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In Collaboration with

Report on the Analysis of Arsenic in Nail clippings, Soil, Food, and Water Samples from the Cayman Islands and the Health Implications.

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Foreword

This report is the published product on the analysis of arsenic in nail clippings, soil, food, and water samples from the Cayman Islands.

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EXECUTIVE SUMMARY

In April 2015, the Government of the Cayman Islands contacted the Pan American Health Organization requesting technical assistance in the investigation of a possible Arsenic Exposure. PAHO/WHO country office communicated with the Toxicologist at PAHO/WHO Head Quarters in Washington DC for technical assistance. Through discussions with PAHO/WHO, WDC it was recommended that The International Centre for Environmental and Nuclear Sciences (ICENS) be contacted to provide technical support in the sampling and analysis.

The International Centre for Environmental and Nuclear Sciences (ICENS), through the Pan American Health Organization (PAHO), was engaged to analyze biological (nail clippings and foods) and environmental samples from an area in the Cayman Islands under investigation for potentially elevated levels of arsenic (As). A team from ICENS visited the site and offered executive assistance in the coordination of sampling efforts. Food, water, soil and nail clippings were collected from the area under investigation, as well as from individuals living in area and locations selected as controls. These samples were shipped to ICENS where they were stored suitably and underwent sample preparation appropriate for the techniques used for analysis. Instrumental neutron activation analysis (INAA) was used for the analysis of arsenic in nail clippings and soil samples. Total reflection X-ray fluorescence (TXRF) was used in the analysis of arsenic in food and water samples.

The findings suggest that there are no significant difference between the As content of soils from the test site and control/background sites although the number of background location samples analyzed was below the number needed for statistical analysis. Approximately 73% of the water samples analysed were below the limit of detection of 10µg/L, which is also the maximum contaminant level for As for the United States Environmental Protection Agency (EPA). The As content of the food samples ranged from 0.08 to 5.63 µg/g (median, 0.25 µg/g, and mean, 0.76µg/g). Approximately 73% of the food samples fall below the United States Food and Drug Administration's (FDA) lower regulatory limit of 0.5µg/g. The food samples that were above the FDA's upper regulatory limit of 2 µg/g are from plants whose taxonomical families

contain known hyperaccumulators of As. The arsenic content of the finger and toenail samples ranged from <0.07 to 0.53µg/g for the persons living in the area under investigation and from <0.03 to 0.12µg/g for the persons living in the control locations. Statistical analysis indicates a significant difference between the means of the control and study area populations with the latter being higher. Since however, the As content in the nail clippings from the study area are within the normal range of As in nail clippings (0.09 to 0.59 µg/g) this cannot be implicitly construed as an indication of arsenic poisoning.

Health effects of arsenic exposures that can be used to monitor arsenic intakes include dermatological examination to check on the characteristic pattern of skin changes caused by arsenic – hyperkeratinization and hyperpigmentation, which are the most sensitive and diagnostic clinical indicators of chronic exposure to arsenic. The examination revealed that none of the persons showed symptoms and/or signs of chronic exposure to Arsenic such as enlarged liver or spleen, ascites, pedal oedema, Mee's lines, hyperpigmentation or keratosis of the skin.

The results of the clinical examination and the environmental analysis revealed that the situation does not warrant an alarm this time. Clinical exams indicate that arsenic exposure effects are likely not occurring among the study population. The health of the residents doesn't seem to have been affected as the levels of arsenic found were within the standards/guidelines in most cases. Arsenic exposure becomes a public health concern when the levels are high enough to impact on health in the short-term and medium term or due to chronic exposure.

The potential source of As contamination is anthropogenic and is not extensive. Strategies for mitigation could include

1. Excavation and subsequent landfill sequestration.

2. Where water abstracted from wells exceeds a determined drinking water limit remediation at source, for example iron oxide filters may be employed.

3. Limiting the use of water with elevated levels of As for irrigation and animal feed may then prevent the uptake of As in plants known to be accumulators and the vertical movement of this potentially toxic element through the food chain.

4. In terms of health, it is recommended that similar annual clinical exams targeting potential medium term health effects, including cancers, neuropathy and other effects that can be potentially associated with arsenic exposures should be conducted.

1 INTRODUCTION

The Pan American Health Organization (PAHO) is the world's oldest international public health agency. It provides technical cooperation and mobilizes partnerships to improve health and quality of life in the countries of the Americas. PAHO is the specialized health agency of the Inter-American System and serves as the Regional Office for the Americas of the World Health Organization (WHO).

The Pan American Health Organization/World Health Organization (PAHO/WHO) country office located in Jamaica provides technical cooperation to Jamaica, Bermuda, and The Cayman Islands. Through this technical cooperation, PAHO provides technical assistance to these countries based on the country priorities and specific needs.

In April 2015, the PAHO/WHO Representative, Dr. Noreen Jack received a correspondence from the then Medical Officer of Health for The Cayman Islands, Dr. Kiran Kumar, requesting technical assistance in the investigation of a possible Arsenic Exposure. The request detailed that the Cayman Water Authority conducted a series of environmental tests of the ground water and soil to measure levels of various metals and possible contaminants such as arsenic. The Water Authority expressed concern in their most recent report of January 2015 that surface soils in the former ash storage area (debris storage area from Hurricane Ivan 2004) had elevated levels of arsenic. In addition, the arsenic levels detected in a domestic well exceeded the WHO drinking water guidelines (the wells were not being used for domestic purposes).

Based on the detailed information received, PAHO/WHO country office communicated with the Toxicologist at PAHO/WHO Head Quarters in Washington DC for technical assistance. Based on discussion the following actions were taken:

1. A laboratory to undertake the sampling and analysis: Given the complex logistics of collection, storage and transportation of samples, it was recommended to use the International Center for Environmental and Nuclear Sciences (ICENS) located at the University of the West Indies. ICENS is internationally recognized and is among the network of 18 research and training centres under the aegis of the Commission for

Science and Technology for Sustainable Development in the South (COMSATS). ICENS was contacted and technical cooperation established under the leadership of its Director General, Mr. Charles Grant.

2. A visit was made to the Cayman Islands by the Disease Prevention and Control Advisor, Dr. Kam Mung, to meet with the Ministry of Health, Cabinet Office and the Families in an effort to gather more details and discuss the way forward.

3. A joint visit was made of PAHO/WHO and ICENS by technical officers to assess the areas of interest, identify and GPS map sampling sites (soils, water, and fruits) and established sampling methodology. This was done in collaboration with the Water Authority and Environmental Health Unit.

4. A health assessment of exposed population was conducted. PAHO assisted in the development of the questionnaire used to assess the exposed population. The assessment was done by local health specialists including a Physician with a Master's in Clinical Dermatology. Nails clippings were taken from exposed persons and non-exposed individuals (controls).

5. ICENS Scientist, Dr. Adrian Spence, visited to collect and transport the samples. Samples were taken from the exposed areas and non-exposed areas (control sample).

Following the completion of the analysis by ICENS, PAHO/WHO country office technical officers, Dr. Taraleen Malcolm and Dr. Kam Mung along with the PAHO/WHO Toxicologist, Dr. Ana Boischio reviewed the findings and prepared the Epidemiological report and health implications.

2 BACKGROUND

2.1 International Centre for Environmental and Nuclear Sciences (ICENS)

ICENS is a state-of-the-art multi-disciplinary research centre and is one of the branches of a network of centres of excellence under the umbrella of the Commission for Science and Technology for Sustainable Development in the South (COMSATS). ICENS operates a miniature research nuclear reactor ("Peaceful Uses of the Atom"), a spectroscopy laboratory and geographic information systems unit and has been at the vanguard of providing authoritative and cutting-edge information in environmental geochemistry and health for over 30 years. The overarching objective of the centre is to contribute to critical socio-economic problems including environmental protection and the development and retention of local scientific talent to enhancing our regional autonomy. As a good example, recent research carried out at ICENS illuminated the problem of high levels of lead (Pb) in blood samples collected from school children in specific areas of Jamaica and informed the necessary intervention to attenuate the effects of such contaminants.

The laboratories at ICENS are not currently certified / accredited to an international standard; however, activities are advanced with the view to achieve accreditation to the ISO/IEC 17025 standard by mid 2016. Notwithstanding, ICENS processes and procedures are well documented and aligned to the management and technical requirements of the standard. There is strict adherence to all documented procedures, governing *inter alia*, sampling protocols, method validation, measurement uncertainty and traceability. ICENS laboratories have participated in local, regional and international inter-laboratory comparisons/ proficiency tests and have received high commendations. Most recently, ICENS laboratories participated in a rigorous inter-laboratory comparisons organized by the Wageningen Evaluating Programs for Analytical Laboratories (WEPAL) which is based in the Netherlands. ICENS was placed at the topmost level with laboratories in Argentina, Brazil, Chile, Peru, Czech Republic, Kazakhstan, Egypt, Portugal, Slovenia, South Africa and Syria, described as a ‘consolidated state of the practice’ which recognizes laboratories that consistently and competently deliver quality chemical analysis.

2.2 Arsenic

Arsenic (As), a metalloid, occurs naturally in the environment and is ranked 20th in elemental abundance in the earth's crust and 12th in the human body. Arsenic can be released from both natural (rock and soil weathering) and anthropogenic (e.g. wood preservatives - CCA, pesticides and mining) sources and may therefore be found in natural waters as oxyanions of arsenite [AsO_3^{3-}, As(III)] and pentavalent arsenate [AsO_4^{3-}, As(IV)]. Contamination of drinking water by inorganic[1]As represents a major environmental source of As exposure to humans. Additionally, crops grown in As-contaminated soils and/or irrigated with As-contaminated water allow for trophic transfer of As through the food chain, while ingestion of soil and/or inhalation of atmospheric dust deposits (e.g coal fly ash) and tobacco smoke are other important environmental sources of As exposure. The consumption of As-tainted drinking water and/or foods represents a significant threat to public health due to the potential toxic and carcinogenic effects of inorganic As. Short-term exposure to high levels of As can be fatal, whereas chronic exposure to trace levels of As can cause skin, bladder and lung cancers.

3 ENVIRONMENTAL GEOCHEMISTRY OF ARSENIC

3.1 Surface soil

Arsenic occurs naturally in over 200 minerals and is found in varying concentrations in soils all over the world. The background values of As in soils of various countries are said to range from 0.1 to 50 µg/g (mean 6 µg/g) with considerable variation among geographic regions.

2.1.1 Action levels

Action levels for As in surface soils vary depending on region and best defined below:

Soil background: 29 µg/g; remediate: 55µg/g (Netherlands).

Agricultural soil, maximum tolerable concentration: 20µg/g (Germany).

[1] Arsenic compounds can be classified into; inorganic, organic, and arsine gas. Inorganic As is generally more toxic the organic form.

3.2 Water and leachates

Arsenic is found in varying concentrations in natural waters. The concentration of As in unpolluted fresh waters typically ranges from 1 to 10 µg/L, rising to 100 to 5000 µg/L in areas of sulfide mineralization and mining.

2.2.1 Action levels

The maximum permissible concentration of As in drinking water is 50 µg/L and recommended value by EPA and WHO is 10 µg/L. However, it is also important to note that mean daily consumption and nutritional status of an individual are also critical factors influencing what level is considered safe. With respect to leachates, the toxicity characteristic[2] (TC) regulatory limit is 5 mg/L, which is generally set at 100 times the maximum contaminant level[3] (MCL).

3.3 Foods

Arsenic is found to be cumulative in living tissue, and the amount of As in a plant depends on the amount of As it is exposed to. Its concentration varies from less than 0.01 to about 5µg/g (dry weight). Where As enters the food chain, fruits and vegetable primarily contains less than 10% of the inorganic form of the element.

2.3.1 Action levels

The regulatory limit of As in foods, as set by the FDA is 0.5 to 2 µg/g.

3.4 Humans

The total human body content varies between 3 and 4 mg As and tend to increase with age. With the exception of hair, nails and teeth, most body tissue contains less than 0.3 to 147µg/g (dry weight).

[2] Leachate from any solid waste having a concentration at or above this level is considered toxic and therefore hazardous.

[3]Maximum concentration of a chemical substance that is allowed in public drinking water (EPA).

3.4.1 Action levels

The normal concentration of As in unwashed hair is approximately 0.08 to 0.276 µg/g with 1 µg/g being indicative of As poisoning, while the normal concentration of As in nail clippings is 0.09 to 0.59 µg/g.

4 METHODOLOGY

4.1 Sample collection

4.1.1 Soils, food and water

Forty five (45) bulk soil samples (0–15 cm) representing different landscape architecture were collected (July 2015) across Grand Cayman Island for As analysis (Figures 1 and 2). One field sampling site was previously dedicated to the storage of post hurricane Ivan debris, while the other sites included two adjacent properties and several areas remote to the debris storage site for use to establish the local background geochemistry of As. Typically, the sampling regime at the debris site and adjacent properties involved the use of a clean stainless steel shovel to collect soils from the corners and centre of a square 5 x 5. Critically, each of the five sub-samples at each sampling site (5 x 5 m) was placed in doubly sealed sterile heavy duty zip lock bags. The rationale was to assess for geochemical variability within each sample site. Background soils were collected as composites and all samples were transported to the laboratory under ambient conditions.

In order to assess the possible transfer of As through the food chain, 11 paired food and fruit types and two grass samples of medium or full maturity were collected from the debris storage site and adjacent properties. The samples were placed in doubly sealed sterile heavy duty zip lock bags and their fresh weights taken before being transported to the laboratory on ice.

Approximately 100 mL of groundwater (n = 11) was collected in sterile Nalgene bottles from domestic and monitoring wells located on the debris storage site and adjacent properties. A single soil porewater sample was collected from the debris storage site. The samples were transported to the laboratory on ice and were frozen before analysis.

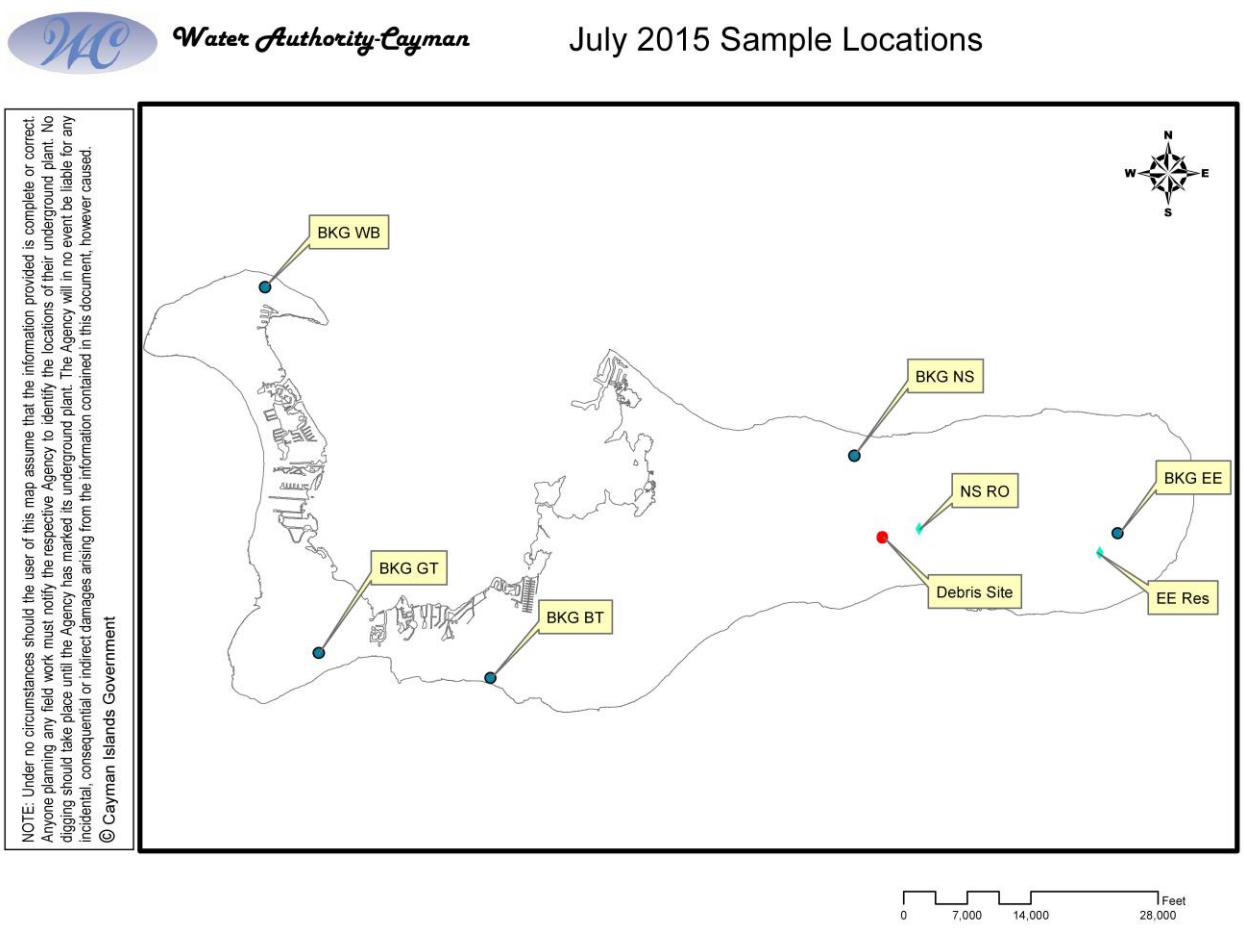

Figure 1: Map of Grand Cayman showing background and debris sampling sites.

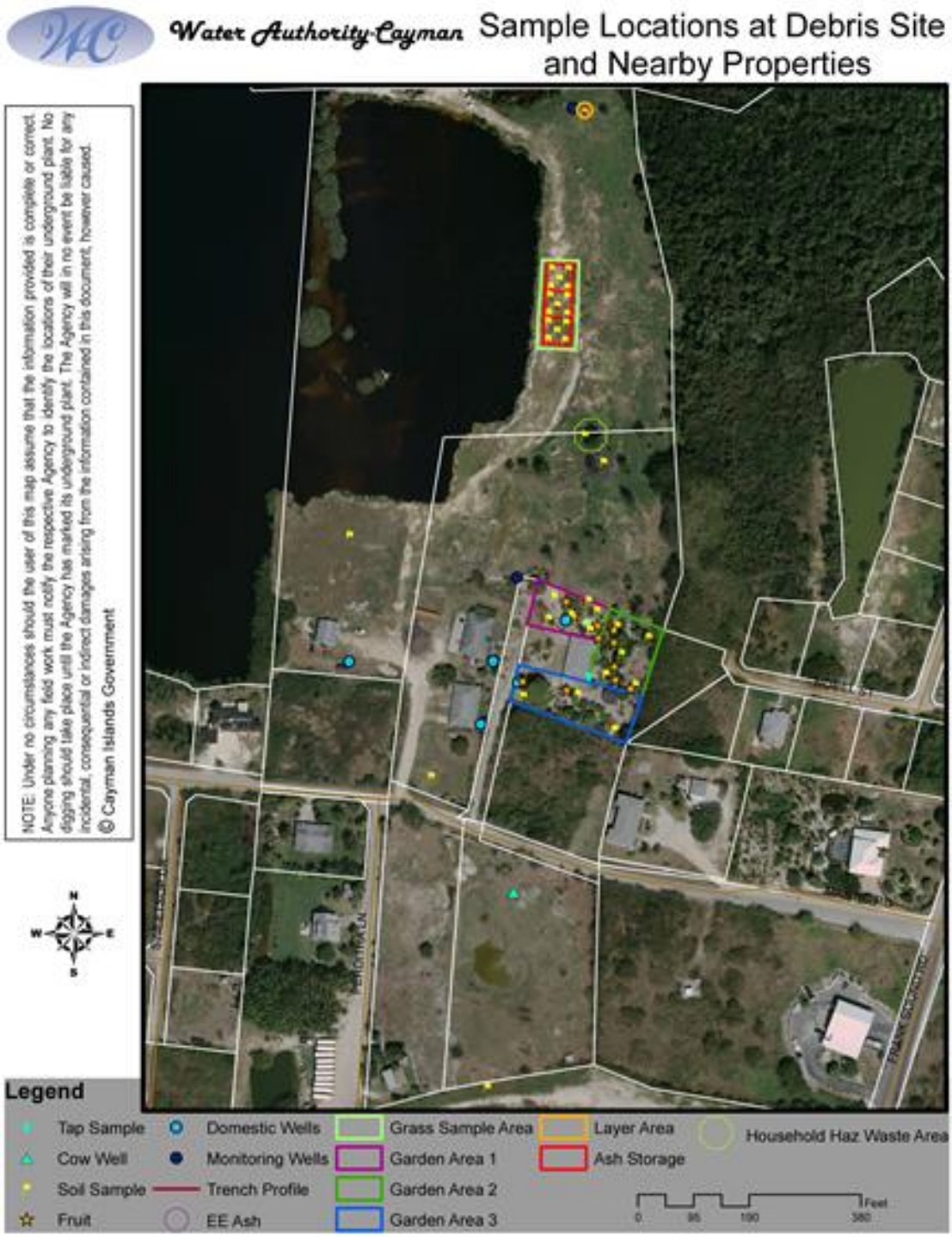

Figure 2: Map showing sample locations at debris site and adjacent properties.

4.1.2 Nail clippings

Fingernail and toenail clippings (n=25) were collected from members (adults and children) of the households proximal to the debris storage site. Nail clippings were also collected from a total of eleven (11) subjects (male and female) ranging in age from 4 to 64 years with no previous history of residency proximal to the debris storage site. The distribution of age for the control group was intended to mirror the gender and age range for participants residing in the study area. Clippings were collected from all toes for all individuals (and fingers, in the majority of the cases), and stored in fresh biohazard bags before analysis.

4.2 Samples preparation

4.2.1 Soil, food and water

Soil samples were sieved using a 100-mesh sieve to retrieve < 2mm fractions, which were then oven dried at approximately 45°C for 12 hours. Using a Fritsch mortar-grinder, samples were ground to a fine consistency stored in acid-treated polyethylene containers before analysis. Leachate extraction was done on composite samples and three randomly selected background samples (<2 mm soil fraction) using the USGS Field Leach Test method and a modified version thereof (deionised water adjusted to pH 5.5 to mimic acid rain),

Foods, fruits and grass samples were washed clean of soil debris using a large excess of distilled water. Samples were then patted dry with paper towels, and where necessary were peeled with a stainless steel knife and cut into small pieces and combined by mixing in a large clean bowl. Samples were weighed and placed in clean non metallic container then oven dried to constant weight at 65°C. After cooling in a desiccator, samples were ground using an automatic agate mortar and pestle and approximately 0.5 g of the ground sample digested in acid before analysis.

Frozen water samples were allowed to thaw at 4°C. Prior to analysis by TXRF, samples were then allowed to equilibrate to room temperature before transferring a well mixed volume of the sample to requisite flask for addition of internal standard.

4.2.2 Nail clippings

Nail clippings were carefully washed to remove external contamination (e.g. nail polish) and visible exogenous material being removed using forceps. The cleaning protocol involved the sonication of clippings in 5ml Triton X-100 (1%) for 20 min. The nails were then subjected to five rinses with 5 ml of deionized water, ensuring complete submersion of the sample during each step. The cleaned samples were then placed in glass beakers and allowed to dry at 60^0C overnight. After cooling the dried samples were prepared for analysis.

4.3 Sample analysis

4.3.1 Instrumental Neutron Activation Analysis (INAA)

Instrumental Neutron Activation Analysis (INAA) when practiced using the relative method, as is employed at the International Centre for Environmental and Nuclear Sciences, has the capability to be described as a primary ratio method of analysis as defined by the Consultative Committee for Amount of Substance- Metrology in Chemistry (CCQM). This is demonstrated by the fact that the method is fully defined by a measurement equation in which all terms are SI traceable and all contributions to the uncertainty budget are fully quantifiable. The CCQM has accepted the basis of this argument and accepted neutron activation analysis as a primary method and added it to their list of primary methods (CCQM, 2007). Neutron Activation Analysis, specifically INAA has been used in the certification of several property values in certified reference materials (CRMs), both biological and geological. Several characteristics of INAA make it ideal for elemental analysis of several sample matrices. INAA is conducted directly on an irradiated mass and analysis is based on nuclear processes rather than chemical properties. For this reason no chemical dissolution is necessary and therefore there is no potential loss due to incomplete digestion of the unknown portion. Furthermore this marks INAA as a technique that can elucidate the true total of the particular analyte of investigation. INAA is also largely matrix independent which is particularly advantageous when faced with samples of unusual physico-chemical properties and especially in the case where there is no reference material of similar matrix or property values. Neutron activation analysis requires a source of neutrons. At ICENS this is the SLOWPOKE-2 (Safe LOW Power K(c)ritical Experiment), a nuclear reactor with a relatively high and stable flux over long periods of time.

This is the only nuclear reactor in the English-speaking Caribbean and operates at a maximum thermal flux of 10^{12} $ncm^{-2}s^{-1}$ at a power of 20kW.

4.3.2 Soils

For the determination of arsenic in soil samples approximately 250 mg was weighed out in acid-washed Polyvial EP 338 (laboratory grade) polyethylene vials and then heat-sealed. These vials were further encapsulated in Polyvial EP 290 (Lg) polyethylene vials which were also heat sealed. Soil samples were irradiated at a neutron flux of 10^{12} $ncm^{-2}s^{-1}$ for 1 hour and allowed a decay period of four (4) days. Samples were then counted on an Ortec High-Purity germanium (HPGe) coaxial gamma photon detector system with an efficiency of 71% and a resolution of 1.8 keV at the ^{60}Co 1332 keV gamma line. Samples were counted at geometry of 3cm from the end-cap of the detector.

4.3.3 Nail clippings

For the determination of arsenic in nail clippings, washed samples were transferred to acid-washed Polyvial EP 338 NAA (prime polyethylene) vials which were then further encapsulated in Polyvial EP 290 (Lg) polyethylene vials. The samples were irradiated at a neutron flux of 10^{12} $ncm^{-2}s^{-1}$ for 4 hours and allowed a decay period of 2 days before counting. After two days the samples were transferred into pre-cleaned inert vials of known mass and the mass of the sample recorded before being heat-sealed to prevent inadvertent loss or potential cross-contamination. Although for the irradiation of the human nail samples prime polyethylene vials were used with lower levels of trace element impurities than the laboratory grade vials, the sample mass of the samples was usually very low and therefore the induced radioactivity of the vial, the low sample mass and the potential arsenic in the vial could confound the low intensity of the arsenic signal. By transferring the sample to inert vials the gamma quanta released by the vial would be eliminated, the background of the spectrum would be reduced and the need for blank correction would be unnecessary. This technique of transferring irradiated samples to unirradiated vials is commonly used in INAA. This would also lower the detection limit and increase the net peak area for ^{76}As. This is particularly important when considering spectral resolution of the arsenic peak at 559.1 keV with ^{82}Br at 554.3 keV, which is ubiquitous in

biological samples and ^{122}Sb at 564 keV. Samples were then counted on an Ortec High-Purity germanium (HPGe) coaxial gamma photon detector system with an efficiency of 71% and a resolution of 1.8 keV at the ^{60}Co 1332 keV gamma line. The samples were counted for 2 hours at a geometry of 2cm from the end-cap of the detector.

4.4 Total Reflection X-Ray Fluorescence (TXRF)

TXRF spectrometry is a sensitive, established analytical technique that is capable of elemental quantification in the range of parts per billion (ppb) levels. TXRF has been used at ICENS in the analysis of body fluids including blood and urine and food samples such as rice, fish and root crops among others. AT ICENS, TXRF has been shown to give reliable results for As in various samples when compared to NAA. However, especially in the case of the food samples in this study, an elemental interference between lead (Pb) and As resulted in the use of a lower intensity As x-ray peak for quantification which increases the level of uncertainty in those values.

4.4.1 Food

Approximately 0.5g of each sample was digested in concentrated nitric acid using a Microwave Accelerated Reaction System (MARS). After digestion, the samples were made up to 30 mL with deionized water. To each digest (900 μL), 100 μL of a 100 μg/L internal standard cobalt (Co) solution was added and the mixture homogenized by vortexing. Ten (10) μL of each sample was pipetted onto a quartz TXRF sample carrier and analysed under vacuum in a Wobistrax TXRF spectrometer operated at 50 kV and 30 mA for 1000 s.

4.4.2 Water

To each water sample (900 μL), 100 μL of a 100 μg/L internal standard cobalt (Co) solution was added and the mixture homogenized by vortexing. Ten (10) μL aliquots of each sample was pipetted onto a quartz TXRF sample carrier and analysed under vacuum using a Wobistrax TXRF spectrometer operated at 50 kV and 30 mA for 1000 s.

4.5 Geochemical characteristics

4.5.1 Soil pH

Soil pH was determined in a water suspension (soil/solution, 1:2.5) after shaking for 1 hour followed by centrifugation at 2,500 rpm for 10 min.

4.6 Statistical analysis

Values of half the detection limit were used in calculations for samples below instrument detection limits. The 'box and whisker' plots illustrate the first and third quartiles (boxes), median (horizontal line), mean (redcross), maximum and minimum values (solid circle), and outliers (open circle mild outliers, asterisk extreme outliers). The whiskers show the range of values that fall within the inner fences (data points that are up to 1.5 times the interquartile range). The statistical significance of differences in concentrations was tested using the non-parametric Mann-Whitney U test.

4.7 Quality control

The reference materials NIST 1643E, IAEA 336, NIST 2709a, and NIST 2711a were analyzed as quality control and the results presented in Table 1.

Table 1: Quality control data for As in water, nail, soil and soil leachate samples

Reference material	Sample Type	Measured Value	Reference Value	Recovery (%)
NIST 1643E (µg/L)	Water	63.87	60.45	106
NIST 1643E (µg/L)	Leachate	57.41	60.45	95
IAEA 336 (µg/g)	Food	0.846	0.63	134
IAEA 336 (µg/g)	Nail clippings	0.73	0.63	116
IAEA 336 (µg/g)	Nail clippings	0.76	0.63	121
IAEA 336 (µg/g)	Nail clippings	0.57	0.63	90
NIST 2709a (µg/g)	Soil clippings	11	10.5	105
NIST 2709a (µg/g)	Soil	12	10.5	114
NIST 2711a (µg/g)	Soil	106	107	99
NIST 2711a (µg/g)	Soil	102	107	95

Routine aspects of quality control for INAA at ICENS include the use of certified reference materials, analysis of replicates, the use of complimentary techniques such as energy-dispersive X-ray fluorescence (ED-XRF) for geological samples or atomic absorption spectrophotometry (AAS) and Total X-ray Fluorescence (TXRF) for biological samples for agreement of results and the periodic assessment of blanks especially when mass fractions are expected to be low and the potential need for blank correction exists. In many cases the potential use of these methods was unnecessary or not possible. Blank correction was unnecessary for the nail samples as these were transferred to inert vials. The analysis of replicates for nail samples was not possible as in all cases the sample mass was not enough for replicate analysis. Blank correction for the soil samples is unnecessary as the arsenic content of the soil samples and the intensity is enough to make any contribution from the vial negligible. This is validated by the results of reference material analysis. Soil samples were also analyzed by ED-XRF and good agreement was found between the two techniques. The detection limit for a particular analyte, in this case arsenic may vary from sample to sample various reasons. Firstly, the gamma spectrum background is matrix dependent. Secondly the detection limit for a given analyte in a particular sample is dependent on irradiation, decay and measurement and counting times. This means that the detection limit is specific to each measurement and therefore each sample.

The uncertainty of NAA analysis is based upon the error on the counting statistic, which is determined as the square root of the background subtracted counts of analytical peak. A 32% threshold value was set for acceptance of analytical results. The data above this limit were reported as detection limit using the Currie definition for detection limit.

There is an approximate 30% uncertainty margin associated with the As concentrations in the food samples. This is due to the use of the lower intensity As K-beta x-ray peak for quantification because there is an interference with the higher intensity K-alpha peak. The food samples will be reanalyzed for As by NAA as soon as the reactor is re-commissioned to obtain more accurate results.

5.1 General geochemical characteristics

The As content of the soil samples from the study area ranged from 5.8 to 111 µg/g (median,17.5 µg/g, mean, 25.8 µg/g) while the background samples ranged from 11 to 85 µg/g (median, 28.8 µg/g; 38.6 µg/g). The geographic coordinates, As content, and pH of all soil samples collected are presented in Table 2. Figure 3 shows the As content of soil samples from this study along with averages reported for Jamaica and the United States.

Table 2: As content, pH, and geographic coordinate of soil samples

Sample ID	Latitude	Longitude	As (µg/g)	pH
030715 02-09E	N 19° 18’ 57.3"	W 081° 11’03. 0”	12	8.3
030715 02-07C	N 19° 18’ 58.5”	W 081° 11’ 02.9”	6	8.9
030715 02-10	N 19° 18’ 55.3”	W 081° 11’ 02.2”	15	8.5
030715 02-04	---	---	10	8.1
030715 02-08D	N 19° 18’ 57.9”	W 081° 11’ 03.2”	111	8.0
030715 02-08B	N 19° 18’ 58.2”	W 081° 11’ 03.1”	22	8.0
030715 02-03	---	---	17	8.6
030715 02-09C	N 19° 18’ 57.4”	W 081° 11’ 03.2”	19	8.5
030715 02-07D	N 19° 18’ 58.3”	W 081° 11’ 03.1”	40	8.4
030715 02-08C	N 19° 18’ 58.0”	W 081° 11’ 03.0”	8	9.0
030715 02-09A	N 19° 16’ 57.7”	W 081° 11’ 02.8”	15	8.7
030715 02-26	N 19° 18’ 55.7”	W 081° 11’ 02.5”	13	8.1
030715 02-07A	N 19° 18’ 58.6”	W 081° 11’ 03.1”	61	7.9
030715 02-07B	N 19° 18’ 58.6”	W 081° 11’ 02.9”	12	8.1
030715 02-07E	N 19° 18’ 58.3”	W 081° 11’ 02.7”	20	8.0
030715 02-09D	N 19° 18’ 57.4”	W 081° 11’ 03.2”	14	8.6
030715 02-08E	N 19° 18’ 57.9”	W 081° 11’ 02.8”	28	7.9
030715 02-02	N 19° 19’ 01.2”	W 081° 11’ 02.6”	56	8.0
030715 02-08A	N 19° 18’ 58.1”	W 081° 11’ 03.1”	65	8.4
030715 02-09B	N 19° 18’ 57.7”	W 081° 11’ 02.9”	24	7.8
030715 02-22	---	---	18	8.2
030715 02-20	---	---	36	7.6
030715 02-13 BKG BT	N 19° 16’ 23.8”	W 081° 11’ 18’ 32.2”	24	8.0
030715 02-11 CHHS	N 19° 18’ 44.7”	W 081° 11’ 04.1”	16	7.7

Table 2 continued

030715 02-39 G3-C	N 19° 18’ 50.8”	W 081° 11’ 01.9”	7.0	8.4
030715 02-28 G1-B	N 19° 18’ 52.8”	W 081° 11’ 02.3”	8.2	8.1
030715 02-12 BKG EE	N 19° 19’ 03.2”	W 081° 11’ 04.1”	34	8.1
030715 02-14 BKG GT	N 19° 16’ 49.5”	W 081° 21’ 50.0”	11	7.9
030715 02-23 BKG NS	N 19° 20’ 26.8”	W 081° 11’ 35.1”	85	7.4
030715 02-07 COMPOSITE	---	---	19	8.1
030715 02-09 COMPOSITE	---	---	16	8.2
030715 02-08 COMPOSITE	---	---	38	8.1
030715 02-21	---	---	To be analysed	8.7
030715 02-35 G2-D	N 19° 18’ 51.6”	W 081° 11’ 02.2”	To be analysed	8.2
030715 02-38 G3-B	N 19° 18’ 51.5”	W 081° 11’ 02.8”	To be analysed	8.5
030715 02-32 G2-A	N 19° 18’ 51.5”	W 081° 11’ 02.8”	To be analysed	8.1
030715 02-34 G2-C	N 19° 18’ 52.2”	W 081° 11’ 01.9”	To be analysed	8.2
030715 02-33 G2-B	N 19° 18’ 52.5”	W 081° 11’ 01.6”	To be analysed	8.0
030715 02-30 G1-D	N 19° 18’ 52.9”	W 081° 11’ 03.3”	To be analysed	8.2
030715 02-37 G3-A	N 19° 19’ 51.6”	W 081° 11’ 03.8”	To be analysed	8.4
030715 02-15 BKG WB	N 19° 23’ 29.3”	W 081° 22’ 53.3”	To be analysed	8.2
030715 02-25 SP GEN #2	N 19° 18’ 50.1”	W 081° 11’ 05.4”	To be analysed	8.5
030715 02-24 SP GEN #1	N 19° 18’ 54.1”	W 081° 11’ 06.4”	To be analysed	8.1
030715 02-36 G2-E	N 19° 18’ 51.4”	W 081° 11’ 01.7”	To be analysed	8.4
030715 02-31 G1-E	N 19° 18’ 52.8”	W 081° 11’ 02.7”	To be analysed	8.2
030715 02-29 G1-C	N 19° 18’ 52.9”	W 081° 11’ 02.9”	To be analysed	8.0
030715 02-27 G1-A	N 19° 18’ 53.2”	W 081° 11’ 03.2”	To be analysed	8.5
030715 02-40 G1-CP SOIL	N 19° 18’ 53.0”	W 081° 11’ 02.4”	To be analysed	8.3
G2 COMPOSITE SOILS	---	--	To be analysed	8.2
G3 COMPOSITE SOILS	---	---	To be analysed	8.3
G1 COMPOSITE SOILS	---	---	To be analysed	8.3

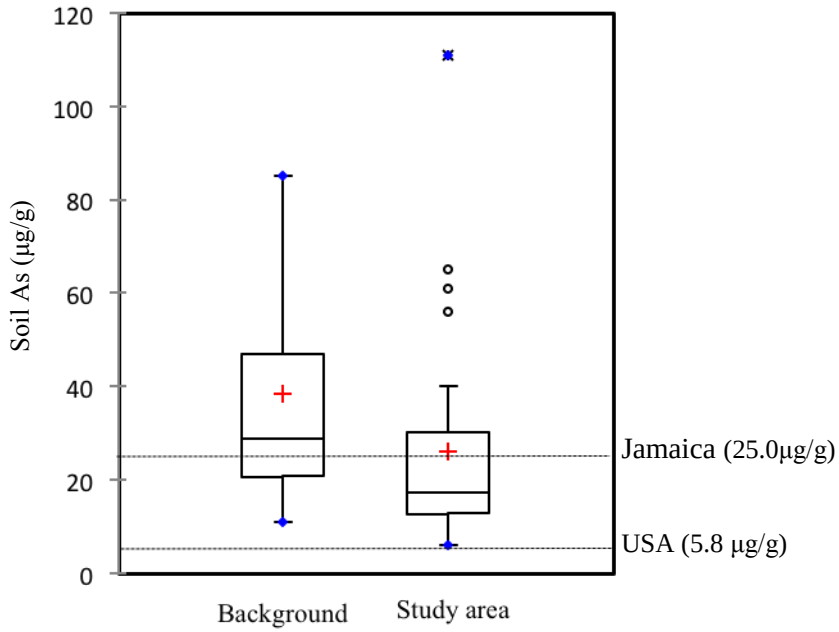

Figure 3: Soil concentration of As in background and study area samples. Jamaica and USA averages are shown for comparison.

There appears to be no significant difference (number of background samples too low to perform statistical test) between the As content of soils from the debris site and those used a background/reference soils. Furthermore, 86% of the samples have As concentration within the world background range (0.1 to 50 µg/g), although the mean As concentration (25.8 µg/g) was higher than the reported world mean of 6.83 µg/g for surface soils. Although elevated relative to world averages, these levels are not unusual for uncontaminated soils. To put even the maximum value in some perspective, the standard reference material©, the NIST 2711a- Montana Soil II is considered only moderately elevated in trace elements, with a certified value of 107 ± 5 µg/g; contaminated soil, NIST 2710a- Montana 1 Soil, has a certified arsenic value of 0.154 ± 0.010 %.

The USGS Field Leach Test and a modified version thereof were used as a proxy for the EPA TCLP/SPLP methods and provide information on the leachable As content of the soils (Table 3; Fig. 2). Similarly the As content of soil porewater provides insights into the *in situ* behavior (mobilization) of dissolved As species. Figure 4 illustrates that more As is leached

under “acid rain” conditions and that soils from the debris site leach higher concentrations of As when compared with the background soils. This would suggest that pH is an important geochemical characteristic influencing the mobility of As in soils. The difference in the concentrations of As leached from the debris site and background soils may be due in part to differences in organic matter content and soil mineralogy. Critically the As content of the leachates (this investigation) is below the regulatory limit (5 mg/L).When considered together, there is likely to be little to no health risks associated with direct exposure to these soils, as drinking water and foods are the main sources of As intake for the general population. Direct intake of As from soil is much less significant. Further assessment of the indirect impact (food chain transfer) of the soil As concentrations reported here could be the focus of future investigations as some plants can accumulate considerable concentrations of As. However it has been reported that the levels of As in edible plants are generally very low even when crops are grown in contaminated soils.

Table 3: As content of soil leachate extracted under neutral and acid rain conditions.

Sample ID	**As in leachate pH 7.0 (µg/L)**	**As in leachate pH 5.5 (µg/L)**
G1 COMPOSITE SOILS	5.13	5.75
G2 COMPOSITE SOILS	3.26	5.02
G3 COMPOSITE SOILS	6.64	7.56
030715 02-07 COMPOSITE	13.45	34.26
030715 02-08 COMPOSITE	7.49	12.44
030715 02-09 COMPOSITE	4.13	7.75
030715 02-10	22.09	25.73
030715 02-11 CHHS	4.00	6.49
030715 02-13 BKG BT	2.25	7.89
030715 02-14 BKG GT	4.75	6.76
030715 02-12 BKG EE	3.298	4.305
06-01 SP LAYER (Soil porewater)	31	

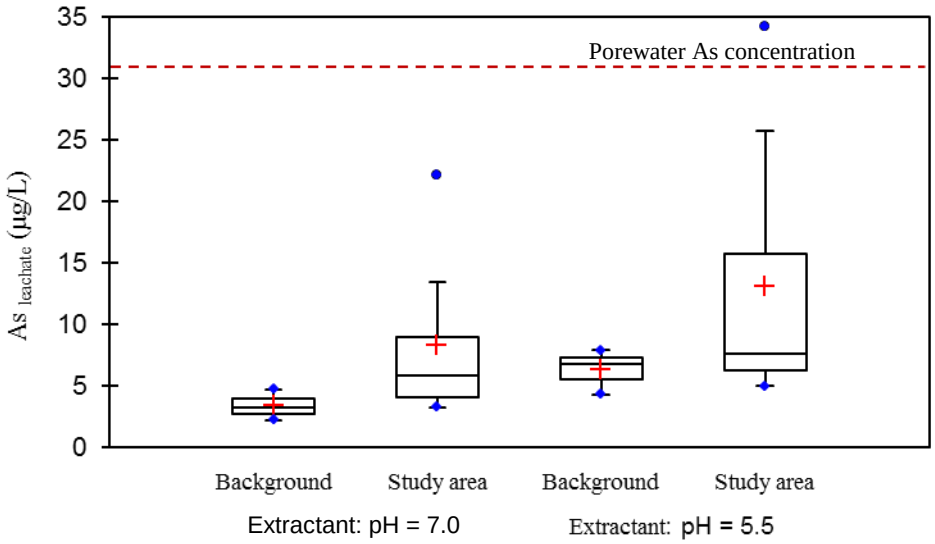

Figure 4: Box plot comparing As content of leachates (study area and background) extracted under neutral and acid rain conditions.

5.2 Water

Table 4: As content of water samples.

Sample ID	As (µg/L)
10-09 SP COW WELL	<10
10-01 SP MW 15	<10
10-08 SP HOUSE TAP	<10
NS RES	<10
10-03 SP MW 13	<10
10-05 APT SOUTH	20
10-04 SP APT NORTH	17
10-07 SP HOUSE EAST 2	23
10-02 SP HOUSE WEST	<10
10-06 SP HOUSE EAST 1	<10
10-11 SP EE RESERVOIR	<10

The arsenic content in ~73% (8/11) water samples measured (Table 4) was below the instrument detection limit and drinking water standard of 10 µg/L. The remaining samples have geometric mean (20 µg/L), similar to the elevated levels first reported by Mr. Hendrik-Jan van Genderen from Water Authority Cayman (19 µg/L). Note also, that the sample with the highest As content is lower than the U.S. Environmental Protection Agency (EPA) defined lowest

adverse effect level (LOAEL)[4] of 170 µg/L for skin lesions in a Taiwanese population. Health effects such as cancer, skin lesions, cardiovascular and neurological effects have been observed in populations exposed to long-term oral intake of inorganic As in water at levels generally greater than 100 µg/L up to over 1000 µg/L.

5.3 Foods

The As content of the food samples analyzed (Table 5) ranged from 0.08 to 5.63 µg/g (median,0.25µg/g, mean, 0.76 µg/g). Approximately 73% of the samples fall below the lower FDA regulatory limit of 0.5µg/g. Two samples were greater than the FDA upper regulatory limit of 2 µg/g and these are seen as outliers in Figure 5. The outliers correspond to As concentrations in lemon grass (*Cymbopogon citratus*) of the family Poaceae and lime (*Citrus aurantifolia*) of the family Rutaceae. These elevated values may be due to the fact that some members of the Poaceae and Rutaceae families are known hyperaccumulators of As.

Table 5: As content of food samples from study area.

Sample ID	As (µg/g)
05-04 G1-E (Plantain)	0.12
05-03-G3-A (Breadfruit)	0.18
05-13 SP (Grass)	0.61
05-02 G1-C (Sweetsop)	0.33
05-07 G2-C (Breadfruit)	0.27
05-01 G1-A (Breadfruit)	0.19
05-09 G2-C (Mango)	0.12
05-14 G1-E (Lemon grass)	5.63
05-08 G2-C (Neseberry) #2	0.14
05-05 G1-D (Cassava)	0.21
05-12 G3-B (Limes)	2.29
05-11-G2-E (Plum)	0.08
05-2A G1-C (Sweet sop)	0.56
05-11A G2-E (Plum)	0.43
05-06 G2-A (June Plum)	0.235

[4]Lowest amount of a substance, found by experiment or observation, which causes an adverse alteration of morphology, functional capacity, growth, development, or life span of a target organism distinguishable from normal (control) organisms of the same species and strain under defined conditions of exposure.

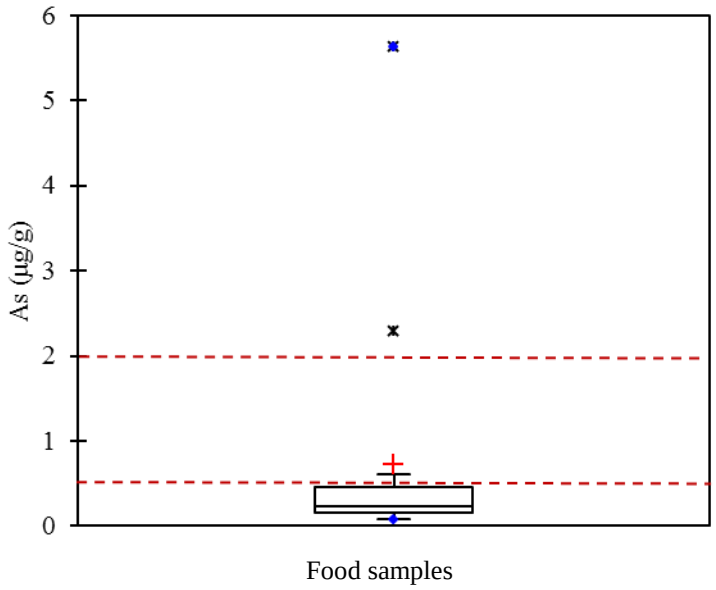

Figure 5: As content of food samples with FDA regulatory limits as dashed red lines.

5.4 Nail clippings

Arsenic in nail clippings ranged from <0.0 3to 0.12 µg/g for the control samples (Table 6) and <0.07to 0.53 µg/g for samples from the study area (Table 7). Figure 6 illustrates that the nail clippings from the study area were significantly (p-value = 0.035) higher in As; however this cannot be interpreted as an indication of excessive exposure to As, since all values fall within the range of 0.09 to 0.59 µg/g for normal concentration of As in nail clippings.

Table 6: As content of control nail samples

Sample ID	**As (µg/g)**
CTRL 1	0.12
CTRL 2	**<0.08**
CTRL 3	**<0.13**
CTRL 4	0.11
CTRL 5	0.08
CTRL 6	**<0.03**
CTRL 7	0.11
CTRL 8	**<0.05**
CTRL 9	0.07
CTRL 10	0.06
CTRL 11	**<0.05**

Table 7: As content of nail samples proximal to the debris storage site.

Sample ID	As (µg/g)
#1	<0.09
#2	0.36
#3	0.09
#4	<0.09
#5	0.08
#6	<0.07
#7	0.19
#8	0.39
#9	0.29
#10	0.19
#11	<0.07
#12	<0.14
#13	0.43
#14	0.18
#15	0.15
#16	0.53
#17	<0.12
#18	0.17
#19	<0.16
#20	0.08
#21	0.1
#22	<0.08
#23	Low sample mass
#24	Low sample mass
#25	Low sample mass

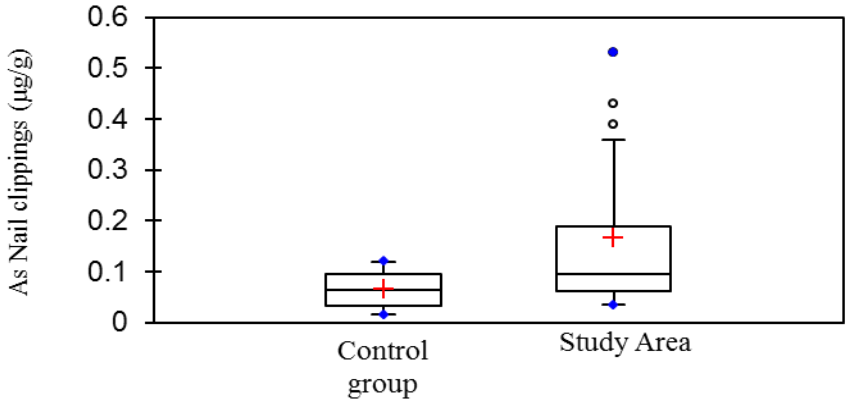

Figure 6: Box plots comparing As content (µg/g) of nail clippings from the control group and subjects proximal to the debris storage area.

6 EPIDEMIOLOGICAL REPORT & HEALTH IMPLICATIONS

Arsenic is natural component of the earth's crust, and is widely distributed throughout the environment in the air, water and land. It is therefore important to note that persons may become exposed to arsenic through consumption of food (including certain types of rice) and water, industrial processes and tobacco smoking. To assess the health implications of the exposure one needs to evaluate the duration of exposure (acute or chronic), the levels of arsenic, the route of exposure (inhalation, consumption, or physical contact) and underlining/existing health conditions. It is also important to note, that while the investigation is being conducted to determine exposure based on the situation surrounding the debris from the 2004 Hurricane Ivan; it is difficult to prove causation as persons may be exposed to arsenic through other sources.

It is possible to monitor human biomarkers to assess arsenic exposures and health effects, depending on the level and duration of arsenic exposures. Given the fact that arsenic stays in the blood stream for a few hours, blood is not a reliable indicator for chronic exposure. Considering arsenic is excreted through urine, measurement of arsenic in urine corrected to creatinine can be used for recent arsenic exposure. However, after ingestion of certain seafood, arsenobetaine (organic arsenic relatively non-toxic) can be excreted in the urine, increasing the total arsenic concentration but not necessarily the inorganic portion, which is of health concern. Hair and nails can be used. However, external contamination must be considered and some correlation among biomarkers and arsenic in water must be used to estimate intake of inorganic arsenic.

Health effects of arsenic exposures that can be used to monitor arsenic intakes include dermatological exam to check on the characteristic pattern of skin changes caused by arsenic – hyperkeratinization and hyperpigmentation, which are the most sensitive and diagnostic clinical indicators of chronic exposure to arsenic.

Based on what is known about arsenic, it was recommended that the cases undergo clinical examination and that nail clippings be taken for laboratory analysis.

The investigation revealed that there were twenty-five (25) persons who reside or had resided in the area of interest and are referred to as the exposed group or cases. Of this number, 11 are males and 14 females and ranges in age from 3 years to 66 years. Majority of the cases (44%) were within the 20-60 age group while the 6-10 age group accounted for 24%.

A standardized assessment tool developed by the Ministry of Health Cayman in collaboration with PAHO/WHO Jamaica was used to take their demographic information, medical history and document result of the clinical examinations. The interview and assessment was conducted by a senior Family Medicine physician within the Cayman Health Services and the acting Head of General Practice Services who has a Master's in Clinical Dermatology.

The examination revealed that none of the persons showed symptoms and/or signs of chronic exposure to Arsenic such as enlarged liver or spleen, ascites, pedal oedema, Mee's lines, hyperpigmentation or keratosis of the skin. From the medical history, it was found that some persons had chronic diseases such as hypertension and diabetes. It was also noted that some individuals were chronic cigarette smokers.

From the laboratory analysis of the nail clippings, it was found that arsenic levels ranged from <0.0 3to 0.12 µg/g for the control samples and <0.07to 0.53 µg/g for samples from the study area. The result showed that there was a statistical difference between the levels found in the control compared to the cases. However, the normal levels of Arsenic in nail clippings range from 0.09 to 0.59µg/g. This would suggest that the levels found in the nail clippings of the cases are within the normal levels.

The primary routes of arsenic entry into the body are through consumption and inhalation. Depending on the frequency and level of exposures these routes most likely leads to illness. Dermal exposure can occur, but is not considered a primary route of exposure.

Smokes from certain activities such as the burning of fossil fuels that contain arsenic and tobacco smoking are key exposures for inhalation. The consumption of arsenic contaminated water and seafood are the main pathways for arsenic through ingestion.

The results of the environmental analysis showed that the concentration of arsenic in the wells tested were less than 10µg/L; this is within the guidelines stipulated by the World Health Organization guidelines for drinking water quality. However, three of the samples exceeded this parameter with a maximum of 23µg/L but was still what would be considered safe values according to studies done. Health effects such as cancer, skin lesions, cardiovascular and neurological effects have been observed in populations exposed to long-term oral intake of inorganic Arsenic in water at levels generally greater than 100µg/L (FAO/WHO, 2011b) or the levels observed among this particular case study.

In 2010, the Joint FAO/WHO Expert Committee on Food Additives (JECFA) re-evaluated the effects of arsenic on human health, taking new data into account. JECFA concluded that for certain regions of the world where concentrations of inorganic arsenic in drinking-water exceed 50–100µg/litre, there is some evidence of adverse effects. In other areas, where arsenic concentrations in water are elevated (10–50µg/litre), JECFA concluded that while there is a possibility of adverse effects, these would be at a low incidence that would be difficult to detect in epidemiological studies. It was reported that the well water was not being used for domestic purpose.

The analysis of the food samples revealed that the majority were within the FDA regulatory limit of 0.5µg/g with exception of two samples. It is well established that long-term exposure to arsenic from drinking-water and food can cause skin lesions and cancer of skin, lung and

bladder. It has also been associated with developmental effects, cardiovascular disease, and neurotoxicity. Given that the situation that gave rise to the issue under investigation took place in 2004, epidemiological investigation would take into consideration exposure of 11 years, taken into account that the arsenic levels overtime since 2004 is not known but at this time the levels are not high. The two items (Lime and Lemon grass) found with arsenic above the standards are products that may not be consumed on a regular basis or in large amount.

In summary, the results of the clinical examination and the environmental analysis revealed that the situation can be considered under control. Clinical exams indicate that arsenic exposure effects are likely not occurring among the study population. The health of the residents doesn't seem to have been affected as the levels of arsenic found were within the standards/guidelines in most cases. Arsenic exposure becomes a public health concern when the levels are high enough to impact on health in the short-term and medium term or due to chronic exposure.

Based on the results of the investigations the following recommendations are made:

Similar annual clinical exams targeting potential medium term health effects, including cancers, neuropathy and other effects that can be potentially associated with arsenic exposures, but also to assess other risk factors such as cardiovascular diseases, diabetes etc. should be conducted.

7 RECOMMENDATIONS AND MITIGATION ADVICE

Since the arsenic present in the soils is anthropogenic and the affected area is not extensive, a suitable course of action may be to:

1. Excavate and remove the soil under consideration and sequester said soil in a landfill area.
2. Alternatively, remediation strategies may be considered as a cost effective option.
    a. Well water with As concentrations exceeding the regulatory limit for drinking water may be remediated at source using, for example, iron oxide filters.
    b. Since some plants (lemon grass and lime) have been shown to accumulate As above the limit permissible in foods, remediation of As-tainted water may become more important where ground water is used to irrigate crop plants.
    c. Alternatively, the use of As-tainted water for irrigation should be avoided as it is difficult to mitigate against the metal content of plants that bioaccumulate these components.

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