarity). Pink box expanded in Figure 4.7. Max C_e is the approximate maximum concentration of F^- in solution before mass precipitation occurs in 0.025 M citric acid.

This figure illustrates that, for solutions containing 0.025 M citric acid, the final equilibrium concentration (C_e) did not exceed values of about 31-32 mg/L, which is over 15 times the 1.5 mg/L drinking water limit. This is in spite of the initial fluoride concentration being as high as 200 mg/L, indicating that another substantial mechanism of fluoride removal (i.e. precipitation) is occurring. An expanded view of the data in Figure 4.6 near the adsorption/desorption origin (where q_e = 0 mg/g) is presented in Figure 4.7. A trendline was fit to the data points at C_e values below 10 mg/L, given their apparent linearity and the R values for linear isotherms of the 0.025 M and 0 M solutions were 0.9944 and 0.9853 respectively.

Table 4.6

Results of Adsorption Isotherm of Fluoride onto Fine Store-Bought Sand with and without 0.025 M Citric Acid

Citric	Initial	Initial [F^-] (mg/L)					Final [F^-]		Adsorbent Capacity	
Acid	[F^-]	Calculated	Measured	pH			Measured		q_e (mg/g)	
(M)	(mg/L)	$C_{o(calc)}$	$C_{o(meas)}$	Initial*	Final		C_e (mg/L)		using $C_{o\ (calc)}$	
0.025	0	0	<LOQ	2.3	6.4	± 0.09	2.05	± 0.03	-0.0123	± 0.0002
0.025	1	1.01	**1.01	2.34	6.42	± 0.09	2.65	± 0.01	-0.0098	± 0.0002
0.025	5	5.04	*4.98	2.36	6.5	± 0.2	5.08	± 0.08	-0.0002	± 0.001
0.025	10	9.79	*9.87	2.37	6.5	± 0.3	8.39	± 0.08	***0.0084***	± 0.0005
0.025	50	49.96	**49.8	2.43	6.5	± 0.2	***31.4***	± 0.4	***0.111***	± 0.002
0.025	100	99.99	**100.5	2.52	6.54	± 0.2	***31.4***	± 0.7	0.41	± 0.003
0.025	200	201.52	**202.8	2.65	6.9	± 0.2	***32***	± 0.5	1.013	± 0.006
0	0	0	nd	4.41	8.6	± 0.4	0.47	± 0.04	-0.0028	± 0.0002
0	1	1.002	**1.04	4.66	8.62	± 0.07	**1.19	± 0.05	-0.0011	± 0.0003
0	5	5.03	**5.12	4.9	8.78	± 0.2	4.67	± 0.07	0.0022	± 0.0004
0	10	10.09	*10.67[1]	4.89	**8.1	± 0.7	9.61	± 0.05	0.0028	± 0.0003
0	50	49.296	*50.73	5.37	8.87	± 0.1	48.76	± 0	**0.00324**	± 0.00002
0	100	99.92	*103.44	4.99	8.8	± 0.2	99.43	± 0	0.00294	± 0.00004
0	200	199.98	*202.74	5.59	8.8	± 0.3	202.74	± 0	-0.0165	± 0.0001

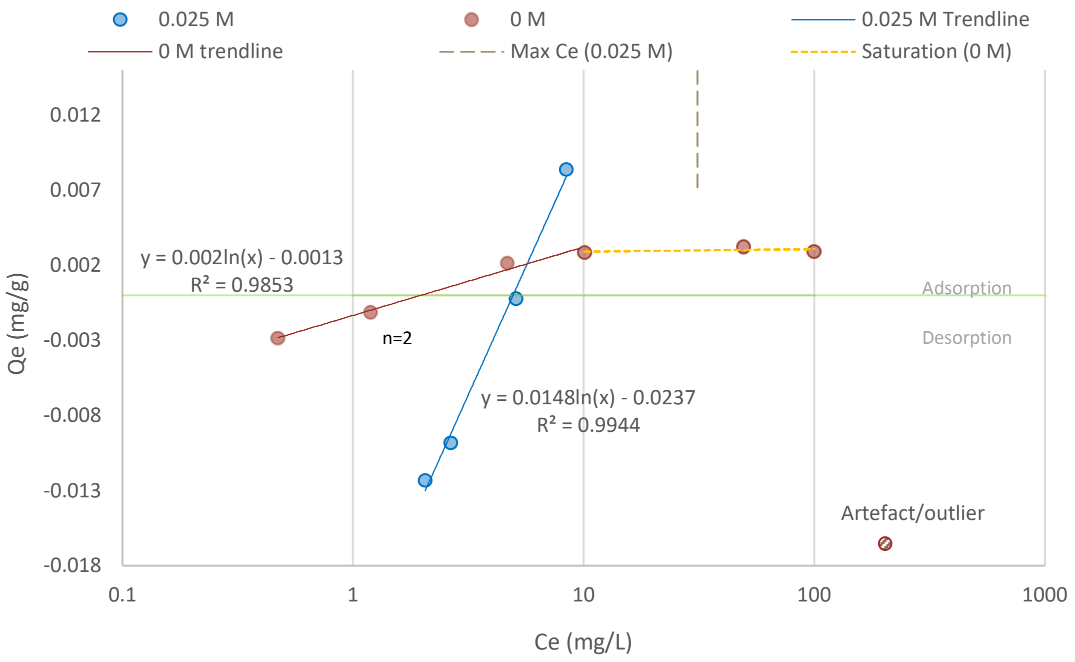
Note. Average ± 2SD (n=3, except *n=1; **n=2); nd = not done, assumed 0 as prepared with no acid. Adsorbent capacity (q_e) determined using initial fluoride concentration as calculated gravimetrically ($C_{o\ (Calc)}$). Values in blue are max C_e, above which mass precipitation occurs (in 0.025 M acid). Max q_e occurs below this point and is indicated in green. Max q_e for non-acidified samples is indicated in orange. Quality control: 0.25 mg/L calibration standard removed thus LOQ <0.25 mg F^-/L; P' = 95-109%;

[1] measured value is 5.7 % different from gravimetrically value, just above quality guidelines.

For non-acidified solutions where the equilibrium concentration (C_e) is above approximately 10, maximal q_e value was reached at approximately 0.00324 mg/g, at which point a saturation or plateau occurred: no additional fluoride could be sorbed onto sand in spite of increasing the fluoride in solution (refer dotted orange line in Figure 4.7 and orange data in Table 4.6).

Figure 4.7

Expanded View of Adsorption Isotherm Near Adsorption / Desorption Origin



Note. Expanded view of trends in adsorption isotherm (T= 22-26 °C) from Figure 4.6 of fluoride on fine store-bought coral sand in 0 M or 0.025 M citric acid, adsorbent dose of 1 g/6 mL. Average (n=3), except where indicated (errors omitted for clarity, included in Table 4.6).

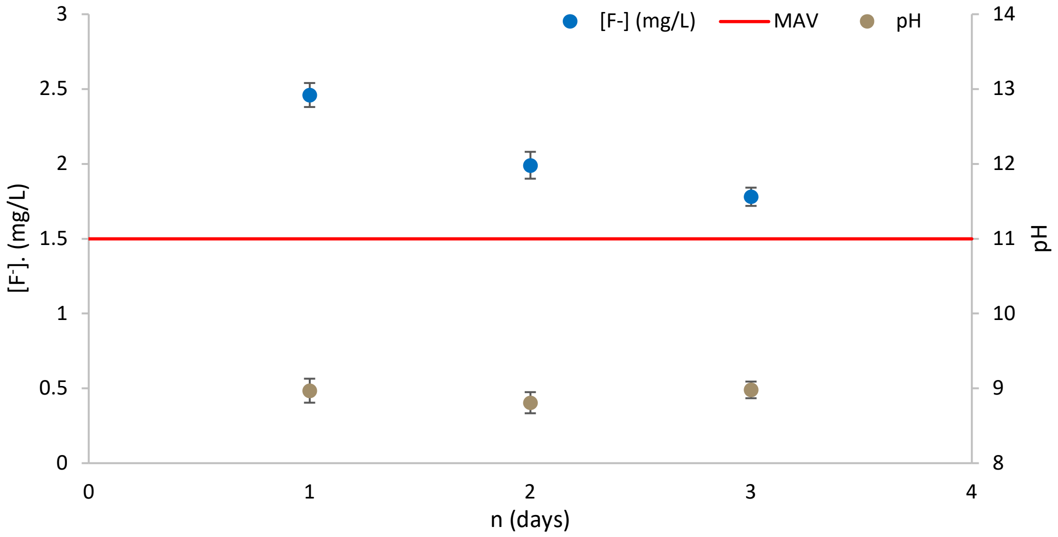
As noted prior, in 0.025 M citric acid solution, a maximum C_e value of 31-32 mg/L is reached where mass precipitation occurs (values in blue in Table 4.6), and the maximum absorption capacity of sand (q_e) would be between 0.0084 and 0.11 (C_e = ~8.4 to ~31) (values in green in Table 4.6). The addition of acid increases adsorption capacity when the C_e is above ~5.75 mg/L (intersection of both trendlines) and may increase sorption by a factor of at least 2-3 above this point. At a C_e of about 5.0 mg/L, no adsorption occurs when there is 0.025 M citric acid in solution (y = 0). This value is approximately 1.9 mg/L when the solution is non-acidified. Below these concentrations, fluoride is released from sand as indicated with negative q_e values and this desorption is more significant in the presence of acid, as indicated by the sharper slope and lower q_e values for 0.025 M solutions. The negative q_e value at 200 mg/L in the non-acidified solution was likely due to an experimental artefact because, the instrumental measurement error at or above 35 mg/L is too large (~8 mg/L) to accurately measure the small difference (< 4 mg/L) between the initial solution concentration (C_o) and the equilibrium concentration (C_e). The standard deviation of the equilibrium concentration (C_e) for non-acidified solutions at approximately 50 mg/L, 100 mg/L, and 200 mg/L is zero, given all replicates measured the same value. This is also due to the lack of instrumental precision at high fluoride concentrations.

4.3.3 EXPERIMENT E – MATRIX RECOVERY (WITH COLUMN REUSE)

A summary of the final fluoride concentrations, pH, and temperature of extracts obtained over three consecutive uses of sand columns with ultrapure water is presented in Figure 4.8 (data in Appendix G – Table G 3). The sand-to-fluid ratios used here were 3.17:1 on day 1 and 9.5:1 on days 2 and 3. All quality control measures were adequate with near perfect standard % recovery, however no duplicates were processed on day 1 or 2.

Figure 4.8

Final pH and Fluoride Concentration of Extracts from Matrix Recovery Experiment



Note. Results of matrix recovery experiment following 4-hour contact with ultrapure water, over three consecutive daily uses, average ± 2SD (n=3). Sand-fluid ratio of 3.17:1 on day 1 and 9.5:1 on days 2 and 3.

Results indicate that a significant amount of fluoride is present in the sand which can be removed via contact with water, without acid. Note that large sand-to-fluid ratios were used (i.e. the pore volume of columns were filled) which explain why fluoride concentration in the extracts remained elevated, even after three days of column use. The sand treatment also increased the pH of water from approximately 4 – 5 to 8.8 ± 0.2.

4.3.4 EXPERIMENT F – AELD: 2:1 SAND-FLUID RATIO; 0.05 & 0.1 M ACID; 4 & 8 HOUR CONTACT

Treated extracts from columns with acidified solution were remarkably sticky and adhered significantly to pipette tips (refer Figure 4.9). Most developed a white precipitate after extraction and all had a very yellow appearance (refer Figure 4.10). Curiously, none of the 0.1 M 8-hour extracts precipitated overnight. Columns filled with water only also produced yellow extracts, however no white precipitate formed. Extracts from reused columns appeared slightly less yellow than those from initial use (refer Figure 4.11) and also did not precipitate overnight.

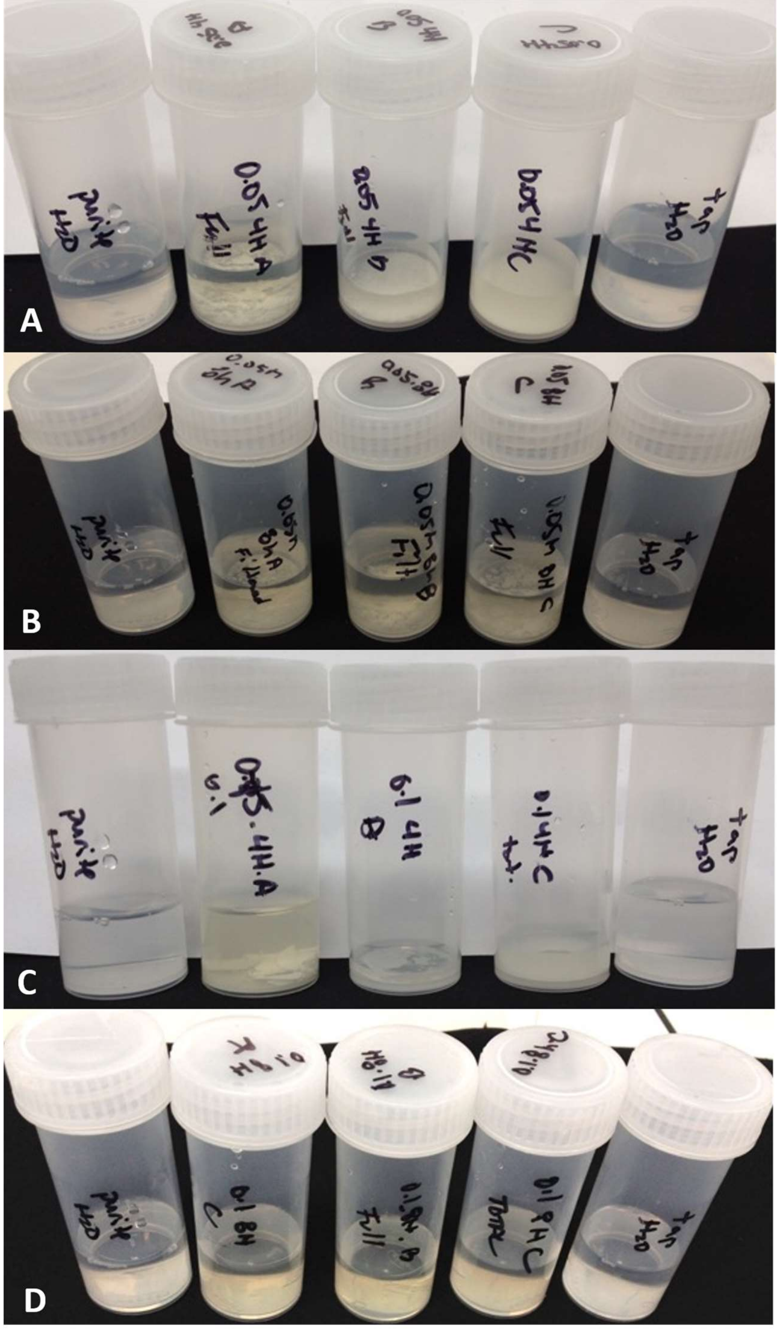
Figure 4.9

Pipette Tip Used on AELD Column Extract Depicting Fluid Consistency

Note. Photograph of a 5 mL pipette tip following pipetting of extract from 0.025 M citric acid & H_2O sand column extract depicting the sticky nature of the extract (Experiment F)

Figure 4.10

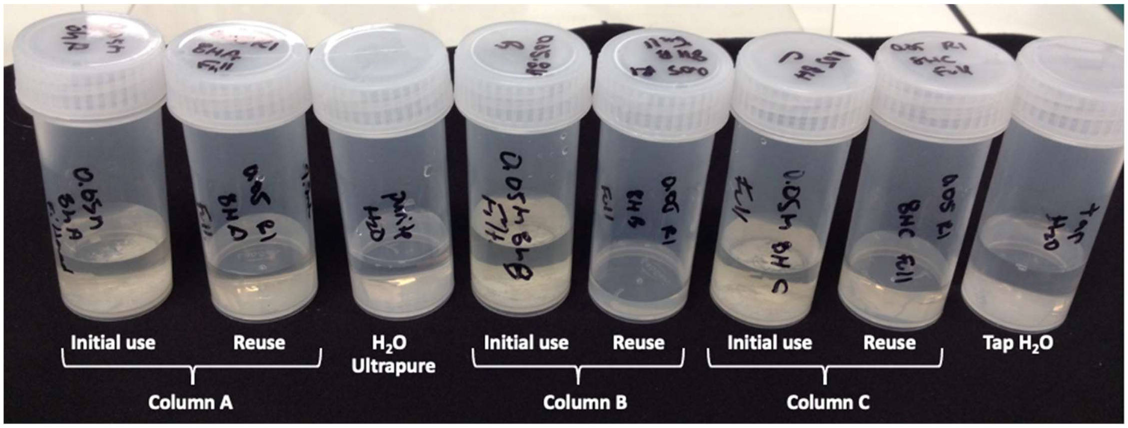
Extracts from 2:1 Sand-Fluid Ratio Columns with 0.05 and 0.1 M Acid (Experiment F), Depicting White Precipitate Formation and Colour



Note. Extracts from sand columns loaded with initial solution of 10 mg F^-/L. White precipitate formed overnight after the following treatments: (A) 4-hour contact with 0.05 M acid; (B) 8-hour contact with 0.05 M acid; (C) 4-hour contact with 0.1 M acid. Compare with (D) 8-hour contact with 0.1 M acid, where no precipitate formed.

Figure 4.11

Extracts from New and Reused Sand Columns with 0.05 M Acid, After 8-Hour Contact (Experiment F)



Note. Photos depict slight decrease in yellowness of extracts and lack of precipitate in reused columns compared to new (initial use).

A summary of final fluoride concentration of extracts after treating initial fluoride solution (10 mg/L) with 0.05 or 0.1 M citric acid, for 4 and 8 hours in new and reused sand columns can be found in Table 4.7. For comparison purposes, this table also includes data from a similar experiment (Experiment G & I) conducted in single columns using 0.025 M or no acid.

All final fluoride concentrations were below 0.5 mg/L regardless or contact time or acid concentration used, with the exception of the 'no acid' column. Values below 0.5 mg/L may be biased by as much as 150 % (EPA, 1996) which may cause larger % differences in duplicate analysis and could influence % recoveries. The standardised % recoveries for all tested acid-containing extracts (67 to 76 %), did not meet quality guidelines and were remarkably low compared to the 96 – 99 % recoveries of the 'no acid' blank and comparative standards. Low standardised spike recoveries (P') indicate that fluoride measurements are compromised by matrix interference. It would therefore be more prudent to analyse at least one spiked sample for each *set* of replicate trials where parameters are varied to ensure results are valid.

Table 4.7

Results of AELD in New and Reused 2:1 Sand-to-Fluid Ratio Columns Following 4 & 8 Hour Contact with Variable Acid Concentrations (Experiment F)

pH (after TISAB addition)	Acid Concentration (M)	Contact Time (hrs)	Column Use	Measured F^- Concentration (mg/L)	Quality Control Data	Fluoride Removal Rates (%)**
5.1	0	4	New	3.39*	P’ = 99%	66%
5	0.025	4	New	0.344*	P’ = 76%	97%
4.9	0.05	4	New	0.40 ± 0.01	n.d.	96%
4.9	0.1	4	New	0.39 ± 0.03	P’ = 75% 6% diff.	96%
4.9	0.05	8	New	0.38 ± 0.04	n.a.	96%
4.9-5.0	0.1	8	New	0.24 ± 0.02	n.a.	98%
5	0.05	4	Reused	0.25 ± 0.2	P’ = 69% 18% diff.	98%
5	0.1	4	Reused	0.282 ± 0.009	P’ = 68%	97%
5	0.1	8	Reused	0.40 ± 0.08	9% diff.	96%
Analysis aborted	0.05	8	Reused	Analysis aborted	n.a.	n.a.

Note. Initial solution of 10 mg F^-/L. Average ± 2SD (n=3), unless stated. Values in red are outside quality guidelines. Diff = duplicate % difference.

* single replicate, data included for comparison, from Experiment G & I.

** validity in doubt due to low standardised spike recovery (P’); n.a. = not analysed

The pH values of samples following TISAB addition are included in Table 4.7 as some were just below the recommended value of 5 to 5.5 (or 9 according to ASTM (2016)). The slightly lower pH of some samples is not the cause of low spike recoveries as the 8-hour columns with 0.05 M acid and the 4-hour columns with 0.1 M acid had pH values within range and recoveries below quality cut-off. In addition, results of samples slightly below pH 5 produced very small % differences (< 5 %) compared to the measured concentration following pH adjustments [data not shown, from Experiment G & I and noted throughout the remainder of the research]. Analysis was aborted given poor recoveries, the ensuing unreliability of measured fluoride concentrations, and likely overinflation of fluoride removal rates.

4.3.5 EXPERIMENT G/I – PRELIMINARY AELD TRIAL: VARIED ACID CONCENTRATIONS & SAND-FLUID RATIOS

A preliminary trial of single sand columns was conducted, where citric acid concentration (0.025 M; 0.05 M) and sand-to-fluid ratios (2:1, 2.5:1, and 3.33:1) varied. Results are tabulated in Table 4.8 and final fluoride concentrations illustrated in Figure 4.12. Temperature varied between 21-25 °C and quality control measures were within guidelines, except where stated. Laboratory notes indicated that the duplicate above quality cut-off was likely inadequately mixed prior preparation (in red in Table 4.8). Matrix interference affected a few acid-containing extracts as indicated by low standardised recovery (refer red values in Table 4.8).

Aesthetically, all filtered extracts were yellow and white precipitate formed overnight in the 0.05 M acid solutions only (refer Figure 4.13). The 0.025 M extracts were examined 6 days later and only a small amount of precipitate was noted. The acidic pH of initial solutions was raised from 2 - 3 to a neutral pH of 6 to 7 following treatment.

Table 4.8

Results of AELD in Columns with Varied Sand-to-Fluid Ratios and/or Acid Concentrations (Preliminary Trial - Experiment G & I)

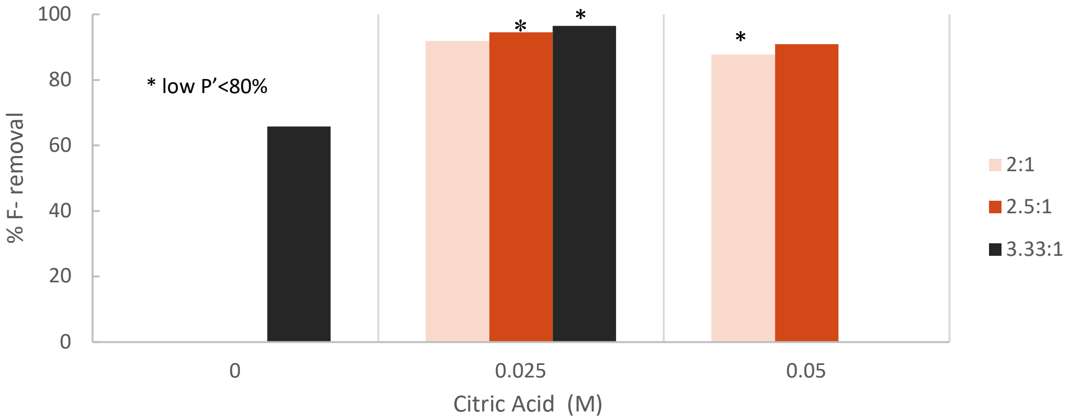
Initial Solution		P'	Acid	Sand-fluid	Measured		% F^-	P'	Dupl.
pH	Measured [F^-]	%	(M)	ratio	[F^-] (mg/L)	pH	Removal	%	% diff
ND	ND	ND	0	2	ND	ND	ND	ND	ND
ND	ND	ND	0	2.5	ND	ND	ND	ND	ND
4.5	9.86	88*	0	3.33	3.39	9.06	65.8	98.7*	ND
2.31	10.5	115	0.025	2	0.81	6.49	91.9	114	ND
2.31	10.5	115	0.025	2.5	0.526	6.8	94.5	***79.7***	***12.7***
2.3	10.2	91	0.025	3.33	0.344	6.85	96.6	***75.9***	12.1
2.25	10.5	115	0.05	2	1.22	6.51	87.8	***73.9***	3.38
2.25	10.5	115	0.05	2.5	0.927	6.42	90.9	92.1	1.26
ND	ND	ND	0.05	3.33	ND	ND	ND	ND	ND
2.3	<LOQ	95	0.025	3.33	0.385	6.65	NA	82.2	**10.5**

Note. Concentrations in mg/L, single replicates, 4-hr contact. Initial solution of 10 mg F^-/L ± 2%. 0.25 mg/L standard removed from calibration curves for samples with 2:1 and 2.5:1 ratios. Values in red are outside quality guidelines.

*spike used was lower than recommended (*25-50% original sample value, as opposed to 2-5X).

Figure 4.12

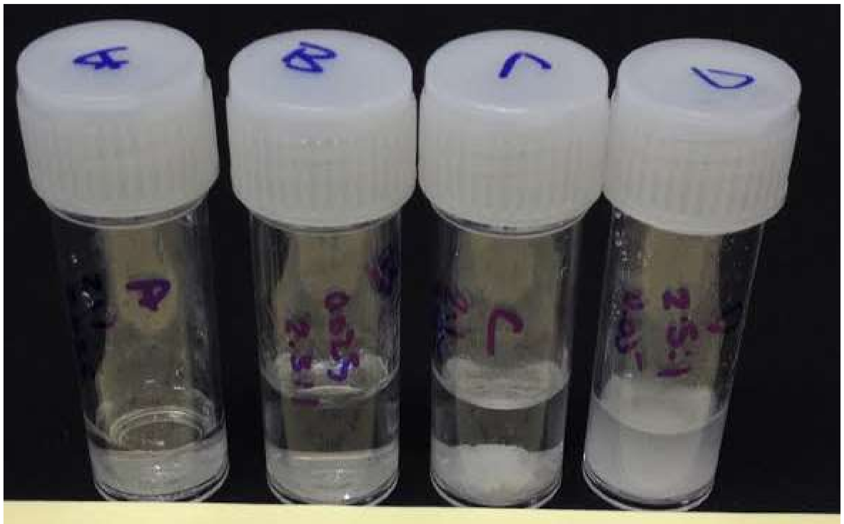
Fluoride Removal from Preliminary Trials with Varied Acid Concentration and/or Sand-Fluid Ratios (Experiment G & I)



Note. % F^- removal from single sand column trials, initial solution of 10 mg F^-/L and various acid concentrations treated with 4-hour contact in columns with sand-to-fluid ratios of 2:1, 2.5:1, or 3.33:1. Raw data in Table 4.8.

Figure 4.13

Precipitate Formation in Some Extracts from Columns with Varied Acid Concentration and/or Sand-Fluid Ratios (Experiment G & I)



Note. Single replicate trial. Extracts approximately 24 hours following column removal. (A) 2:1 ratio with 0.025 M citric acid; (B) 2.5:1 ratio with 0.025 M; (C) 2:1 ratio with 0.05 M; (D) 2.5:1 ratio with 0.05 M. White precipitate is present in the 0.05 M samples only.

This preliminary data suggests that higher sand-to-fluid ratios remove more fluoride, as does a lower acid concentration. Lower acid concentrations would be preferred to avoid formation of white precipitate in extracts. In addition, extracts from less acidic solutions may be less affected by matrix interferences and thus easier to analyse.

4.3.6 EXPERIMENT H – PRELIMINARY TRIAL: SAFETY OF AELD EXTRACTS USING 0.025, 0.05 & 0.1 M ACID

Single columns were filled with 10 mg/L fluoride solution and various acid concentrations. A column loaded with ultrapure water as well as a 'no sand' blank column were included. Observations and conductivity readings of treated extracts are listed in Table 4.9. The yellow colour of the extracts is noted in Figure 4.14 in addition to white precipitate in the 0.05 and 0.1 M acid extracts. The 0.025 M acid and 'water only' extracts contained a small amount of sand but no obvious precipitate.

Table 4.9

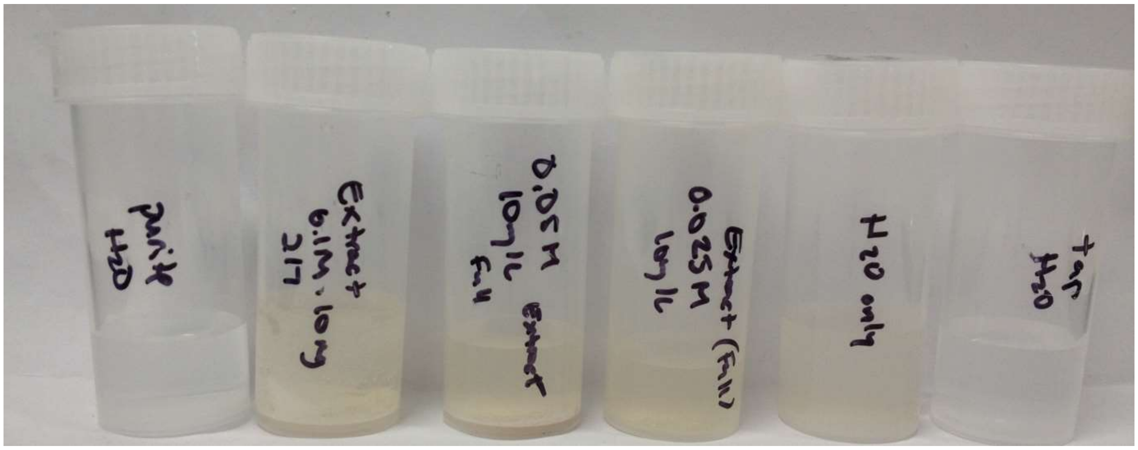
Observations and Conductivity of Extracts with Various Acid Concentrations Before and After Sand Treatment (Experiment H)

Solution	Observations Day After Extraction / weight of extract	pH / temperature		Conductivity Before and after AELD		Est'd TDS	
		Before	After	Before	After	Before	After
0.1 M & 10 mg F^-/L	Obvious white precipitate; 12.57 g extracted	2.0 at 23.5 °C	6.40 at 23.8 °C	3.19 mS/cm at 23.4°C	2.69 mS/cm at 23.2°C	2.04 g/L	1.72 g/L
0.05 M & 10 mg F^-/L	Obvious white precipitate; 11.96 g extracted	2.16 at 24.2 °C	6.71 at 23.4 °C	2182 µS/cm at 22.6°C	2.76 mS/cm at 23.7°C	1.40 g/L	1.77 g/L
0.025 M & 10 mg F^-/L	Sand remnants only; 10.88 g extracted	2.22 at 23.9 °C	6.95 at 23.4 °C	1514 µS/cm at 23.4°C	2.52 mS/cm at 22.6°C	0.97 g/L	1.61 g/L
H_2O only	Sand remnants only; 10.33 g extracted	3.86 at 21.9 °C	8.66 at 24.7 °C	2-5 µS/cm (unstable)	4.92 µS/cm	3.2 mg/L	3.15 mg/L
H_2O (no sand)	Clear; 28.41 g of solution	3.86 at 21.9 °C	4.77 at 23.3 °C	2-5 µS/cm (unstable)	1.03 µS/cm	3.2 mg/L	0.66 mg/L

Note. Single sand column extracts (sand-fluid ratio 3.33:1), using initial solutions of 0.025, 0.05, and 0.1 M citric acid with 10 mg/L fluoride.

Figure 4.14

Extracts from Columns Used with 0.1 & 0.05 M Citric Acid and Four-Hour Contact Depicting Colour and White Precipitate (Experiment H)



Note. Small amount of sand in 0.025 M acid and H_2O only extracts. White precipitate in 0.05 and 0.1 M extracts. Samples placed between ultrapure water (Purite) and tap water for comparative purposes.

As prior, the pH of the solutions increased after treatment with coral sand, to a more neutral and acceptable value. Of interest, there is an apparent correlation between the weight (and thus volume) of extracts and acid concentration; more voluminous extracts were noted with higher concentrations. This may be due to an increase in carbon dioxide generation which was noted in columns with more concentrated acid.

ICP-MS analysis was completed on filtered extracts and results, as well as pH, conductivity, hardness and estimated TDS, are tabulated in Table 4.10. The citric acid used in this experiment was stored for an extended period in glass Schott bottles which had not been acid-washed prior to use and no acidified initial solution was analysed alongside the extracts for comparative purposes. Arsenic and Cr were above maximum allowable values (MAV) whereas Al, Fe, Mn, Ca + Mg (hardness), and TDS exceeded guidelines (GL) for aesthetic purposes.

Table 4.10

Select Trace Elements in Extracts from 3.33:1 Sand-to-Fluid Ratio Columns with Varied Citric Acid Concentrations (Experiment H)

Element	Units	Initial 10 mg F^-/L with Citric Acid				(no sand)	LOQ	Published Limits	
		0.1 M	0.05 M	0.025 M	0 M	0 M blank		MAV	GL
Al	mg/L	***3.36***	***2.39***	<LOQ	<LOQ	<LOQ	2.1		0.1
As^{75}	µg/L	***39.6***	***29***	***22.3***	<LOQ	<LOQ	21	10	
B	µg/L	1300	1010	849	187	11.2	2.1	1400	
Cd	µg/L	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	2.1	4	
Co	µg/L	4.01	3.26	2.42	<LOQ	<LOQ	2.1	NIS	
Cr	µg/L	***396***	***208***	***108***	<LOQ	<LOQ	21	50	
Cu	µg/L	48.5	33.6	24.7	15.4	50.5	2.1	2000	1000
Fe^{56}	mg/L	***2.75***	***1.83***	***1.29***	<LOQ	0.158	0.021		0.2
Mn	µg/L	***327***	***216***	***111***	<LOQ	<LOQ	21	400	40
Mo	µg/L	5.54	4.2	3.95	4.47	<LOQ	2.1	70	
Ni	µg/L	73.3	56.6	43.8	3.44	<LOQ	2.1	80	
Pb	µg/L	<LOQ	<LOQ	<LOQ	<LOQ	3.99	2.1	10	
S	mg/L	53.5	36.8	30.9	22.7	<LOQ	2.1		NIS
Ti	µg/L	24.8	<LOQ	<LOQ	<LOQ	<LOQ	21		NIS
Zn	µg/L	664	436	242	<LOQ	<LOQ	210		1500
Ca	mg/L	***986***	***1520***	***1220***	7.03	0.213	0.21		100-300 Ca + Mg
Mg	mg/L	***373***	***208***	***127***	5.3	<LOQ	0.21		
Na	mg/L	92.7	77.2	71.6	36	<LOQ	0.21		200
K	mg/L	135	134	131	87.6	<LOQ	2.1		NIS
Conductivity	µS/cm	2700	2760	2520	4.92	1.03			See TDS
Est'd TDS	mg/L	***1730***	***1770***	***1610***	3.15	0.66			1000
Hardness		***3990***	***4650***	***4160***	39.3	0.5			200
pH	mg/L	***6.4***	***6.71***	***6.95***	***8.66***	***4.81***			7.0 – 8.0
Temperature	°C	23.8	23.4	23.4	24.7	23.2			cool

		Initial solutions			
Conductivity	µS/cm	3190	2182	1514	6
Est'd TDS	mg/L	2040	1400	969	3.84
pH		2	2.16	2.22	3.86
Temperature	°C	23.4	22.6	22.6	22

Note. Elements measured (with ICP-MS) in extracts from sand columns loaded with 10 mg F^-/L solutions after 4 hours contact (n=1). Highlighted values are above NZ limits (MAV in red, GL in blue) (MOH, 2018). NIS: not in standard.

4.3.7 EXPERIMENT J – AELD: 2:1 SAND-FLUID RATIO; 0.025 M ACID; 4 & 8 HR CONTACT

Results from extracts collected 4 or 8 hours after loading triplicate columns with 0.025 M citric acid and 10 mg F^-/L solution are tabulated in Table 4.11 and depicted in Figure 4.15. The pH of the initial solution was between 2.2 to 2.4 and the final temperature of analysed samples was 19.5 ± 1 °C. The calibration standard of 0.25 mg/L was removed from the calibration curves to improve results. All quality control measures were adequate except for slightly low standardised percent recovery of day 1, 8-hour column extracts. In spite of the lower acid concentration used (0.025 M), white precipitate formed overnight in extracts from day 1 and 2.

Trends can be noted in the data, whereby an increase in column use (in days) correlates with: increase in fluoride concentration; increase in standardised % recovery (for the most part); and lack of precipitate formation over time. Regardless of citric acid concentration used or contact time, sand columns could only be used twice to reduce fluoride from 10 mg/L to below the MAV of 1.5 mg/L (Figure 4.15). The columns were successful in remediating the low pH of initial acidified fluoride solution to neutral pH (6.5 – 7) over all four consecutive days of use.

Table 4.11

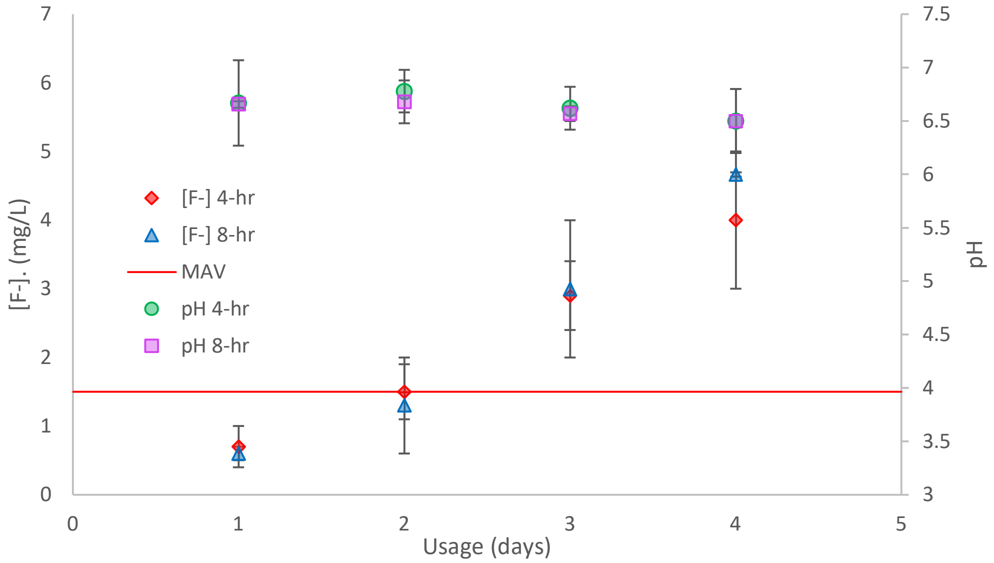
Results of AELD in 2:1 Sand-Fluid Ratio Columns with 0.025 M Acid, 4 & 8 Hour Contact, Reused Over Four Days (Experiment J)

Contact Time (hr)	n (days)	F^- Concentration (mg/L)	2SD	Standardised % recovery	pH of extracts Ave	2SD	$\%F^-$ Removal Ave	2SD	White Precipitate?
4	1	0.7	± 0.3	84-91	6.67	± 0.4	93.5	± 0.9	Yes
4	2	1.5	± 0.4	92-96	6.78	± 0.2	86	± 2	Yes
4	3	2.9	± 0.5	99-102	6.62	± 0.2	71	± 2	Nil
4	4	4	± 1	96-97	6.5	± 0.3	56	± 4	Nil
8	1	0.6	± 0.1	***79***-84	6.66	± 0.03	94	± 1	Yes
8	2	1.3	± 0.7	88-93	6.68	± 0.2	86	± 2	Yes-slight
8	3	3	± 1	100-102	6.57	± 0.07	71	± 9	Nil
8	4	4.67*	± 0.03	98-99	6.5	± 0.3	54	± 0.3	Nil

Note. Initial solution of 10 mg F^-/L, columns reused over 4 days. Average ± 2SD (n=3, except where indicated * n = 2). Value in red is slightly below quality guideline (80 % < P' < 120 %).

Figure 4.15

Final pH and Fluoride Concentration of Extracts vs. Use of 2:1 Sand-Fluid Ratio Columns According to Contact Time (Experiment J)



Note. Initial solution of 10 mg F^-/L prepared in 0.025 M citric acid with 4 and 8 hour of contact time. Average ± 2SD (n=3, n=2 on day 4, 8 hours).

4.3.8 EXPERIMENT K – AELD: 5:1 SAND-FLUID RATIO; 0.025 & 0.05 M ACID; THREE TYPES OF SAND

The general characteristics and composition of the initial solutions as well as the measured pH and temperature from the extracts are detailed in Table 4.12. The measured fluoride concentration from all initial solutions as well as the control column extracts were within 5 % error of the calculated initial fluoride concentration. Detailed figures of final pH and fluoride concentration of extracts from three types of sand columns, using two acid concentrations following repeated use are presented in Appendix G Figures G 1 to G 3. The overall data is condensed into Figure 4.16 and a 2-per moving average trendline (available in Excel) was added to assist visualisation. All quality control measures were within specified limits except those highlighted in Appendix G and discussed here.

Table 4.12

Composition of Initial Solutions and Final pH and Temperature of Extracts from 5:1 Sand-to-Fluid Ratio Columns of Three Sand Types (Experiment K)

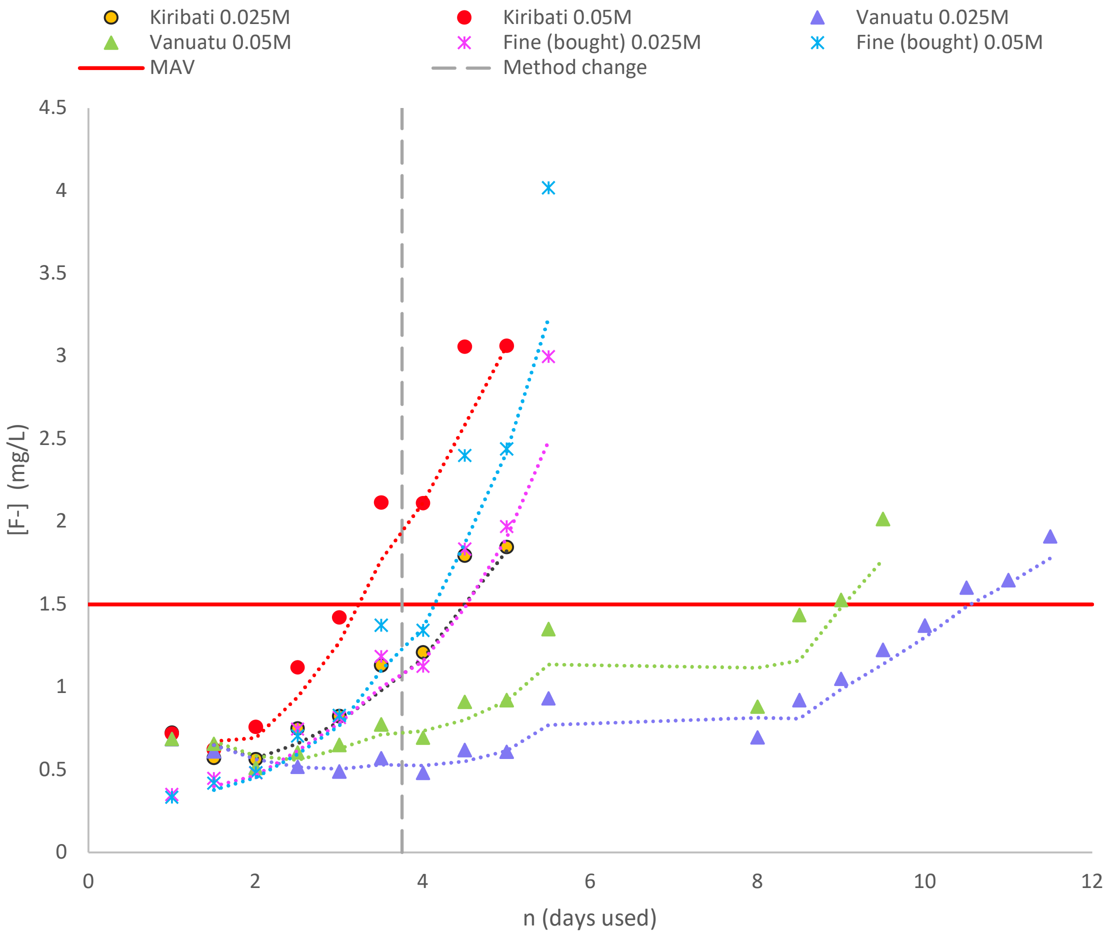
Sand	Initial solution composition				Extracts	
Type	[F$^-$] (mg/L)	Citric Acid (M)	pH	Temp. (°C)	pH	Temp. (°C)
Kiribati	10.0 ± 0.1	0.025 ± 1%	2.38 ± 0.03	19.3 – 24.4	6.57 – 7.08	19.5 – 20.4
		0.05 ± 1%	2.23 ± 0.07	19.6 – 21.1	6.59 – 6.91	19.5 – 20.7
Vanuatu	10.0 ± 0.1	0.025 ± 1%	2.41 ± 0.05	18.9 – 20.4	6.71 – 7.24	19 – 21
		0.05 ± 1%	2.28 ± 0.02	19.8 – 20.5	6.51 – 6.95	19 – 21
Fine	10.0 ± 0.2	0.025 M ± 4%	2.46 ± 0.1	19.6 – 21.2	6.50 – 7.15	19.8 – 20.5
sand		0.05 M ± 1%	2.37 ± 0.1	19.6 – 21.2	6.55 – 7.21	19.8 – 20.5

Note. Concentrations in mg/L. Error are maximum and minimum values, calculated in % or units, as indicated. Fine sand is store-bought coral sand.

Due to significant matrix interference prior to day 4, FISE samples from days 1-4 were also diluted 1:1 with ultrapure water and the resulting fluoride concentrations back-calculated. These values were always slightly higher than those measured in non-dilute FISE samples and dilute FISE samples had improved percent recoveries (data not shown). The decreased matrix interference in diluted samples implies that measured concentrations would be closer to their true value. These back-calculated values were therefore plotted up to day 4 In Figure 4.16 but matrix interference still affected results on day 1, 1.5, and 2 (refer brackets in Figures G1 and G3 in Appendix G). The dotted line labelled 'method change' in all figures demarks the point where fluoride analysis was undertaken on full extracts. The small dip or flatlining in the data at this point is likely due to the methodology change and subsequent change in percent fluoride recovery from stronger matrix interference in non-dilute FISE samples. In spite of this improvement, some interference occurred from day 4 onwards as standardised percent recoveries were consistently lower than comparative standards, although within quality limit (80 % < P' < 120 %).

Figure 4.16

Final Fluoride Concentration of Extracts vs. Column Use According to Sand Type and Acid Concentration Used (5:1 Sand-Fluid Ratio – Experiment K)



Note. Columns used twice daily with 4-hour contact time. Average of n=3 (except day 1, use 1 where n=1 or n=2); 2-per-moving-average trendline added. Errors omitted for clarity but present in Appendix G – Figure G1 to Figure G 3). Standardised percent recovery (P') of some extracts on days 1-3 were < 80%.

The first major trend observed was that Vanuatu sands performed much better than other sand types, regardless of acid concentration used. The columns could be reused more often to reduce the fluoride concentration from an initial value of 10 mg/L to below the MAV of 1.5 mg/L. Fine sand columns could be reused for 4 days; Kiribati sand columns for 3 to 3.5 days (depending on acid concentration); and Vanuatu sand columns could be reused for at least five days. The gap in data for days 6 and 7 in the Vanuatu results are weekend days, where no column use was undertaken. The fact that the columns could be used an additional two days on top of the original 5, was likely assisted by this 2-day 'incubation' period where any fluoride present in the fluid trapped in the sand would have additional time to be absorbed and removed prior to the experiment continuing on week 2.

Secondly, columns filled with 0.025 M acid solutions outperformed those with higher 0.05 M solution. This trend is applicable to all sand types, though the difference is not significant for fine store-bought sand, given the overlapping error below the MAV (refer Appendix G – Figure G 1). The Kiribati and store-bought sands performed quite similarly when the initial solutions contained 0.025 M citric acid however, the store-bought sand performed best when the acid was raised to 0.05 M.

As noted prior, coral sand treatment neutralised acidic pH: the pH of sample extracts was just below neutral throughout the entire use of the treatment system, demonstrating the ability of coral sand to neutralise the acidic nature of the initial solutions, which varied between 2.2 to 2.5. Precipitate developed overnight in the first extract removed from the Kiribati and fine sand columns with 0.05 M acid however none was visible using 0.025 M acid. In contrast, Vanuatu sand column extracts did not have obvious precipitate develop overnight, regardless of acid concentration. With regards to the volume taken up by a particular weight of sand, the same weight of Vanuatu sand took up larger volumes in the columns. Additionally, it also appeared that higher acid concentrations correlated with more voluminous extracts, which was noted on the first use only, likely as these extracts were always significantly smaller in volumes than subsequent uses (refer diagram in Appendix H for additional details, if required).

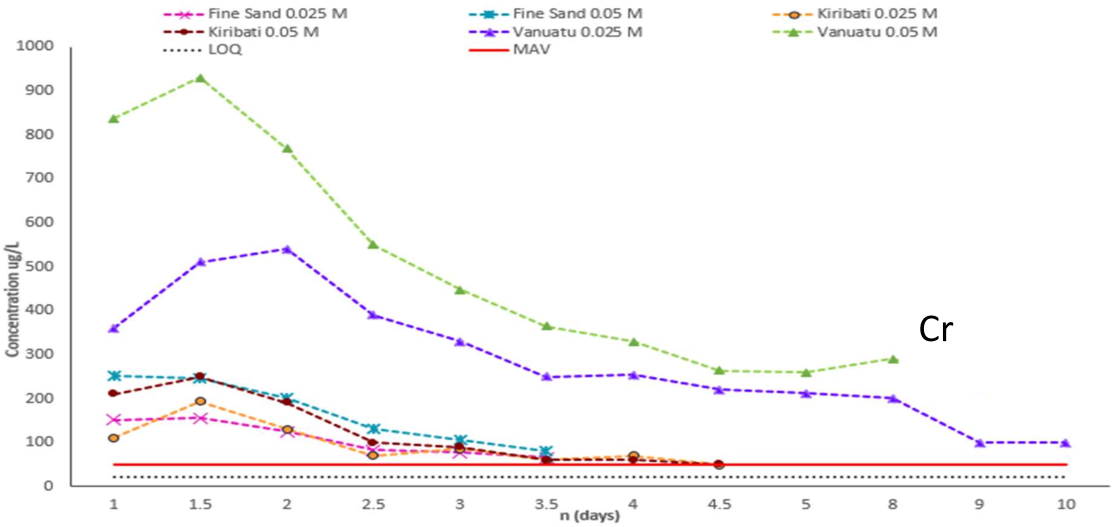
4.3.9 EXPERIMENT K – TRACE ELEMENTS IN AELD EXTRACTS FROM 5:1 SAND-FLUID RATIO COLUMNS

Select extracts were analysed with ICP-MS to ascertain the presence and concentrations of potentially problematic elements for drinking water safety and aesthetics. Six detailed summary tables for fine store-bought sand, Kiribati sand and Vanuatu sand columns are presented in Appendix G (Table G 8 to Table G 13). Concentrations measured in initial solutions or control column extracts, whichever highest, were deducted from the sand column extracts and values presented in the tables. Results are juxtaposed to aesthetic guidelines (GL) and maximum allowable values (MAV) for elements of health concern, as published by the MOH (2018). None of the initial solutions or control column extracts contained elements above standards and most were below the LOQ. These elements present (Cu; Fe; Mg; Na; Ni; Zn), were at least five times lower than published limits. A gross comparison of values from 0.025 M vs. 0.05 M acid extracts indicate that, for the most part, slightly higher contaminant concentrations are present in extracts with more acid.

A summary of significant trace elements present in the treated extracts is found in Table 4.13. This table lists elements above limit and length of time above limit (in days, or LT if element is present for the duration of the trial). The value in brackets is the highest average concentration measured, and was usually measured within the first 1 to 3 uses of the columns. Generally, all element concentrations decreased with usage and this is visible in Figure 4.17 to Figure 4.20.

Figure 4.17

Concentration of Chromium in Extracts vs. Repeated Column Use with Citric Acid (Experiment K)



Note. 5:1 sand-fluid ratio columns with varied sand type were reused multiple times with initial solution of 10 mg F$^-$/L and 0.025 or 0.05 M acid. Columns were used twice daily, with 4-hr contact (no use on days 6 & 7). Replicates and errors detailed in Appendix G (Table G 8 to Table G 13).

Table 4.13

Trace Elements Above Published Limits in Extracts Following Repeated Use of Columns of Three Sand Types with 0.025 or 0.05 M Citric Acid (Experiment K)

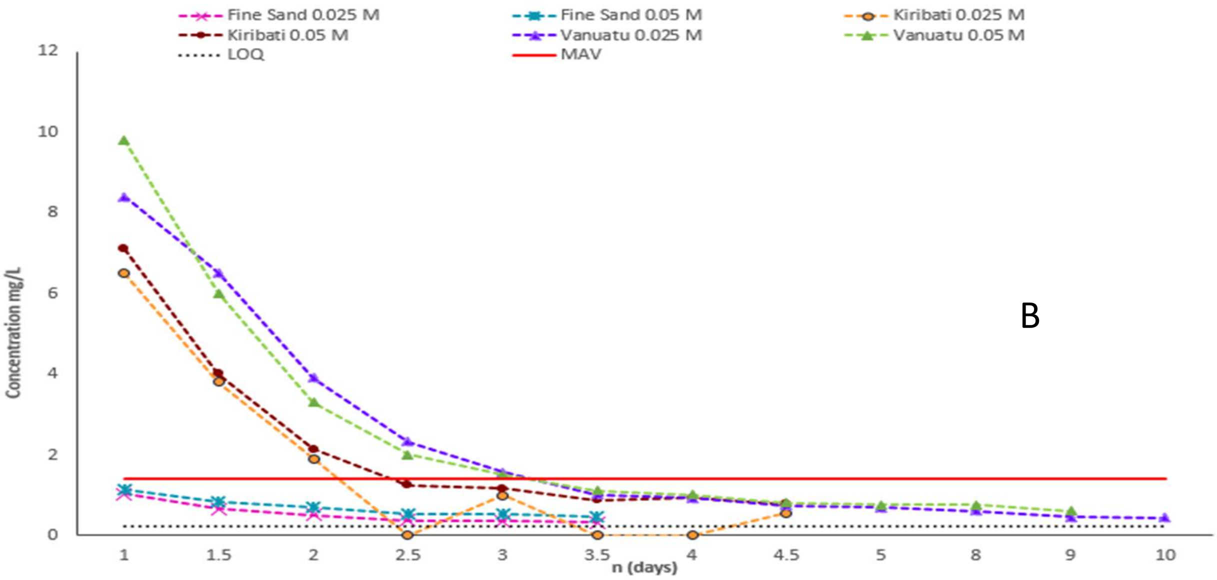
Element	Published Limit		Units	Bought (fine)		Kiribati		Vanuatu	
	MAV	*GL*		0.025 M	0.05 M	0.025 M	0.05 M	0.025 M	0.05 M
As$^{75-91}$	10		µg/L	Day 1-2 (31.4)	Day 1-3 (38.9)	LT (570)	LT (640)	LT (99)	LT (114)
B	1.4		mg/L	---	---	Day 1-2 (6.5)	Day 1-2 (7.1)	Day 1-3 (8.4)	Day 1-3 (9.8)
Cr	50		µg/L	LT (155)	LT (251)	LT (194)	LT (250)	LT (540)	LT (930)
Ni	80		µg/L	---	---	Day 1 (165)	Day 1 (180)	Day 1 (92)	Day 1 (140)
Al		0.1	mg/L	LT (2.43)	LT (2.38)	LT (1.33)	LT (1.3)	LT (2.5)	LT (3.2)
Ca		100-300	mg/L	LT (1374)	LT (1552)	LT (1490)	LT (2240)	LT (1250)	LT (2350)
Cu	2000	1000	µg/L	---	---	~*Day 1* (1000)	~*Day 1* (1000)	---	---
Fe		0.2	mg/L	LT (1.92)	LT (2.27)	LT (6.19)	LT (6.7)	LT (2.49)	LT (3.449)
Mg		100-300	mg/L	LT (142)	LT (205)	LT (670)	LT (730)	LT (780)	LT (830)
Mn	400	40	µg/L	LT (151)	LT (238)	LT (183)	LT (261.1)	LT (280)	**LT* (490)**
Na		200	mg/L	---	---	Day 1-2 (3300)	Day 1-2 (3000)	Day 1-3 (7800)	Day 1-3 (7000)

Note: Initial solution of 10 mg F^-/L with 0.025 or 0.05 M citric acid. Number of days where extracts were above limit is listed (LT indicates above limit for duration of the trial). Number in brackets is highest average value measured. MAV (red) and GL (blue) according to the MOH (2018).

~ = value is at the published limit. * Mn above MAV on day 1, and above GL for duration of the trial.

Figure 4.18

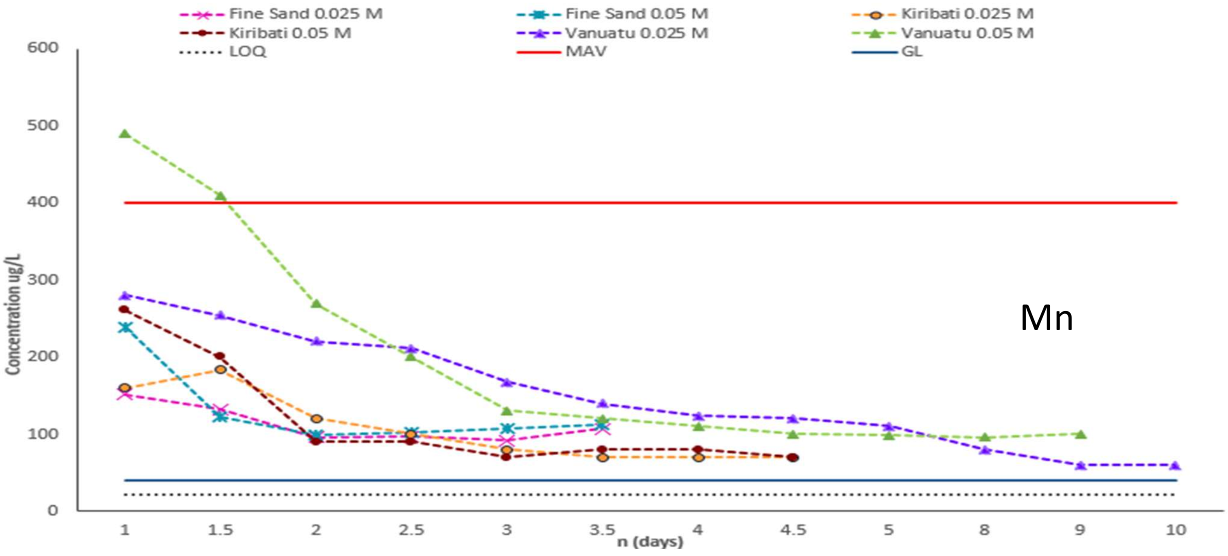
Concentration of Boron in Extracts vs. Repeated Column Use with Citric Acid (Experiment K)



Note. 5:1 sand-fluid ratio columns with varied sand type were reused multiple times with initial solution of 10 mg F^-/L and 0.025 or 0.05 M acid. Columns were used twice daily, with 4-hr contact (no use on days 6 & 7). Replicates and errors detailed in Appendix G (Table G 8 to Table G 13).

Figure 4.19

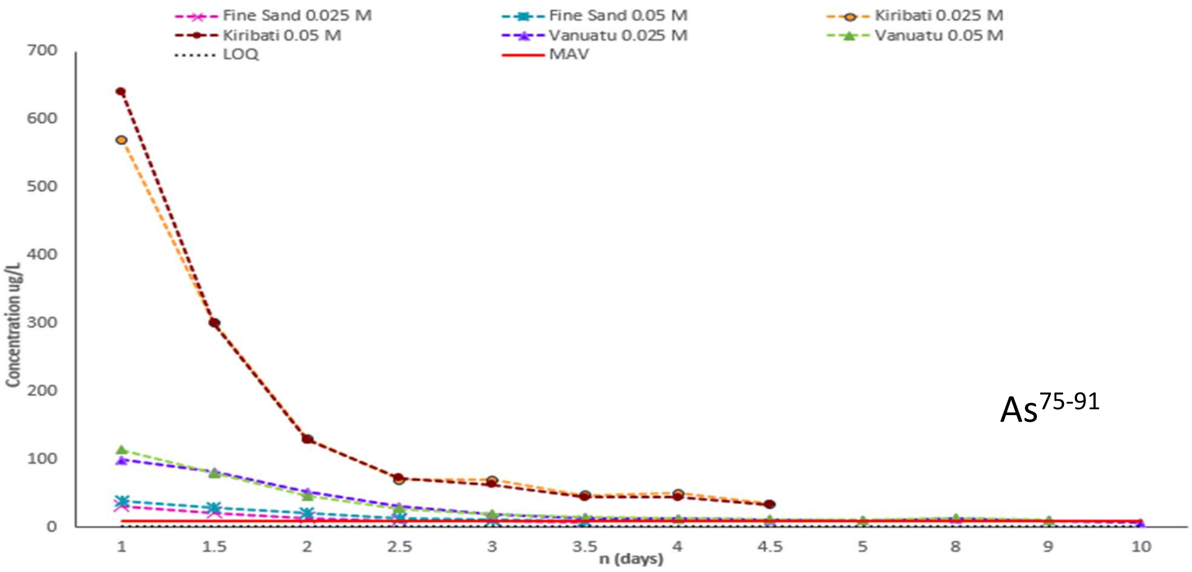
Concentration of Manganese in Extracts vs. Repeated Column Use with Citric Acid (Experiment K)



Note. 5:1 sand-fluid ratio columns with varied sand type were reused multiple times with initial solution of 10 mg F^-/L and 0.025 or 0.05 M acid. Columns were used twice daily, with 4-hr contact (no use on days 6 & 7). Replicates and errors detailed in Appendix G (Table G 8 to Table G 13).

Figure 4.20

Concentration of Arsenic in Extracts vs. Repeated Column Use with Citric Acid (Experiment K)



Note. 5:1 sand-fluid ratio columns with varied sand type were reused multiple times with initial solution of 10 mg F$^-$/L and 0.025 or 0.05 M acid. Columns were used twice daily, with 4-hr contact (no use on days 6 & 7). Replicates and errors detailed in Appendix G (Table G 8 to Table G 13).

Of all elements measured, chromium is the most concerning as it is present in all extracts at both acid concentrations, for the entire duration of the trial (or 'long-term' as referred to herein). This is evident in Figure 4.17 where its concentration in treated extracts is plotted over use (in days). Aluminium and Fe are present long-term in all sand extracts and would explain the matrix interference issues detailed prior. Sodium and boron are above-limit only in Pacific sands, and only during the first few days of usage. These two elements may be less prevalent in Kiribati sands as opposed to Vanuatu sands, as they are above MAV for an extra day in the Vanuatu sand extracts. The boron concentration present in sand column extracts over the duration of the trial is depicted in Figure 4.18 and the decreasing concentration with increased column usage is obvious. Copper is present at or near the published limit in Kiribati sand extracts but the large 2SD renders it unclear if copper truly exceeded guideline. Calcium is present long-term but this is expected as citric acid reacts with the sand ($CaCO_3$), releasing the ion. Manganese is only above the MAV in the 0.05 M Vanuatu sand extracts on day 1, and above aesthetic guidelines for all sands long term: this is illustrated in Figure 4.19. As illustrated in Figure 4.20, arsenic is persistently above MAV for Pacific sand extracts (and especially elevated in Kiribati sand), but only above the MAV in store bought sand for 2 or 3 days.

4.4 DISCUSSION – BATCH AND COLUMN EXPERIMENTS

Acid enhanced lime defluoridation is effective in reducing fluoride in contaminated waters, however little is known about the ability of coral sand to be used as an adsorbent with this technique. Investigation of operational variables including contact time, adsorbent dose, and acid concentration was undertaken with the aim of creating an effective, simple, and reusable system able to produce safe, treated water with fluoride below the safe limit of 1.5 mg/L.

4.4.1 ADSORPTION CAPACITY OF CORAL SAND

The adsorption capacity of coral sand determined using isotherm experiments, with and without 0.025 M citric acid and an adsorbent dose of 1 g / 6 mL, was significantly lower than published results and further supports the notion that the overall adsorption capacity of calcium carbonate is poor (Fan et al., 2003; Gogoi & Dutta, 2015; Nath & Dutta, 2010a, 2012). The best adsorption capacity obtained in this study in non-acidified environment was 0.0335 mg/g with an equilibrium fluoride concentration (C_e) of 194 mg/L (from the preliminary isotherm experiment reported in Appendix F – Table F 1). In acidified solutions, this value was between 0.0084 to 0.11 mg/g at an equilibrium concentration between 10 mg/L up to 32 mg/L, where mass precipitation occurred.

Comparisons are made herein between limestone and coral sand as high purity limestone is primarily calcite or aragonite (Spiropoulos, 1985). The reported adsorption capacity of limestone varies greatly between investigators as it is influenced by experimental variables including adsorbent dose, initial fluoride concentration (C_o), pH, etc. Some report the adsorption capacity (q_e) established experimentally whereas others, the maximum adsorption capacity (Q_o) based on Langmuir modelling, even if experimental data does not fit the model very well. The fluoride adsorption capacity (q_e) of calcium carbonate encountered during literature review ranged from 0.0035 to over 30 mg/g when the initial fluoride concentration was 0.0634 and 100 mg/L respectively (Fan et al., 2003; Jain & Jayaram, 2009). Batch studies conducted with a slightly higher adsorbent dose to that used here (1 g / 5 mL) and smaller particles of 63 to 125 µm, produced a q_e of 0.38 mg/g when the initial fluoride concentration was 100 mg/L (Labastida et al., 2017). This q_e value is 10-fold better than results obtained here with coral sand. The poor fluoride adsorption capacity of coral sand may be due to several reasons. Firstly, there is some level of error present in the calculation of q_e, based on whether the initial fluoride concentration (C_o) used was measured or calculated from the prepared fluoride solution. This error affected results presented here by as much as a factor of 2 (as noted in the preliminary isotherm experiment detailed in Appendix F). Secondly, the coral sand had lower specific surface area compared to many limestone particles used by researchers. The average diameter of particles was 552 µm compared to diameters as low as ~63 to 125 µm (Jain & Jayaram, 2009; Labastida et al., 2017). Most authors state that fluoride removal is generally more effective on smaller particles (Camlek, 2017; Nath & Dutta, 2010a; Wong & Stenstrom, 2018), with an exception encountered by Labastida et al. (2017) where only two of three types of limestone had increased removal with smaller particles. Thirdly, the coral sand used here contained fluoride prior to AELD experiments.

4.4.1.1 PRE-EXISTING FLUORIDE CONTENT OF CORAL SAND

The pre-existing presence of fluoride in coral sand was first noted in the isotherm experiment conducted in absence of acid, where fluoride was released from store-bought sand into initial solutions containing low fluoride (< 1.9 mg/L). This release was more evident during the acidified trials where fluoride was desorbed up to an equilibrium concentration of 5.0 mg/L. Consequentially, the fluoride adsorption capacity of coral sand as noted herein was poor, because its capacity was partly taken up by fluoride prior to starting defluoridation trials.

Further review identified that coral sand can contain fluoride. Analysis of soils from the Red Sea "show clearly that fluoride content and distribution are generally associated with calcium and calcium carbonate contents of sediments" (Abu-Hilal, 1986, p. 230). This indicates that $CaCO_3$ tends to retain fluoride in natural environments (Labastida et al., 2017; Reardon & Wang, 2000), and seawater contains an appreciable fluoride concentration of 1.3 mg/L (Millero et al., 2008). If local water sources are contaminated with elevated concentrations of fluoride, it logically follows that nearby environments and materials, such as beaches and coral sand, would also be affected.

Limestone, in contrast, does not appear to contain appreciable concentrations of fluoride. Research by Fan et al. (2003), examined fluoride removal with calcite at incredibly low fluoride concentrations and adsorption (not desorption) occurred throughout their study. This supports the idea that limestone is not a relevant source of fluoride. This was further stated by Mondal et al. (2016) and demonstrated by Labastida et al. (2017). Batch treatment of limestone in 1 g / 5 mL solid-to-water ratio provided a final fluoride concentration of 0.2 mg/L with FISE analytical method (this concentration is at or near the limit of quantitation of the method). The absorption study presented here, in contrast, was conducted with similar but even lower adsorbent doses of 1 g / 6 mL and a final concentration of 0.47 mg F$^-$/L was measured in treated water. This is more than twice the concentration obtained with limestone reported by Labastida et al. (2017) and further supports the finding that store-bought coral sand contained fluoride which can desorb in the right conditions. With regards to trace analysis of calcium carbonate material prior to defluoridation, Turner et al. (2005) performed XRF analysis on limestone from New South Wales (Australia) and did not detect fluoride at concentrations above 40 ppm.

The desorption of fluoride from sand used in this isotherm study meant that fitting data onto models and comparing results between acidified and non-acidified solutions was not possible. Many data points at low fluoride concentrations were within the desorption range ($Y < 0$ in Figure 4.7), producing negative q_e values that cannot be used in log form. Attempts to transform the data by using a '$q_e + 1$' method skewed and misrepresented results. Other data points from the acidified trials were in the precipitation range ($C_e >$ 31-32 mg/L – refer dotted grey line in Figure 4.6), where adsorption is negligeable in terms of fluoride removal mechanism.

In summary, the adsorption capacity of coral sand in the tested conditions was remarkably low and the sand, as received, was not an efficient fluoride sorbent. 0.025 M citric acid improved the adsorption of fluoride onto coral sand up to a maximum amount of 31 – 32 mg/L, where mass precipitation occurred. Acid also greatly enhanced desorption of fluoride already present in the sand into solutions containing less than 5.0 mg/L. The matrix recovery experiment confirmed the presence of significant fluoride in the store-bought coral sand which released into water for a minimum of three days.

4.4.2 FLUORIDE REMOVAL EFFICIENCY IN COLUMNS WITHOUT CITRIC ACID

A single column trial with high sand-fluid ratio (varying from 3:1 to 9:1), could be reused at least three times without acid, to remove up to circa 60 % fluoride from initial solutions of 10 mg/L. These results are similar to those reported in the literature. For example, Labastida et al. (2017) obtained 60-65 % fluoride removal for a two-week period, from limestone-filled columns in absence of acid. Their experiment differed substantially from the current study, in that an initial fluoride solution of only 3 mg/L was continuously fed through a percolation column filled with 0.84 to 1.41 mm particles. More similar to the study conducted here, is a limestone chip reactor which removed ca 40 % fluoride, 12-hours after being filled with a pore volume of 10 mg/L fluoride solution (Nath & Dutta, 2010a). This reactor contained larger particles of 2-3 mm which may explain the lower % fluoride removal compared to the circa 60 % obtained here.

4.4.3 FLUORIDE REMOVAL EFFICIENCY IN COLUMNS WITH CITRIC ACID

The 5:1 sand-fluid ratio column studies conducted here using a 4-hour contact time and 0.025 M citric acid, could reduce fluoride from 10 mg/L to below the MAV of 1.5 mg/L, twice daily, for at least 3.5 to 7 days. These results are comparable to the successful results of Nath and Dutta (2010a) described above when using AELD with 0.1 M citric acid, particularly when considering the shorter contact time, lower acid concentration, and likely smaller sand-fluid ratio used here. The authors did not report their sand-fluid ratio nor the dimensions of their reactor in this particular article, but coarser particles (2-3 mm) and only a pore volume of fluid was used. (Using a pore-volume only, generally maximises the sand-fluid ratio.) Their system removed ca 85 % fluoride, from 10 mg/L to 1.5 mg/L, for an estimated 9 days using 0.1 M citric acid and 12-hour contact. (The uncertainty in this statement relates to difficulties in interpreting their results from very small figures and lack of numerical data.)

4.4.3.1 MORPHOLOGY OF SANDS BEFORE AND AFTER AELD

SEM micrograms at 150X magnification illustrate the large intra-sample variability in surface characteristics and appearance of sands. No obvious differences were noted in surface morphology between sand types, except that the Vanuatu sand particles were larger, which is apparent from the mean particle size of the sands. Images pre- and post-AELD also did not reveal any obvious differences from the treatment process. This lack of findings could be caused by the magnification used. Crystals on the surface of citric acid treated limestone were noted by Nath and Dutta (2010a) using 6000X magnification. The SEM-EDS methodology used here could not produce non-blurry images above 1500X magnification. The lack of morphological differences may also be due to small subsample size (i.e. three particles from 75 g of sand) whereby chance, none of the imaged particles displayed characteristic changes due to acid treatment. Slight reduction in sub-10 µm structures on coral sand surfaces was noted by Camlek (2017) after AELD, although he used acetic acid not citric acid in his study. Results obtained are consistent with Camlek (2017) and also those of Nath et al. (2011) who specifically studied the morphology of calcite after AELD with acetic and citric acids. Their study concluded that acetic acid has a greater morphological effect on limestone compared to citric acid and that the only significant change in morphology after AELD was deposition of precipitate on particles (Nath et al., 2011). Success in locating morphological differences pre- and post-AELD may have been aided had particles with a powdery appearance been specifically targeted, as opposed to imaging a homogenised subsample of all the used sand from a column, following drying and thorough mixing. This process, of mixing and breaking up sand clumps to obtain a homogenous sample of treated sand, dislodged white powder which was noted and collected from the containers. XRD analysis of this powder revealed a complex mixture, which likely contained a hydrate of calcium citrate (M. Polson, personal communication, April 28, 2021). Neither calcium carbonate (in calcite or aragonite form) nor fluorite (i.e. CaF_2, the precipitation product expected from the defluoridation process with $CaCO_3$) were obviously present in the mixture. These results align with those of Nath et al. (2011) who used citric acid in AELD and determined the white powder to be calcium citrate. In addition, they applied a lengthy procedure to isolate and detect the CaF_2 present in much smaller amounts in the white powder.

4.4.3.2 WHITE PRECIPITATE FORMATION IN EXTRACTS

The addition of acid to initial fluoride solution and subsequent coral sand treatment had several effects, including the formation of white precipitate in some extracts, a few hours following removal. It is uncertain what combination of conditions caused precipitation as it did not follow an obvious trend. The time delay in formation may be due to temperature decrease following extraction as adsorption is exothermic (Mondal et al., 2016); or a gradual pH change from exposure to ambient air, and/or removing the source of CO_3^- (i.e. the sand). This precipitation effect was often more substantial in newer columns and with higher initial acid concentrations (0.05 M or 0.1 M) compared to low (0.025 M), but not always the case (as was noted in Experiments F, G & I).

4.4.3.3 MATRIX INTERFERENCE

The presence of acid also caused significant matrix interference issues that were not present in non-acidified extracts. This interference would artificially lower fluoride concentration measured and in turn, artificially enhance removal rates. This effect was particularly problematic for Experiment F, (see Table 4.7) using 0.05 and 0.1 M acid where the standardised percent fluoride recoveries were too low (P’< 80 %). As a result, the fluoride analysis method was modified. The interference may be more substantial in more highly acidified solution extracts, but this trend was not consistent throughout the study. The likely cause of the interference is that the addition of acid releases contaminants present in the sand more effectively, which increases the concentration of ions in solution. Interference of ions with fluoride measurement is well documented and the FISE method is particularly sensitive to Al, B, Fe, and OH^- (ASTM, 2016; Baird & Bridgewater, 2017; EDT directION, n.d.-b). Ions in solution may bind with fluoride and once bound, fluoride is undetected by the electrode. The correlation in contaminant concentration in extracts and the addition of acid or increase in acid concentration can be noted directly in Table 4.10. Comparison of trace element results from 0.025 and 0.05 M acid conducted in Experiment K on three types of sands (which are detailed in Table G 8 to G 13 in Appendix G), also generally supports this notion. Select elements presented in Figure 4.17 to Figure 4.20 also illustrate this broad trend. Visual observations also suggested an increase in yellow colouration of extracts with increased acid concentration (see Figure 4.11 and Figure 4.14), which could be indicative of increased contaminant concentrations such as iron.

4.4.4 EFFECT OF ACID CONCENTRATION

4.4.4.1 INCREASED ACID – REDUCES FLUORIDE REMOVAL EFFICIENCY

Results of preliminary trials (Experiment G & I) using various sand-to-fluid ratios and acid concentrations contradicted findings from most published AELD studies, whereby increased acid concentration enhanced fluoride removal (M. Ashworth, personal communication [Pioneer], 2021; Nath & Dutta, 2010a, 2012). The increase in fluoride removal with lower acid concentrations was confirmed multiple times here with triplicate column experiments, using 0.025 & 0.05 M citric acid and three types of sand. This major contradiction could be attributed to one or both of the following reasons.

<u>Pre-existing fluoride in coral sand:</u> As established during the isotherm and matrix recovery experiments, the coral sand already contained fluoride. The fluoride present desorbed more extensively into solutions of low fluoride concentration, especially in the presence of acid. As mentioned, limestone appears to be free of fluoride contamination. The only known AELD studies using coral sand (Camlek, 2017) did not investigate the process in low fluoride concentrations (i.e. 10 mg/L was used) and therefore would not have encountered this desorption phenomenon. Further research conducted at ESR did however, investigate fluoride removal at various acetic acid concentrations (0; 0.025; 0.05; 0.075, and 0.1 M) which resulted in fluoride removal reaching a

maximal capacity value (M. Ashworth, personal communication [*Pioneer*], 2021). Results did not indicate a decrease in fluoride removal efficiency with increased acid concentration.

<u>% extractable volume:</u> (Refer Appendix H for illustration if required) During a preliminary trial of ICP-MS analysis of single column extracts (refer Experiment H), an increase in acid concentration correlated with an increase in weight, and thus volume of extracts recovered (with slight error given a small amount of sand escaped the columns). It is likely that more concentrated acid generates more gas, which aerates the sand pack sufficiently to alter the extractable volume from columns (refer diagram in Appendix H for visual representation if required). This factor, referred to as '% extractable volume', was not encountered during the literature review and thus not taken into account or examined at depth here. Only in hindsight, when trying to decipher counterintuitive results obtained in this study, was it noted. This increase in extracted volume correlated with an increase in final fluoride concentration of extracts and is broached in more detail following Experiment L (refer end of Section 5.1).

4.4.4.2 INCREASED ACID – QUESTIONABLE ENHANCEMENT OF MATRIX INTERFERENCE

The standardised % recovery obtained with lower acid concentration (i.e. 0.025 M) were sometimes slightly better than more acidic solutions (i.e. 0.1 M and possibly 0.05 M) but not always the case. A lower standard % recovery with higher acid concentrations would likely be caused by more acidic solutions extracting contaminants from sand more efficiently, increasing the concentration of dissolved ions in the extracts and finally interfering with electrode measurement. This hypothesis is supported by ICP-MS data from preliminary trials (Experiment G & I) as well as the 5:1 sand-fluid ratio columns (Experiment K) using three types of sand: for most elements, slightly higher contaminant concentrations in extracts are correlated with more acidic solutions (data in Appendix G – Tables G 8 to G 13 and four elements are graphically represented in Figure 4.17 to Figure 4.20). However, correlation between higher acid concentration and lower % recoveries was not consistent throughout all experiments.

4.4.4.3 INCREASED ACID – INCREASED PRECIPITATION IN EXTRACTS

The use of lower acid concentrations (0.025 M) in initial solutions seemed to prevent or at least reduce the formation of precipitate in extracts following sand removal. Precipitation was generally more prevalent in more acidic initial solutions (i.e. 0.1 and 0.05 M), particularly when the sand treatment system was newer, which also happened to coincide with when fluoride adsorption was at its highest. However, some exceptions were noted and could be related to contact time. In spite of using low 0.025 M acid, precipitation developed in some extracts from the 5:1 sand columns, a short time following removal (i.e. overnight). Obvious precipitation in extracts using 0.025 M solution generally occurred on the first use of the column but some extracts required longer than an overnight period to precipitate.

4.4.5 EFFECT OF CONTACT TIME

Increasing contact or residence time has been reported to increase fluoride removal (Fu, 2014; Gogoi et al., 2015; Nath & Dutta, 2010b). Varying the time (4 vs. 8 hours) in the 2:1 sand-fluid ratio experiments did not result in a significant difference in final fluoride concentration of extracts. Though the contact time was doubled, this was evidently too short to significantly impact fluoride removal. It has been stated that AELD by limestone column filtration is a long process taking over 20 hours (Reardon & Wang, 2000), which is particularly relevant in this study given the static nature of the columns. Data reported by Camlek (2017) using coral sand, showed an 8 % increase in fluoride removal from non-acidified solution when the residence time was increased from 4 to 24 hours. However, given the studies were batch agitated experiments, comparison of results with experiments conducted here is not necessarily equitable.

Studies with AELD and oxalic acid resulted in enhanced fluoride removal when longer contact times were used (6 vs. 24 hours), particularly with very low acid concentrations of 0.01 M (Nath & Dutta, 2012). The presentation of results in small separate graphs and no numerical data made assessing the degree of improvement difficult. Fluoride removal efficiencies using very low acid concentrations may be particularly informative for future studies with coral sand, as minimising acid content would reduce material consumption and could result in less contaminant leaching.

4.4.6 EFFECT OF ADSORPTION DOSE / SAND-TO-FLUID RATIO

Single-column trials (Experiment G & I) using various sand-fluid ratios and acid concentrations support previous reports that higher adsorbent doses reduce final fluoride concentration and improves removal (Mondal et al., 2016; Turner et al., 2005). This effect is further supported when comparing results of the 2:1 and 5:1 sand-fluid ratio columns conducted in triplicate (Experiments J & K respectively). Successful reduction of fluoride from 10 mg/L to below MAV could only be achieved twice with 2:1 ratio columns (Experiment J) but reduction was successful for seven consecutive reuses with 5:1 columns (Experiment K). Though the usage regime for the experiments differed slightly (i.e. one-daily use in the 2:1 columns vs. twice-daily use in the 5:1 columns), the comparison is valid given the 2:1 columns, which performed poorly in comparison, had a longer lag period between reuses (20 hours vs. 4 and 16 hours, respectively) providing additional time for fluoride removal to occur. Results obtained here confirm that the sand-to-fluid ratio is critical in fluoride removal, but results were not as substantial as other authors. In a follow-up study of coral sand AELD, adsorbent doses of 100; 250; 500; and 750 g of sand to 500 mL of fluoride solution were used in agitated batch experiments (M. Ashworth, personal communication [*Pioneer*], 2021). The increase in sand-fluid ratio from 1:1 to 3:2 resulted in lower final fluoride concentration by a factor of 5 (from 1 mg/L down to 0.2 mg/L).

Though a variety of sand-fluid ratios were trialled throughout this research, a point at which an increase in dose did not enhance fluoride removal was never reached. This contrasts studies conducted on $CaCO_3$ by Mondal et al. (2016) who obtained improved fluoride reduction with increased adsorbent dose up to a maximum of 2 g/L. Their experimental set-up was different, in that it incorporated stirring, very small particles of 100-300 µm, and was only conducted once (i.e. the material was not reused) therefore direct comparison of results is problematic.

4.4.6.1 INCREASED ADSORBENT – INCREASED MATRIX INTERFERENCE

Matrix spikes were performed on select samples and the % recovery of fluoride calculated to ascertain the validity of fluoride concentrations measured in samples. The fluoride spike recoveries in the 5:1 sand-to-fluid ratio column experiments were lower than the 2:1 ratio columns. This was likely due to the increased amount of sand in the 5:1 ratio columns. More sand equates to more contaminants available for desorption, and this, combined with a lower total volume, concentrates the contaminants extracted. The increase in contaminants adds complexity to the matrix, which interferes with the electrode and reduces spike recoveries. Low recoveries prompted an FISE methodology change where extracts were diluted 1:1 with ultrapure water, prior to sample preparation with TISAB. This change improved spike recoveries enough so that most of the data was reliable (P’ > 80 %). Some level of matrix interference remained, however, as all acidified samples had lower spike recoveries compared to non-acidified samples and comparative blanks. Any further research using similar parameters and coral sand may benefit from a TISAB formulation that can more effectively counterbalance large loads of electrode interferents and provide more accurate measurements.

4.4.6.2 INCREASED ADSORBENT – INCREASED FLUORIDE REMOVAL

The amount of fluid in excess of the pore volume is directly related to adsorbent dose (and/or sand-to-fluid ratio). A diagram in Appendix H illustrates this concept. The significance of this factor on the effectiveness of fluoride removal in non-agitated systems became apparent in the early stages of this research. Any fluoride present in solution in excess of the pore volume will have much higher external mass transport requirements, which is the rate-determining step of the fluoride removal process (Fan et al., 2003). Therefore, this volume is likely to have very little, if any fluoride removal. Essentially, what occurs during the extraction of treated fluid from containers with more solution than the pore volume, is a mixture of low and high fluoride solutions. The solution from the pore volume of the sand, which is lower in fluoride, is concentrated by the high fluoride solution which resided outside the pore volume. Any increase of this excess volume into the final extract, be it caused by a lower sand-fluid ratio or an increase in % extractable volume, will alter the fluoride concentration of the extract accordingly.

4.4.7 EFFECT OF SAND TYPE

Columns filled with Vanuatu sand outperformed both Kiribati and fine store-bought sand columns in fluoride removal, over multiple uses. It is likely that the resulting fluoride concentration would have exceeded the MAV sooner, had a 2-day gap in the Vanuatu sand column trial not occurred (refer Figure 4.16). Regardless, the Vanuatu sands still outperformed other sand types during the initial 5-day period.

The mineral composition of the sands was considered as a possible explanation, as aragonite is more soluble than calcite (Stenzel, 1963) and therefore a higher aragonite content would be expected to improve fluoride removal. However XRD analysis revealed greater aragonite content in store-bought sands and similar composition in Kiribati and Vanuatu sands, yet fluoride removal using the purchased sand was poorer than Vanuatu sand. If mineral content does have an effect on fluoride removal, it appears to be masked by other factors. It is also plausible that Vanuatu sand had less pre-existing fluoride content compared to other sands, which would therefore increase its adsorption capacity.

At first glance, it seemed counterintuitive that larger particles removed fluoride better than smaller particles (1.32 mm mean diameter for Vanuatu sand compared to 0.55 and 0.615 mm) since larger particles have lower surface area (Mavura et al., 2004). BET analysis could have provided additional information on specific surface area but this analysis was not prioritised given other findings in this study. Most authors report either no appreciable difference in fluoride removal based on particle size (in low concentrated solutions as studied by Mondal et al. (2016)) or increased removal with smaller particle sizes (Mondal et al., 2016; Nath & Dutta, 2010a; Wong & Stenstrom, 2018). One study reports of a limestone which did not produce an increase in fluoride removal with smaller particles (Labastida et al., 2017). Particle size can indirectly alter the fluid present in excess of the pore volume (refer diagram in Appendix H if required). It is hypothesised that the Vanuatu sand columns could be reused more often because the particles were larger and the same weight of sand took up more space in the columns, as noted during column preparation. This increase in sand volume, increased the pore volume in the column, and thus reduced fluid residing above the sand line. As such, there was less high fluoride solution in the columns to concentrate the pore volume of fluid where fluoride reduction had occurred. This resulted in a lower final fluoride concentration in extracts.

5 RESULTS & DISCUSSION – SCALED-UP PROTOTYPES

To ascertain if the promising fluoride reduction results obtained from the 5:1 sand-fluid ratio column experiments are transferable to a larger format, 1 L prototypes containing 1 kg of store-bought coral sand were used to treat initial acidified and non-acidified fluoride solutions (10 mg/L). The 1 L prototypes and operational regime (i.e. twice-daily use, with 4-hours of contact) are a close 1-to-20 approximation to a 20 L gravity-fed household treatment system which could produce 8 L of treated water daily. Elemental analysis of extracts and conductivity readings were completed to assess the safety of the treated fluid produced.

5.1 EXPERIMENT L – PROTOTYPES: FINE & COARSE SAND; 5:1 SAND-FLUID RATIO; 0.025 M ACID

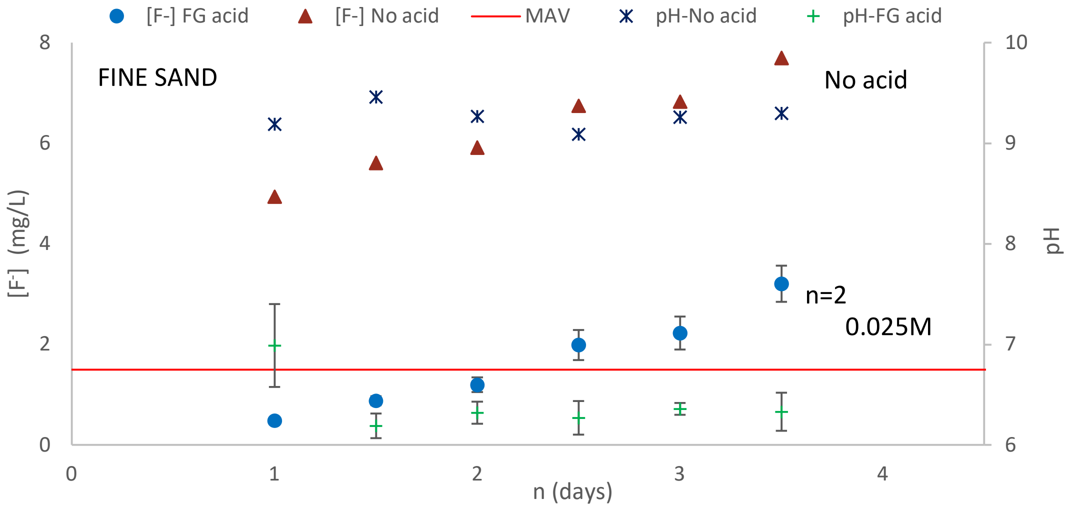
The prototype trials were completed in triplicate with 0.025 M food grade citric acid (i.e. store-bought) as opposed to analytical grade, while other variables used in the 5:1 sand-fluid ratio column experiment kept constant. It was assumed that the food grade (FG) citric acid is a monohydrate, with the same molar mass as the analytical grade used prior. A single 0 M or 'no acid' prototype was run alongside and a blank (no sand) prototype was also processed on day 1.

Data obtained from the fine-sand prototype experiment with and without 0.025 M food grade acid is summarised in Figure 5.1. The prototypes could only be used successfully to lower the initial fluoride from 10 mg/L to below 1.5 mg/L, for three uses. The 0 M acid prototype removed close to 50 % of the fluoride on first use (i.e. 3:1 sand-fluid ratio), which is comparable but lower than the ~66 % value obtained from the single replicate trial of 3.33:1 sand-fluid ratio (refer Experiment G & I - Table 4.8).

The prototype experiment was repeated with coarse store-bought sand with almost identical results as seen in Figure 5.2 and a direct comparison of 0.025 M citric acid trials are included in Figure 5.3. With regards to the non-acidified initial solution trials, a difference in performance between the sands used was noted (refer Figure 5.4). Coarse sand reduced the fluoride concentration more so than fine sand but only single replicate prototypes were run. The resulting pH from the coarse sand extracts was also lower than the fine sand. A correlation between lower pH and lower fluoride concentrations in the extracts fits, given fluoride removal works better at lower pH. Note also that the 'no acid' prototypes did not release the same amount of fluid as the acidified replicates, but no obvious pattern existed (i.e. on some reuses, the 'no acid' extracts were larger, whereas on other reuses, it was smaller, often by 10-12 mL or more).

Figure 5.1

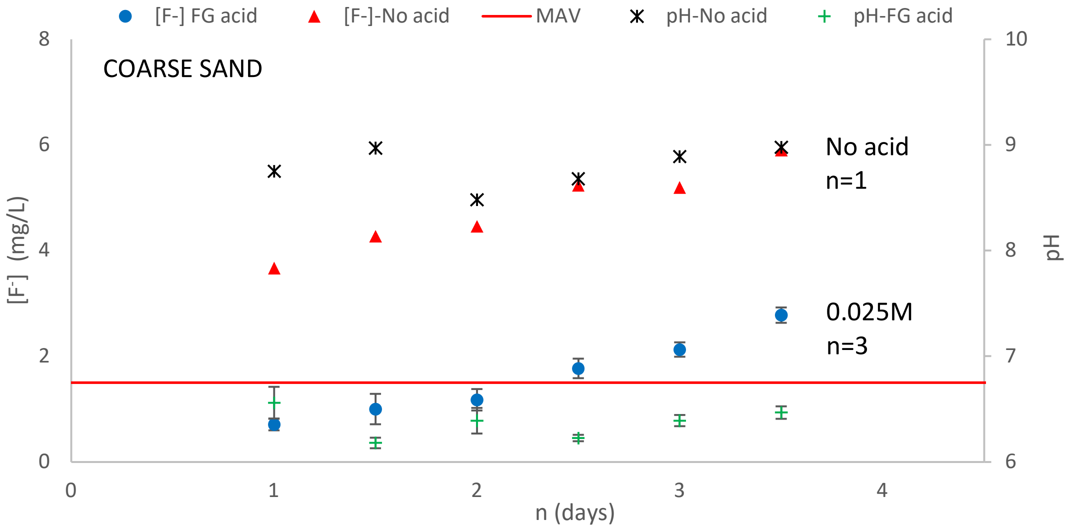
Final Fluoride Concentration and pH of Extracts from Fine-Sand Prototypes vs. Use with 0 M & 0.025 M Citric Acid (Experiment L1)



Note. Initial solution of 10 mg F$^-$/L; food grade citric acid; Prototypes with 5:1 sand-fluid ratio, used twice daily. Average ± 2SD for 0.025 M citric acid (n=3, n=2 on day 3.5); no acid solutions (n=1).

Figure 5.2

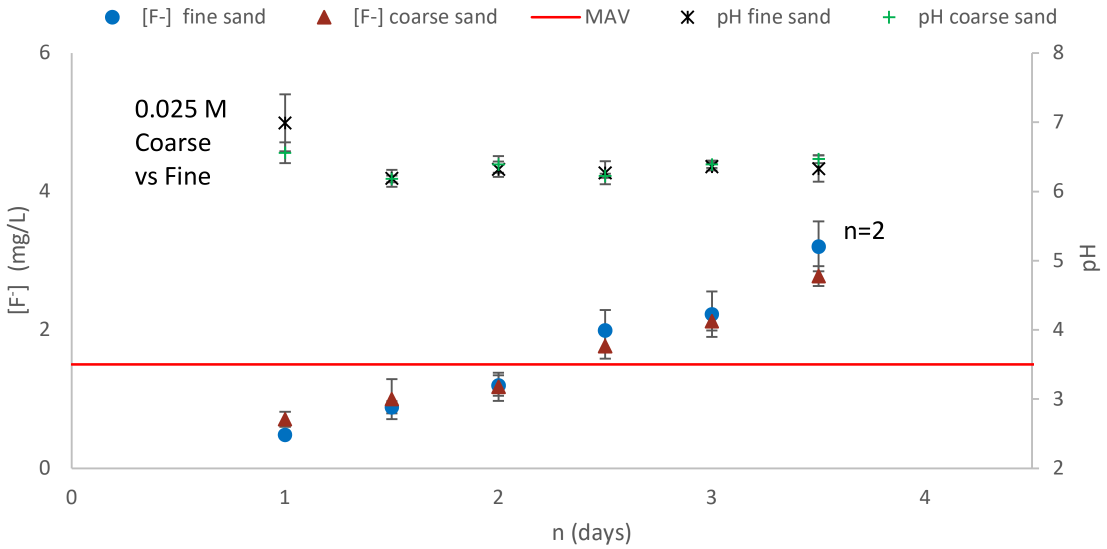
Final Fluoride Concentration and pH of Extracts from Coarse Sand Prototypes vs. Use with 0 M & 0.025 M Citric Acid (Experiment L2)



Note. Initial solution of 10 mg F$^-$/L; food grade citric acid; Prototypes with 5:1 sand-fluid ratio, used twice daily. Average ± 2SD for 0.025 M citric acid (n=3); no acid (n=1). (Duplicate differences slightly above quality guidelines: for day 2.5 (0.025 M) = 5.99%; day 3 (0.025 M) = 5.15%.)

Figure 5.3

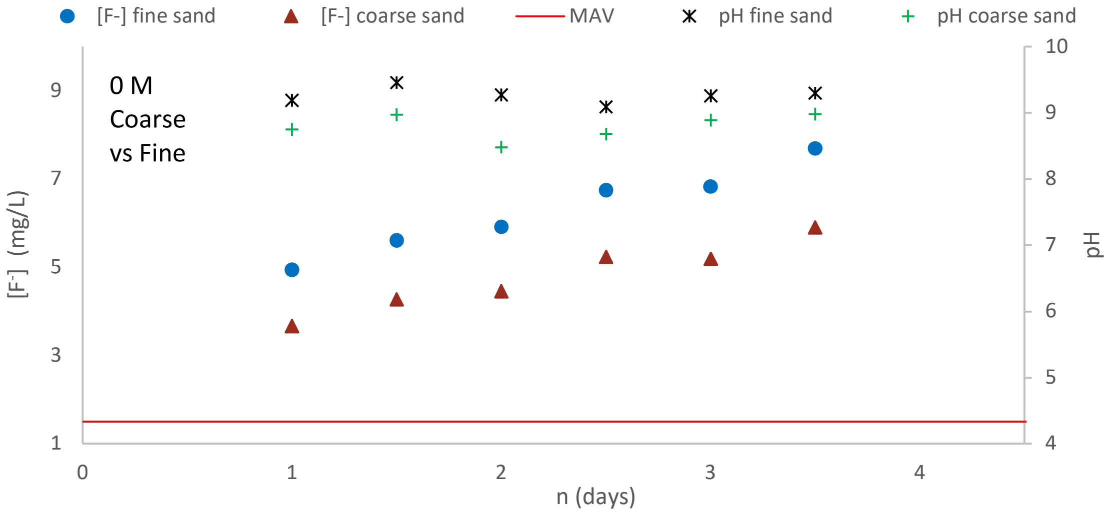
Comparison of Final Fluoride Concentration and pH of Extracts from Fine vs. Coarse Sand Prototypes with 0.025 M Citric Acid, Following Repeated Use



Note. Initial solution of 10 mg F$^-$/L; food grade citric acid; Prototypes with 5:1 sand-fluid ratio, used twice daily. Average ± 2SD (n=3, n=2 fine sand on day 3.5).

Figure 5.4

Comparison of Final Fluoride Concentration and pH of Extracts from Fine vs. Coarse Sand Prototypes Used without Acid, Following Repeated Use

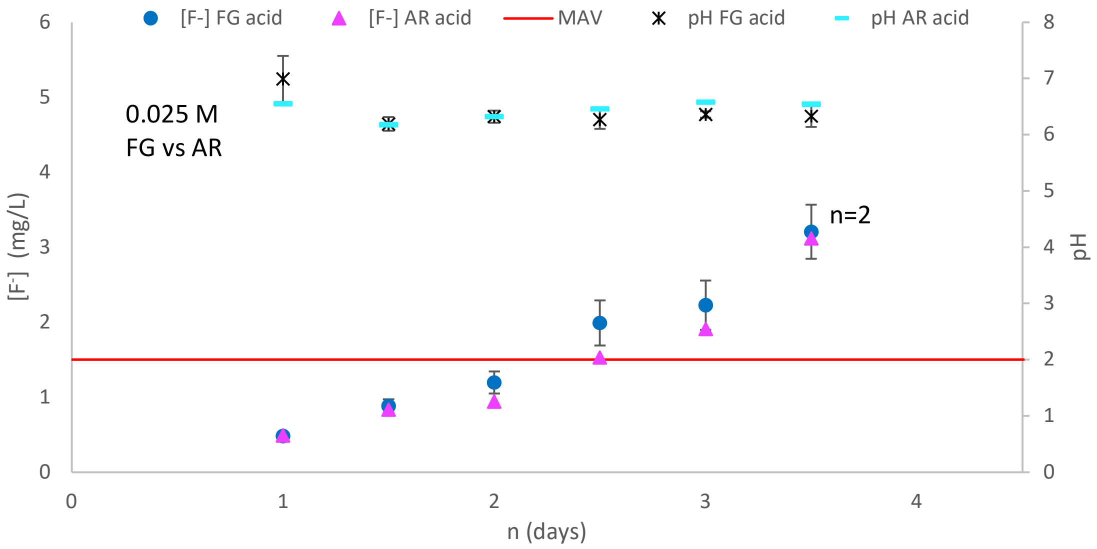


Note. Initial solution of 10 mg F$^-$/L; food grade citric acid; Prototype with 5:1 sand-fluid ratio, used twice daily (n=1).

To ascertain if the poor fluoride removal capability of the prototypes compared to the columns may be due to the acid grade used, the prototype experiment was repeated with the same lot of analytical grade (AR) acid as used with the columns. The results obtained are compared with those of the food grade (FG) acid in Figure 5.3. The fluoride concentrations from the AR trial were slightly lower, however the difference was minimal. Acknowledging that the AR acid trial was a single replicate, the treatment system with AR acid was not successful in reducing fluoride concentrations to below MAV any longer than the food grade acid. Other than the grade of acid used and the scaled-up container, all other variables were kept constant, indicating the difference in performance between columns and prototypes is not due to the acid grade.

Figure 5.5

Comparison of Final Fluoride Concentration and pH of Extracts from Fine Sand Prototypes Used with 0.025 M Citric Acid (AR vs. FG), Following Repeated Use



Note. Initial solution of 10 mg F$^-$/L; Fine sand prototypes with 5:1 sand-fluid ratio, used twice daily with 0.025 M analytical grade (AR; n=1) vs. food grade (FG; n=3) acid. Average ± 2SD (n=3 where applicable, n=2 on day 3.5 with FG acid).

During the course of this research, it was noted that, though a column or prototype was ‘topped’ up with 200 mL or 15 mL respectively, the volume extracted was not exactly 200 mL or 15 mL. There was a difference in the % of volume which could be extracted via gravity from the columns vs. the prototypes compared to how much fluid was loaded in. Any difference in this ratio would affect the final concentration of the extract. An initial attempt at measuring the differences in extractable volume after the initial 3:1 ‘wash-step’ revealed that the columns released about 95-98 % of the 15 mL volume added whereas the prototypes released about 99-103 % of the 200 mL added. This small 1 to 5 % difference can have a large impact on the final concentration of extracts, especially when fluoride removal in the treatment system is high. Given the extra 1-5 % fluid would be outside the pore volume and external mass transport requirements very high, fluoride removal would be minimal and the concentration of fluoride in this fluid would be at or near 10 mg/L. If only 1 % extra fluid was added to, for example a low fluoride extract of 0.3 mg/L, the final concentration would be about 30% higher; if 1 % volume was added to an extract measuring 1 mg/L, the final concentration would be about 9 % higher, as demonstrated below:

Low concentration (0.3 mg/L):

Concentration of solution if 100% of volume extracted from column:

$$0.3\ \text{mg/L} * 0.015\ \text{L} * 100\ \% = \frac{0.0045\ \text{mg}}{(0.015\text{L} * 100\ \%)} = 0.3\ \text{mg/L}$$

Concentration of solution if 101 % of volume extracted from prototype with low F^- concentration:

$$\frac{(0.3\ \text{mg/L} * 0.2\ \text{L} * 100\ \%) + (10\ \text{mg/L} * 0.2\ \text{L}* 1\ \%)}{(0.2\ \text{L} * 100\ \% + 0.2\ \text{L} * 1\ \%)} = \frac{(0.06 + 0.02\ \text{mg})}{(0.2 + 0.002)\ \text{L}} = 0.396\ \text{mg/L}$$

0.3 mg/L vs. 0.396 mg/L → 32% difference in concentration

Moderate concentration (1.0 mg/L):

Concentration of solution if 100% of volume extracted from column:

$$1\ \text{mg/L} * 0.015\ \text{L} * 100\ \% = \frac{0.015\ \text{mg}}{(0.015\ \text{L} * 100\ \%)} = 1\ \text{mg/L}$$

Concentration of solution if 101 % of volume extracted with moderate acid concentration:

$$\frac{(1\ \text{mg/L} *0.2\ \text{L} *100\ \%) + (10\ \text{mg/L} * 0.2\ \text{L}*(1\ \%))}{(0.2\ \text{L} * 100\ \% + 0.2\ \text{L} * 1\ \%)} = \frac{(0.2 + 0.02\ \text{mg})}{(0.2 + 0.002)\ \text{L}} = 1.09\ \text{mg/L}$$

1 mg /L vs. 1.09 mg/L → 9% difference in concentration

5.1.1 TRACE ELEMENTS IN PROTOTYPE EXTRACTS

Extracts where the final fluoride concentration was below the MAV were analysed with ICP-MS to ascertain the presence and concentrations of potentially problematic elements. Concentrations of select elements measured in extracts from prototypes containing fine or coarse sand are presented in Table 5.1 and Table 5.2, respectively. Values obtained from initial solutions or controls (whichever highest), were deducted from the extract concentration. Results were compared to aesthetic guideline (GL) and maximum acceptable values (MAV) for elements of health concern as published by the MOH (2018). Values above GL or MAV are highlighted in the tables, in blue or red, respectively. None of the initial solutions measured or control column extracts had values above standards; most elements were below the LOQ. Those elements which were not, (Fe; Mg; Na; Pb; Zn) were at least five times lower than published limits. A brief summary of the elements present in the prototype extracts above published limits, as well as their persistence in above limit in days/uses throughout the experiment is provided in Table 5.3.

Table 5.1

Trace Elements Present in AELD Extracts Following Repeated Use of Fine Sand Prototypes, with or without 0.025 M Food Grade Citric Acid (Experiment L1)

					Initial Solutions			Blank Prototype		**Fine Store-Bought Coral Sand**					
Element	Limit[1]		Units	LOQ	0M	0.025M		0.025M		**No Acid**			**0.025M Citric Acid**		
	MAV	***GL***			Day 1 Use 1	Day 1 Use 1	Day 1 Use 2	Day 1 Use 1	Day 1 Use 2	Day 1 Use 1	Day 1 Use 2	Day 2 Use 1	Day 1 Use 1	Day 1 Use 2	Day 2 Use 1
Al		100	µg /L	210	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	***1680 ± 40***	***1300 ±100***	***1420 ± 90***
As $^{75-91}$	10		µg /L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	3.7	2.8	2.4	**23 ± 3**	**15.7 ± 0.9**	**13 ± 2**
B	1400		µg /L	210	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	700 ± 100	500 ± 100	410 ± 70
Ca		*100-300	mg/L	212.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	***1500±100***	***1600 ±100***	***1200 ± 300***
Cd	4		µg /L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Cr	50		µg /L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5.9	4.7	3.1	**128 ± 8**	**110 ± 10**	**90 ± 10**
Cu	2000	1000	µg /L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	29 ± 4	<LOQ	<LOQ
Fe $^{56-72}$		200	µg /L	21	<LOQ	<LOQ	22	***23***	<LOQ	<LOQ	<LOQ	<LOQ	***1300±100***	***1050 ± 40***	***1030 ± 50***
Mg		*100-300	mg/L	2.121	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4.5	4.4	3.8	***110 ± 3***	***109 ± 2***	***106 ± 5***
Mn	400	40	µg /L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	***120 ± 20***	***116 ± 9***	***120 ± 10***
Mo	70		µg /L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Na		200	mg/L	21.21	21	<LOQ	<LOQ	***22***	<LOQ	<LOQ	<LOQ	<LOQ	43 ± 2	30 ± 10	26 ± 6
Ni	80		µg /L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	36 ± 4	25 ± 3	<LOQ
Pb	10		µg /L	2.1	<LOQ	<LOQ	<LOQ	***2.1***	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Zn		1500	µg /L	21	<LOQ	<LOQ	***40***	30	34	<LOQ	<LOQ	<LOQ	400 ± 300	230 ± 150	110 ± 20
Hardness		200	mg /L	212	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	4200 ± 300	4500 ± 300	3400 ± 800
Conductivity			mS/cm		0.0484	1.385	1.382	1.39	1.371	Insuff.	0.223	0.225	2.33 ± 0.09	2.25 ± 0.03	1.98 ± 0.04
TDS		1	g/L		0.0310	0.886	0.884	0.890	0.877	Insuff.	0.143	0.144	1.49 ± 0.06	1.44 ± 0.02	1.27 ± 0.02

Note. Select elements as measured with ICP-MS; Initial solution of 10 mg F$^-$/L. Average ± 2SD (n=3), control blank or initial solution values deducted (whichever highest, *bolded* above). Values in red or blue are above MAV or GL, respectively (as published by the [1]MOH (2018)).

Table 5.2

Trace Elements Present in AELD Extracts Following Repeated Use of Coarse Sand Prototypes, with or without 0.025 M Food Grade Citric Acid (Experiment L2)

Element	Limit[1]		Units	LOQ	Initial Solutions			Blank Prototype		**Coarse Store-Bought Coral Sand**					
					0M	0.025M		0.025M		**No Acid**			**0.025M Citric Acid**		
	MAV	***GL***			Day 1 Use 1	Day 1 Use 1	Day 2 Use 1	Day 1 Use 1	Day 1 Use 2	Day 1 Use 1	Day 1 Use 2	Day 2 Use 1	Day 1 Use 1	Day 1 Use 2	Day 2 Use 1*
Al		100	µg /L	210	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	***1316***	***220***	<LOQ	***1700 ± 200***	***1400 ± 100***	***1330 ± 80***
As [75-91]	10		µg /L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	8.2	<LOQ	<LOQ	**12 ± 2**	**9.9 ± 0.8**	7.8 ± 0.5
B	1400		µg /L	210	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	436	<LOQ	<LOQ	600 ± 100	500 ± 100	440 ± 20
Ca		*100-300	mg/l	212.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	***1700 ± 500***	***1570 ± 80***	***1100 ± 100***
Cd	4		µg /L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Cr	50		µg /L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**85.3**	<LOQ	<LOQ	**130 ± 5**	**110 ± 10**	**89.8 ± 0.7**
Cu	2000	1000	µg /L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Fe [56-72]		200	µg /L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	***898***	<LOQ	<LOQ	***1200 ± 100***	***1000 ± 100***	***930 ± 70***
Mg		*100-300	mg/l	2.121	***3***	<LOQ	2.4	<LOQ	<LOQ	6	4.7	5.6	***120 ± 7***	***113 ± 7***	***109 ± 3***
Mn	400	40	µg/L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	***99.4***	<LOQ	<LOQ	***90 ± 2***	***98 ± 4***	***104 ± 1***
Mo	70		µg/L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Na		200	mg/l	21.21	23	<LOQ	***25***	23	22	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Ni	80		µg/L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	25 ± 3	<LOQ	<LOQ
Pb	10		µg/L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Zn		1500	µg/L	21	<LOQ	<LOQ	***80***	21	59	67	<LOQ	<LOQ	220 ± 80	180 ± 60	70 ± 20
Hardness		200	mg/L	212	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	5000 ± 1000	4400 ± 200	3200 ± 300
Conductivity			mS/cm		0.048	1.387	1.391	1.383	1.381	0.1638	0.1483	0.1589	2.26 ± 0.02	2.15 ± 0.07	1.86 ± 0.03
TDS		1	g/L		0.031	0.888	0.890	0.885	0.884	0.1048	0.0949	0.1017	1.45 ± 0.01	1.38 ± 0.05	1.19 ± 0.02

Note. Average ± 2SD (n=3, n=2 on *Day 2 – Use 1), control blank or initial solution values deducted (whichever highest – ***bolded*** above). Values in red or blue are above MAV or GL, respectively (as published by [1]the MOH (2018)).

Table 5.3

Trace Elements Above Published Limits in Extracts Following Repeated Use of Prototypes (Fine or Coarse Sand) with or without 0.025 M Citric Acid (Experiment L)

Element	Published Limit[1]		Units	Fine		Coarse	
	MAV	*GL*		0 M	0.025 M	0 M	0.025 M
As	10		µg/L	---	LT (23)	---	Day 1 (12)
Cr	50		µg/L	---	LT (128)	Use 1 (85.3)	LT (130)
Al		100	µg/L	---	LT (1680)	Day 1 (1316)	LT (1700)
Ca		100-300	mg/L	---	LT (1600)	---	LT (1700)
Fe		200	µg/L	---	LT (1300)	Use 1 (898)	LT (1200)
Mg		100-300	mg/L	---	LT (110)		LT (120)
Mn	400	40	µg/L	---	LT (120)	Use 1 (99.4)	LT (98)

Note: Initial solution of 10 mg F^-/L in 5:1 sand-fluid ratio prototypes. Number of days or uses above limit is listed or if presence is above limit long-term (i.e. throughout duration of the trial, LT). Values above MAV (red) and GL (blue) according to [1]MOH (2018). Number in brackets is highest average value measured.

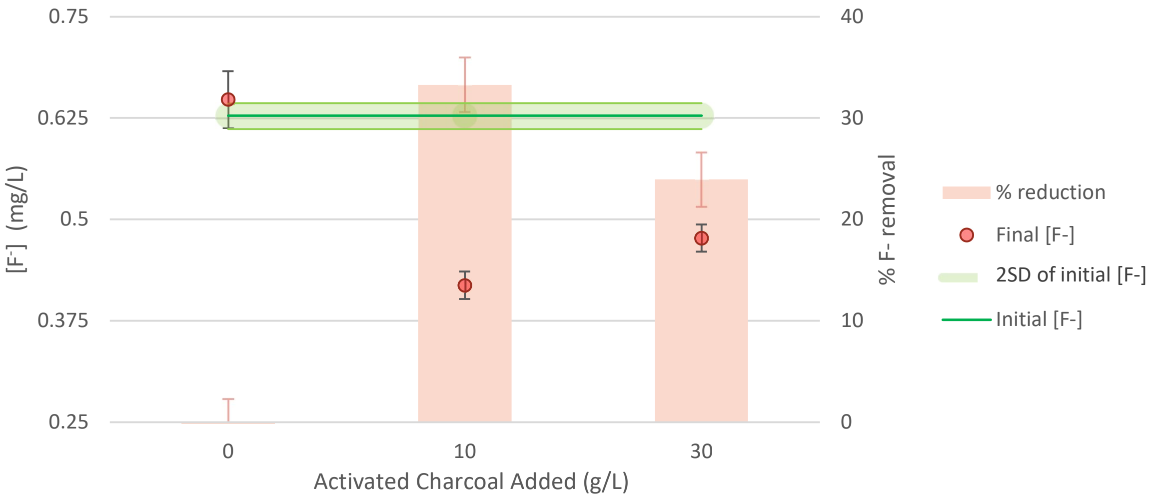
5.2 EXPERIMENT M – ACTIVATED CHARCOAL CLEAN-UP

The fluoride concentration of the initial acidified solution treated with coral sand was measured as a baseline. The fluoride concentrations obtained after this extract was treated with activated charcoal (10 g/L, 30 g/L or 0 g/L – time control) was compared to this baseline and the % fluoride removal calculated. Results are depicted in Figure 5.6. Standardised % recoveries were between 80-89 %.

The activated charcoal treatment step further decreased fluoride present in solution, even when the initial concentration was quite low, about 0.675 mg/L. This additional reduction however, appears to have an optimal point as adding larger amounts of activated charcoal (30 g/L) removed less fluoride than lower doses (10 g/L). There was no indication that fluoride concentrations lowered over time only (i.e. through precipitation), as the concentration after 4 hour without AC was essentially the same as the initial (within the margins of error).

Figure 5.6

Fluoride Removal from Prototype Extract Following Activated Charcoal Treatment



Note. Final fluoride concentration and % removal following AC treatment (4hr contact with initial agitation). Initial solution used was a fine-sand prototype extract following coral sand treatment (extract from day 1.5, third extract from the column). Average ± 2SD (n=3).

5.2.1 TRACE ELEMENTS IN ACTIVATED CHARCOAL EXTRACTS

A comparison of the concentration of selected elements present in extracts before and after AC treatment, but after the original coral sand treatment is presented in Table 5.4. The same elements which were above limit in the original fine-sand prototype experiment conducted prior (refer Table 5.1) were above limit prior to start of this AC experiment – they were: Al; As; Ca; Cr; Fe; Mg; and Mn. Some elements (Ca; Cr; Cu; Mg; Ni; Zn) were partly removed with AC treatment but many increased in concentration: Al; As; Fe; Mn; Mo; P; S; and Zn (refer greyed boxes in Table 5.4). Most importantly, two of three elements of health concern, As and Mn, increased following AC treatment whereas Cr may have slightly decreased. Mg and Ca decreased but only by 20 % at best, and concentrations were still about 3 to 10 times above published guidelines.

Table 5.4

Changes in Element Concentrations of AELD Extract Following 4-Hour Treatment with Varied Doses of Activated Charcoal (Experiment M)

Element	LOQ	Limit		Units	Prior to treatment (0 hrs; 0g/L)		After 4hr contact with or without Activated Charcoal						CRM % Rec.
		MAV	*GL*				0g/L	(control)	10g/L		30g/L		
Al	0.21		0.1	mg/L	1.8	± 0.1	***1.72***	***± 0.02***	***2.7***	***± 0.2***	***32***	***± 0.05***	119
As	2.1	10		ug/L	13.7	± 0.3	**13.8**	**± 0.3**	**15**	**± 1**	**19.2**	**± 0.1**	104
B	210	1400		ug/L	560	± 60	590	± 80	520	± 70	600	± 100	118
Cd	2.1	4		ug/L	<LOQ		<LOQ		<LOQ		<LOQ		101
Cr	2.1	50		ug/L	115	± 4	**113**	**± 4**	**112**	**± 4**	**104**	**± 3**	110
Cu	2.1	2000	1000	ug/L	13	± 1	17	± 1	4	± 2	6	± 2	111
Fe	0.021		0.2	mg/l	1.2	± 0.03	***1.26***	***± 0.008***	***2.3***	***± 0.1***	***2.17***	***± 0.03***	105
Mn	21	400	40	ug/L	158	± 7	***154***	***± 4***	**400**	**± 30**	**960**	**± 8**	106
Mo	2.1	70		ug/L	2.18	n=1	**2.27**	**n=1**	**3.8**	**± 0.5**	3.7	± 0.4	91
Ni	2.1	80		ug/L	20	± 2	21.6	± 0.6	13.9	± 0.4	15.4	± 0.3	110
Pb	2.1	10		ug/L	<LOQ		3	n=1	<LOQ		3	n=1	93
S	0.21		HS=0.05*	mg/L	16	± 1	**14.9**	**± 0.7**	**20**	**± 1**	**32**	**± 2**	na
Zn	21		1500	ug/L	240	± 20	260	± 40	60	± 30	**118**	**± 8**	na
Ca	21.21		100-300	mg/L	1300	± 100	***1270***	***± 40***	***1100***	***± 100***	***990***	***± 40***	106
Mg	21.21		100-300	mg/L	102	± 9	***101***	***± 4***	***100***	***± 10***	***86***	***± 3***	*na*
Na	2.121		200	mg/L	38	± 4	40	± 10	40	± 10	44	± 6	na
P	21.21	---		mg/L	<LOQ		**<LOQ**		**80**	**± 10**	**320**	**± 9**	111
Hardness	21.21		200	mg/L	***3700***	***± 100***	***3700***	***± 100***	***3600***	***± 300***	***2800***	***± 100***	n/a

Note. An extract from an acidified prototype jerrycan from Day 2, Use 1 (refer experiment L1) was used as an initial solution and trace elements measured prior to treatment. Average ± 2SD (n=3). **Red** = Questionable trend or no trend, above MAV; ***Blue*** = Decreasing trend, above GL; **Black** = Decreasing trend, below limit / no limit; Grey = No trend, below limit. * No limit listed for S alone, only as hydrogen suphide.

Red	Increasing trend, above MAV	***Blue***	Increasing trend, above GL	**Black**	Increase trend, below limits / no limit

5.3 DISCUSSION – SCALED-UP 1 L PROTOTYPES WITH 1 KG SAND

The functional parameters of the 75 g sand column experiment were scaled-up to 1 kg of sand in 1 L prototype jerrycans and experimental trials conducted with food grade citric acid, as opposed to analytical grade which was used in all prior trials. The prototypes were not as effective as the smaller columns in reducing fluoride concentration. The 5:1 sand-to-fluid ratio columns could be reused seven to ten times successfully, depending on the sand type used. In comparison, the prototypes could only be used to reduce 10 mg/L of fluoride to below the MAV three times, regardless of the particle size.

5.3.1 EFFECT OF ACID GRADE (ANALYTICAL VS. FOOD GRADE)

The prototype trials were initially conducted in triplicate with fine and coarse sand and acidified with food grade citric acid purchased in-store, to simulate locally available product. A single prototype was also trialled with analytical grade acid and fine sand. Marginally better fluoride removal was obtained with analytical grade acid, but the improvement was not substantial enough to explain the difference in long-term success between columns and prototypes. All prototypes, regardless of acid grade used, could only successfully reduce fluoride to below MAV for three uses.

5.3.2 EFFECT OF PARTICLE SIZE

No noticeable effect on fluoride removal rates was noted in the acidified prototype jerrycans when comparing different particle sizes. It was hoped that an increase from fine to coarser grains (0.55 to 0.9 mm mean diameter) would enhance fluoride removal, as occurred in the Vanuatu sand columns, however this was not the case. The increase in particle size in the prototypes was by a factor of 1.6, whereas the increase in the columns was 2.4 (from 0.55 to 1.32 mm), therefore the increase may not have been sufficient to create a measurable difference. The pre-existing fluoride load of the coarse vs. fine sands is unknown but could have impacted fluoride removal, if different. It is also possible that the effect of other variables, such as the larger amount of extractable volume, masked any effect of the particle size. There may also be some unidentified factor which caused better fluoride removal with Vanuatu sands. In absence of acid, a slight improvement in fluoride removal was noted with coarse sand over fine sand, and coincidentally, the coarse sand extracts also had lower pH. It is difficult to assess which factor, particle size, pH or both, improved fluoride removal in the single replicate trial.

5.3.3 EFFICIENCY OF FLUORIDE REMOVAL IN COLUMNS VS. DRUMS

Fine-sand columns could be successfully reused seven times compared to three when the same experimental parameters were used on bigger 1 L prototypes with 1 kg sand. This aligns with Fawell et al. (2006) who discusses sorption defluoridation of bone charcoal filters in buckets and columns. Operational capacity in buckets is ⅓ of theoretical capacity whereas it is ⅔ theoretical in columns, equating to columns being twice as effective as buckets (Fawell et al., 2006, p. 45). Observations and insights from experiments conducted here indicate differences in extractable volume between columns and prototypes could be a plausible reason for the difference in operational capacities. It is hypothesized that the format and shape of containers could affect processes such as fluid mechanics, retention, preferential flow, sand compaction, and/or capillary forces, causing columns to drain less effectively than prototypes. Any fluid retained longer in sand will benefit from enhanced fluoride removal. As calculated at the end of Experiment L (Section 5.1), a small difference of 1 to 5% in extractable volume can make a significant difference in fluoride concentration of extracts and therefore explain the improved success of columns, keeping other parameters constant.

5.3.4 SAFETY OF TREATED SAMPLES

The treated water from both the columns and the scaled-up prototypes contained multiple elements of concern above NZ drinking water quality limits, including: Al, As, Ca, Cr, Fe, Mg, and Mn. Column extracts also contained B, Ni , Na and potentially Cu above limit. These findings indicate that elements are leaching from the coral sand, particularly in acidic environments. There appears to be an inverse relation existing between lower final fluoride concentration and increased concentration of contaminants extracted.

Studies conducted here (preliminary trials Experiment G & I as well as the 5:1 sand-fluid columns in Experiment K) indicate that for most elements, an increase in acid is correlated to an increase in contaminant concentration of sand extracts. Some contaminants are only aesthetically problematic (Al, Fe, Mn, hardness or Mg & Ca) however a few are important health concerns (As, B, Cr and to a lesser degree Mn and Ni). Pacific Island sands, compared to store-bought sand, released slightly more trace elements at concerning concentrations, particularly from newer treatment systems (i.e. B, Ni). This could be due to the purchased sand having been processed prior to sale (as noted on packaging and given it is targeted for marine aquariums) or different geographical origin of the sands. These results are somewhat contradictory to other findings. A report by Nath and Dutta (2010a) who also studied AELD with citric acid but with limestone as an adsorbent, stated that heavy metal contamination was not a problem in their treated water, however, they did not specify the detection limits for their analyses. A similar study with oxalic acid indicated an increase post-treatment of Cr, Fe, Mg, and Ni (Nath & Dutta, 2012). Of these, only iron and nickel were above the NZ drinking water limits. The authors deemed their method safe with regards to heavy metals but did not report results for As or Al.

Limestone is created from the sedimentation of carbonate materials in shallow waters which converted into rock over millions of years; its characteristics are influenced by the environment where they were formed (Oates, 1998). The origin of limestone used by various authors could potentially be very different to the coral sands used here. These sands, which are mainly coral alga, shells, and snails (Roseth, 2000), were obtained from the Pacific Region or purchased in-store from a Chinese supplier. As such, the types and concentrations of trace contaminants are likely to differ. The sands used here were unprocessed except for sieving and drying at low temperatures. Prior studies using AELD with coarse store-bought coral sand did not encounter as many problematic elements in sand extracts using acetic acid (Camlek, 2017). Manganese was detected above limit at 0.144 ± 0.009 mg/L as well as Ca and Na, which is not unexpected given coral sand is composed of $CaCO_3$, would be in contact with seawater, and the requirement of NaF to prepare initial fluoride solutions. Boron was also detected but below the MAV; As was not reliably measured; and Al, Cr, Cu, Fe, and Ni were not detected. That said, the experimental parameters used herein differed: the sand-fluid ratio was much greater (5:1 vs. 1:1); the acid was different (citric vs. acetic) and lower in concentration (0.025 vs. 0.1 M); and the contact time was shorter (4 vs. 24 hours). It is more likely that the increase in sand-fluid ratio increased the concentration of contaminants, given the shorter time and lower acid concentrations used.

Total hardness and dissolved solids in all extracts would render them palatably unacceptable according to NZ guidelines (MOH, 2018). The TDS and hardness is likely related to the eventual formation of white precipitate in extracts although this was not investigated in any detail. The sand treatment did however, neutralise the acidic pH of initial solutions to just below 7, much closer to the recommended guideline of 7-8 (MOH, 2018).

5.3.4.1 TRACE ELEMENTS IN CORAL SAND

EDS analysis detected low % weights of Cl, Mg, Na, and Sr in the sand samples, which is consistent with coral sand being in contact with sea water (Lebrato et al., 2020) as sea water contains: Na; Mg; Ca; K; Cl; and Sr (Millero et al., 2008) as well as sulphur in concentrations of ~900 ppm (Anthoni, 2006). EDS also potentially detected Al, B, and Fe though concentrations were near the detection limit of the instrument. ICP-MS analysis of sand digests not only confirmed the presence of Al, B, and Fe in the sands, but detected other elements of health and aesthetic concern. The presence of Al, As, B, Cr, Fe, Mg, Mn, and Ni in the coral sand digests suggest that the sand is the source of contaminants, as opposed to the materials used in this study. The Council of Europe has published suggested limits (SRL) on the release of specific heavy metals from food contact materials to aid industry on minimising the endangerment of human health (Cederberg et al., 2015). These limits are measured in mg / kg of food. The concentration of elements in coral sand is not indicative of how much would leach into food through normal contact, but indicates a maximum amount per kg if all the element present did leach. A comparison of measured concentrations in sands with the SRL can indicate which elements may be problematic in terms of food contact. Aluminium and Pb were present in all sand types at concentrations at least 10 times higher than the recommended SRL, whereas As was present in concentrations over 100 times the SRL.

Many of the contaminants located in the sand and their extracts may originate from the volcanic environment of the Pacific region. Arsenic is prevalent in regions with volcanic and hydrothermal activity and volcanic ash is a source of As contamination (Bundschuh et al., 2010; Gonzalez Rodriguez et al., 2019; Masuda, 2018). Manganese and Cr were measured in the thousand ppm range in Ambae lava and Ni ranged between 200 – 500 ppm (Park et al., 2012). In consequence, their presence has been measured far and wide. For example, Ni and Cr were detected in the urine of New-Caledonians, especially children, at concentrations in excess of reference values (St-Jean et al., 2018). Chromium, which was of particular concern in all sands and extracts analysed here, is a carcinogen contributing to ocean pollution (Wise et al., 2009). It has been detected in 99% of sperms whales across the globe, with the highest concentrations from whales located near Kiribati (Wise et al., 2009). An analysis of road dust and soils in Suva, Fiji measured concentrations of chromium at 34-40 mg/kg and iron at 39-41 g/kg (Maeaba et al., 2019). Analysis of sediments from the Suva lagoon in Fiji indicate that As, Cr, and Zn are present above the USEPA guidelines (Garimella S. et al., 2002). The presence of trace contaminants in coral sand from the Pacific region is consistent with these findings.

The presence of problematic elements in the prototype extracts were consistent with results from the column extracts, albeit column extracts contained higher trace element concentrations. This higher concentration in column extracts is likely caused by a difference in extractable volume, as discussed earlier, as any excess fluid would dilute the contaminant concentration in the extracts. If the prototypes are less efficient in fluoride removal, it follows that they may also be less efficient in contaminant leaching.

It was also noted that the concentration of elements measured in sand digests were not necessarily proportional to the concentrations measured in the sand extracts. This is particularly noticeable in the As concentration of Kiribati sands. The As concentrations in all sands measured between 1 to 4 mg/kg (Table 4.4) whereas the concentration in extracts on day 1 varied from < 50 ug/L in fine store bought sand, to approximately 100 ug/L in Vanuatu sands and finally to 300 – 700 ug/L in Kiribati sand extracts (refer Figure 4.40 or Tables G 8 to G 13 in Appendix G). This disproportional difference may be in part due to sampling variability as only 0.3 g of sand was digested and analysed compared to 75 g of sand placed into columns to create sand extracts. The high As concentrations measured in Kiribati sand extracts relative to the lower concentrations in the sand digests may also be related to the large and highly variable iron concentrations in the sand (refer underlined values in Table 4.4). Arsenic is strongly adsorbed onto iron hydroxide surfaces (Bang & Meng, 2004), as such iron is commonly used to remove As from contaminated waters (Hao et al., 2018; Wang et al., 2018).

Very little differences were noted in trace element concentrations of the fine vs. coarse sand extracts, with the exception that arsenic and sodium might be slightly higher in the fine sand prototypes. The similarity in contaminants and concentrations could indicate the purchased sands originating from the same or similar source (which is consistent with purchase from the same supplier). The similarity in mineral content (aragonite and calcite) also supports this thought.

5.3.4.2 WHITE PRECIPITATE

The exact composition of the white substances collected, either from the extracts after overnight settling period or those obtained from the sand columns themselves, could not be elucidated with the XRD analysis undertaken and spectral library search available at UC. The powders and precipitates analysed were complex mixtures likely containing calcium citrate in various hydrated forms. They did not appear to contain calcite or aragonite (i.e. coral sand – M. Polson, personal communication, April 28, 2021) or fluorite (CaF_2), the precipitate expected from defluoridation with calcium carbonate material. This is consistent with the results of Nath et al. (2011) and Nath and Dutta (2010a) who determined that the white powder located in used citric acid limestone reactors was calcium citrate. The authors also noted that if solutions containing more than 0.1 M citric acid were used, calcium citrate would precipitate out (Nath & Dutta, 2010a). There was no indication from this article that white precipitate formed in treated extracts some time after removal from their reactor.

There may be some advantage in terms of TDS, total hardness and trace element content, to allow formation and remove the precipitate prior to 'consumption' or trace element analysis. Given the complex mixture of the white powders and precipitates obtained, there is potential for some problematic contaminants to be removed by precipitation, thus improving the safety of the treated extracts.

5.3.4.3 CLEAN-UP OF SAND EXTRACTS USING ACTIVATED CHARCOAL

Clean-up attempts of sand extracts using 4-hour contact and initial agitation with activated charcoal were unsuccessful. Though other authors have reported success in reducing As (Alchouron et al., 2021), Fe (Baharudin et al., 2021; Corral-Bobadilla et al., 2021), and Mn (Baharudin et al., 2021), the activated charcoal treatment used here increased the concentration of these elements, as well as Al, P, and S. The treatment was successful in reducing fluoride from solutions with low initial fluoride concentrations of <1 mg /L, by ca 30 %, which aligns with previous authors (Choong et al., 2020). A slight reduction in Ni and Ca was also noted (20-30%) as well as a reduction of Cu and Zn by a factor of 2 to 3. The method used here with an adsorbent dose of 10 or 30 g/L was developed after a short literature review. In hindsight, though one study did use 10 g/L (Alchouron et al., 2021), the doses may have been too excessive as many authors used anywhere between 0.1 to 4 g/L (Alkurdi et al., 2020; Bakhta et al., 2020; Corral-Bobadilla et al., 2021).

6 CONCLUSIONS

In general, coral sand was a poor fluoride adsorbent. The maximum fluoride removal capacity obtained in this study using non-acidified solution was < 0.04 mg/g with an initial fluoride concentration of 200 mg/L (adsorbent dose of 1 g / 6 mL, mean particle diameter of 0.55 mm). In acidified solution, this capacity was between 0.008 to 0.11 mg/g when using solutions of 10 to 32 mg/L fluoride (at which point mass precipitation occurred). The likely cause of poor fluoride adsorption was that coral sand already contained fluoride, which took up part of its adsorption capacity. There was a balance between adsorption of fluoride onto sand vs. desorption of fluoride into solution, which was governed by the presence of acid and initial fluoride concentration of the solution (as well as other factors not examined in this study). The adsorption/desorption process could be affected by how much fluoride was pre-existing in the sand, which could vary according to the origin of the sand.

Column experiments indicated that 8 hours of contact did not significantly improve fluoride removal compared to 4 hours, and high sand-to-fluid ratios worked best at fluoride removal. A column-shaped treatment system used twice daily, with a 5:1 sand-to-fluid ratio, 4-hours of contact time, and 0.025 M citric acid effectively reduced fluoride from 10 mg/L to below the MAV of 1.5 mg/L, for at least 3.5 to 7 days. These results were greatly affected by the type of sand used. Columns containing larger Vanuatu sand particles, with a mean particle size of 1.32 mm, removed fluoride successfully for the maximum number of days (7). Generally, larger particles are not as effective in fluoride removal but results from these experiments contradicted this general trend. The mineral composition of the sand was disregarded as a potential reason because Vanuatu and Kiribati sand had very similar mineral content, yet their fluoride removal capability differed. Another possibility could be that Vanuatu sand contained less sorbed fluoride, increasing its adsorbent capacity. The most likely explanation was that the larger particles increased the pore volume of the column, which in turn decreased the excess fluid outside the pore volume. This extra pore space equated to more solution in closer contact with sand where fluoride removal occurred, which reduced the final fluoride concentration of the extract.

Increasing the acid concentration lowered fluoride removal efficiency, which also contradicts reported trends. The fact that coral sand contained fluoride, which can be released easily in acid, is a plausible explanation for this difference. In addition, preliminary observations indicated that this trend may be partly due to variation in extractable volumes. An increase in acid generated more carbon dioxide, which altered the sand pack and appeared to increase the volume which could be extracted. Given the original solution contained higher concentrations of fluoride and resided outside the pore volume, where little to no fluoride removal would have occurred, this increase in extractable fluid concentrated the final extract accordingly.

Scaling-up the 75 g sand columns to 1 kg sand prototypes and using food grade citric acid did not yield the same removal of fluoride. The prototypes could only be used three times to reduce 10 mg/L of fluoride to below the MAV, compared to seven times when columns of the same sand type were used. A preliminary trial with a single prototype jerrycan using analytical grade acid did not significantly improve fluoride removal when compared with results from food grade acid. Increasing the sand mean diameter also did not significantly improve results however, the increase from 0.55 to 0.9 mm may not have been substantial enough. The lower efficiency rate, by a factor of two, for buckets compared to columns has been documented in similar fluoride treatment systems (Fawell et al., 2006) and aligns with results from this study. A possible explanation derived from observations and results obtained here is again, due to differences in extractable volume. In the presence of acid, prototypes released on average 1-5 % more solution, which would concentrate the fluoride in the treated extracts.

There is a fine balance between multiple variables for effective fluoride removal to occur in a non-agitated system so that a sufficient volume of treated water is produced (i.e. 2 L ppd). Although a treatment system was developed in column format that functioned for at least 5 to 7 days, the system was not successfully scaled-up to a 1 L jerrycan format. Most importantly, the treated extracts were unacceptable in terms of drinking water quality.

The coral sands not only contained fluoride, but other contaminants which were confirmed via acid digestion and ICP-MS analysis of sands directly. These contaminants leached into the extracts, particularly when acid was added to the treatment protocol. Contaminants of health concern present in extracts at concentrations above drinking water guidelines, throughout the duration of the experiment included: As and Cr. Nickel and B were present in some Pacific sand extracts but their concentrations lowered below MAV after 1 to 3 days of use. Manganese was above the health limit only in Vanuatu sands on first use of the columns and was present in all sand extracts above aesthetic guidelines, for the duration of the trials. Other factors and elements were present in extracts above published limits throughout the duration of the trials, that would render the treated water unpalatable. These included: Al; Fe; total dissolved solids; and total hardness. Unfortunately, preliminary attempts at cleaning up extracts with activated charcoal treatment were unsuccessful, particularly for the main contaminants of concern: As, B, Cr, and Mn. Contaminant concentrations increased, for the most part, though fluoride was further reduced as were Ca, Cu, Ni, and Zn.

6.1 LIMITATIONS AND POTENTIAL IMPROVEMENTS

Many potential improvements and suggested further research points have been discussed above. The main limitation of this study was analytical in nature. The analytical FISE technique used here, though functional, had inherent issues mostly due to elevated contaminant concentrations, especially Al, B and Fe present in most extracts. Their concentrations, confirmed by ICP-MS, were sufficiently elevated to cause significant matrix interference and variation in fluoride measurement. Aluminium was detected in some extracts at concentrations of 2-3 mg/L. Aluminium present in concentrations of 3 mg/L can cause a 10 % measurement reduction of fluoride, when containing 1 mg F^-/L. Therefore, fluoride measurements, especially on first use when contaminant concentrations were generally highest, may be reduced by 10% from the presence of Al alone. This 10 % reduction does not account for other interfering ions such as iron (which was detected at concentrations up to 7 mg/L) and boron. Trialling other TISAB formulations more effective at counterbalancing Al and Fe (as described in the literature review), could simplify analysis and improve fluoride measurements. However, TISAB is not effective for boron tetrafluoride and boron was measured at concentrations up to 9 mg/L. Based on earlier experiments, it became apparent that at least one duplicate and one spiked sample should be analysed per treatment type or parameter variation (not per batch of samples) as each variation may alter the matrix differently, and in turn alter fluoride % recovery. Modifications to FISE methodology sufficiency circumvented the matrix interference encountered to provide reliable results. Use of the standard addition method or distillation may also have been an option, though more time consuming.

Sample variation, which is inherent given the heterogenous nature of the sand, could introduce some error in results. This was noted during sand characterisation (i.e. PSD, XRD) and trace element analysis of sands (i.e. ICP-MS and EDS), particularly Pacific sands, and sample heterogeneity would have introduced some random error in fluoride and trace contaminant measurements.

Contaminants present in the sand were likely introduced at the source, however, the possibility cannot be excluded that sand characterisation steps as well as manipulations prior to receipt introduced additional contaminants (Pacific Island sands were graciously donated by ESR whereas store-bought sands were purchased from a Chinese supplier and likely treated prior to sale). There is potential that some trace elements detected in the coral sands were introduced during the current study, for example, through equipment used for drying, sand characterisation, and splitting. Kiribati and Vanuatu sands were obtained from ESR and were likely sieved prior to use. However, the coarse bought sand was not sieved or split prior to use in the prototype experiment and yet significant concentrations of problematic elements were detected in its extracts and sand digests. Contaminants may also have been introduced through the columns or prototypes (i.e. the rubber plunger had been inside the 50 mL syringe body; five prototype devices were cleaned and reused at least 1-2 times during the research; metal mesh in the spout of the prototypes was a second-hand donation from the UC workshop) or from chemicals, as most were pre-opened on receipt. Citric acid solutions were also stored in glass for an extended period of time during the sand column experiments. Low contaminant concentrations in controls (i.e. in blank treatment devices and initial solutions) however, do not support this.

The ambient laboratory temperature varied from approximately 14 to 24 °C throughout the course of the study, which may have introduced some error in fluoride measurements conducted on different days. It may also have influenced the formation of precipitation in extracts. Solution concentrations were calculated gravimetrically in consequence, with an assumed value of 1 g/mL which would introduce a small skew to solution concentration, in particular those with higher citric acid concentration as these would be slightly denser. Another source of variability in fluoride and trace element analysis was caused by the consistency of the extracts. The unavoidable sticky nature of the extracts, combined with the low volumes used for FISE and trace analysis, may have introduced some degree of error in measured values, potentially increased the 2SD of average values, and caused differences in duplicate sample analysis larger than 5 %.

6.2 IMPLICATIONS FOR TREATMENT DEVICES FOR USE IN LOCAL SETTINGS

Results of this study highlight important factors to consider in the design of water treatment systems (of any kind) using coral sands, particularly if the water is to be consumed following treatment or released into waters which could subsequently be consumed. First and foremost, contaminants are present in coral sands which can be released into solution during sand contact. This release is more extensive in acidic conditions. Contaminants of health concern detected in coral sands which were also measured in concentrations above the MAV in their extracts included: As; B; Cr; Mn; and Ni. Fluoride was also indirectly detected in sand but not quantitated. Other elements, Al, Ca, Fe, Mg and Na, are also released into treated fluid which affect the aesthetics and desirability of water as a drinking source. Different geographical sources of sand may reveal different contaminants present in variable concentrations therefore, trace analysis of sands collected from different locations is recommended. It would be most prudent to analyse treated waters for the presence and concentration of elements of health concern (particularly As and Cr, and to a lesser extent, Ni and Mn) from any treatment system which incorporates contact with coral sand.

Given the significant leaching of contaminants when using high sand-to-fluid ratios and acidified solutions, these devices are less likely to be a successful solution to fluoride removal as they are more likely to create other health issues. Designing systems with lower ratios may be safer and is recommended. A remedy to these high contaminant concentrations in treated extracts is required before similar treatment devices should be used and their product consumed. Solutions could include removing contaminants from the sand prior to use in filter production; removing contaminants from processed water after fluoride removal treatment; or limiting the leaching of contaminants into treated samples. Field testing of prototype filters would benefit from trace element analysis of extracts. If coral sands systems were eventually field-implemented, a monitoring program might be valuable to ensure safety of treated water long-term.

When considering the design of a filter, sand particle size has a big influence on fluoride removal efficiency, and may need some level of control during filter production. Use of only very small particles, though usually enhances fluoride removal, is generally problematic in terms of filter clogging and is not recommended. There is a limit at which point grains are too small, and thus the pore volume too small, to be a practical filter material to produce an adequate volume of drinking water (2 L ppd). Another factor of importance includes assessing volume ratios (i.e. the pore volume vs. the total volume of fluid put into the treatment device), as this factor was quite important in fluoride removal success of non-agitated systems as developed here.

Column-shaped filters functioned better than jerrycans. The question of whether large columns, as opposed to drums or buckets, would be acceptable, practical and easily accessible in rural settings remains. Consideration of cultural implications is critical in designing or re-designing a prototype filter, as better solutions may be obvious from observing local practices but also, insufficient cultural attention can result in project failure (Schoeffel, 1995). For example, the process of collecting and carrying water could be incorporated into the fluoride removal treatment. Starting the removal process at the point of collection and having it take place whilst the water is carried back to the household could add agitation to the equation, which could enhance removal. This option may not be as suitable if using rainwater tanks, as is the case for 53-78 % of households in Vanuatu (String et al., 2020), or if the distance to the source is short (< 200 m reported by Foster and Willetts (2018)). That said, seasonal changes in water source is common in Pacific Island Countries where use of natural springs, rivers, and public standpipes increases significantly in the dry season (Elliott et al., 2017). In addition, String et al. (2020) reports the following on Vanuatu practices: residents take 2 to 20 water gatherings trips daily, ranging from < 1 to 150 minutes per trip; 61 – 78 % of households had water storage capability in-house, of which 48 – 60 % were buckets. This information also highlights the importance of local knowledge of year-round practices in treatment system design.

A final factor to consider is temperature, as it will influence fluoride removal given it affects solubility of compounds (such as those which developed in the extracts overnight) and is not particularly controllable in field settings. Ambient laboratory temperatures in New Zealand are about 19-22 °C but outdoor temperatures in Vanuatu or other Pacific region would reach significantly higher values, therefore temperature-controlled laboratory results may differ from field testing. Devices successful in laboratory could be trialled at ambient local temperatures prior to field testing to further ensure their local suitability.

6.3 FUTURE DIRECTION

Given the extent and concentration of contaminants of aesthetic and health concern present in the treated extracts, further work is necessary to ensure treated samples are safe for consumption, particularly with regards to arsenic and chromium. Research into decontamination methods for coral sand prior to use could be attempted and is potentially feasible. Some authors discovered that limestone could be fairly easily regenerated by removing the precipitate and grinding the limestone particles or, by washing the adsorbent with fluoride-free water (Nath et al., 2011; Nath & Dutta, 2012). If true, regeneration after an initial clean-up step to remove contaminants present, could potentially turn coral sand into a safer adsorbent. A mechanical method to regenerate the adsorbent would be ideal as fluoride-free water may not be available in fluoride affected areas, and hence the reason for studying fluoride removal. During the preparation of XRD sand samples following AELD treatment, drying and mechanical agitation of used sands visibly dislodged white precipitate formed during treatment. Similar methodology followed by sieving could potentially rid enough of the precipitate to regenerate the sand. Alternatively, seawater, which contains about 1.3 mg/L of fluoride (Millero et al., 2008) may be of low enough concentration to wash and remove some fluoride and other contaminants from the sand. Removing contaminants from solution after coral sand treatment is another potential solution. Activated charcoal or other adsorbents useful in arsenic and chromium remediation could be evaluated. Concurrent removal of fluoride and other toxins such as As and Mn has been documented (Bora et al., 2018; Gogoi et al., 2018; Kanaujia et al., 2015b; Mlilo et al., 2009) therefore exploration of combination filters to remove the added toxins would be valuable.

The use of lower sand-fluid ratios and agitation, as done by Camlek (2017), produced extracts of better quality with regards to trace contaminant concentrations. Additional fine-tuning of variables pertinent in AELD using coral sand could maintain or improve fluoride reduction as well as concurrently reduce contaminant leaching, rendering treated water safer to consume. Insights from this study and prior work with coral sand or other calcium carbonate materials indicate that the following adjustments may assist: increasing contact time; reducing or maintaining low acid concentrations; use of larger particles in a fixed-bed format; use of finer particles or pulverised sand in low sand-fluid ratios combined with some form of agitation. Many questions relating to the adsorption capacity of coral sand and its potential use as a fluoride adsorbent remain unanswered. How adsorbent is coral sand if it were decontaminated and regenerated? How adsorbent is coral sand in powdered format? How much agitation, in terms of frequency, duration, and intensity, is required for effective fluoride removal? Exploration of large-scale columns vs. drum-shaped treatment systems may further elucidate whether container shape is important in long-term filter efficiency.

Regarding analytical methods, trialling different TISAB formulations and/or altering the FISE methodology may simplify or improve fluoride analysis in future, particularly if treated extracts contain high contaminant concentrations. Ideally, designing a treatment system which generates treated extracts with lower contaminant concentrations may not require methodology adjustments and more importantly, the extracts may be safer to consume.

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APPENDIX A – CHEMICAL TRACKING

Table A 1

List of Chemicals Used, Batch Numbers, UC Tracking Numbers and Uses

Chemical Name	Batch No.	UC Tracking Number	Use
HI conductivity solution sachets HI70031	lot 7882; Exp 07/19	n/a	Conductivity meter calibration
Coral sand (fine 0.8-1 mm)	product code GB91	n/a	Adsorbent studied
Coral sand (coarse 1-2 mm)	GB88 – barcode 9419423 102184	n/a	Adsorbent studied
Vanuatu coral sand	n/a	n/a	Adsorbent studied
Kiribati coral sand	n/a	n/a	Adsorbent studied
Sodium Fluoride	unclear	CA0007845	LCS / CCV
Sodium Fluoride	6E 20215 (30105)	CA0005525	Calibration standards; Initial solutions
EDTA		CA0023689	TISAB
Sodium Chloride		CA0015241	TISAB
Sodium Chloride		CA0024576	TISAB
Glacial Acetic Acid		CA0024743	TISAB
Glacial Acetic Acid		CA0015241	TISAB
Fluoride Standard for IC	Lot BCBX0081 Exp Apr 21	CA0033775	Reference Standard, Spike
AR Citric Acid	10.248004	CA0018015	Initial solutions
FG Citric Acid	#7300 Best before 03.12.22	n/a	Initial solutions
pH buffer 7	BSPA98.500	CA0029970	pH meter calibration
pH buffer 4	BSPA97.500	CA0029962	pH meter calibration
pH buffer 10	BSPA99.500	CA0029946	pH meter calibration
Activated Charcoal	Purchased at Piko Wholefoods	n/a	Experiment M

APPENDIX B – SPIKE SOLUTION CONCENTRATION CALCULATIONS

The highest expected fluoride concentration in this study would be 10 mg/L, the initial fluoride concentration prior to fluoride removal. The spike should create a concentration 10 to 50 times the detection limit or 2 to 5 times the analyte concentration present in the natural (unspiked) sample (ASTM, 2016), that is:

2 x 10 mg / L = 20 mg/L
5 x 10 mg / L = 50 mg/L

20 mg/L was chosen in order to fit within the calibration range, thus the spike should add:

10 mg/L = 20 mg/L – 10 mg/L (assumed to be present in the original sample)

Given the 1/50 dilution of the spike to sample ratio used i.e. a 0.1 mL spike per 5 mL or 0.08mL for 4 mL of sample already mixed with TISAB, the spike concentration should measure:

50 (dilution factor) x 10 mg / L
= 0.5 g / L

However, the spike is not diluted with TISAB. To account for this 1:1 sample dilution, the spike concentration is halved giving a final concentration of 0.25 g/L.

A 10 mg/L spike is good for use in samples that are 1 to 4 times smaller, since the spike should create a sample 2 to 5 times that of the initial concentration:

[spike] + [unspiked] = 2 x [unspiked] → [spike] = [unspiked]
[spike] + [usnpiked] = 5 x [unspiked] → [spike] = 4 x [unspiked]

Thus:

A 10 mg/L spike (0.25 g/L spike solution concentration) to be used with samples measuring
→ **2.5 mg/L to 10 mg/L**.

A 8 mg/L spike (0.2 g/L spike solution concentration) to be used with samples measuring
→ **2 mg/L to 8 mg/L**.

A 4 mg/L spike (0.1 g/L spike solution concentration) to be used with samples measuring
→ **1 mg/L to 10 mg/L**.

A 2 mg/l spike (0.05 g/L spike solution concentration) to be used with samples measuring
→ **0.5 to 4 mg/L** (and also below 0.5 mg/L).

APPENDIX C – TISAB FORMULATION

Email from N. Alexander (personal communication, March 2, 2020)

- 0.05M Na2H2EDTA.2H_2O (13.60 g)
- 1.00 M NaCl (58.44 g)
- 0.122 M AcOH (7.33 g)
- 0.378 M NaOAc.3H_2O (51.44 g)
- pH (in theory) ~5.25

Dissolve in ~ 900 mL MilliQ water, adjust pH to between 5-5.5 and make up to 1L

If you don't have sodium acetate handy you can make it up using just glacial acetic acid (30.03 g) and adjusting pH with 8M NaOH until pH between 5-5.5 then make up to 1 L

Cheers

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APPENDIX D – METHODOLOGY DEVELOPMENT

EXPERIMENT A – TRIAL OF COLUMN SET-UP AND TISAB FORMULATIONS

This experiment was undertaken as a preliminary trial to assess the column set-up, gain experience using the instrumentation, develop a working methodology, as well as compare the modified TISAB 'B' formulation (refer 'TISAB Buffer B' below) with the TISAB formulation used in the UC Chemistry Undergraduate laboratory (Appendix C).

Experimental set-up: One 50 mL BD Plastipak™ syringe with a 26-gauge needle with cap was used without the plunger as a column. With an outer diameter of 29.4 mm and a length of 133 mm (Thermo FisherThermo Fisher Scientific, 2020), filling these syringes up to near the top approximately fulfils the recommended 1:4 ratio of diameter to length which minimise sidewall flow effects (Lewis & Sjöstrom, 2010). (Note that adhering to the 1:4 ratio was abandoned later in the study when acid was used because the carbon dioxide generated greatly disturbed any column packing.)

60 mL of fine coral sand (~84.5 g) which had previously been wetted with distilled H_2O and oven-dried, was added to one column and approximately 28 mL of non-acidified 10 mg/L fluoride solution was added at the plunger opening (referred to hereon in as the top of the column). This caused some sand compaction to about 57-58 mL and about 2 mL of fluid was noted above the sand line. Although the needle gauge used was the smallest available, a slow leak of solution was escaping from the tip, which instigated the search for a better stopper mechanism. Rubber septa and bungs were trialled. Both worked adequately but the bung was preferred as its larger size was easier and safer to manipulate.

FISE sample/calibration preparation with modified TISAB 'B': The loss of fluid meant that the column contained enough volume for only one sample, which was collected after about 24 hours of contact. This sample was filtered through a GVS 0.2 µm filter, 3.50 mL was mixed 1:1 with modified TISAB 'B' and analysed. The calibration curve was prepared using fluoride solutions of 0.5, 2, 5, 10, 15, 25 mg/L and quality control measures included one reagent blank and two laboratory control samples (4 and 20 mg/L). pH of FISE calibration standards, controls and samples were between 5.40 and 5.42.

(Additional detail regarding quality assessment of the modified TISAB 'B' formulation can be found in TISAB Buffer 'B' - Troubleshooting and Table D 2 below.)

No spike or duplicate samples were analysed in this trial experiment. Controls were made from the same stock fluoride solution as the calibration standards. This insured any variation or issues with the controls was more likely due to the method as opposed to the fluoride source itself.

RESULTS: In summary, the sample extract resulted in a measured fluoride value of 0.67 mg/L (see Table D 1). The laboratory controls LCS4 and LCS20 were within the cut off value of 15 % (13 and 4.3 % respectively), the reagent blank measurement was slightly elevated (0.13 mg/L), much more so than the blank values obtained with the UC TISAB formulation (refer below), and the slope of -53.6 was slightly outside the manufacturer range of -54 to -59. Removal of the 25 mg/L calibration standard from the calibration curve did not improved quality results and gave a similar value of 0.66 mg/L. (Note: the 25 mg/L standard is unnecessary given the measured fluoride values were not that concentrated). The slope and the blank were still too high at -52.9 and 0.127 mg/L respectively, but the laboratory control samples remained in an acceptable range.

Table D 1

Summary Trial Experiment A: Assessing and Comparing TISAB Formulations

Contact Time	pH		TISAB Formulation	Measured Fluoride Concentration (mg/L)	Comments
	After Coral Sand Treatment	After TISAB Addition			
n/a – initial solution	n/a	4.95	UC laboratory	10.5 mg/L.	Calculated concentration 10.0 mg/L
~24 hrs	Not measured Volume too low	5.42	Modified TISAB 'B'	0.67 mg/L	~93 % F^- removal*

Note. Single replicate trial using non-acidified 10 mg/L fluoride solution in ~3.3:1 sand-to-fluid ratio column. *No spike or duplicates performed and some quality issues with the experiment.

Upon further inspection, the quality issues were likely caused by the 0.5 mg/L calibration standard as the electrode seemed to require additional time to reach equilibrium at low fluoride concentrations. Removal of the 0.5 mg/L standard in the calibration curve equation put the slope in the correct range. Longer pre-conditioning of the electrode with a low concentrated sample prior to analysis would also have likely rectified the slope issue. A fresh calibration curve was later analysed which resolved the slope issue. That said, the blank values were still quite elevated even after a longer immersion time of 5 minutes.

FISE initial sample/calibration preparation with UC TISAB formulation: A 4 mL sample of the initial 10 mg/L fluoride solution was collected and mixed, unfiltered in a 1:1 ratio with the TISAB prepared by N. Alexander. The calibration curve was prepared from fluoride solutions of 2, 5, 10, 15, 25 mg/L and a reagent blank and two laboratory control samples of 4 and 20 mg/L were utilised. All FISE standards, controls, blank and sample had pH between 4.95 to 4.97.

RESULTS: The initial solution of 10 mg/L of fluoride resulted in a measured fluoride concentration of 10.5 mg/L (see Table D 1). The slope of the calibration curve (-60.4) was outside the manufacture range of -54 to -59. Laboratory control samples were less than 4 % different from the prepared values and the blank was quite low (<0.04 mg/L) and did not take a noticeably long time to reach equilibrium. Removal of calibration standard point 25 mg from the curve gave a similar initial sample value of 10.5 mg/L and did not improve quality control results: the slope was still too low at -60.3. In retrospect, though the pH values of all samples and standards were just below the recommended value of 5 to 5.5, it is plausible that the slope and results may have potentially benefitted from pH adjustment and re-analysis.

Given the trial nature of this experiment, re-analysis was not undertaken however this data provides some indication that 24 hours of contact between coral sand and a pore volume amount of 10 mg/L fluoride solution (circa 3.3:1 sand-to-fluid ratio) can potentially remove a significant portion of fluoride from solution without the addition of acid (over 93 % fluoride removal in this rough experiment). *Note that the initial and extract samples were analysed using different TISAB formulations and quality issues existed with the calibration curves and blanks, thus this result is a broad indication of potential removal rates only. No spike was performed and thus matrix interference, which would lower the fluoride value measured in sample extracts, is not known. A summary of observations of quality control variables with FISE using both TISAB formulations can be found in Table D 2.

Table D 2

Summary of Observations When Trialing Two TISAB Formulations from Experiment A.

Quality Control Variables	Observations	
	Modified TISAB B	**UC TISAB Formulation**
Blank measured value	*Higher* (0.13) but still less than half lowest calibration standard.	Low (<0.1). much less than half lowest calibration point.
Slope	*Slightly outside range*, within range if low calibration point (0.5 mg/L) removed.	*Outside range*
Equilibrium	Reached **very slowly,** unable to reach values below 0.14 mg/L	No obvious issues.
	Even 15 mins with blank did not reach equilibrium.	Could reach low values with a reasonable time.
LCS 4 &	13%	<3%
LCS 20	4.30%	4.10%
pH	Within 5 to 5.5	Rounded to 5.0, *may need adjustment upwards*
Comments and recommendations	Additional troubleshooting required.	May benefit from longer equilibration time for low concentrated samples.
	Requires fair amount of time for equilibration. Would benefit from electrode conditioning prior to analysis of low concentrated samples/blanks.	Slope to be checked.

Note. Summary of quality control measures, observations, and comparison of two TISAB formulation.

TISAB BUFFER 'B' – TROUBLESHOOTING

TISAB Buffer 'B': The formulation for TISAB buffer 'B' in Standard D1179 (ASTM, 2016) was adjusted due to a lower specific gravity of ammonium hydroxide (i.e. more concentrated) available through the UC Chemistry Department. Surprisingly, given hydroxide ions interfere with the FISE, the D1179 Standard does not specify the pH range required for this buffer as it does with the other formulation published.

The following chemicals were dissolved in approximately 800 mL of ultrapure water and made up to 1 L using a glass volumetric flask: citric acid (60.0170 g); sodium citrate dihydrate (210.3 g); ammonium chloride (53.64 g); and ammonium hydroxide (specific gravity of 0.88) 55 mL. The solution was incredibly viscous, with a pH of 6.25 at 24.2°C. As this pH is higher than the recommended value for other TISAB formulations used with a FISE (N. Alexander, personal communication, March 2, 2020; Agarwal et al., 2002; Camlek, 2017; EPA, 1996; Yuwono, 2005), a modified version of this TISAB formula was made with less ammonium hydroxide to keep the pH within the 5 to 5.5 range.

Modified Buffer 'B'

The modified buffer 'B' contained the following chemicals in a total of 250 mL: citric acid (15 g); sodium citrate dihydrate (50.5 g); ammonium chloride (13.4 g); and ammonium hydroxide – specific gravity of 0.88 (8.125 mL). The pH of this formulation was 5.33 at a temperature of 19.1 °C. No further ammonium hydroxide was added so the total amount of ammonium hydroxide in this modified version is about 60% of the original formulation.

This modified TISAB buffer B was trialled twice: in Experiment A (detailed above) and also by preparing a new calibration curve and re-analysing sample 'A' from Experiment A (detailed here). The sample value measured was similar to the original (0.71 vs. 0.67 mg/L). The blank was not reaching potential equilibrium even after 15 minutes of immersion time and the lowest measured fluoride concentration was above 0.14 mg/L. Though this value is less than half the value of the lowest calibration standard, it is much higher than the blank values obtained using the UC TISAB formulation (of 0.03 to 0.07 mg/L). The inability of the potential readings to get below 0.14 mg/L could be due to several reasons including but not limited to: a) the electrode requiring longer conditioning time; b) the extreme viscosity of the buffer which could also affect the equilibrium time; c) the presence of less ammonium ions given the TISAB formulation was modified from the published version.

Though the R values of 0.998 to 0.999 were good when compared to the published requirements of 0.995 (Baird & Bridgewater, 2017), the slope of one of two curves was slightly outside the manufacture range of -54 to -59 mV/decade (EDT directION, n.d.-b). Further troubleshooting was halted at this point and the formulation used in the UC Undergraduate Chemistry laboratory (refer Appendix C) which is known to work well, was used from this point forward. A summary of the findings and observations are listed in Table D 2.

In hindsight, preparing and trialling the formulation as published, ignoring the pH of the TISAB solution itself, but ensuring the pH of samples and controls mixed with TISAB are within the 5 to 9 range (as stated elsewhere in the standard method), may have been more successful. Insuring the pH of samples are similar to the values of the calibration curve standards would also have been beneficial.

EXPERIMENT B – PRELIMINARY TRIAL WITH 10 MG/L OF FLUORIDE AND NO ACID

Experimental Set-up: 3 X 50 mL BD Plastipak™ syringes fitted with a 26-gauge needle with the tip plugged into a rubber-septa were filled (not packed) with 85.0 g of fine coral sand (designated BI, BII, and BIII). A fluoride solution of 10.1 mg/L was added to the syringe to fill the pore volume of the column, that is, until the water level reached the top of the sand level. Approximately 25 mL was added, providing a sand-fluid ratio of approximately 3.4: 1. Column BI and BII had a total volume/sand combination of approximate 60 mL whereas column BIII had a small volume of water above the sand line: the fluid reached up to ~61 mL whereas the sand settled down to 58 - 59 mL only.

Sample extraction and preparation: After 8 hours, ~4 mL of fluid was removed from the columns, mixed and filtered with a 0.2 µm GVS filter and Chirana syringe. Results are tabulated in Table D 3. Extracts were collected from the columns by either removing the rubber septa and allowing the fluid to drip out of the needle or by twisting off the needle/septa assembly and collecting the fluid directly from the tip of the syringe body. Expelling the fluid from the syringe body was much speedier, required less force, and created less clogging but resulted in a small amount of sand loss. Use of the plunger to force out the fluid sped up the process drastically and increased the volume which could be collected from the column compared to using gravity alone. Plunger assistance and removal of the needle/septa assembly was the method of choice and used throughout the rest of this study, unless gravity was used. 3.5 mL of filtered sample extracts were mixed 1:1 with the UC TISAB formulation prepared by N. Alexander (refer Appendix C for formulation).

After 24 hours, attempts were made to collect a second sample from each column however the fluid was very difficult to extract and required repeated pressurisation with the plunger. It appears that this ratio of sand-to-fluid may be insufficient to obtain two ~4 mL samples per column, especially if duplicate and spike analysis is to be completed.

RESULTS: A 92-94 % fluoride removal rate was obtained by allowing 8 hours of contact between 85.0 g of sand and a pore volume (approximately 25 mL) of 10.1 mg/L non-acidified fluoride solution. This experimental set-up decreased the fluoride concentration from 10.1 mg/L down to 0.7 ± 0.1 mg/L, which is below the recommended guideline of 1.5 mg/L.

Table D 3

Results of Preliminary Trial (Experiment B) Single Sand Column with Non-Acidified F^- Solution.

Column Number	Contact Time	pH /Temperature		Measured Fluoride Concentration (mg/L)	% F^- removal*
		After Coral Sand Treatment	After TISAB Addition		
Bi	8	7.79 at 19.5 °C	4.97 at 20.1 °C	0.61	94%*
Bii	8	8.04 at 19.5 °C	4.99 at 20.2 °C	0.82	92%*
Biii	8	7.81 at 19.3 °C	4.97 at 20 °C	0.66	94%*
	Average ± 2SD	7.9 ± 0.2		0.7 ± 0.2	93 ± 2 %*
(Initial 10.1 mg/L)	0	N/A	5.01 at 20.1 °C	10.3	(1.9 % different from initial concentration)

Note. Pore volume (~25 mL) of non-acidified 10.1 mg/L fluoride solution added to triplicate columns containing 85g of coral sand, with contact time of 8 hours. (Sand-to-fluid ratio of approximately 3.4:1). No duplicates or spike performed.

The pH of the extracts, controls and calibration standards mixed in a 1:1 ratio with TISAB were slightly below the recommended value of 5. pH adjustments and re-analysis of samples was not undertaken given the trial nature of this experiment and decimal point rounding. Additionally, later experimental results demonstrated that re-analysis of samples adjusted for such small pH deviances had % differences of only about 1-2%.

All quality control measures were acceptable (slope = -58.4; R-value = 0.9999; blank <0.05 mg/L; LCS4 = 4.6 % bias; rerun of LCS4 = 0.4 % difference) instilling confidence in the use of this TISAB formulation. No duplicates were processed due to limited volume and no matrix spike was performed during this trial, thus it is unknown whether a matrix effect could be influencing measured fluoride concentrations.

ELAPSED TIME BETWEEN FISE SAMPLE PREPARATION AND ANALYSIS

In the matrix recovery experiment (Experiment E), samples were reanalysed 1 to 2 days following initial measurement. The measured fluoride concentration according to the number of days between preparation and analysis is detailed in Table D 4. The data indicates that the measured fluoride concentration decreases as more time elapses between sample preparation and analysis. The values decreased by ~2 - 4 % two days following preparation and 7 ± 1 % three days following preparation. The spiked water samples, which therefore had not been in contact with sand, were not affected by an extended lapse (up to a day) between sample preparation and analysis.

These results are somewhat inconsistent with the results obtained from the 1-week old samples analysed in Experiment C, Section 4.3.1. The % difference in measured fluoride concentration was ± 3 % a week following sample preparation, and some values were higher than the original measurement, not always lower. The major differences between these two experiments is the presence of acid in the earlier experiment as well as the refrigeration of samples which took place. Based on all results, preference would be for FISE sample analysis to be completed on the day of preparation, or no later than a day after.

Table D 4

Summary of Re-Analysis of Fluoride in Matrix Recovery Extracts Two & Three Days Following Preparation to Assess Measurement Error

Samples	**pH**	**[F$^-$] after # days decomplexing**			**% Difference based on # days decomplexed**		
(Column Use)		**(mg/L ± 2SD)**			**+ 1 day**		**+2 days**
		1 day	**2 days**	**3 days**	**(day 1 to 2)**	**(day 2 to 3)**	**(day 1 to 3)**
Day 1	9.0 ± 0.2	2.46 ± 0.08	2.38 ± 0.05	2.3 ± 0.1	-3.5 ± 1.4	-3.5 ± 2.4	**-7.0 ± 1.4**
Day 2	8.8 ± 0.1	1.99 ± 0.09	1.94 ± 0.11		-2.4 ± 1.4	na	na
Day 3	9.0 ± 0.1	1.78 ± 0.06	na		na	na	na
Day 1 (spikes)		5.0 ± 0.1	4.8 ± 0.1		-3.0 ± 0.8	na	na
H_2O (spikes)		2.58 ± 0.04	2.56 ± 0.01		0 ± 2	na	na

Note. Retesting sand extracts from Day 1, Day 2 and Day 3 of Matrix Recovery experiment, 1 and 2 days after original analysis. Difference in [F$^-$] compared to original concentration measured to assess change, if any, is above 5%. Samples stored at room temperature. Values are Averages ± 2SD (n=3, in mg/L). Value in red indicate % difference is above 5% error (quality cut off for duplicates).

OTHER OBSERVATIONS AND METHODOLOGY CHANGES

pH Meter: A 'Hanna HI8314' membrane pH meter (UC# 8041) was originally trialled but due to the numerous and very small volumes of sample used herein (5 to 8 mL), the electrode could not be immersed deep enough for consistent, reliable and accurate measurements. In addition, this probe does not measure temperature, thus the Mettler Toledo Unit was preferred.

Syringes: Terumo 10 mL syringes were eventually replaced with Chirana™ rubber-free syringes, to reduce contaminants from the rubber plunger for ICP-MS analysis. However, note that all columns were created from 50 mL BD Plastipak™ syringe bodies which had rubber plungers removed prior to use.

FISE 0.1 mg/L calibration standard: The 0.1 mg/L calibration standard used early on during this research, often reduced the R value of the curve to below 0.999 and thus was often omitted from the linear calibration curve equation. This was likely due to the difficulty or lengthy time required for the electrode to reach equilibrium at such a low concentration. This calibration standard was eventually replaced with a 0.25 mg/L standard from the Matrix Recovery Experiment (Experiment E) onwards.

Filtering of initial solution FISE samples: The 0.2 µm filtration step had no noticeable effect on analytical FISE results: measured fluoride values for filtered vs. non-filtered initial solution samples were within a 5 % difference from each other and from the calculated fluoride concentration. Therefore, filtering initial samples, which did not contain any particulate matter, was not undertaken on every initial sample throughout this study.

The laboratory control samples were used directly (i.e. not filtered, thus these were CCVs) in Experiments A to C. As mentioned, the filtering step had no noticeable effect on measured fluoride concentration and is used to remove particulate matter and interfering material from samples which can foul and damage the fluoride electrode or ICP-MS instrument.

FISE sample pH / TISAB: FISE samples with a pH just below the cut off value of 5, when pH adjusted and re-analysed, had only very small differences in measured fluoride values (1-2 % difference). Nevertheless, samples were pH adjusted to the recommended range of 5 to 5.5 and re-analysed from Experiment G onwards. It was noted that the pH of some FISE samples and standards were often and consistently just slightly below the recommended value of 5. To avoid adjusting the pH of each FISE sample individually, the pH of the stock TISAB solution itself was increased. A few NaOH pellets were dissolved into it and the new pH confirmed to be between 5 and 5.5, preferably around the mid-point of this range.

pH of ultrapure water / initial solutions: It was noted that the pH of non-acidified solutions and ultrapure water seemed to change and increase following preparation or removal from the filtration 'Purite' system and exposure to ambient air/temperature.

APPENDIX E – GRADISTAT ANALYSIS PRINT-OUTS

Figure E 1

GRADISTAT[1] Analysis of Fine Store-Bought Sand Sample A1.2

SAMPLE STATISTICS

SIEVING ERROR: 0.1%
SAMPLE IDENTITY: **A1.2**
ANALYST & DATE: ,
SAMPLE TYPE: Bimodal, Moderately Well Sorted
TEXTURAL GROUP: Slightly Gravelly Sand
SEDIMENT NAME: Slightly Very Fine Gravelly Medium Sand

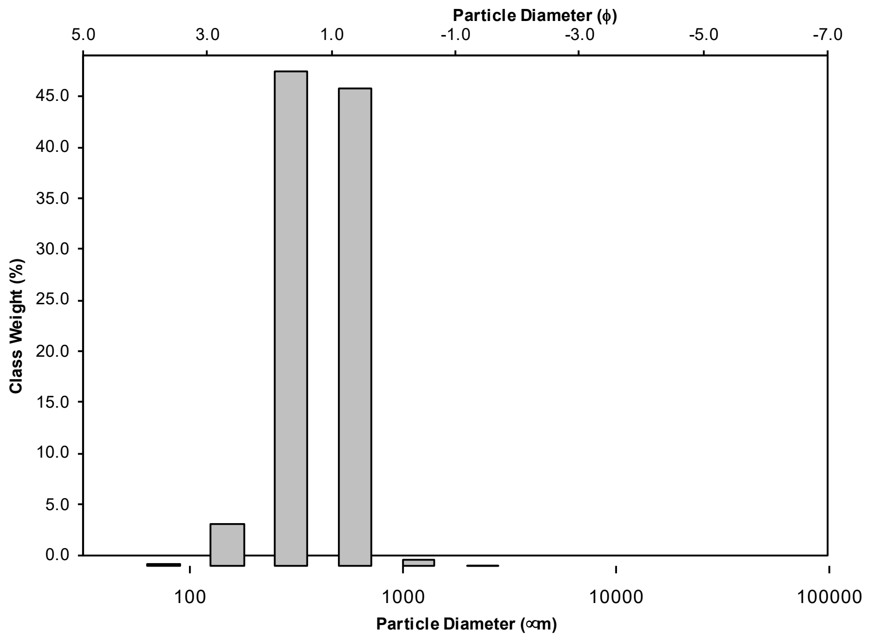
	∝m	ϕ
MODE 1:	302.5	1.747
MODE 2:	605.0	0.747
MODE 3:		
D$_{10}$:	260.2	0.596
MEDIAN or D$_{50}$:	347.9	1.523
D$_{90}$:	661.5	1.942
(D$_{90}$ / D$_{10}$):	2.542	3.258
(D$_{90}$ - D$_{10}$):	401.3	1.346
(D$_{75}$ / D$_{25}$):	2.037	2.352
(D$_{75}$ - D$_{25}$):	300.8	1.026

GRAIN SIZE DISTRIBUTION

GRAVEL:	0.0%	COARSE SAND:	46.6%
SAND:	99.9%	MEDIUM SAND:	48.3%
MUD:	0.1%	FINE SAND:	4.3%
		V FINE SAND:	0.2%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.0%	V FINE SILT:	0.0%
V COARSE SAND:	0.6%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic ∝m	Geometric ∝m	Logarithmic ϕ	Geometric ∝m	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	442.0	401.1	1.318	391.0	1.355	Medium Sand
SORTING (σ):	171.3	1.525	0.609	1.439	0.525	Moderately Well Sorted
SKEWNESS (Sk):	0.539	-0.815	0.815	0.383	-0.383	Very Coarse Skewed
KURTOSIS (K):	4.682	6.959	6.959	0.580	0.580	Very Platykurtic

GRAIN SIZE DISTRIBUTION



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 2

GRADISTAT[1] Analysis of Fine Store-Bought Sand Sample D1

SAMPLE STATISTICS

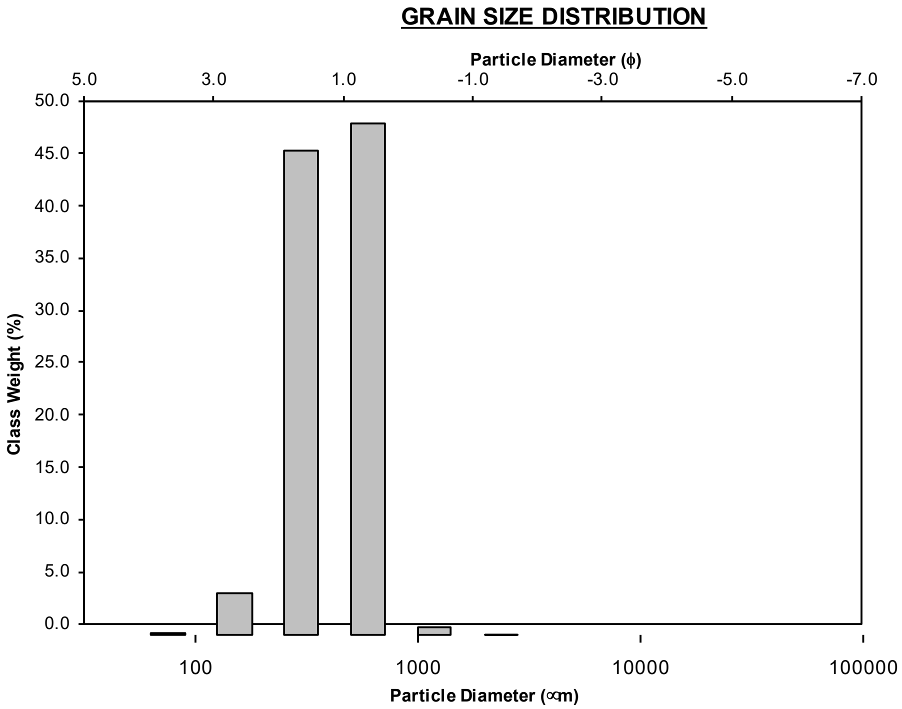
SIEVING ERROR: 0.1%
SAMPLE IDENTITY: **D1**
ANALYST & DATE: mel,
SAMPLE TYPE: Bimodal, Moderately Well Sorted
TEXTURAL GROUP: Slightly Gravelly Sand
SEDIMENT NAME: Slightly Very Fine Gravelly Coarse Sand

	∝m	ϕ
MODE 1:	605.0	0.747
MODE 2:	302.5	1.747
MODE 3:		
D_{10}:	260.9	0.591
MEDIAN or D_{50}:	353.6	1.500
D_{90}:	664.1	1.938
(D_{90} / D_{10}):	2.545	3.282
$(D_{90} - D_{10})$:	403.2	1.348
(D_{75} / D_{25}):	2.039	2.377
$(D_{75} - D_{25})$:	303.8	1.028

GRAIN SIZE DISTRIBUTION

GRAVEL:	0.0%	COARSE SAND:	48.8%
SAND:	99.9%	MEDIUM SAND:	46.2%
MUD:	0.1%	FINE SAND:	4.1%
		V FINE SAND:	0.2%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.0%	V FINE SILT:	0.0%
V COARSE SAND:	0.7%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic ∝m	Geometric ∝m	Logarithmic ϕ	Geometric ∝m	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	449.8	408.3	1.292	394.5	1.342	Medium Sand
SORTING (σ):	173.8	1.526	0.610	1.439	0.525	Moderately Well Sorted
SKEWNESS (Sk):	0.594	-0.839	0.839	0.356	-0.356	Very Coarse Skewed
KURTOSIS (K):	5.631	6.810	6.810	0.580	0.580	Very Platykurtic



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 3

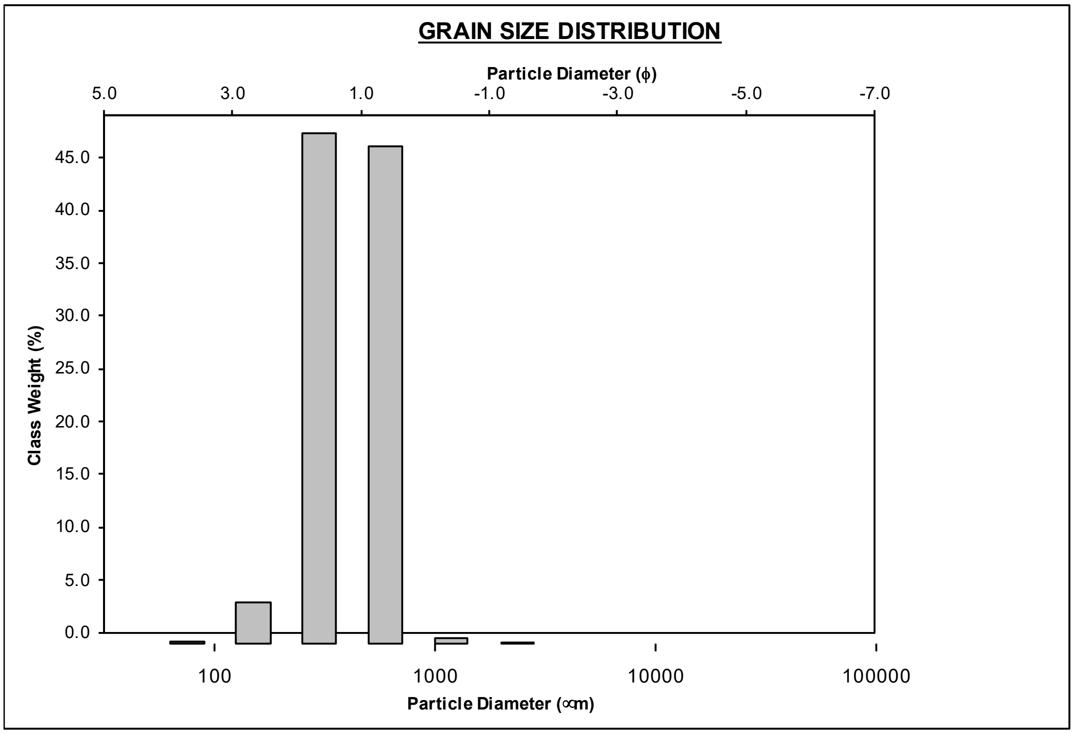
GRADISTAT[1] Analysis of Fine Store-Bought Sand Sample C1

SAMPLE STATISTICS

SIEVING ERROR:	0.2%		
SAMPLE IDENTITY:	**C!**	ANALYST & DATE:	Mel,
SAMPLE TYPE:	Bimodal, Moderately Well Sorted	TEXTURAL GROUP:	Slightly Gravelly Sand
SEDIMENT NAME:	Slightly Very Fine Gravelly Medium Sand		

	∝m	ϕ	GRAIN SIZE DISTRIBUTION			
MODE 1:	302.5	1.747	GRAVEL:	0.1%	COARSE SAND:	46.9%
MODE 2:	605.0	0.747	SAND:	99.8%	MEDIUM SAND:	48.2%
MODE 3:			MUD:	0.1%	FINE SAND:	4.0%
D_{10}:	260.6	0.595			V FINE SAND:	0.2%
MEDIAN or D_{50}:	348.7	1.520	V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
D_{90}:	661.9	1.940	COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
(D_{90} / D_{10}):	2.540	3.259	MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
$(D_{90} - D_{10})$:	401.3	1.345	FINE GRAVEL:	0.0%	FINE SILT:	0.0%
(D_{75} / D_{25}):	2.036	2.355	V FINE GRAVEL:	0.1%	V FINE SILT:	0.0%
$(D_{75} - D_{25})$:	301.0	1.026	V COARSE SAND:	0.5%	CLAY:	0.0%

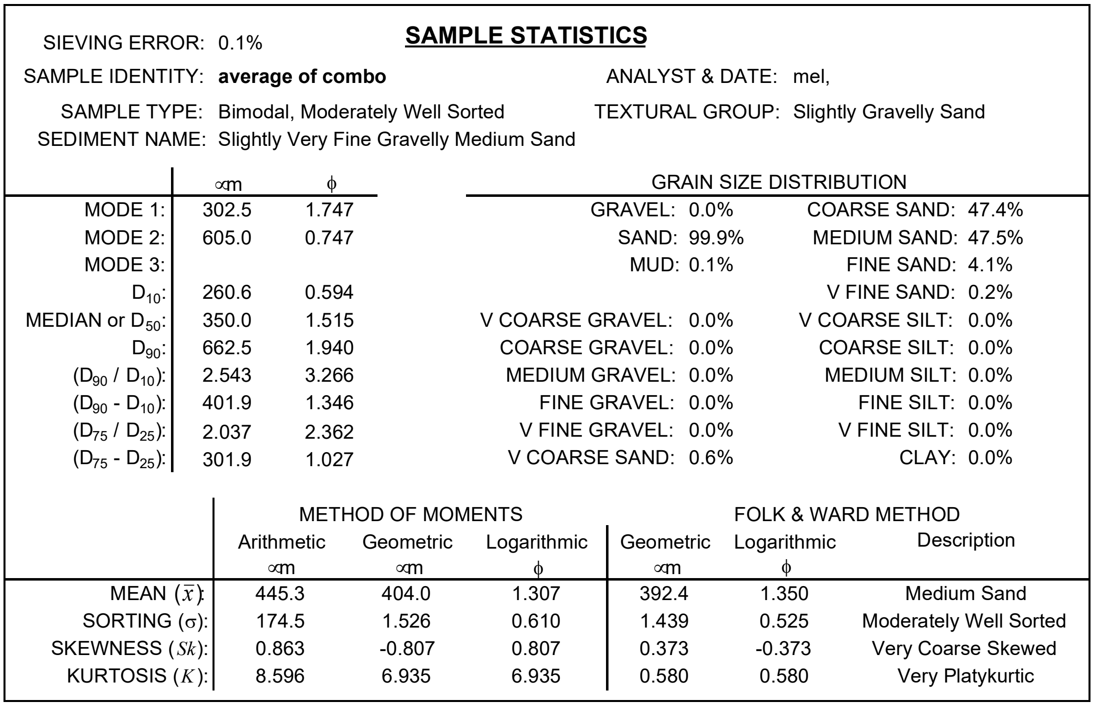
	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic ∝m	Geometric ∝m	Logarithmic ϕ	Geometric ∝m	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	444.5	402.8	1.312	391.6	1.352	Medium Sand
SORTING (σ):	180.1	1.527	0.610	1.438	0.524	Moderately Well Sorted
SKEWNESS (Sk):	1.586	-0.755	0.755	0.381	-0.381	Very Coarse Skewed
KURTOSIS (K):	16.64	7.072	7.072	0.580	0.580	Very Platykurtic



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 4

GRADISTAT[1] Analysis of Mean Fine Store-Bought Sand



SAMPLE STATISTICS

SIEVING ERROR: 0.1%

SAMPLE IDENTITY: **average of combo**

ANALYST & DATE: mel,

SAMPLE TYPE: Bimodal, Moderately Well Sorted

TEXTURAL GROUP: Slightly Gravelly Sand

SEDIMENT NAME: Slightly Very Fine Gravelly Medium Sand

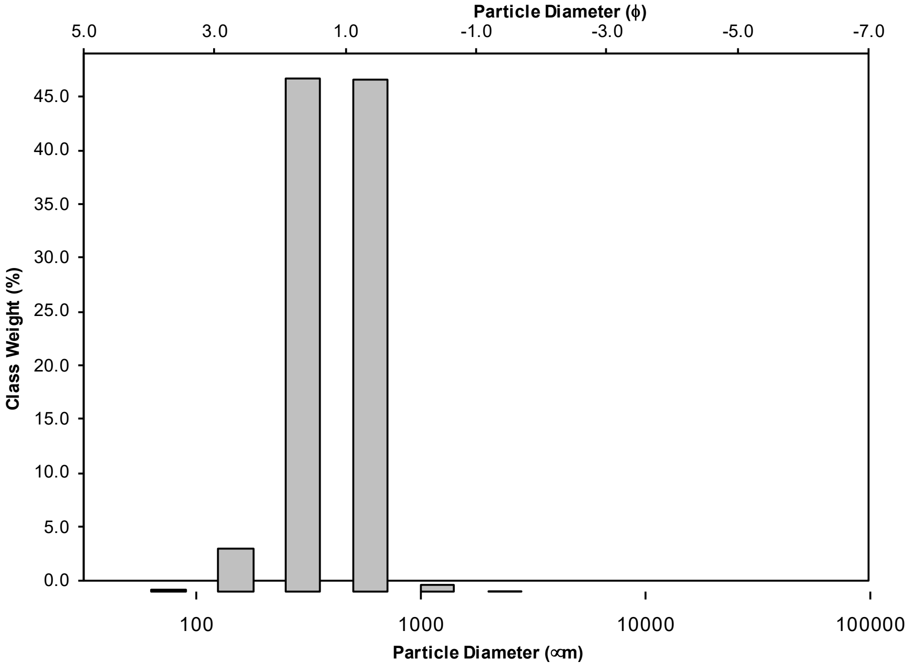
	∝m	ϕ
MODE 1:	302.5	1.747
MODE 2:	605.0	0.747
MODE 3:		
D_{10}:	260.6	0.594
MEDIAN or D_{50}:	350.0	1.515
D_{90}:	662.5	1.940
(D_{90} / D_{10}):	2.543	3.266
(D_{90} - D_{10}):	401.9	1.346
(D_{75} / D_{25}):	2.037	2.362
(D_{75} - D_{25}):	301.9	1.027

GRAIN SIZE DISTRIBUTION

GRAVEL:	0.0%	COARSE SAND:	47.4%
SAND:	99.9%	MEDIUM SAND:	47.5%
MUD:	0.1%	FINE SAND:	4.1%
		V FINE SAND:	0.2%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.0%	V FINE SILT:	0.0%
V COARSE SAND:	0.6%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic ∝m	Geometric ∝m	Logarithmic ϕ	Geometric ∝m	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	445.3	404.0	1.307	392.4	1.350	Medium Sand
SORTING (σ):	174.5	1.526	0.610	1.439	0.525	Moderately Well Sorted
SKEWNESS (Sk):	0.863	-0.807	0.807	0.373	-0.373	Very Coarse Skewed
KURTOSIS (K):	8.596	6.935	6.935	0.580	0.580	Very Platykurtic

GRAIN SIZE DISTRIBUTION



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 5

GRADISTAT[1] Analysis of Coarse Store-Bought Sand – Sample 1

SAMPLE STATISTICS

SIEVING ERROR: 0.1%

SAMPLE IDENTITY: **Coarse 1**

ANALYST & DATE: Mel, 28/2/2021

SAMPLE TYPE: Trimodal, Moderately Well Sorted

TEXTURAL GROUP: Sand

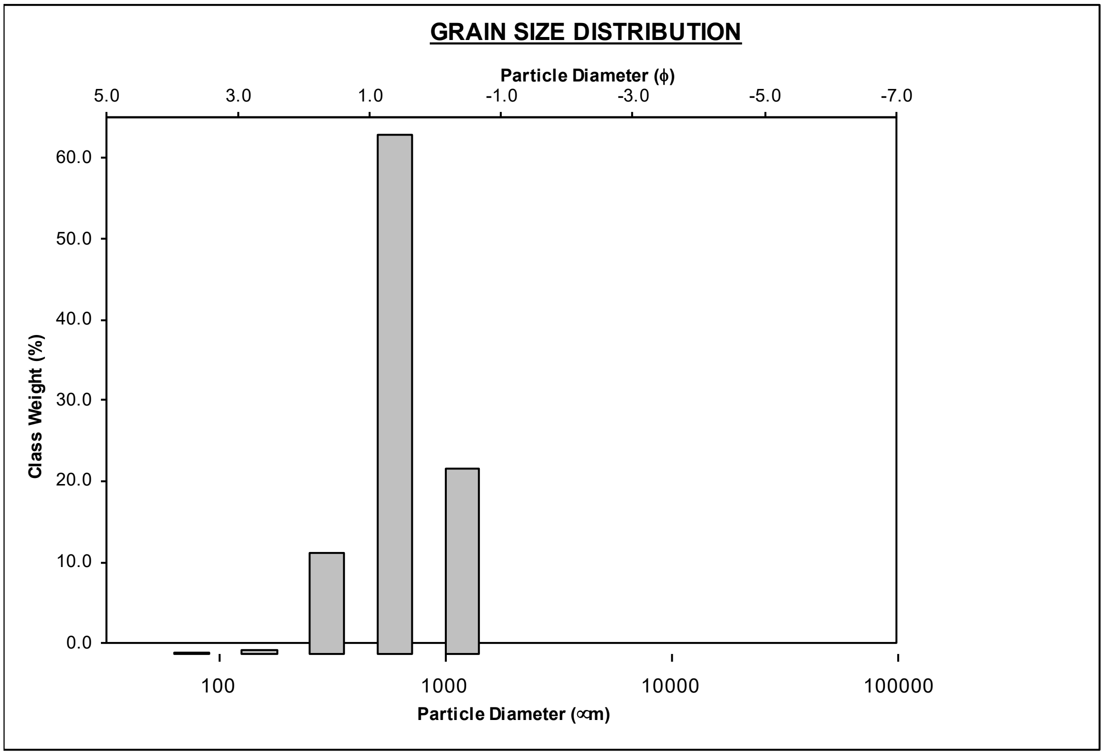
SEDIMENT NAME: Moderately Well Sorted Coarse Sand

	µm	ϕ
MODE 1:	605.0	0.747
MODE 2:	1200.0	-0.243
MODE 3:	302.5	1.747
D_{10}:	323.6	-0.266
MEDIAN or D_{50}:	610.2	0.713
D_{90}:	1202.3	1.628
(D_{90} / D_{10}):	3.715	-6.122
$(D_{90} - D_{10})$:	878.7	1.893
(D_{75} / D_{25}):	1.312	1.758
$(D_{75} - D_{25})$:	166.2	0.392

GRAIN SIZE DISTRIBUTION

GRAVEL:	0.0%	COARSE SAND:	64.6%
SAND:	99.9%	MEDIUM SAND:	12.6%
MUD:	0.1%	FINE SAND:	0.5%
		V FINE SAND:	0.2%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.0%	V FINE SILT:	0.0%
V COARSE SAND:	22.1%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic µm	Geometric µm	Logarithmic ϕ	Geometric µm	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	694.9	626.7	0.674	697.8	0.519	Coarse Sand
SORTING (σ):	288.9	1.555	0.637	1.529	0.612	Moderately Well Sorted
SKEWNESS (Sk):	0.788	-1.147	1.147	0.254	-0.254	Coarse Skewed
KURTOSIS (K):	2.621	11.86	11.86	2.307	2.307	Very Leptokurtic



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 6

GRADISTAT[1] Analysis of Coarse Store-Bought Sand – Sample 2

SAMPLE STATISTICS

SIEVING ERROR: 0.1%
SAMPLE IDENTITY: **Coarse 2**
ANALYST & DATE: Mel, 28/2/2021
SAMPLE TYPE: Bimodal, Moderately Well Sorted
TEXTURAL GROUP: Sand
SEDIMENT NAME: Moderately Well Sorted Coarse Sand

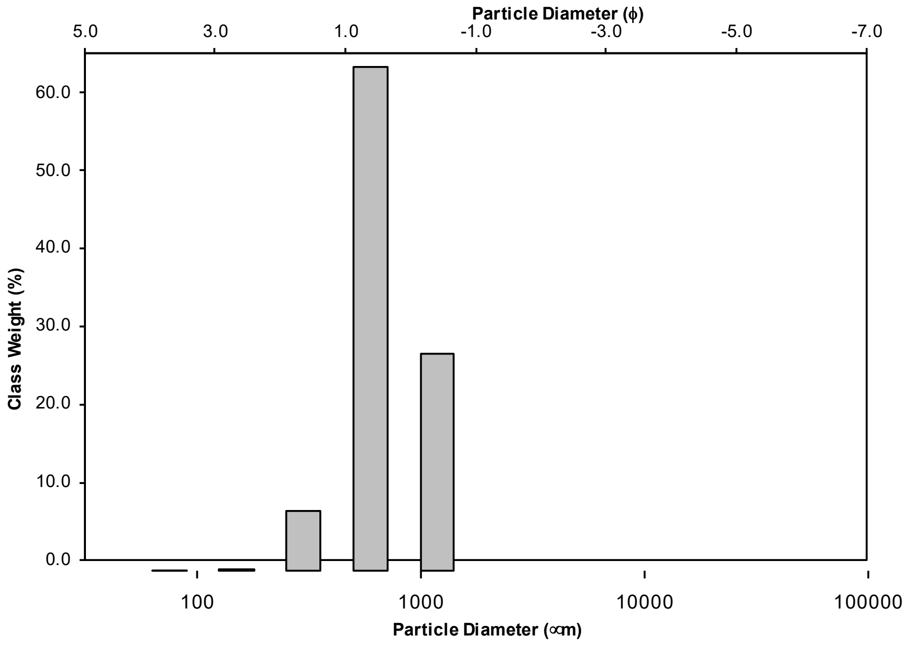
	µm	ϕ
MODE 1:	605.0	0.747
MODE 2:	1200.0	-0.243
MODE 3:		
D_{10}:	505.4	-0.305
MEDIAN or D_{50}:	626.9	0.674
D_{90}:	1235.4	0.985
(D_{90} / D_{10}):	2.445	-3.228
(D_{90} - D_{10}):	730.1	1.290
(D_{75} / D_{25}):	1.869	-25.243
(D_{75} - D_{25}):	476.2	0.902

GRAIN SIZE DISTRIBUTION

GRAVEL:	0.0%	COARSE SAND:	65.1%
SAND:	99.9%	MEDIUM SAND:	7.7%
MUD:	0.1%	FINE SAND:	0.2%
		V FINE SAND:	0.0%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.0%	V FINE SILT:	0.0%
V COARSE SAND:	26.9%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic µm	Geometric µm	Logarithmic ϕ	Geometric µm	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	740.3	675.3	0.566	721.2	0.472	Coarse Sand
SORTING (σ):	291.0	1.498	0.583	1.516	0.600	Moderately Well Sorted
SKEWNESS (Sk):	0.703	-0.809	0.809	0.279	-0.279	Coarse Skewed
KURTOSIS (K):	2.162	10.81	10.81	0.948	0.948	Mesokurtic

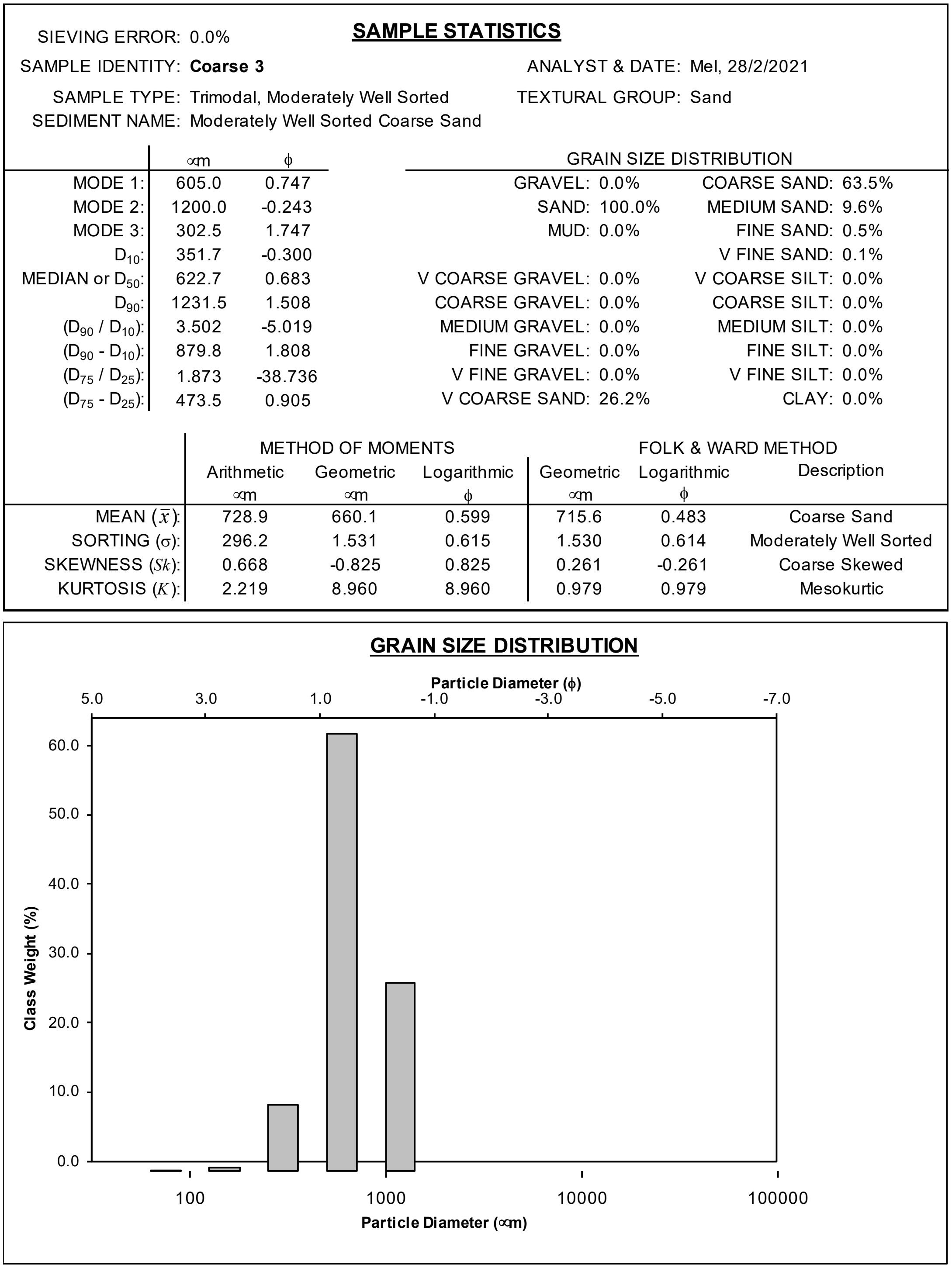
GRAIN SIZE DISTRIBUTION



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 7

GRADISTAT[1] Analysis of Coarse Store-Bought Sand – Sample 3



SAMPLE STATISTICS

SIEVING ERROR: 0.0%
SAMPLE IDENTITY: **Coarse 3**
ANALYST & DATE: Mel, 28/2/2021
SAMPLE TYPE: Trimodal, Moderately Well Sorted
TEXTURAL GROUP: Sand
SEDIMENT NAME: Moderately Well Sorted Coarse Sand

	µm	ϕ
MODE 1:	605.0	0.747
MODE 2:	1200.0	-0.243
MODE 3:	302.5	1.747
D_{10}:	351.7	-0.300
MEDIAN or D_{50}:	622.7	0.683
D_{90}:	1231.5	1.508
(D_{90} / D_{10}):	3.502	-5.019
$(D_{90} - D_{10})$:	879.8	1.808
(D_{75} / D_{25}):	1.873	-38.736
$(D_{75} - D_{25})$:	473.5	0.905

GRAIN SIZE DISTRIBUTION

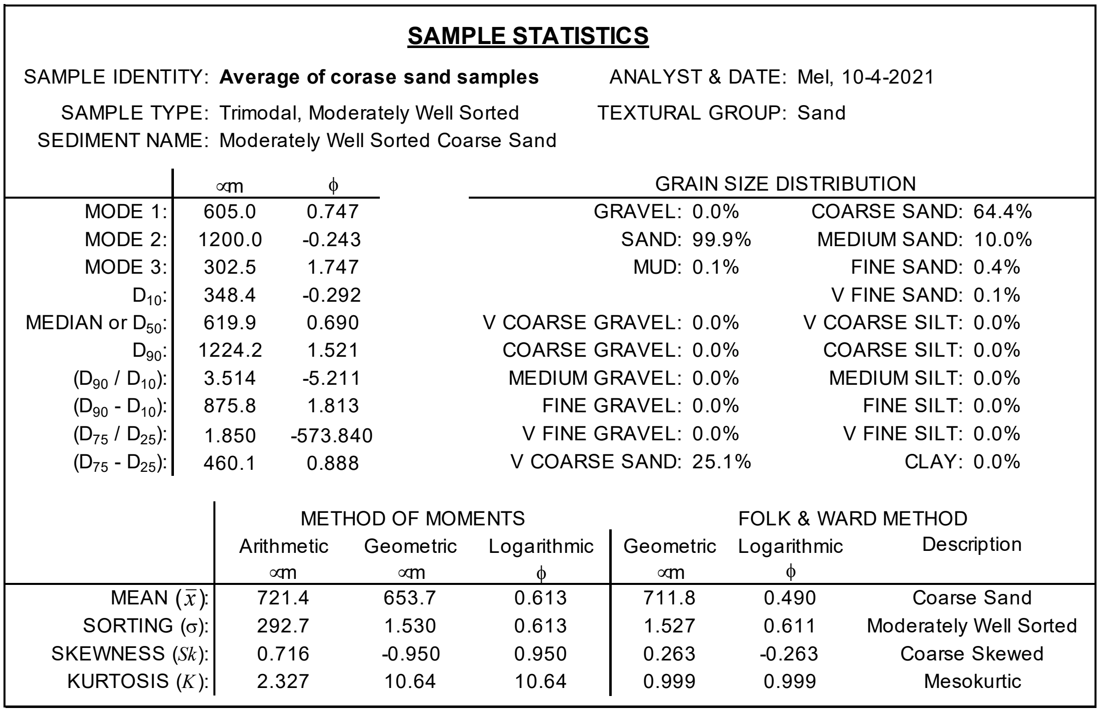
GRAVEL:	0.0%	COARSE SAND:	63.5%
SAND:	100.0%	MEDIUM SAND:	9.6%
MUD:	0.0%	FINE SAND:	0.5%
		V FINE SAND:	0.1%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.0%	V FINE SILT:	0.0%
V COARSE SAND:	26.2%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic µm	Geometric µm	Logarithmic ϕ	Geometric µm	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	728.9	660.1	0.599	715.6	0.483	Coarse Sand
SORTING (σ):	296.2	1.531	0.615	1.530	0.614	Moderately Well Sorted
SKEWNESS (Sk):	0.668	-0.825	0.825	0.261	-0.261	Coarse Skewed
KURTOSIS (K):	2.219	8.960	8.960	0.979	0.979	Mesokurtic

Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 8

GRADISTAT[1] Analysis of Mean Coarse Store-Bought Sand



SAMPLE STATISTICS

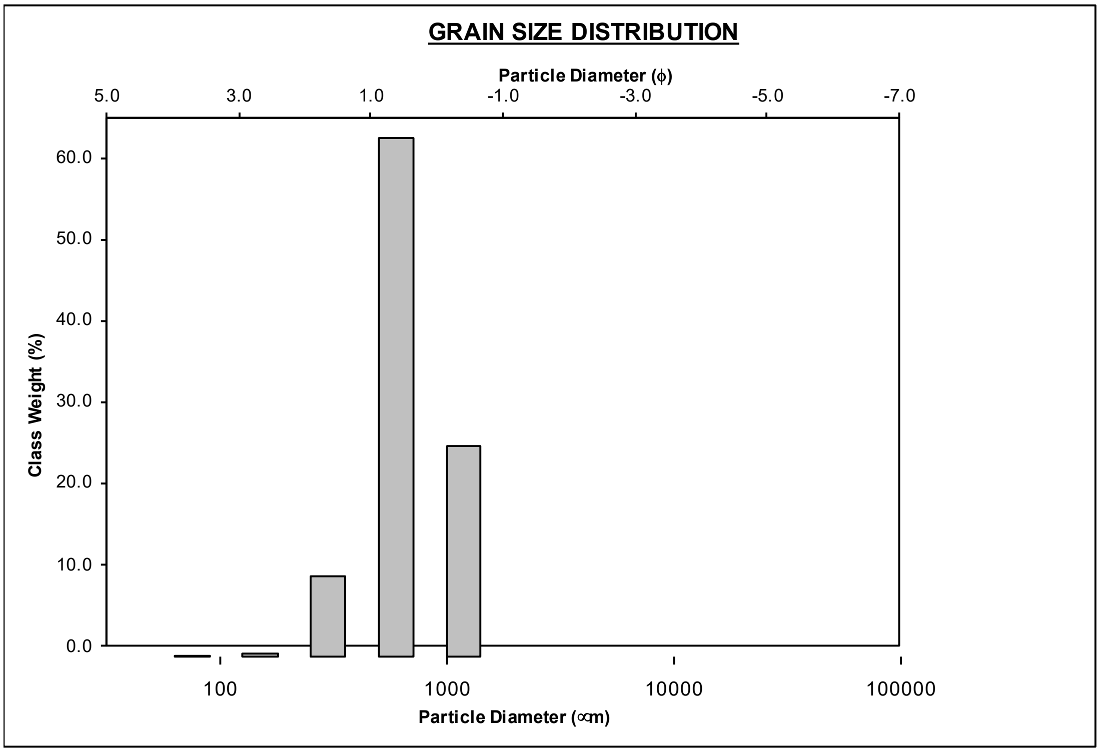
SAMPLE IDENTITY: **Average of corase sand samples**
ANALYST & DATE: Mel, 10-4-2021
SAMPLE TYPE: Trimodal, Moderately Well Sorted
TEXTURAL GROUP: Sand
SEDIMENT NAME: Moderately Well Sorted Coarse Sand

	∝m	ϕ
MODE 1:	605.0	0.747
MODE 2:	1200.0	-0.243
MODE 3:	302.5	1.747
D_{10}:	348.4	-0.292
MEDIAN or D_{50}:	619.9	0.690
D_{90}:	1224.2	1.521
(D_{90} / D_{10}):	3.514	-5.211
(D_{90} - D_{10}):	875.8	1.813
(D_{75} / D_{25}):	1.850	-573.840
(D_{75} - D_{25}):	460.1	0.888

GRAIN SIZE DISTRIBUTION

GRAVEL:	0.0%	COARSE SAND:	64.4%
SAND:	99.9%	MEDIUM SAND:	10.0%
MUD:	0.1%	FINE SAND:	0.4%
		V FINE SAND:	0.1%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.0%	V FINE SILT:	0.0%
V COARSE SAND:	25.1%	CLAY:	0.0%

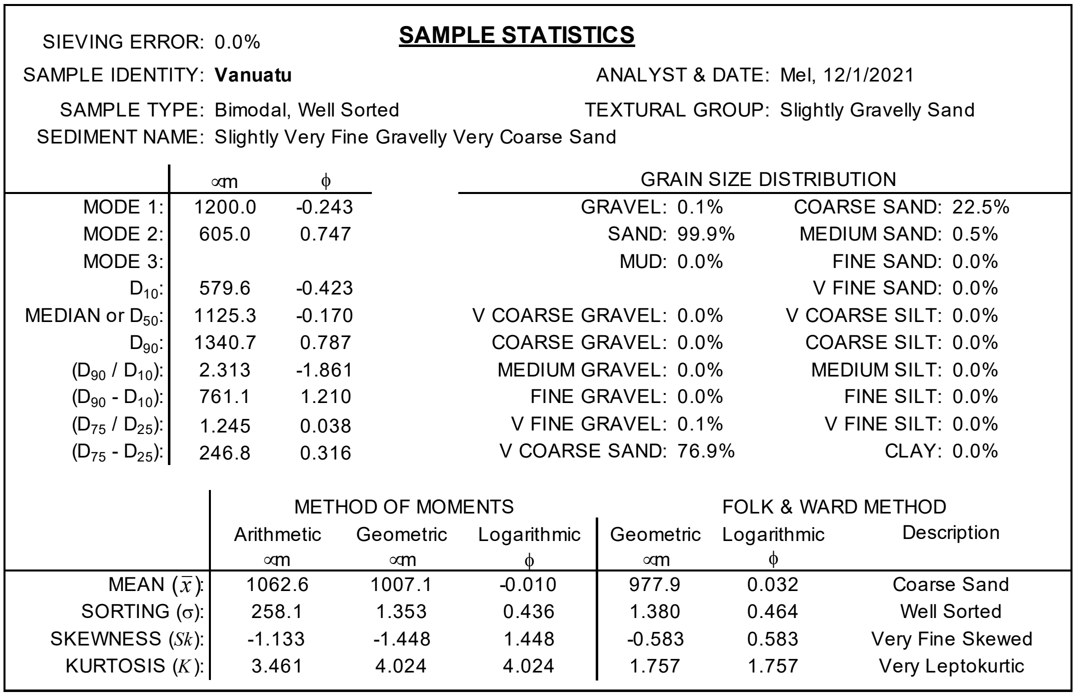
	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic ∝m	Geometric ∝m	Logarithmic ϕ	Geometric ∝m	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	721.4	653.7	0.613	711.8	0.490	Coarse Sand
SORTING (σ):	292.7	1.530	0.613	1.527	0.611	Moderately Well Sorted
SKEWNESS (Sk):	0.716	-0.950	0.950	0.263	-0.263	Coarse Skewed
KURTOSIS (K):	2.327	10.64	10.64	0.999	0.999	Mesokurtic



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 9

GRADISTAT[1] Analysis of Total Vanuatu Sand



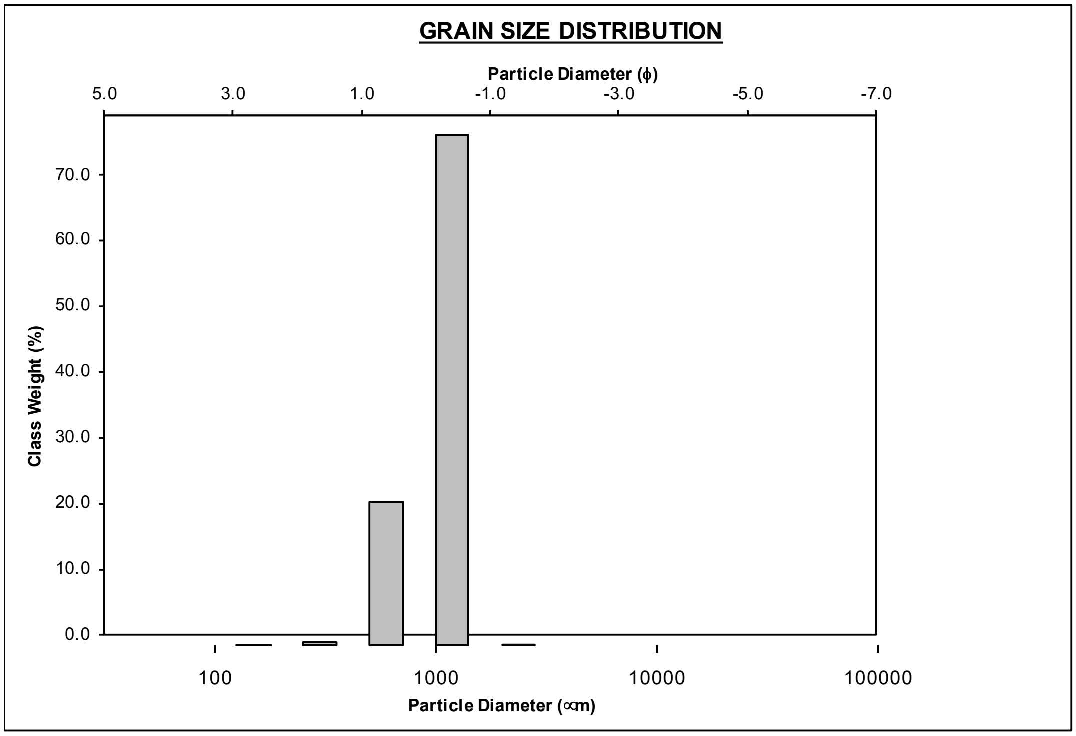
SAMPLE STATISTICS

SIEVING ERROR: 0.0%
SAMPLE IDENTITY: **Vanuatu**
ANALYST & DATE: Mel, 12/1/2021
SAMPLE TYPE: Bimodal, Well Sorted
TEXTURAL GROUP: Slightly Gravelly Sand
SEDIMENT NAME: Slightly Very Fine Gravelly Very Coarse Sand

	µm	ϕ
MODE 1:	1200.0	-0.243
MODE 2:	605.0	0.747
MODE 3:		
D_{10}:	579.6	-0.423
MEDIAN or D_{50}:	1125.3	-0.170
D_{90}:	1340.7	0.787
(D_{90} / D_{10}):	2.313	-1.861
$(D_{90} - D_{10})$:	761.1	1.210
(D_{75} / D_{25}):	1.245	0.038
$(D_{75} - D_{25})$:	246.8	0.316

GRAIN SIZE DISTRIBUTION			
GRAVEL:	0.1%	COARSE SAND:	22.5%
SAND:	99.9%	MEDIUM SAND:	0.5%
MUD:	0.0%	FINE SAND:	0.0%
		V FINE SAND:	0.0%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.1%	V FINE SILT:	0.0%
V COARSE SAND:	76.9%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic µm	Geometric µm	Logarithmic ϕ	Geometric µm	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	1062.6	1007.1	-0.010	977.9	0.032	Coarse Sand
SORTING (σ):	258.1	1.353	0.436	1.380	0.464	Well Sorted
SKEWNESS (Sk):	-1.133	-1.448	1.448	-0.583	0.583	Very Fine Skewed
KURTOSIS (K):	3.461	4.024	4.024	1.757	1.757	Very Leptokurtic



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 10

GRADISTAT[1] Analysis of Kiribati Subsample BB1

SAMPLE STATISTICS

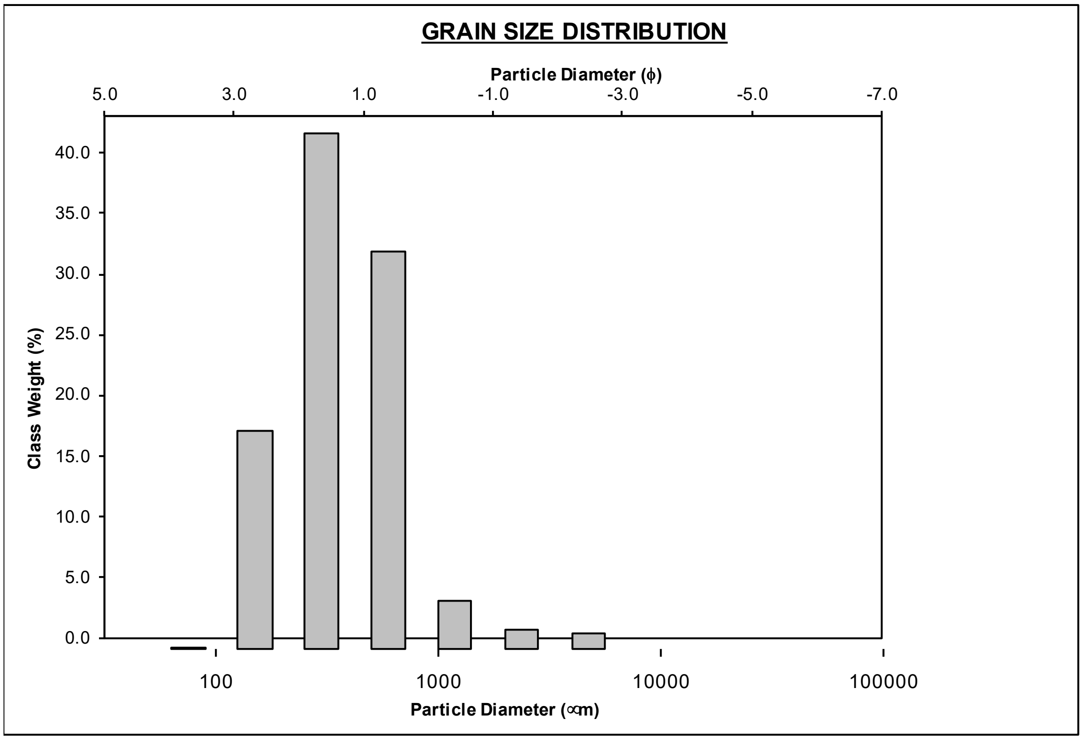
SIEVING ERROR: -0.1%
SAMPLE IDENTITY: **Kiribati sand sml sample**
ANALYST & DATE: MHL , 02-11-2020
SAMPLE TYPE: Trimodal, Moderately Sorted
TEXTURAL GROUP: Slightly Gravelly Sand
SEDIMENT NAME: Slightly Very Fine Gravelly Medium Sand

	∝m	φ
MODE 1:	302.5	1.747
MODE 2:	605.0	0.747
MODE 3:	152.5	2.737
D_{10}:	151.7	0.548
MEDIAN or D_{50}:	324.2	1.625
D_{90}:	683.9	2.721
(D_{90} / D_{10}):	4.508	4.964
$(D_{90} - D_{10})$:	532.2	2.173
(D_{75} / D_{25}):	2.209	2.463
$(D_{75} - D_{25})$:	318.4	1.143

GRAIN SIZE DISTRIBUTION

GRAVEL:	2.7%	COARSE SAND:	32.5%
SAND:	97.2%	MEDIUM SAND:	42.2%
MUD:	0.0%	FINE SAND:	18.6%
		V FINE SAND:	0.1%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	1.2%	FINE SILT:	0.0%
V FINE GRAVEL:	1.5%	V FINE SILT:	0.0%
V COARSE SAND:	3.8%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic	Geometric	Logarithmic	Geometric	Logarithmic	Description
	∝m	∝m	φ	∝m	φ	
MEAN ($\bar{x}$):	493.7	368.7	1.439	328.6	1.606	Medium Sand
SORTING (σ):	585.8	1.933	0.951	1.919	0.941	Moderately Sorted
SKEWNESS (Sk):	5.421	0.839	-0.839	0.111	-0.111	Coarse Skewed
KURTOSIS (K):	37.70	5.138	5.138	1.096	1.096	Mesokurtic



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 11

GRADISTAT[1] Analysis of Remainder of Kiribati Sand

SAMPLE STATISTICS

SIEVING ERROR: -0.1%

SAMPLE IDENTITY: **Kiribati remainder**

ANALYST & DATE: Mel,

SAMPLE TYPE: Polymodal, Moderately Sorted

TEXTURAL GROUP: Sand

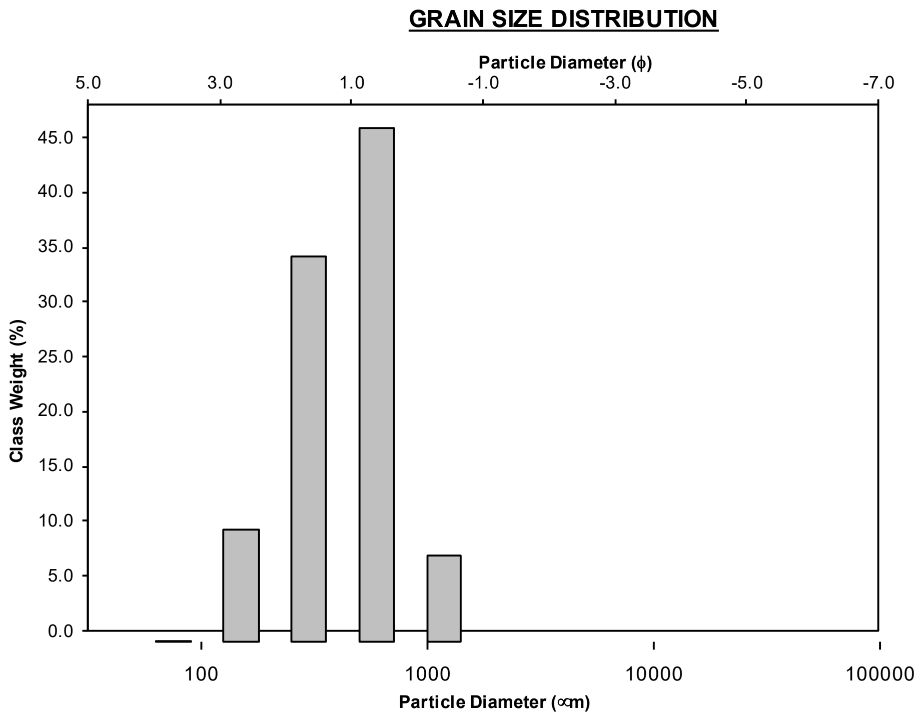
SEDIMENT NAME: Moderately Sorted Coarse Sand

	∝m	ϕ
MODE 1:	605.0	0.747
MODE 2:	302.5	1.747
MODE 3:	152.5	2.737
D_{10}:	175.9	0.521
MEDIAN or D_{50}:	516.3	0.954
D_{90}:	697.0	2.507
(D_{90} / D_{10}):	3.963	4.814
$(D_{90} - D_{10})$:	521.1	1.987
(D_{75} / D_{25}):	2.159	2.625
$(D_{75} - D_{25})$:	334.3	1.110

GRAIN SIZE DISTRIBUTION

GRAVEL:	0.0%	COARSE SAND:	46.7%
SAND:	100.0%	MEDIUM SAND:	35.1%
MUD:	0.0%	FINE SAND:	10.6%
		V FINE SAND:	0.1%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.0%	FINE SILT:	0.0%
V FINE GRAVEL:	0.0%	V FINE SILT:	0.0%
V COARSE SAND:	7.5%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic ∝m	Geometric ∝m	Logarithmic ϕ	Geometric ∝m	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	495.4	424.5	1.236	449.3	1.154	Medium Sand
SORTING (σ):	262.0	1.719	0.782	1.713	0.777	Moderately Sorted
SKEWNESS (Sk):	1.119	-0.244	0.244	-0.342	0.342	Very Fine Skewed
KURTOSIS (K):	4.373	2.606	2.606	1.077	1.077	Mesokurtic



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 12

GRADISTAT[1] Analysis of 2 mm+ Kiribati Sand

SAMPLE STATISTICS

SAMPLE IDENTITY: **large Kiribati 2m+**
ANALYST & DATE: Mel,
SAMPLE TYPE: Bimodal, Moderately Well Sorted
TEXTURAL GROUP: Gravel
SEDIMENT NAME: Very Fine Gravel

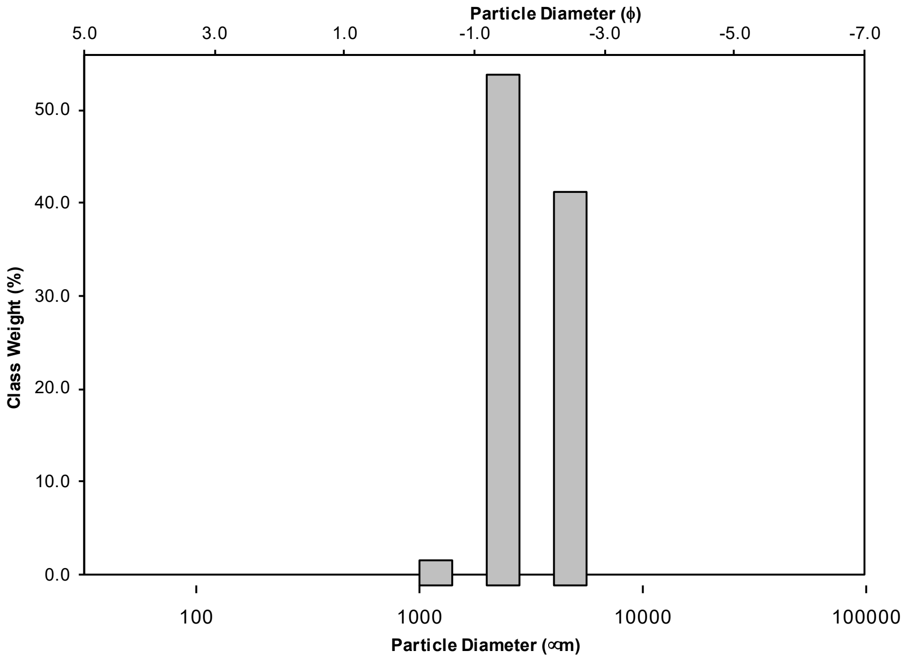
	∝m	ϕ
MODE 1:	2400.0	-1.243
MODE 2:	4800.0	-2.243
MODE 3:		
D_{10}:	2091.4	-2.371
MEDIAN or D_{50}:	2671.8	-1.418
D_{90}:	5172.2	-1.064
(D_{90} / D_{10}):	2.473	0.449
$(D_{90} - D_{10})$:	3080.8	1.306
(D_{75} / D_{25}):	2.003	0.544
$(D_{75} - D_{25})$:	2298.5	1.002

GRAIN SIZE DISTRIBUTION

GRAVEL:	97.3%	COARSE SAND:	0.0%
SAND:	2.7%	MEDIUM SAND:	0.0%
MUD:	0.0%	FINE SAND:	0.0%
		V FINE SAND:	0.0%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	42.3%	FINE SILT:	0.0%
V FINE GRAVEL:	55.0%	V FINE SILT:	0.0%
V COARSE SAND:	2.7%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic ∝m	Geometric ∝m	Logarithmic ϕ	Geometric ∝m	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	3383.8	3114.7	-1.639	3057.6	-1.612	Very Fine Gravel
SORTING (σ):	1228.8	1.456	0.542	1.423	0.509	Moderately Well Sorted
SKEWNESS (Sk):	0.214	-0.093	0.093	0.464	-0.464	Very Coarse Skewed
KURTOSIS (K):	1.242	2.005	2.005	0.576	0.576	Very Platykurtic

GRAIN SIZE DISTRIBUTION



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Figure E 13

GRADISTAT[1] Analysis of Composite Kiribati Sand

SIEVING ERROR: 0.0%

SAMPLE STATISTICS

SAMPLE IDENTITY: **Kiribati composite final**
ANALYST & DATE: Mel,
SAMPLE TYPE: Polymodal, Moderately Sorted
TEXTURAL GROUP: Slightly Gravelly Sand
SEDIMENT NAME: Slightly Very Fine Gravelly Coarse Sand

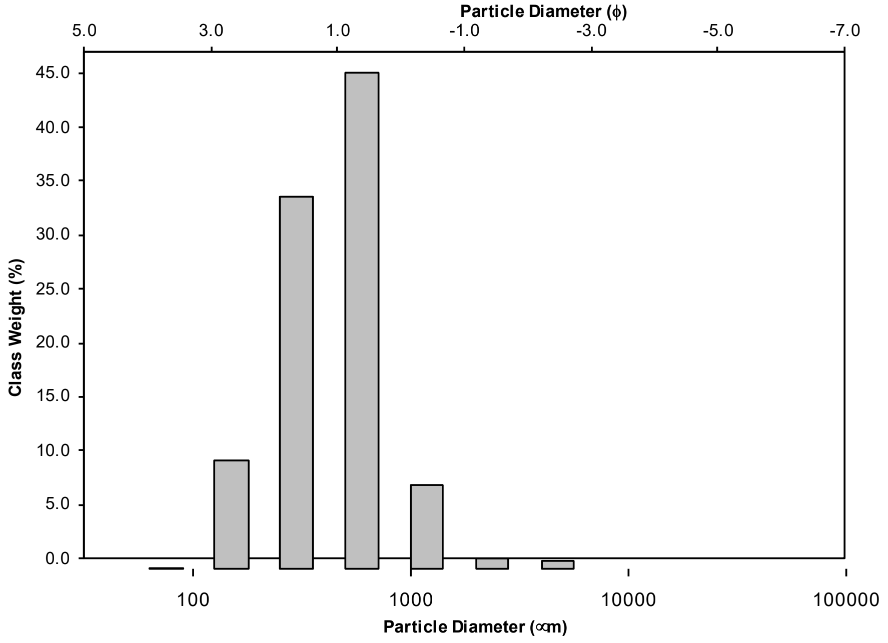
	∝m	ϕ
MODE 1:	605.0	0.747
MODE 2:	302.5	1.747
MODE 3:	152.5	2.737
D_{10}:	176.9	0.504
MEDIAN or D_{50}:	519.6	0.945
D_{90}:	705.0	2.499
(D_{90} / D_{10}):	3.985	4.955
$(D_{90} - D_{10})$:	528.1	1.995
(D_{75} / D_{25}):	2.170	2.670
$(D_{75} - D_{25})$:	339.0	1.118

GRAIN SIZE DISTRIBUTION

GRAVEL:	1.6%	COARSE SAND:	46.0%
SAND:	98.4%	MEDIUM SAND:	34.5%
MUD:	0.0%	FINE SAND:	10.4%
		V FINE SAND:	0.1%
V COARSE GRAVEL:	0.0%	V COARSE SILT:	0.0%
COARSE GRAVEL:	0.0%	COARSE SILT:	0.0%
MEDIUM GRAVEL:	0.0%	MEDIUM SILT:	0.0%
FINE GRAVEL:	0.7%	FINE SILT:	0.0%
V FINE GRAVEL:	0.9%	V FINE SILT:	0.0%
V COARSE SAND:	7.5%	CLAY:	0.0%

	METHOD OF MOMENTS			FOLK & WARD METHOD		
	Arithmetic ∝m	Geometric ∝m	Logarithmic ϕ	Geometric ∝m	Logarithmic ϕ	Description
MEAN ($\bar{x}$):	543.6	438.9	1.188	452.3	1.145	Medium Sand
SORTING (σ):	479.2	1.816	0.861	1.734	0.794	Moderately Sorted
SKEWNESS (Sk):	5.578	0.340	-0.340	-0.321	0.321	Very Fine Skewed
KURTOSIS (K):	46.39	4.164	4.164	1.106	1.106	Mesokurtic

GRAIN SIZE DISTRIBUTION



Note. [1] GRADISTAT V8.0 (Blott & Pye, 2001).

Table E 1

Back-Calculation of Composite PSD for Kiribati Sand

Composite Kiribati PSD	Kiribati Remainder		Upscaled Remainder	2mm+ Weight	Final Composite	
Sieve size (mm)	Weight (g)	(% w/w)	(g)	(g)	(g)	(% w/w)
4	0	0	0	9.4	9.4	0.71
2	0	0	0	12.2	12.2	0.92
1	64.2	7.5	98.52	0.6	99.12	7.45
0.5	398.4	46.7	611.35	0	611.35	45.96
0.25	298.8	35.1	458.51	0	458.51	34.47
0.125	90.5	10.6	138.87	0	138.87	10.44
0.063	0.5	0.06	0.77	0	0.77	0.06
<0.063	0	0	0	0	0	0
Total	852.4		1308.02	22.2	1330.22	

Note. % fractions back-calculated as follows: Total Kiribati sand received = 1501.8 g.

BB1 subsample (171.59 g) removed leaving 1330.21 g.

2 mm+ fraction removed (22.2 g) and PSD determined, leaving 1308.01 g.

Sand remaining after experiments = 851.7 g and PSD determined (‘remainder’ or ‘large’).

% w/w of 851.7 g ‘remainder’ proportionally scaled up to total of 1308.01 g and added to PSD of 2mm+ for final weight of 1330.21 g (Note small errors in rounding.)

PSD determined on fractional sum.

APPENDIX F – PRELIMINARY ISOTHERM STUDY (WITH NO ACID)

An initial adsorption study of fluoride onto coral sand without the addition of acid was studied by using a fixed amount of oven-dried coral sand (5 g) gently agitated at room temperature (21 ± 2 °C) in 30 mL of fluoride solution of varying concentrations (0; 1; 5; 10; 50; 100; and 200 mg/L). (Section 3.9.2 details solutions preparation.) A 'no sand' blank was also prepared using 200 mg/L fluoride solution in an empty falcon tube. The 50 mL plastic tubes were placed onto a head-over shaker at low rotation (speed setting of '3') for 24 hours to achieve equilibrium. Aliquots were extracted at 24 hours, filtered and analysed for pH, temperature and fluoride as detailed in Section 3.8.4. The calibration curve was created from prepared 0.5; 2; 5; 10; 15; 25; 100; 200 mg/L fluoride solutions as detailed in Section 3.3.1 and provided a slope of -58.9 and an R value of 0.9999. Note that the same stock solution (hence chemical source) was used for the standards and the unknown sample solutions. Quality controls used included a reagent / method blank, one duplicate, a spiked sample and spiked LCS created from a 10 % spike-to-sample ratio (i.e. 0.5 mL spike solution to 5 mL of analysed extract).

FISE samples were prepared from 3.5 mL of filtered extract and 3.5 mL of TISAB, decomplexed overnight. The initial (C_o) and equilibrium (C_e) concentrations were measured with the FISE and the q_e calculated as described above in Section 3.9.2. Results are tabulated in Table F 1. The LCS spike had 107 % recovery but spike was slightly below (1.81X) the recommended 2-5X the original sample value.

This preliminary data indicated that there is fluoride present in the sand, which is being released when the initial fluoride concentration in solution added to the sand is low (i.e. 0, 1 mg). In addition, the adsorption capacity (q_e) of the sand in these non-acidified conditions appears to be fairly low (< 0.05 mg/g). Note also the large difference in q_e values based on whether the q_e is calculated from the measured C_o vs. the calculated C_o.

Table F 1

Results of Preliminary Isotherm Experiment with No Acid

Solution Concentration (mg/L)	C_o calculated (mg/L)	C_o measured (mg/L)	pH prior	pH after	C_e (mg/L)	q_e From Co(calc) (mg/g)	q_e From Co(meas) (mg/g)
0	0	0.11 (<LOQ)	5.2	9.42	0.67	-0.00402	-0.00334
1	1.005	1.13	5.31	9.47	1.35	-0.00209	-0.00134
5	5.000	**5.23**	5.4	9.5	4.71	0.00175	0.00315
10	10.1	10.4	5.53	9.5	***9.18***	0.00519	0.0071
50	50.14	49.3	5.75	9.65	45.6	0.02703	0.0223
100	99.26	99.7	5.93	9.72	95.9	0.02067	0.0229
200	199.4	202	6.13	9.78	194	0.0335	0.0464
‘No sand’ blank with 200 mg/L	199.4	202	6.13	5.46	202	-0.01287	0

Note. Preliminary isotherm experiment (T = 23-25°C) without acid, following coral sand treatment, using an adsorbent dose of 1g / 6mL. QC checks: **spike** = 101 % recovery (P). ***duplicate*** = 1.2 % different. Blank, CCV & LCS within limits.

Improvements for Triplicate Isotherm Experiment

The isotherm was further studied in triplicate, with 0 M and 0.025 M citric acid. The original calibration curve processed with the 0 M samples using the general calibration standards in Section 3.3.1 (0.25; 0.5; 2; 5; 10; 25; 100; and 200 mg/L) was inadequate. To improve results, two curves were subsequently used with new calibration standards with a wider range up to 250 mg/L. One curve was used for samples below 25 mg/L and one for samples above 10 mg/L, as detailed in Section 3.9.2.

Large % bias in low concentrated samples has been reported (EPA, 1996), thus the 0.25 mg/L calibration standard solution was removed from the calibration curves for both the 0 M and 0.025 M citric acid experiments. This improved the R value of the slope and decreased the % difference by 3-5 % for all standards 0.5 mg/L and above but increased the error of the 0.25 mg/L standard by about 8-15 %. Given very few samples had measurements below 0.4 mg/L (with the exception of the initial solutions of 0 mg/L with and without 0.025 M acid) and the difficulties reaching equilibrium at lower sample concentrations, it was deemed acceptable to do this.

APPENDIX G – SUPPLEMENTARY DATA & FIGURES

Table G 1

Raw Data from Elemental Analysis using SEM-EDS Imaging from Three Types of AELD Treated and Untreated Sands

Sand	Site #	% weight ± sigma error												
		O	Ca	C	Mg	Sr	S	Fe	Si	Al	W	P	Na	Cl
Store	site 1	44.1 ±0.2	33.5 ±0.2	20.6 ±0.2	0.4 ±0	*0.7 ±0.1*	*0.1 ±0*	*0.2 ±0.1*	*0.1 ±0*	*0.1 ±0*	--	--	*0.2 ±0*	--
Store	site 2	45.4 ±0.2	32.8 ±0.2	20.3 ±0.2	0.5 ±0	*0.5 ±0.1*	*0.1 ±0*	--	*0.1 ±0*	*0.1 ±0*	--	--	*0.2 ±0*	--
Store	site 3	46.2 ±0.2	30.2 ±0.1	19.4 ±0.2	2.7 ±0	*0.3 ±0.1*	0.3 ±0	*0.2 ±0.1*	0.3 ±0	0.2 ±0	--	--	*0.3 ±0*	--
Kiribati	site 4	46.1 ±0.2	29.2 ±0.1	20.1 ±0.2	3 ±0	--	0.3 ±0	--	0.3 ±0	--	--	--	0.6 ±0	0.4 ±0
Kiribati	site 5	45.3 ±0.2	29.4 ±0.1	22.6 ±0.2	0.5 ±0	--	0.3 ±0	--	--	--	*0.5 ±0.1*	0 ±0	0.8 ±0	0.5 ±0.2
Kiribati	site 6	46.4 ±0.2	27.4 ±0.1	22.2 ±0.2	2.8 ±0	--	*0.1 ±0*	--	--	--	--	*0.1 ±0*	0.4 ±0	0.4 ±0
Vanuatu	site 7	39.1 ±0.3	19.4 ±0	30.8 ±0.4	1.7 ±0.1	--	*0.2 ±0*	--	0.8 ±0	--	--	--	4.2 ±0.1	3.8 ±0.1
Vanuatu	site 8	49 ±0.2	27.1 ±0.2	21.7 ±0.2	0.4 ±0	*0.6 ±0.1*	*0.3 ±0*	--	--	--	--	--	0.5 ±0	0.4 ±0
Vanuatu	site 9	43.6 ±0.3	31.9 ±0.2	21.9 ±0.3	0.9 ±0	0.4 ±0.1	*0.2 ±0*	--	--	--	--	--	0.5 ±0.1	*0.4 ±0*
Store (used)	site 10	47.3 ±0.2	23.6 ±0.1	28.3 ±0.1	*0.2 ±0*	0.5 ±0	--	--	--	--	--	--	*0.1 ±0*	--
Store (used)	site 11	45.8 ±0.2	19.9 ±0.1	33.8 ±0.2	*0.1 ±0*	*0.3 ±0.1*	--	--	--	--	--	--	--	--
Store (used)	site 12	45.8 ±0.2	31.9 ±0.1	21.1 ±0.2	*0.2 ±0*	*0.6 ±0.1*	*0.1 ±0*	--	*0.1 ±0*	--	--	--	*0.2 ±0*	--
Kiribati (used)	site 13	37.3 ±0.3	43.5 ±0.3	17.1 ±0.2	1.7 ±0.1	--	*0.2 ±0*	--	--	--	--	--	*0.2 ±0*	--
Kiribati (used)	site 14	44.3 ±0.2	31.3 ±0.1	21.2 ±0.2	2.9 ±0	--	*0.2 ±0*	--	--	--	--	--	*0.1 ±0*	--
Kiribati (used)	site 15	42.9 ±0.2	30.6 ±0.1	25.6 ±0.2	0.2 ±0	0.3 ±0.1	--	--	*0.1 ±0*	--	--	--	*0.2 ±0*	--
Vanuatu (used)	site 16	36 ±0.2	41.7 ±0.2	20.9 ±0.2	*0.2 ±0*	0.8 ±0.1	*0.2 ±0*	--	--	--	--	--	*0.2 ±0*	--
Vanuatu (used)	site 17	44.7 ±0.3	29.6 ±0.2	23.1 ±0.2	2.7 ±0.1	--	--	--	--	--	--	--	--	--
Vanuatu (used)	site 18	43.2 ±0.2	32.2 ±0.2	21.8 ±0.2	1.9 ±0	--	*0.3 ±0*	--	--	--	*0.4 ±0.1*	--	*0.2 ±0*	--
Vanuatu	site 9*	3.4 ±0.2	4 ±0.1	37.4 ±0.7	*0.2 ±0*	--	--	--	--	--	--	--	**19.9 ±0.3**	**35.2 ±0.4**
Kiribati	site 4*	39.6 ±0.2	35.2 ±0.2	20.3 ±0.2	3.8 ±0.1	--	0.4 ±0	--	--	--	*0.3 ±0.1*	--	0.3 ±0	--
Kiribati	site 4*	43.1 ±0.2	31.7 ±0.1	20.5 ±0.2	3.7 ±0	*0.3 ±0.1*	0.4 ±0	--	--	--	--	--	0.4 ±0	--
Kiribati	site 4*	47.5 ±0.2	26.7 ±0.1	21.4 ±0.2	3.2 ±0	--	0.3 ±0	--	--	--	--	--	0.5 ±0	0.3 ±0

Note. Store = Store-bought fine coral sand; sands were treated (used) or untreated; 3 'sites' or particles imaged per sample. % weights are indicated with sigma error of instrument. Values in red are near the detection limit/background of the instrument, thus their presence is uncertain. Values in green are indicative of salt deposit.

* indicates small area/site targeted for analysis as white appearance seemed to indicate presence of concentrated element/deposit in the region

Table G 2

Maximum and Minimum Elemental Composition (in mg/kg) of Untreated Coral Sands as Determined by Acid Digestion and ICP-MS Analysis

Element	**Vanuatu**		**Kiribati**		**Fine**		**Coarse**		**LOQ**	**SRM %**	**CRM %**	**SRL**
	Min	**Max**	**Min**	**Max**	**Min**	**Max**	**Min**	**Max**		**Recovery**		**(µg/g)**
Al	147	**1400**	49	72	145	156	97	115	3.5	88	111	5
As$^{75 \rightarrow 75}$	0.615	0.794	0.724	1.45	0.268	0.402	0.244	0.308	0.35	***77***	108	0.002
B	45.5	53	72.2	80.7	66.2	75	56.3	61.2	3.5	n/a	98	n/a
Cd	*<LOQ*	<LOQ	0.084	0.09	*<LOQ*	<LOQ	0.04	0.052	0.035	93	106	0.005
Co	0.026	0.11	0.061	0.43	0.039	0.046	*<LOQ*	<LOQ	0.035	87	99	0.02
Cr	5.9	10.4	2.1	4.6	1.9	2.2	2.1	2.5	0.035	80	101	0.25
Cu	0.627	0.7	1.313	5.79	0.183	0.249	0.135	0.145	0.035	87	106	4
Fe$^{56 \rightarrow 72}$	121	**406**	**2362**	**12851**	88	171	25	35	0.35	***68***	101	40
Mn	9.1	12.3	**15.1**	**45.4**	7.7	9.5	8.7	12.3	3.5	96	99	1.8
Ni	0.373	0.56	0.501	2.55	0.357	0.389	0.275	0.311	0.035	84	103	0.08
Pb	1.744	2.01	**3.836**	**99.41**	0.381	0.45	0.391	0.447	0.035	85	113	0.01
Zn	0.99	1.82	6.2	8.57	1.19	1.53	1.2	21.45	0.35	120	103	5
Ca (mg/g)	323	344	311	352	311	347	318	341	0.035	***73***	104	n/a
Mg (mg/g)	11.94	15.81	16.17	18.9	5.9	6.45	6.72	10.31	0.0035	88	92	n/a
Na (mg/g)	4.16	4.61	4.13	4.38	3.35	3.48	2.97	3.2	0.00035	***72***	106	n/a
S (mg/g)	1.46	1.71	1.6	1.89	1.36	1.49	1.29	1.55	0.035	***62***	n/a	n/a

Note. Maximum and minimum (n=3) concentrations in mg/kg unless indicated with the average of two blanks was deducted. Acid digestion of 0.3 g in 5 mL concentrated acid. Values in red are outside the quality guideline (80 – 120 % recovery range).

Table G 3

Summary of Matrix Recovery Experiment Data: pH and Final Fluoride Concentration

Sample	**Temperature (°C)**	**pH of Extract**	**Final Fluoride Concentration (mg / L)**	**Standardized % Recovery (P')**
MR – day 1	25.3 ± 0.06 °C	9.0 ± 0.1	2.46 ± 0.08	104
MR – day 2	22.6 ± 0.2 °C	8.8 ± 0.1	1.99 ± 0.08	103
MR – day 3	21.8 ± 0.1 °C	8.9 ± 0.1	1.78 ± 0.06	100
H_2O – day 1*	24.1 °C	~5**	< LOQ	104
H_2O – day 2*	22.5 – 22.8 °C	~4.45 – 4.66**	< LOQ	103
H_2O – day 3*	21.5 – 22 °C	~4.21 – 4.93**	< LOQ	100

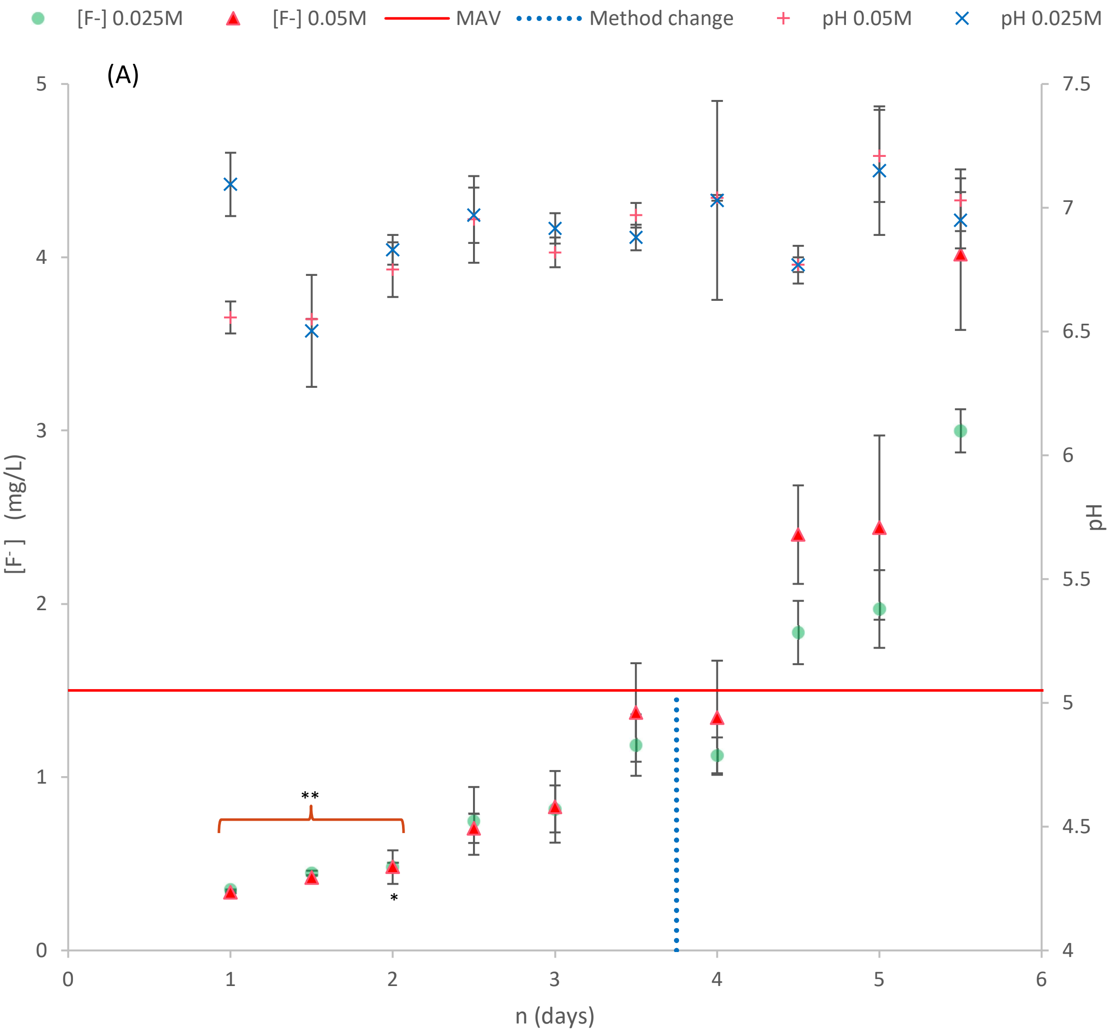
Note. Columns reused daily with ultrapure water and 4 hour contact, over three consecutive days. Average ± 2SD (n=3).

* = duplicate on day 1 and 2, single replicate on day 3.

** = pH of ultrapure water at start of experiment. The pH varied quite rapidly following removal from the purification unit.

Figure G 1

Final Fluoride Concentration and pH of Extracts vs. Repeated Use of Fine Store-Bought Sand Columns with 5:1 Sand-Fluid Ratio (Experiment K)



Note. Columns twice-daily use, with 4-hour contact. Initial 10mg/L fluoride solution prepared in 0.025 or 0.05M citric acid. Average of triplicates ± 2SD (except for day 1 – first use, where n=2). Method change = change in FISE analytical method from analysing 1:2 diluted sample to non-diluted sample.

* P'=67% (for 0.025M) ** P' < 80% (for 0.05M samples).

Table G 4

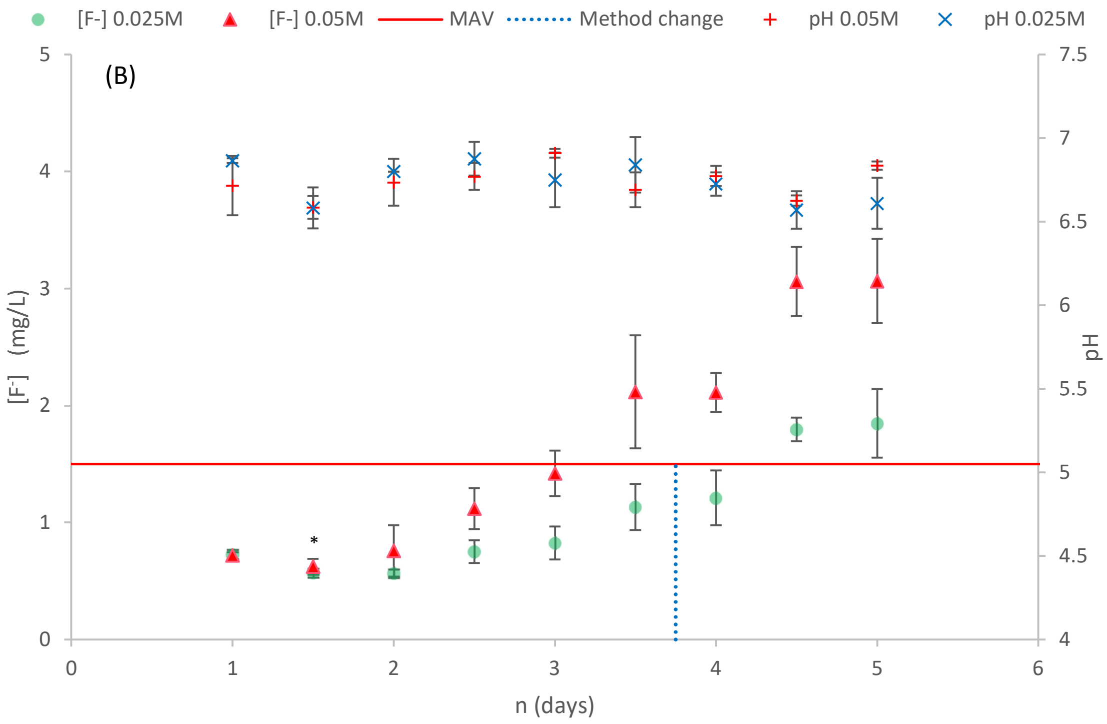
Raw Data for 0.025 & 0.05 M Citric Acid, 5:1 Sand-Fluid Columns – Experiment K – Store-Bought Fine Coral Sand (Figure G 1)

[Acid]	Initial				Use	Final				P'	Dilute
(M)	$[F^-]$ (mg/L)		pH	n	(days)	$[F^-]$		pH			FISE
	Measured	Calculated				(mg/L)	2SD		2SD		Sample
0.025	9.99	10.14	2.36	2	1	0.35	0	7.1	0.1	83	Y
0.025	9.99	10.13	2.50	3	1.5	0.45	0.01	6.5	0.2	81	Y
0.025	10.06	10.14	2.55	3	2	0.48	0.1	6.83	0.06	***68***	Y
0.025	10.06	10.14	2.55	3	2.5	0.75	0.2	7	0.1	90	Y
0.025	9.91	10.20	2.43	3	3	0.8	0.1	6.92	0.06	93	Y
0.025	9.91	10.20	2.43	3	3.5	1.2	0.2	6.88	0.05	98	Y
0.025	10.04	10.15	2.45	3	4	1.1	0.1	7.03	0.4	95	N
0.025	10.04	10.15	2.45	3	4.5	1.8	0.2	6.77	0.03	96	N
0.025	10.49	10.02	2.48	3	5	2	0.2	7.2	0.3	95	N
0.025	10.49	10.02	2.48	3	5.5	3	0.1	7	0.1	98	N
0.05	9.87	10.16	2.32	3	1	0.34	0	6.56	0.06	***73***	Y
0.05	9.87	10.12	2.27	3	1.5	0.42	0.02	6.55	0	***78***	Y
0.05	9.79	10.20	2.46	3	2	0.48	0.03	6.8	0.1	n.d.	Y
0.05	9.79	10.20	2.46	3	2.5	0.7	0.08	7	0.2	87	Y
0.05	9.91	10.20	2.34	3	3	0.8	0.2	6.82	0.06	90	Y
0.05	9.91	10.20	2.34	3	3.5	1.4	0.3	6.97	0.05	96	Y
0.05	9.92	10.12	2.37	3	4	1.3	0.3	7.04	0.01	94	N
0.05	9.92	10.12	2.37	3	4.5	2.4	0.3	6.77	0.08	98	N
0.05	9.88	10.03	2.34	3	5	2.4	0.5	7.2	0.2	95	N
0.05	9.88	10.03	2.34	3	5.5	4	0.4	7	0.1	98	N

Note. Columns used twice daily (second use of the day represented as n = 0.5 days). Values in red are outside quality guidelines.

Figure G 2

Final Fluoride Concentration and pH of Extracts vs. Repeated Use of Kiribati Sand Columns with 5:1 Sand-Fluid Ratio (Experiment K)



Note. Columns twice-daily use, with 4-hour contact. Initial 10 mg/L fluoride solution prepared in 0.025 or 0.05 M citric acid. Average of triplicates ± 2SD (except for day 1 – first use, where n=2). Method change = change in FISE analytical method from analysing 1:2 dilute FISE sample to non-diluted sample.

*0.025M = duplicate % difference of 5.7% (outside 5% quality guideline)

Table G 5

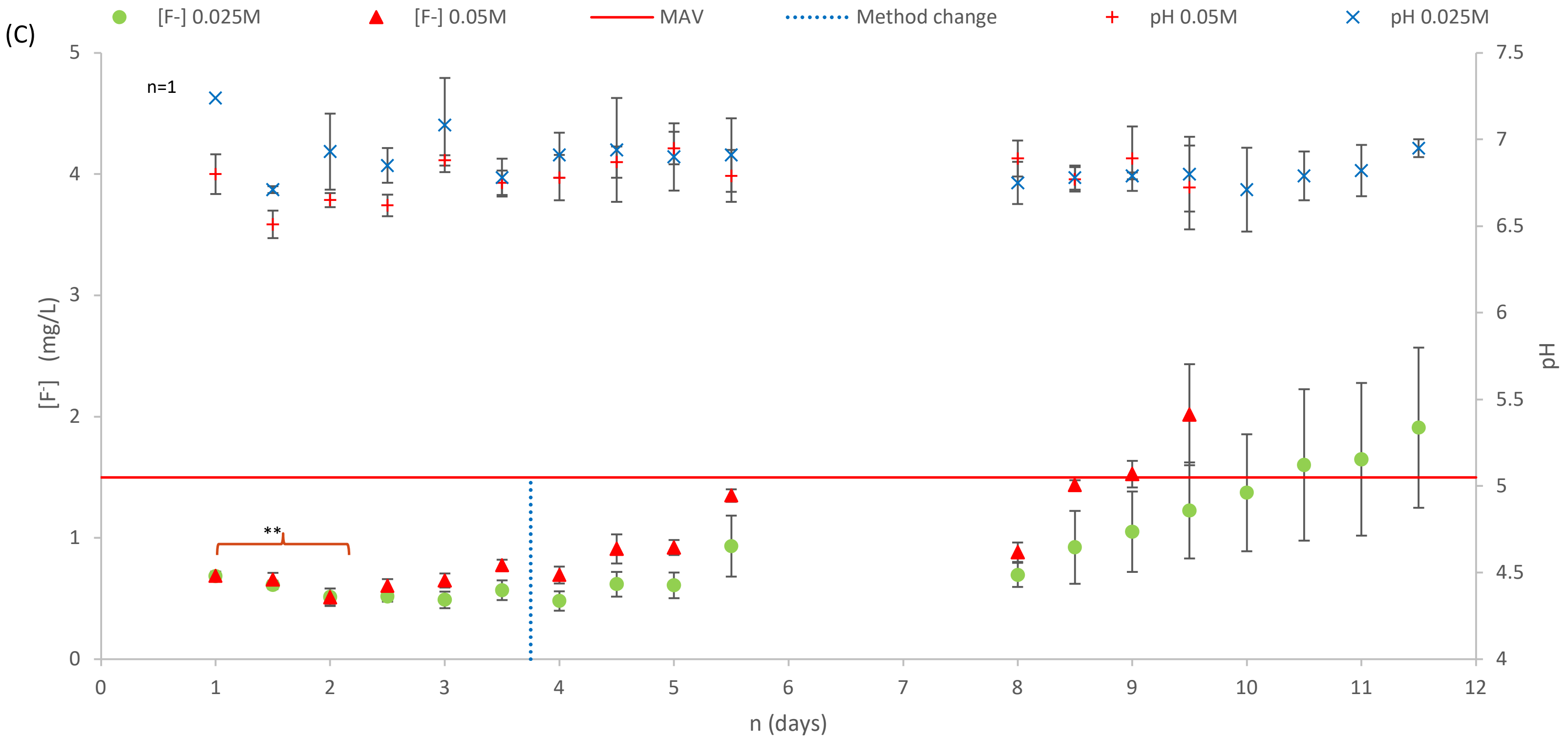
Raw Data for 0.025 & 0.05 M Citric Acid, 5:1 Sand-Fluid Columns – Experiment K – Kiribati Sand (Figure G 2)

[Acid]	Initial				use	Final				P'	Dilute	
(M)	[F$^-$] (mg/L)		pH	n	(days)	[F$^-$]		pH			FISE	Comment
	Measured	Calculated				(mg/L)	2SD		2SD		Sample	
0.025	10.38	10.03	2.38	2	1	0.73	0.04	6.87	0.01	85	Y	
0.025	10.38	10.03	2.38	3	1.5	0.57	0.04	6.6	0.1	86	Y	Dupl = 5.7%
0.025	10.36	10.02	2.39	3	2	0.57	0.04	6.8	0	86	Y	
0.025	10.36	10.02	2.39	3	2.5	0.8	0.1	6.9	0.1	92	Y	
0.025	10.30	10.02	2.38	3	3	0.8	0.1	6.8	0.2	93	Y	
0.025	10.30	10.02	2.38	3	3.5	1.13	0.2	6.8	0.2	95	Y	
0.025	10.22	10.02	2.41	3	4	1.2	0.2	6.73	0.07	96	N	
0.025	10.22	10.02	2.41	3	4.5	1.8	0.1	6.6	0.1	98	N	
0.025	10.20	10.02	2.35	3	5	1.8	0.3	6.6	0.2	97	N	
0.05	10.22	10.02	2.16	2	1	0.72	0.03	6.7	0.4	85	Y	
0.05	10.22	10.02	2.16	3	1.5	0.62	0.07	6.6	0.1	87	Y	
0.05	10.16	10.00	2.23	3	2	0.8	0.2	6.7	0.3	89	Y	
0.05	10.16	10.00	2.23	3	2.5	1.1	0.2	6.8	0.2	94	Y	
0.05	10.26	10.00	2.19	3	3	1.4	0.2	6.91	0.05	94	Y	
0.05	10.26	10.00	2.19	3	3.5	2.1	0.5	6.7	0.2	99	Y	
0.05	10.20	10.00	2.22	3	4	2.1	0.2	6.8	0.1	96	N	
0.05	10.20	10.00	2.22	3	4.5	3.1	0.3	6.63	0.06	97	N	
0.05	10.12	10.01	2.30	3	5	3.1	0.4	6.84	0.05	90	N	

Note. Columns used twice daily (second use of the day represented as n = 0.5 days). Duplicate % difference for day 1, use 2 outside 5 % range.

Figure G 3

Final Fluoride Concentration and pH of Extracts vs. Repeated Use of Vanuatu Sand Columns with 5:1 Sand-Fluid Ratio (Experiment K)



Note. Columns twice-daily use, with 4-hour contact. Initial 10 mg/L fluoride solution prepared in 0.025 or 0.05 M citric acid. Method change = change in FISE analytical method from analysing 1:2 diluted sample to non-diluted sample. Average of triplicates ± 2SD (except as indicated and for day 1 – first use, where n=2). ** P' for 0.05M and 0.025 M samples = 70-80 % (below quality guideline)

Table G 6

Raw Data for 0.025 M Citric Acid, 5:1 Sand-Fluid Columns – Experiment K – Vanuatu Sand (Figure G 3)

[Acid]	Initial				use	Final				P'	Dilute	
(M)	$[F^-]$ (mg/L)		pH	n	(days)	$[F^-]$		pH			FISE	Comment
	Meas'd	Calc'd				(mg/L)	2SD		2SD		Sample	
0.025	9.97	10.02	2.42	2	1	0.69	0.03	7.24	0	78	Y	
0.025	9.97	10.02	2.42	3	1.5	0.61	0.03	6.71	0	80	Y	
0.025	9.66	10.01	2.4	3	2	0.51	0.07	6.9	0.2	76	Y	
0.025	9.66	10.01	2.4	3	2.5	0.52	0.04	6.85	0.1	89	Y	
0.025	9.83	9.99	2.36	3	3	0.49	0.07	7.1	0.3	83	Y	
0.025	9.83	9.99	2.36	3	3.5	0.57	0.08	6.8	0.1	88	Y	
0.025	9.61	9.93	2.38	3	4	0.48	0.08	6.9	0.1	81	N	
0.025	9.61	9.93	2.38	3	4.5	0.6	0.1	6.94	0.3	88	N	
0.025	9.72	9.99	2.41	3	5	0.6	0.1	6.9	0.2	83	N	
0.025	9.72	9.99	2.41	3	5.5	0.9	0.3	6.9	0.2	88	N	
0.025	9.91	10.07	2.43	3	8	0.7	0.1	6.8	0.1	90	N	
0.025	9.91	10.07	2.43	3	8.5	0.9	0.3	6.78	0.1	96	N	
0.025	9.81	10.05	2.43	3	9	1.1	0.3	6.79	0	94	N	
0.025	9.81	10.05	2.43	3	9.5	1.23	0.4	6.8	0.2	95	N	
0.025	9.8	10	2.46	3	10	1.4	0.5	6.7	0.2	94	N	removed 0.25 mg/L from cal’n curve
0.025	9.8	10	2.46	3	10.5	1.6	0.6	6.8	0.1	108	N	removed 0.25 mg/L from cal’n curve
0.025	9.72	10.02	2.4	3	11	1.6	0.6	6.8	0.1	95	N	
0.025	9.72	10.02	2.4	3	11.5	1.9	0.7	6.95	0.1	96	N	

Note. Columns used twice daily (second use of the day represented as n = 0.5 days). Values in red are outside quality guidelines.

Table G 7

Raw Data for 0.05 M Citric Acid, 5:1 Sand-Fluid Columns – Experiment K – Vanuatu Sand (Figure G 3)

[Acid]	Initial				use	Final				P'	Dilute
(M)	$[F^-]$ (mg/L)		pH	n	(days)	$[F^-]$		pH			FISE
	Meas'd	Calc'd				(mg/L)	2SD		2SD		Sample
0.05	9.82	9.97	2.29	2	1	0.69	0.04	6.8	0.1	77	Y
0.05	9.82	9.97	2.29	3	1.5	0.66	0.06	6.51	0.08	78	Y
0.05	9.54	9.99	2.3	3	2	0.51	0.07	6.65	0.04	77	Y
0.05	9.54	9.99	2.3	3	2.5	0.61	0.06	6.62	0.06	88	Y
0.05	9.75	10.01	2.26	3	3	0.65	0.06	6.88	0.03	85	Y
0.05	9.75	10.01	2.26	3	3.5	0.77	0.05	6.75	0.07	91	Y
0.05	9.53	9.96	2.26	3	4	0.69	0.07	6.8	0.1	82	N
0.05	9.53	9.96	2.26	3	4.5	0.9	0.1	6.87	0.09	82	N
0.05	9.61	9.99	2.27	3	5	0.92	0.06	6.95	0.09	87	N
0.05	9.61	9.99	2.27	3	5.5	1.35	0.05	6.8	0.2	92	N
0.05	9.84	10.05	2.27	3	8	0.88	0.08	6.9	0.1	87	N
0.05	9.84	10.05	2.27	3	8.5	1.44	0.04	6.77	0.07	92	N
0.05	9.70	10.03	2.27	3	9	1.5	0.1	6.9	0.2	91	N
0.05	9.70	10.03	2.27	3	9.5	2.0	0.4	6.7	0.2	93	N

Note. Columns used twice daily (second use of the day represented as n = 0.5 days). Values in red are outside quality guidelines.

Table G 8

Concentrations of Elements Present in Extracts from Fine Store-Bought Sand with 0.025 M Citric Acid Following Repeated Column Use

Element	Limits		Unit	LOQ	**Day 1**	**Day 1**	**Day 2**	**Day 2**	**Day 3**	**Day 3**	Initial	Control
	MAV	***GL***			**Use 1**	**Use 2**	**Use 1**	**Use 2**	**Use 1**	**Use 2**	High	0.025M
Al		0.1	mg/L	0.21	***2.43***	***1.85***	***1.38***	***0.8***	***0.97***	***0.71***	<LOQ	<LOQ
As^{75-91}	10		µg/L	2.1	**31.4**	**21.9**	**13.8**	**10**	9.6	7.6	<LOQ	<LOQ
B	1.4		mg/L	0.21	1.02	0.65	0.51	0.36	0.35	0.31	<LOQ	<LOQ
Ca		*100-300	mg/L	2.1	***1374***	***1364***	***601***	***565***	***479***	***538***	<LOQ	<LOQ
Cd	4		µg/L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Cr	50		µg/L	21	**152**	**155**	**124**	**82**	**77**	**66**	<LOQ	<LOQ
Cu	2000	1000	µg/L	21	39.9	21.7	<LOQ	<LOQ	113	<LOQ	<LOQ	**4.5**
$Fe^{56/57}$		0.2	mg/L	0.0021	***1.92***	***1.44***	***1.03***	***0.616***	***0.665***	***0.546***	**0.011**	<LOQ
Mg		*100-300	mg/l	0.021	***142***	***132***	***104***	***106***	***111***	***115***	**0.066**	<LOQ
Mn	400	40	µg/L	21	***151***	***132***	***96***	***97***	***92***	***107***	<LOQ	<LOQ
Mo	70		µg/L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Na		200	mg/L	0.21	59.2	39.8	25.2	15.9	17.1	15.9	13.3	**14.5**
Ni	80		µg/L	2.1	41.9	22.5	4.8	<LOQ	<LOQ	<LOQ	**14**	9.5
Pb	10		µg/L	210	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Zn		1500	µg/L	21	311	142	<LOQ	<LOQ	<LOQ	<LOQ	**122**	77

Note. Concentrations measured with ICP-MS. Sand-fluid ratio of 5:1, columns used twice daily with 4hr contact with 0.025 M analytical grade citric acid & 10mg F^-/L solution. 'Initial High' is highest measured concentration of two initial solutions (0.05 M AR citric acid and 10 mg F^-/L solution) measured. Value indicated is a single replicate with control column or 'Initial High' deducted, whichever highest (**bold**). Values in red and blue are above MAV or GL respectively, as published by the MOH (2018). Fe^{56} measured on day 1 and Fe^{57} on subsequent days. * is hardness measured as Ca + Mg expressed in mg/L of $CaCO_3$.

Table G 9

Concentrations of Elements Present in Extracts from Fine Store-Bought Sand with 0.05 M Citric Acid Following Repeated Column Use

Element	Limits		Unit	LOQ	**Day 1**	**Day 1**	**Day 2**	**Day 2**	**Day 3**	**Day 3**	Initial	Control
	MAV	*GL*			**Use 1**	**Use 2**	**Use 1**	**Use 2**	**Use 1**	**Use 2**	High	0.05M
Al		0.1	mg/L	0.21	*2.38*	*2.09*	*1.63*	*0.99*	*1.02*	*0.68*	<LOQ	<LOQ
As^{75-91}	10		µg/L	2.1	**38.9**	**27.9**	**20.4**	**13.7**	**11.9**	8.6	<LOQ	<LOQ
B	1.4		mg/L	0.21	1.15	0.83	0.71	0.53	0.53	0.45	<LOQ	<LOQ
Ca		*100-300	mg/L	2.1	*1552*	*669*	*504*	*463*	*444*	*424*	<LOQ	<LOQ
Cd	4		µg/L	2.1	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Cr	50		µg/L	21	**251**	**246**	**200**	**130**	**105**	**80**	<LOQ	<LOQ
Cu	2000	1000	µg/L	21	43	23	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	**6.9**
$Fe^{56/57}$		0.2	mg/L	0.0021	*2.27*	*1.68*	*1.08*	*0.771*	*0.735*	*0.511*	**0.011**	<LOQ
Mg		*100-300	mg/l	0.021	*205*	*203*	*202*	*192*	*202*	*189*	**0.066**	<LOQ
Mn	400	40	µg/L	21	*238*	*123*	*99*	*102*	*108*	*113*	<LOQ	<LOQ
Mo	70		µg/L	21	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Na		200	mg/L	0.21	57.5	46.2	39.8	31.1	31.5	26.3	13.3	**13.5**
Ni	80		µg/L	2.1	50.7	25.8	11.2	6.2	3.8	1.5	14	**15**
Pb	10		µg/L	210	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ	<LOQ
Zn		1500	µg/L	21	452	158	10	<LOQ	<LOQ	<LOQ	**122**	114

Note. Concentrations measured with ICP-MS. Sand-fluid ratio of 5:1, columns used twice daily with 4hr contact with 0.025 M analytical grade acid & 10 mg F^-/L solution. 'Initial High' is highest of two initial solutions (0.05 M AR citric acid and 10 mg F^-/L solution) measured. Value indicated is a single replicate with control column or 'Initial High' value deducted, whichever highest (**bold**). Values in red and blue are above MAV or GL respectively, as published by the MOH (2018). Fe^{56} measured on day 1 and Fe^{57} on subsequent days. * is hardness measured as Ca + Mg expressed in mg/L of $CaCO_3$.

Table G 10

Concentrations of Elements Present in Extracts from Kiribati Sand with 0.025 M Citric Acid Following Repeated Column Use

Element	Published Limit		Units	LOQ	Day 1		Day 1	Day 2		Day 2		Day 3		Day 3		Day 4		Day 4		Control
	MAV	*GL*			Use 1		Use 2$^{\#}$	Use 1		Use 2		Use 1		Use 2		Use 1		Use 2		0.025M
Al		0.1	mg/L	0.29	*0.7*	*± 0.01*	*1.33*	*1.1*	*± 0.2*	*0.6*	*± 0.2*	*0.88*	*± 0.02*	*0.55*	*± 0.02*	*0.65*	*± 0.05*	*0.43*	*± 0.02*	>LOQ
As $^{75-91}$	10		µg/L	2.9	**570**	**± 20**	**301**	**130**	**± 30**	**70**	**± 10**	**70**	**± 10**	**47**	**± 7**	**50**	**± 7**	**34**	**± 4**	>LOQ
B	1.4		mg/L	0.21	**6.5**	**± 0.1**	**3.8**	**1.9**	**± 0.3**	1	± 0.1	0.99	± 0.02	0.7	± 0.02	0.7	± 0.003	0.56	± 0.04	>LOQ
Ca		*100-300	mg/L	2.9	*1130*	*± 60*	*1490*	*1040*	*± 30*	*800*	*± 40*	*610*	*± 40*	*570*	*± 70*	*520*	*± 80*	*540*	*± 50*	>LOQ
Cd	4		µg/L	2.9	>LOQ		>LOQ	>LOQ		>LOQ		>LOQ		>LOQ		>LOQ		>LOQ		>LOQ
Cr	50		µg/L	29	**110**	**± 10**	**194**	**130**	**± 40**	**70**	**± 20**	**86**	**± 8**	**60**	**± 10**	**70**	**± 10**	**49**	**± 6**	>LOQ
Cu	2000	1000	µg/L	2.9	*1000*	*± 200*	790	860	± 90	500	± 300	400	± 100	400	± 300	300	± 100	300	± 200	4.5
Fe^{56}		0.2	mg/L	0.21	*4.7*	*± 0.3*	*6.19*	*4*	*± 2*	*2*	*± 1*	*2.2*	*± 0.4*	*1.8*	*± 0.8*	*1.8*	*± 0.5*	*1.6*	*± 0.6*	>LOQ
Mg		*100-300	mg/L	2.1	*670*	*± 20*	*333*	*180*	*± 40*	*150*	*± 30*	*160*	*± 20*	*150*	*± 40*	*150*	*± 30*	*160*	*± 20*	>LOQ
Mn	400	40	µg/L	29	*160*	*± 20*	*183*	*120*	*± 40*	*100*	*± 40*	*80*	*± 30*	*70*	*± 30*	*70*	*± 20*	*70*	*± 30*	>LOQ
Mo	70		µg/L	29	>LOQ		>LOQ	>LOQ		>LOQ		>LOQ		>LOQ		>LOQ		>LOQ		>LOQ
Na		200	mg/L	2.1	*3300*	*± 300*	*1100*	*400*	*± 100*	120	± 30	120	± 20	60	± 10	70	± 10	41	± 6	14.5
Ni	80		µg/L	2.9	**165**	**± 5**	**92**	40	± 10	13	± 8	13	± 8	7	± 7	7.6	± 0.5	4	± 4	9.5
Pb	10		µg/L	290	>LOQ		>LOQ	>LOQ		>LOQ		>LOQ		>LOQ		>LOQ		>LOQ		>LOQ
Zn		1500	µg/L	29	240	± 40	460	400	± 200	280	± 70	200	± 100	200	± 70	120	± 70	180	± 90	77

Note. Concentrations measured with ICP-MS. Sand-fluid ratio of 5:1, columns used twice daily with 4hr contact, initial solution of 0.025 M analytical grade acid & 10 mg F$^-$/L. Average ± 2SD (n=2, n=1 on day 1, use 2$^{\#}$) with control column deducted. Values in red and blue are above MAV or GL respectively, as published by the MOH (2018). * is hardness measured as Ca + Mg expressed in mg/L of $CaCO_3$.

Table G 11

Concentrations of Elements Present in Extracts from Kiribati Sand with 0.05 M Citric Acid Following Repeated Column Use

Element	Published Limit		Units	LOQ	Day 1 Use 1	Day 1 Use 2	Day 2 Use 1	Day 2 Use 2	Day 3 Use 1	Day 3 Use 2	Day 4 Use 1	Day 4 Use 2	Control 0.05M
	MAV	*GL*											
Al		0.1	mg/L	0.29	*0.83 ± 0.03*	*1.2 ± 0.2*	*1.3 ± 0.1*	*0.72 ± 0.1*	*0.8 ± 0.3*	*0.5 ± 0.3*	*0.6 ± 0.4*	*0.5 ± 0.3*	>LOQ
As $^{75\text{-}91}$	10		µg/L	2.9	**640 ± 20**	**300 ± 100**	**129 ± 4**	**73 ± 2**	**63 ± 7**	**44 ± 4**	**44 ± 5**	**33 ± 2**	>LOQ
B	1.4		mg/L	0.21	**7.1 ± 0.8**	**4 ± 2**	**2.13 ± 0.03**	1.24 ± 0.02	1.16 ± 0.01	0.88 ± 0.0002	0.92 ± 0.02	0.78 ± 0.06	>LOQ
Ca		*100-300	mg/L	2.9	*2240 ± 70*	*1600 ± 600*	*600 ± 100*	*500 ± 100*	*500 ± 100*	*500 ± 100*	*440 ± 80*	*440 ± 50*	>LOQ
Cd	4		µg/L	2.9	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ
Cr	50		µg/L	29	**210 ± 10**	**250 ± 60**	**190 ± 20**	**100 ± 20**	**90 ± 30**	**60 ± 10**	**60 ± 10**	**50 ± 10**	>LOQ
Cu	2000	1000	µg/L	2.9	*1000 ± 600*	800 ± 200	500 ± 500	300 ± 300	300 ± 400	300 ± 300	200 ± 300	200 ± 200	6.9
Fe ^{56}		0.2	mg/L	0.21	*6.7 ± 0.9*	*6 ± 2*	*3.1 ± 0.2*	*2.2 ± 0.2*	*2 ± 0.3*	*1.7 ± 0.2*	*1.7 ± 0.3*	*1.4 ± 0.3*	>LOQ
Mg		*100-300	mg/L	2.1	*730 ± 5*	*420 ± 20*	*310 ± 40*	*280 ± 50*	*290 ± 60*	*280 ± 60*	*290 ± 40*	*270 ± 40*	>LOQ
Mn	400	40	µg/L	29	*261 ± 0.2*	*200 ± 20*	*90 ± 30*	*90 ± 40*	*70 ± 40*	*80 ± 50*	*80 ± 40*	*70 ± 30*	>LOQ
Mo	70		µg/L	29	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ
Na		200	mg/L	2.1	*3000 ± 200*	*1200 ± 600*	*410 ± 30*	163 ± 1	140 ± 30	80 ± 10	90 ± 20	70 ± 40	13.5
Ni	80		µg/L	2.9	**180 ± 10**	**90 ± 30**	28 ± 7	13 ± 5	9 ± 4	7 ± 6	7 ± 5	3 ± 3	15
Pb	10		µg/L	290	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ	>LOQ
Zn		1500	µg/L	29	700 ± 200	370 ± 90	60 ± 30	40 ± 40	20 ± 100	60 ± 100	10 ± 70	40 ± 80	114

Note. Concentrations measured with ICP-MS. Sand-fluid ratio of 5:1, columns used twice daily with 4hr contact, initial solution of 0.05 M analytical grade citric acid & 10 mg F$^-$/L. Average ± 2SD (n=2) with control column deducted. Values in red and blue are above MAV or GL respectively, as published by the MOH (2018). * is hardness measured as Ca + Mg expressed in mg/L of CaCO$_3$.

Table G 12

Concentrations of Elements Present in Extracts from Vanuatu Sand with 0.025 M Citric Acid Following Repeated Column Use

Element	Published Limit		Units	LOQ	Day 1		Day 1		Day 2		Day 2		Day 3		Day 3		Day 4	
	MAV	***GL***			Use 1		Use 2		Use 1		Use 2		Use 1		Use 2		Use 1	
Al		0.1	mg/L	0.21	*1.6*	*± 0.09*	*2.2*	*± 0.2*	*2.5*	*± 0.3*	*1.8*	*± 0.1*	*1.9*	*± 0.1*	*1.5*	*± 0.4*	*1.55*	*± 0.05*
As$^{75-91}$	10		µg/L	2.1	**99**	**± 3**	**81.01**	**± 0.09**	**52**	**± 1**	**30**	**± 1**	**19**	**± 1**	**13.7**	**± 0.5**	**12.3**	**± 0.5**
B	1.4		mg/L	0.21	**8.4**	**± 0.1**	**6.51**	**± 0.02**	**3.9**	**± 0.5**	**2.32**	**± 0.03**	**1.56**	**± 0.03**	1	± 0.2	0.92	± 0.02
Ca		*100-300	mg/L	21.21	*1210*	*± 10*	*1160*	*± 30*	*1210*	*± 0*	*1250*	*± 40*	*1120*	*± 90*	*850*	*± 40*	*740*	*± 30*
Cd	4		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	
Cr	50		µg/L	2.1	**360**	**± 20**	**510**	**± 40**	**540**	**± 30**	**390**	**± 10**	**330**	**± 20**	**250**	**± 10**	**254**	**± 7**
Cu	2000	1000	µg/L	2.1	450	± 20	390	± 10	380	± 60	208	± 7	66	± 5	35	± 5	25	± 4
Fe$^{56-72}$		0.2	mg/L	0.021	*2.17*	*± 0.03*	*2.49*	*± 0.004*	*2.4*	*± 0.2*	*1.82*	*± 0.09*	*1.5*	*± 0.1*	*1.061*	*± 0.003*	*1.06*	*± 0.08*
Mg		*100-300	mg/L	21.21	*780*	*± 30*	*579*	*± 2*	*384.5*	*± 0.5*	*229*	*± 8*	*168*	*± 3*	*127*	*± 6*	*120*	*± 20*
Mn	400	40	µg/L	21	*280*	*± 10*	*254*	*± 6*	*220*	*± 30*	*211*	*± 9*	*167*	*± 1*	*140*	*± 20*	*124*	*± 4*
Mo	70		µg/L	2.1	9.4	± 0.6	7	± 1	6	± 1	3.6	± 0.1	2.44	± 0.06	<LOQ		<LOQ	
Na		200	mg/L	2.121	*7800*	*± 300*	*4120*	*± 30*	*1730*	*± 90*	*580*	*± 30*	*240*	*± 20*	100	± 20	80	± 10
Ni	80		µg/L	2.1	**92**	**± 6**	75	± 3	55	± 8	37.5	± 0.4	26	± 2	13	± 1	8	± 2
Pb	10		µg/L	2.1	2.43	± 0.03	2.2	± 0.2	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	
Zn		1500	µg/L	21	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	

Note. Concentrations measured with ICP-MS. Sand-fluid ratio of 5:1, columns used twice daily with 4 hour contact, initial solution of 0.025 M analytical grade citric acid & 10 mg F$^-$/L. Average ± 2SD (n=2) with control column deducted. Values in red and blue are above MAV or GL respectively, as published by the MOH (2018). * is hardness measured as Ca + Mg expressed in mg/L of CaCO$_3$.

Table G 12 (Continued from previous page)

Concentrations of Elements Present in Extracts from Vanuatu Sand with 0.025 M Citric Acid Following Repeated Column Use (Continued from previous page)

Element	Published Limit		Units	LOQ	Day 4		Day 5		Day 8		Day 9		Day 10		Input Solution		Control
	MAV	***GL***			**Use 2**		**Use 1**		**Use 1**		**Use 1**		**Use 1**		Day 2	Day 4	0.025M
Al		0.1	mg/L	0.21	*1.3*	*± 0.2*	*1.41*	*± 0.01*	*1*	*± 1*	*0.5*	*± 0.6*	<LOQ		<LOQ	<LOQ	>LOQ
$\text{As}^{75\text{-}91}$	10		µg/L	2.1	**10.5**	**± 0.4**	**10**	**± 1**	**13**	**± 5**	**10**	**± 2**	7	± 2	<LOQ	<LOQ	>LOQ
B	1.4		mg/L	0.21	0.74	± 0.06	0.68	± 0.04	0.6	± 0.1	0.46	± 0.01	0.43	± 0.03	<LOQ	<LOQ	>LOQ
Ca		*100-300	mg/L	21.21	*720*	*± 30*	*590*	*± 20*	*800*	*± 100*	*600*	*± 30*	*620*	*± 2*	<LOQ	<LOQ	>LOQ
Cd	4		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	<LOQ	>LOQ
Cr	50		µg/L	2.1	**220**	**± 30**	**212**	**± 5**	**200**	**± 200**	**100**	**± 60**	**100**	**± 40**	<LOQ	<LOQ	>LOQ
Cu	2000	1000	µg/L	2.1	25	± 1	18	± 6	3	± 8	<LOQ		<LOQ		3.84	4.01	*4.5*
$\text{Fe}^{56\text{-}72}$		0.2	mg/L	0.021	*0.85*	*± 0.03*	*0.9077*	*± 0.0008*	*0.5*	*± 0.5*	*0.6*	*± 0.5*	*0.7*	*± 0.6*	<LOQ	<LOQ	>LOQ
Mg		*100-300	mg/L	21.21	*120*	*± 20*	*109*	*± 1*	*120*	*± 1*	*105*	*± 5*	*100*	*± 2*	<LOQ	<LOQ	>LOQ
Mn	400	40	µg/L	21	*120*	*± 20*	*110*	*± 10*	*80*	*± 30*	*60*	*± 30*	*60*	*± 50*	<LOQ	<LOQ	>LOQ
Mo	70		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	<LOQ	>LOQ
Na		200	mg/L	2.121	50	± 3	40	± 20	53	± 1	30	± 20	20	± 30	<LOQ	<LOQ	*14.5*
Ni	80		µg/L	2.1	8	± 2	4	± 4	<LOQ		<LOQ		<LOQ		5.88	6.76	*9.5*
Pb	10		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	<LOQ	>LOQ
Zn		1500	µg/L	21	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		25.6	58.1	*77*

Note. Concentrations measured with ICP-MS (quality control duplicate check on Day 9 for Na was 15% different, others within 7%). Sand-fluid ratio of 5:1, columns used twice daily with 4hr contact, initial solution of 0.025 M analytical grade citric acid & 10 mg F^-/L. Average ± 2SD (n=2) with control column deducted. Values in red and blue are above MAV or GL respectively, as published by the MOH (2018). * is hardness measured as Ca + Mg expressed in mg/L of $CaCO_3$.

Table G 13

Concentrations of Elements Present in Extracts from Vanuatu Sand with 0.05 M Citric Acid Following Repeated Column Use

Element	Published Limit		Units	LOQ	Day 1		Day 1		Day 2		Day 2		Day 3		Day 3	
	MAV	***GL***			**Use 1**		**Use 2**		**Use 1**		**Use 2**		**Use 1**		**Use 2**	
Al		0.1	mg/L	0.21	*2.8*	*± 0.1*	*3.2*	*± 0.1*	*2.9*	*± 0.1*	*2.3*	*± 0.4*	*1.944*	*± 0.008*	*1.8*	*± 0.5*
As$^{75-91}$	10		µg/L	2.1	**114**	**± 2**	**79.5**	**± 0.1**	**46**	**± 3**	**27**	**± 1**	**20**	**± 1**	**15**	**± 1**
B	1.4		mg/L	0.21	**9.8**	**± 0.2**	**6.0**	**± 0.2**	**3.3**	**± 0.3**	**2.0**	**± 0.2**	**1.5**	**± 0.1**	1.11	± 0.01
Ca	*	100-300	mg/L	21.21	*2270*	*± 90*	*2350*	*± 60*	*1300*	*± 3*	*950*	*± 50*	*600*	*± 200*	*524*	*± 2*
Cd	4		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	
Cr	50		µg/L	2.1	**837**	**± 5**	**930**	**± 30**	**769**	**± 9**	**550**	**± 10**	**448**	**± 2**	**364**	**± 6**
Cu	2000	1000	µg/L	2.1	420	± 80	270	± 60	230	± 70	130	± 20	66	± 9	30	± 7
Fe$^{56-72}$		0.2	mg/L	0.021	*3.42*	*± 0.04*	*3.449*	*± 0.003*	*2.75*	*± 0.07*	*1.8*	*± 0.2*	*1.2*	*± 0.2*	*1.03*	*± 0.07*
Mg	*	100-300	mg/L	21.21	*830*	*± 10*	*610*	*± 20*	*380*	*± 30*	*277*	*± 4*	*230*	*± 30*	*212*	*± 6*
Mn	400	40	µg/L	21	**490**	**± 40**	**410**	**± 20**	*269*	*± 7*	*200*	*± 10*	*130*	*± 40*	*120*	*± 10*
Mo	70		µg/L	2.1	10.3	± 0.7	7.3	± 0.4	4.6	± 0.6	<LOQ		<LOQ		<LOQ	
Na		200	mg/L	2.121	*7000*	*± 300*	*3216*	*± 6*	*1100*	*± 100*	*400*	*± 50*	*200*	*± 20*	119	± 8
Ni	80		µg/L	2.1	**140**	**± 10**	**99**	**± 3**	53	± 5	25	± 4	10	± 5	5	± 2
Pb	10		µg/L	2.1	5.7	± 0.7	5	± 2	<LOQ		<LOQ		<LOQ		<LOQ	
Zn		1500	µg/L	21	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	

Note. Concentrations measured with ICP-MS. Sand-fluid ratio of 5:1, columns used twice daily with 4hr contact, initial solution of 0.05 M analytical grade citric acid & 10 mg F^-/L. Average ± 2SD (n=2) with control column deducted. Values in red and blue are above MAV or GL respectively, as published by the MOH (2018). * is hardness measured as Ca + Mg expressed in mg/L of $CaCO_3$.

Table G 13 (Continued from previous page)

Concentrations of Elements Present in Extracts from Vanuatu Sand with 0.05 M Citric Acid Following Repeated Column Use (Continued from previous page)

Element	Published Limit		Units	LOQ	**Day 4**		**Day 4**		**Day 5**		**Day 8**		**Day 9**		Initial solution		Control
	MAV	***GL***			**Use 1**		**Use 2**		**Use 1**		**Use 1**		**Use 1**		Day 2	Day 4	0.05M
Al		0.1	mg/L	0.21	*1.7*	*± 0.2*	*1.47*	*± 0.04*	*1.63*	*± 0.07*	*1.9*	*± 0.3*	*1.6*	*± 0.2*	<LOQ	<LOQ	>LOQ
As^{75-91}	10		µg/L	2.1	**13**	**± 2**	**11.3**	**± 0.3**	**10.42**	**± 0.06**	**13.7**	**± 0.6**	**10.5**	**± 0.1**	<LOQ	<LOQ	>LOQ
B	1.4		mg/L	0.21	1	± 0.2	0.81	± 0.05	0.75	± 0.05	0.76	± 0.02	0.61	± 0.06	<LOQ	<LOQ	>LOQ
Ca	*	100-300	mg/L	21.21	*530*	*± 70*	*460*	*± 20*	*390*	*± 50*	*500*	*± 300*	*490*	*± 50*	*38.8*	<LOQ	>LOQ
Cd	4		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	<LOQ	>LOQ
Cr	50		µg/L	2.1	**330**	**± 60**	**264**	**± 8**	**260**	**± 10**	**290**	**± 9**	**230**	**± 40**	<LOQ	<LOQ	>LOQ
Cu	2000	1000	µg/L	2.1	18	± 6	13	± 3	9	± 4	<LOQ		<LOQ		7.08	*7.25*	6.9
Fe^{56-72}		0.2	mg/L	0.021	*0.9*	*± 0.07*	*0.8*	*± 0.1*	*0.76*	*± 0.04*	*0.8*	*± 0.2*	*0.9*	*± 0.1*	<LOQ	<LOQ	>LOQ
Mg	*	100-300	mg/L	21.21	*220*	*± 20*	*194*	*± 4*	*182*	*± 4*	*180*	*± 10*	*168*	*± 2*	<LOQ	<LOQ	>LOQ
Mn	400	40	µg/L	21	*110*	*± 10*	*100*	*± 10*	*98*	*± 6*	*96*	*± 7*	*100*	*± 40*	<LOQ	<LOQ	>LOQ
Mo	70		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	<LOQ	>LOQ
Na		200	mg/L	2.121	93	± 1	60	± 2	52	± 2	60	± 7	36	± 5	3.87	2.75	*13.5*
Ni	80		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		12.33	13.59	*15*
Pb	10		µg/L	2.1	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		<LOQ	<LOQ	*>LOQ*
Zn		1500	µg/L	21	<LOQ		<LOQ		<LOQ		<LOQ		<LOQ		48.8	53.8	*114*

Note. Concentrations measured with ICP-MS. Sand-fluid ratio of 5:1, columns used twice daily with 4hr contact, initial solution of 0.05 M analytical grade citric acid & 10 mg F$^-$/L. Average ± 2SD (n=2) with control column deducted. Values in red and blue are above MAV or GL respectively, as published by the MOH (2018). * is hardness measured as Ca + Mg.

Table G 14

Summary of AELD Results and Data from Extracts of All Prototype Trials (Experiments L & M)

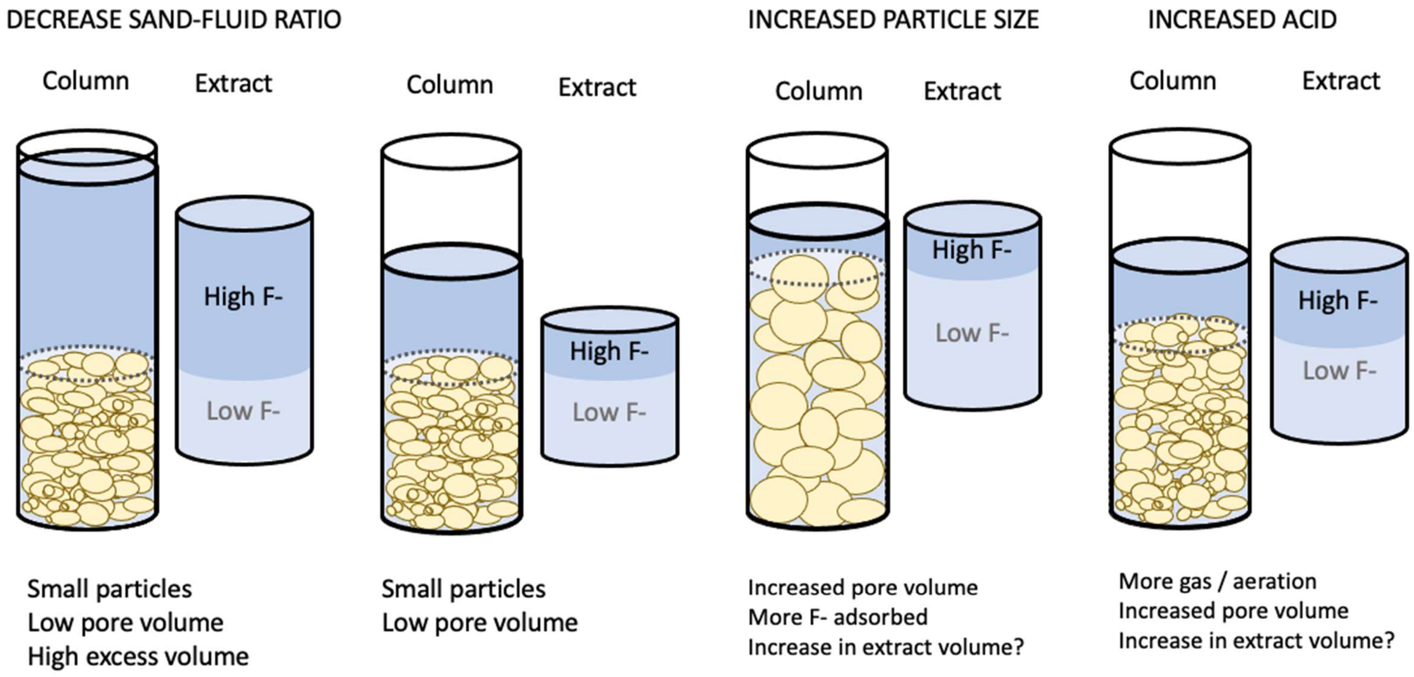
Acid Conc. (M)	Acid Type	Day & Use	Sand Type	Repl. # (n=)	Measured $[F^-]$ (mg/L)		Standard % Recovery	pH		Conductivity (mS/cm)		Estimated TDS (mg/L)	
0.025	FG	1	Coarse	3	0.71	± 0.1	86.0	6.6	± 0.2	2.26	± 0.02	1.45	± 0.01
0.025	FG	1.5	Coarse	3	1.0	± 0.3	90.3	6.18	± 0.05	2.15	± 0.07	1.38	± 0.05
0.025	FG	2	Coarse	3	1.18	± 0.2	91.6	6.4	± 0.1	1.86	± 0.03	1.19	± 0.02
0.025	FG	2.5	Coarse	3	1.77	± 0.2	99.9	6.23	± 0.03	1.78	± 0.04	1.14	± 0.03
0.025	FG	3	Coarse	3	2.13	± 0.1	96.9	6.39	± 0.05	1.59	± 0.01	1.019	± 0.009
0.025	FG	3.5	Coarse	3	2.78	± 0.1	94.9	6.47	± 0.06	1.58	± 0.03	1.01	± 0.02
0	N/A	1	Coarse	1	3.67	- - -	105.3	8.75	- - -	0.164	- - -	0.1048	- - -
0	N/A	1.5	Coarse	1	4.27	- - -	103.0	8.97	- - -	0.148	- - -	0.0949	- - -
0	N/A	2	Coarse	1	4.46	- - -	99.1	8.48	- - -	0.159	- - -	0.1017	- - -
0	N/A	2.5	Coarse	1	5.24	- - -	101.3	8.68	- - -	0.129	- - -	0.0822	- - -
0	N/A	3	Coarse	1	5.2	- - -	97.1	8.89	- - -	0.131	- - -	0.0841	- - -
0	N/A	3.5	Coarse	1	5.9	- - -	101.1	8.98	- - -	0.115	- - -	0.0736	- - -
0.025	FG	1	Blank	1	9.96	- - -	103.7	2.5	- - -	1.383	- - -	0.8851	- - -
0.025	FG	1.5	Blank	1	10.1	- - -	100.3	2.38	- - -	1.381	- - -	0.8838	- - -
0.025	FG	1	Fine	3	0.48	± 0.04	86.9	7.0	± 0.4	2.33	± 0.09	1.49	± 0.06
0.025	FG	1.5	Fine	3	0.88	± 0.09	94.8	6.2	± 0.1	2.25	± 0.03	1.44	± 0.02
0.025	FG	2	Fine	3	1.2	± 0.1	92.8	6.3	± 0.1	1.98	± 0.04	1.27	± 0.02
0.025	FG	2.5	Fine	3	2.0	± 0.3	96.5	6.3	± 0.2	1.85	± 0.02	1.18	± 0.02
0.025	FG	3	Fine	3	2.2	± 0.3	94.2	6.36	± 0.06	1.69	± 0.07	1.08	± 0.04
0.025	FG	3.5	Fine	**2**	3.2	± 0.4	95.9	6.3	± 0.2	1.57	± 0.09	1.01	± 0.06
0	N/A	1	Fine	1	4.94	- - -	100.1	9.19	- - -	*insuff*	- - -	*insuff*	- - -
0	N/A	1.5	Fine	1	5.61	- - -	102.4	9.46	- - -	0.223	- - -	0.143	- - -
0	N/A	2	Fine	1	5.92	- - -	102.1	9.27	- - -	0.225	- - -	0.144	- - -
0	N/A	2.5	Fine	1	6.75	- - -	ND	9.09	- - -	0.17	- - -	0.1086	- - -
0	N/A	3	Fine	1	6.83	- - -	102.1	9.26	- - -	0.158	- - -	0.1014	- - -
0	N/A	3.5	Fine	1	7.7	- - -	97.6	9.3	- - -	0.132	- - -	0.0842	- - -
0.025	FG	1	Blank	1	9.89	- - -	101.6	2.44	- - -	1.39	- - -	0.8896	- - -
0.025	AR	1	Fine	3	0.49	- - -	85.5	6.55	- - -	2.3	- - -	1.47	- - -
0.025	AR	1.5	Fine	3	0.84	- - -	88.4	6.18	- - -	2.23	- - -	1.43	- - -
0.025	AR	2	Fine	3	0.94	- - -	90.4	6.32	- - -	1.92	- - -	1.23	- - -
0.025	AR	2.5	Fine	3	1.53	- - -	93.6	6.46	- - -	1.826	- - -	1.169	- - -
0.025	AR	3	Fine	3	1.91	- - -	91.1	6.58	- - -	1.678	- - -	1.074	- - -
0.025	AR	3.5	Fine	3	3.12	- - -	93.2	6.54	- - -	1.617	- - -	1.035	- - -

Note. ND = not done; Insuff = insufficient sample volume; N/A = no acid; FG = Food Grade; AR = Analytical Grade. Average ± 2SD of replicates as indicated.

APPENDIX H – DIAGRAM OF PORE VOLUME CHANGES AND EFFECT ON FINAL [F$^-$]

Figure H 1

Diagram of Variables and Their Effect on Pore Volume and Final Fluoride Concentration of Extracts



Outside the Pore Volume: (Adsorption & precipitation is low)
= High [F-]

Inside the Pore Volume: (Adsorption & precipitation is high)
= Low [F-]