Environmental Studies of Constructed Wetlands in Akumal, Mexico: New Comparisons of Geotechnical and Botanical Parameters

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By

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Dedication

This work is dedicated to my family. This would not have been possible without their patience, support and encouragement throughout the course of this work.

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Abstract

ENVIRONMENTAL STUDIES OF CONSTRUCTED WETLANDS IN AKUMAL, MEXICO: NEW COMPARISONS OF GEOTECHNICAL AND BOTANICAL PARAMETERS

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Wastewater management is major concern in the Yucatan Peninsula, as sewage pollution has been linked to a rise in human health concerns as well as the decline of the Meso-American coral reef. Subsurface flow constructed wetlands (SFCWs) are engineered ecosystems which involve the use of hydrological, biological and mineralogical processes to reduce wastewater volume and decrease or ideally eliminate the polluting components. Geotechnical properties, plant cover and water quality characteristics of 30 SFCWs in Akumal, Quintana Roo were investigated to determine efficacy of the systems and assess causes for variability of performance.

The number of cells, shape and size varied mostly according to the space available for construction. Of the 38 plant species found in these wetlands, *Colocasia* spp., *Cyperus* spp. and *Acrostichum danaeifolium* were common. Concentrations of

ammonia and phosphate in effluents varied widely. Around 96 and 92% reductions to 354 and 250% gains were observed in ammonia and phosphate concentrations respectively in the effluent. The coefficient of permeability (k) for aggregate varied from 0.019 cm/s to 0.06 cm/s with an average of 0.041 cm/s. The average porosity was 43.89% and the minimum and maximum porosity was found to be 26% and 52% respectively.

The limestone aggregate is angular to subangular with an average uniformity coefficient of 1.52 and average aspect ratio of 2.3 indicating elongated aggregate particles. X-ray diffraction of powdered aggregate from the wetlands indicated four types i.e. (1) calcite (2) calcite and aragonite (3) calcite, quartz and boehmite (4) calcite, quartz, boehmite and aragonite. SEM analysis of samples indicates that the aggregate was highly porous with distinct dissolution and reprecipitation textures. Rare occurrences of Cassiterite (SnO_2) were found in few samples however no other heavy metal bearing minerals were observed. The bio-films on the aggregate have a distinct chemical composition with high phosphate content.

Many of the systems in Akumal seem to be undersized, overloaded and poorly maintained and planted with vegetation that might not be optimal for expected results. Aggregate dissolution might pose a risk of releasing pollutants into the environment. This study identifies several problems with these SFCWs and indicates a more efficient design and maintenance regime is needed.

Chapter 1: Introduction

The Location and its Issues with Wastewater

The Yucatán peninsula in Mexico is one of the major tourism destinations in the world and is an exemplar of the globalization to the tourism industry. Over the last several decades this region has seen tremendous growth. Murray (2007) reported that six million tourists entered the region in 2006, up from an estimated three million tourists in 2003. The economic development in this region has been accompanied by extensive social and environmental impacts (*e.g.*, Krekeler *et al*., 2007; Murray, 2007; Torres and Momsen, 2005; Aguilar and Fuentes, 2007). Much of the environmental impacts occur in the state of Quintana Roo where runaway economic growth is continuing, particularly to the south of Cancun (Murray, 2007).

Central to many environmental problems in the region is wastewater. Wastewater management is a growing concern for both human health reasons and because of the damaging effect of untreated or poorly treated wastewater on the environment (Krekeler *et al*., 2007; UNESCO, 2000; WHO, 2007; Pacheco and Cabrera, 1997; Alcocer *et al*., 1998; Aguilar and Fuentes, 2007). The Meso-American reef extends along the coast of Quintana Roo and is heavily impacted by sewage related pollution (Nicholls, 2009). The Meso-American Reef is similar to other coral reefs which are declining worldwide and sewage pollution is a contributing factor (Carpenter *et al*., 2008; Hoegh-Guldberg *et al*., 2007; Pandolfi *et al*., 2005; Pandolfi *et al*., 2003; Huges *et al*., 2003; Gardner *et al*., 2003; Pennisi, 2002; Pastorok and Bilyard, 1985). The geologic environment of the eastern Yucatán peninsula is characterized by karst aquifers that are extensively connected to the marine environment and thus are directly tied to the Meso-American coral reef. The overall health of the Meso-American coral reef has declined over the past several years and this decline has been attributed to the wastewater effluent that enters the marine environment through the karst aquifers. These aquifers are also used as a source of drinking water by the population in rural areas and it has resulted in an increase in human health concerns in the region (Krekeler *et al*., 2007). Prior investigations of groundwater in the Yucatán Peninsula have indicated that the water quality is poor due to the high contents of nitrate and coliform bacteria (e.g., Shaw, 1997). The decline in poor water quality has been attributed to local contamination of groundwater due to improper domestic wastewater management (Pacheco *et al*., 1997).

Currently there are no large scale water treatment options available for the region. A few modern wastewater treatment plants are present in Cancun. However, smaller communities to the south of Cancun do not have such treatment plants or wastewater treatment facilities. Some residents use septic tanks which are not effective in treating sewage as these systems simply retain the solid waste and discharge the untreated wastewater into the environment. The solids are occasionally pumped out and disposed of in the ecologically and hydrologically sensitive forest areas (Krekeler *et al*., 2007, personal communication with local people).

Constructed wetlands are engineered ecosystems which involve the use of hydrologic, biologic and mineralogical processes to reduce wastewater volume and decrease or ideally eliminate the polluting components of wastewater. Constructed wetlands have a wide variety of designs (e.g., Kadlec and Knight, 1996; Shutes, 2001). Wetlands can be horizontal surface and subsurface flow, vertical flow and floating raft systems (Shutes, 2001). Subsurface flow constructed wetlands (SFCWs) are being utilized as inexpensive wastewater treatment alternatives in many developing regions (Vymazal and Krőpfelová, 2008; Decamp and Warren, 2000**).**

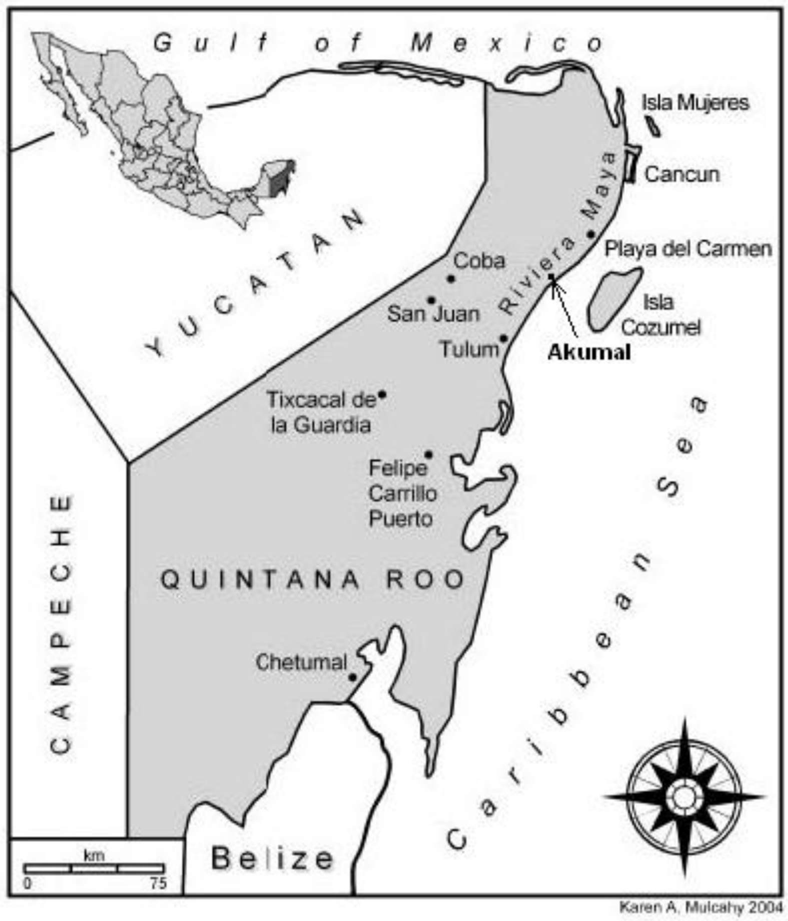


Figure 1: Map of Quintana Roo located in Yucatan Peninsula, Mexico. Map adapted from Torres and Momsen (2005)

Akumal is an ocean side tourist village in the east central coast of Quintana Roo, Yucatán (Fig. 1), located approximately 90 kilometers south of Cancun that uses constructed wetlands for wastewater treatment (Krekeler *et al*., 2007, Whitney *et al*., 2003). Akumal was founded in 1970 as a resort community and attracts tourists owing to its beaches, coral reefs and diving and snorkeling activities.

Wetlands in Akumal and Previous Work Done

In Akumal, constructed wetlands commonly consist of concrete boxes filled with mineral aggregate and planted with vegetation and they may have single or multiple cells. The size and shape of these wetlands varies according to available space. Wastewater is passed through the subsurface of the wetland where the microbial processes break down organic matter and reduce the BOD levels in the wastewater. Minerals in the aggregate take up some of the inorganic and organic pollutants improving wastewater quality and the total volume of wastewater is reduced by evapotranspiration (Krekeler *et al*., 2007). The wastewater is released into the surrounding environment after passing through these systems.

Centro Ecológico Akumal (CEA) was formed in 1993 to address environmental issues in the region. Mark Nelson from University of Florida, with the help of sponsorship from Planetary Coral Reef Foundation (PCRF) and CEA, began to install wetland systems in the region in mid 1990's as an inexpensive alternative for wastewater management. Initially two SFCWs were installed and Nelson conducted research on those two wetlands for his doctoral dissertation (1998). He worked on the design aspects of the wetlands and how to make them more efficient in processing wastewater. A total of six wetlands were constructed under Nelson's guidance in the 1990's and now more than 50 wetland systems exist in the region for treatment of wastewater from domestic as well as commercial sources.

Only limited work on SFCWs in Akumal has been done. Krekeler *et al*. (2007) conducted a basic survey of 20 subsurface wetlands in the Akumal region and determined the number of cells, control boxes, holding tanks, areas and estimated plant cover. Volume of aggregate and water level were also determined. Krekeler *et al*. reported a drop in aggregate levels in the wetlands. Mineralogy was determined for the CEA 1 and the Las Casitas wetland and was primarily found to consist of calcite and aragonite. New geologic Ca-montmorillonite clay material was reported to occur locally that could be used as liner in the wetland systems. Whitney *et al*. (2003) conducted a preliminary evaluation of CEA 1 wetland and examined the bulk properties and their study primarily focused on basic hydraulic characterization and chemical oxygen demand (COD) analysis on this single wetland. No detailed survey was done for other wetlands in Akumal. Whitney *et al*. (2003) reported very low dissolved oxygen levels and also low nitrification levels in this wetland. Improper plant choice was also pointed out in this study.

CEA wetland 1 was studied in detail by Probst *et al*. in 2003. This wetland was reportedly overloaded during peak tourist season and was receiving an inflow that was almost double its original capacity for which it was designed. The study indicated preferential flow and water accumulation at the surface. The wastewater effluent was analyzed for fecal coliform bacteria, nitrate concentration and dissolved oxygen concentration in order to evaluate the efficiency of the system. The investigation suggested that more efficient systems could be designed for future use.

Many biological aspects of these wetlands have not been investigated and little is known about what exact role the biotic factors play in the performance of these particular wetlands. The plant cover has not been studied for all the wetlands in the region and no data is available on the plant diversity in these wetlands except the plant coverage estimates done by Krekelar *et al*. (2007) and the plant diversity studies done by Nelson (1998) on the first two wetlands (CEA 1 and 2). Plants are very important component of constructed wetland systems as they are involved in removal of nutrients, pollutants, and microorganisms and recycling of water through transpiration. At present, plant assemblages is a major focus of on site management of wetlands in the region and it is assumed that if the plant cover is good, the wetland is functioning well (CEA staff, personal communication).

Mineralogy of aggregate in the constructed wetlands of Akumal was investigated in a limited way by Krekeler *et al*. (2007). Most work centered on two wetlands and one additional aggregate source. Powder X-ray diffraction was the primary tool of investigation for aggregate in the constructed wetlands. However more detailed electron microscopy studies were done on alternative dolomite aggregate sources and Ca-montmorillonite materials. Krekeler *et al*. (2009) has also investigated beach sands for use in constructed wetlands. Although these investigations are useful for future construction or aggregate replacement, it is undetermined whether or not the limestone mineralogy of the aggregate is similar in all constructed wetland systems. Furthermore, the mineralogy of the insoluble fraction (which is commonly dominated by phyllosilicates and oxyhydroxides in carbonate rocks) of the aggregate in the wetland systems has not been investigated in detail.

Basic geotechnical and environmental parameters of the systems also remain largely unquantified. Parameters such as influent and effluent volumes, grain-size and permeability coefficients of aggregate, total phosphorus and total nitrogen concentrations of influent and effluent have not been studied extensively. Another parameter which is poorly understood is the process of evapotranspiration. This process is key because the water that is evaporated and transpired through plants contribute highly to faster recycling of wastewater.

The goal of this study is to investigate the variability of geotechnical aspects, including vegetation, of a larger population of the Akumal constructed wetlands and assess how variability may impact performance. A comparative analysis with previous work will identify areas of new knowledge creation regarding these systems and identify gaps in our understanding. Understanding the variability of the geotechnical properties of these systems is critical in improving their overall performance so as to meet the government's wastewater effluent quality standards and also in designing and creating next generation SFCWs for the region.

Chapter 2: Methods

General Wetland Survey

A general survey was conducted for 30 SFCWs in Akumal. The condition, size, and GPS coordinate location of each SFCW was determined. Construction factors such as cracks and leakage, position of control box and number of cells was determined. Whether the wetland system is in shaded area or is exposed to sunlight was also determined.

Plant Cover and Diversity

30 SFCWs were surveyed for plant species count and percentage coverage. The percentage cover was determined by visual estimation of the total wetland area covered by plants. Very densely covered wetlands with dense plant canopy and growth to edges of the wetlands were given a score of 100%. Lower percentages were given when there were areas in the wetland that did not have plant cover or if the plant cover was not as dense as compared to the ones designated as being covered 100%. The dominant species in the wetlands were visually estimated by considering the plant canopy covering most of the surface area of the individual wetlands. The total numbers of plants were determined

by manually counting the number of individuals of each species that occurred in the wetlands. Plants such as taro, fern and cypress produce ramets and these were considered as one individual along with the parent plant as they had a continuous root system. This can be considered as an approximate plant count value and approximate diversity value as the number of plants could not be determined accurately due to difficulties such as dense growth, inaccessibility and possible error in counting of individual plants due to presence of ramets. However, accurate numbers are available for constructed wetlands which were newly planted. Weed plants which constitute a minor percentage (<15) of all plants, were not taken into account for this study. Plant diversity was calculated for all the 30 wetlands using Shannon-Weiner (Shannon's) plant diversity index which is the most commonly used and widely accepted diversity index.

Shannon-Weiner's plant diversity is derived using the following equation

$$H = -\sum_{i=1}^{s} (p_i) \ln(p_i), \text{ (Krebs, 1989)}$$

Where:

H= index of species diversity
S = number of species (species richness)
p_i = proportion of total sample belonging to the *i*th species
ln = natural log

Due to its logarithmic nature, the Shannon-Weiner index is sensitive to uncommon plant species and less sensitive to very common species. More value is given to presence of each species than is given to abundance of each species. A higher Shannon-Weiner index indicates higher number of unique species as well as higher evenness in distribution of plant species within the area.

Geotechnical Properties

A 1.0 kg bulk sample of aggregate from each wetland was obtained. Grain size of samples was determined using electronic caliper measurements. The long axis and the short axis of 100 aggregate grains were measured for each sample to get the average grain size. The uniformity coefficient was calculated for aggregate samples from each wetland by arranging their long axis measurements in an ascending order and then dividing the 60^{th} percentile reading by the 10^{th} percentile reading. This basically represents the ratio of the sieve size that will permit 60% of the aggregate to the sieve size that will permit passage of 10% of the aggregate (d_{60}/d_{10}). Hydraulic conductivity (K) values were determined using a standard GEOTEST permeameter. The bulk porosity was measured using a standard graduated cylinder. Aggregate was filled up to the 1000 ml. mark and water was poured in the cylinder commensurate with the 1000 ml mark. The amount of water held by the aggregate was then poured off and measured using a separate graduated cylinder. Organic matter was removed by washing thoroughly with water and when possible estimated volumetrically visually.

Water Quality Parameters

Water quality parameters that were investigated from influent and/or effluent include field tests of phosphate, ammonia, dissolved oxygen, pH, temperature, and conductivity. Water samples from influent and/or effluent was brought back to the CEA lab in clean plastic/glass sampling bottles/vials and tested immediately for pH, ammonia (NH_3) and phosphate. A standard multimeter was used for pH. A Hach brand ammonia nitrogen test kit (Model NI -8) and phosphate pocket colorimeter test kit was used to determine the concentrations of total P and ammonia. Dilution of samples with distilled water was done for samples with high concentrations of phosphate and ammonia so as to bring the concentrations within the readable range of the test kits. The actual concentrations were then accordingly calculated from the observed readings. The ammonia test kit gives results in terms of ammonia-nitrogen concentration. Therefore, the obtained final result was multiplied by 1.2 to express results as mg/L NH_3. A YSI datasonde was used to determine on site pH, conductivity and dissolved oxygen concentration of the influent and effluent wastewater for as many wetlands as possible. Access to the control box or final effluent stand pipes for several wetlands was not possible due to one or several portions of the systems being purposefully sealed to prevent access or lack of maintenance or care. Some systems were in disrepair, or apparently “dry”. Accordingly wastewater data from all systems was not collected.

X-Ray Diffraction and Scanning Electron Microscopy of Aggregate

Samples were collected in the field in clear, labeled plastic bags. For powder X-ray diffraction (XRD) investigation of aggregate samples, particles were dried at 105°C for 8 hours then powdered using a tungsten carbide mill for 10 minutes. The powdered samples were stored in polystyrene vials. Insoluble residues were collected from selected samples using acetic acid wash treatments. These materials were exchanged with 0.1 N Mg^{2+} solution five times and then washed with deionized water. The < 2 μm size fraction (upper 5 cm of suspension collected after a 2.5 hour settling time) was collected and centrifuged. Clay material was removed and smear mounts were prepared on slide mounts. Slides were analyzed under air-dry and glycerol-exchanged conditions.

X-ray diffraction scans were made using a Scintag X-1 powder diffractometer equipped with a Peltier detector, using Cu Kα2 radiation (0.1548 nm) radiation operating at 40 kV and 35 mA. The computer program "Data Scan" was used to operate the diffractometer. Samples were scanned from 5 to 65° 2θ at 0.02 degrees steps using a count time of 1s per step. Mineral identification was accomplished using the standard parameters outlined in Moore and Reynolds (1997), using the computer program Jade and PDF cards for aragonite (PDF# 041-1475), boehmite (PDF# 021-1307), calcite (PDF#047-1743), and quartz (PDF#046-1045).

For scanning electron microscopy (SEM) investigation, samples were broken down into smaller fragments of 1-3 mm in size. Fragments with relatively flat surfaces were chosen for SEM investigation to aid in energy dispersive spectroscopy (EDS) data collection. Carbon adhesive tapes were used to mount the samples on aluminum stubs using clean forceps. About 4-6 fragments were placed on each aluminum stub and these stubs were then mounted on the SEM stage. SEM investigation was done with a field emission scanning electron microscope (FESEM, Zeiss Supra 35VP FEG) at Miami University, Ohio. Textures of carbonate aggregate as well as the chemical composition of minerals in the aggregate were determined. Energy dispersive spectroscopy (EDS) chemical mapping and back scatter electron microscopy were used to investigate composition and textures when appropriate.

Chapter 3: Results

General Characteristics and Construction of SFCWs

Most SFCWs in Akumal are located in the front yard of beach/ocean front properties that were using it and in close vicinity of the coastline. These systems are typically constructed after the residence of commercial property and are not part of the original layout of the buildings. Most of the wetlands are located by the road connecting these buildings and therefore are easily accessible. El Eden, Casa Redonda, Casa Mayanah and Casa Christensen wetlands were located within gated, private properties. The CEA 1 and CEA 2 wetlands are being used for influent from commercial properties and public restrooms. These wetlands are located in close vicinity of restaurants. The CEA Dive Shop wetland receives influent from a shower and washing facility while the CEA New wetlands receive influent from the residential complex run by the CEA. The Las Casitas wetland system is located in an open plot and gets its influent from surrounding residential properties along the coastline. Luna Azul, La Bahia, Villas Flamingo, Casa Redonda, Playa Blanca are rental condominiums/villas which can accommodate multiple group of guests at a time and they have their wetlands across the road from the property the SFCWs serve.

Visual inspection indicates that all the wetlands surveyed are in good physical status and were built using concrete blocks and mortar except one wetland which was constructed using coral skeletons and mortar (Corals Wetland). There was no apparent structural flaw such as cracks or spalling in any of the 30 SFCWs surveyed, however systems were not excavated. Inspection of an incomplete wetland however showed that there was spalling at the wall-floor interface (Fig. 2) and suggests that such defects may be present in other SFCWs. An unfinished example of a concrete block wall is shown in Fig. 3.

Figure 2: Spalling at the wall-floor interface in an unfinished constructed wetland

Figure 3: An unfinished constructed wetland built using concrete blocks

The survey of SFCWs indicates a range of different sizes, number of cells; shapes and conditions exist in Akumal (Table 1). The sizes of the surveyed wetlands ranged from a maximum of 351.79 sq. meters to a minimum of 4.70 square meters. The average wetland size for the investigated wetlands is 50.41 sq. meters. Of the 30 SFCWs, 9 (37 %) are two celled systems and the remaining 21 (63 %) are one celled systems (Table 1). All of the two celled SFCWs had cells of the same or similar dimensions. The Las Casitas system has a total of 4 rectangular cells in two tandem wetlands fed by the same wastewater storage tank. For the purpose of this investigation, both the tandem wetlands at Las Casitas are treated as separate systems. All of the two celled wetlands were rectangular in shape. One celled wetlands were constructed in a variety of shapes ranging from rectangular, L-shaped, figure “8”, polygonal or irregularly shaped SFCWs (Table 1). The Que Onda wetland was the only two celled wetland that had octagon/irregular shaped cells. The U shaped wetland at Casa Aurora had an aeration system installed. This system was installed in December 2001 (Krekeler, personal communication) to circulate air in the inner layers of the aggregate and thereby aiding in better microbial action on the wastewater flowing through the system. The system appeared non functional in January 2009.

The capacity of the wetlands was calculated for per person per day on 5 m^2 equivalency based on the recommendations by the Danish EPA (1999) for constructed wetlands. The capacity of the investigated wetlands ranged from a minimum of ~1 person per day to a maximum of ~ 70 people per day with an average capacity of ~10 people per day (Table 1). Of all the investigated wetland systems, the Las Casitas system is the largest while the Akumal Real Estate wetland is the smallest in size and therefore they also had the highest and the lowest capacity respectively.

Table 1: Basic structural/dimensional data for the studied wetlands

No.	Wetland Name	Area (m^2)	No. of cells	Shape	Capacity* (People)
1	Akumal real estate	4.70	1	L-shaped	0.94
2	Alam Ek	20.47	1	Rectangular	4.09
3	Casa Aurora	9.57	1	U-Shaped	1.91
4	Casa Caribe	16.80	1	L-shaped	3.36
5	Casa Christensen	13.90	1	8-shaped	2.78
6	Casa Del Mar	10.63	2	Rectangular	2.13
7	Casa Del Sol	32.38	2	Rectangular	6.48
8	Casa Maleno	9.06	2	Rectangular	1.81
9	Casa Mayanah	12.35	1	8-Shaped	2.47
10	Casa Papagayo	12.01	1	Rectangular	2.40
11	Casa Redonda	21.61	2	Rectangular	4.32
12	Casa Zama	20.45	1	Rectangular	4.09
13	CEA 1	87.60	2	Rectangular	17.52
14	CEA 2	53.10	2	Rectangular	10.62
15	CEA Dive Shop	10.67	1	Rectangular	2.13
16	CEA New	51.20	1	Rectangular	10.24
17	Corals wetland	21.40	2	Rectangular	4.28
18	Dos Palamos	20.95	1	L-shaped	4.19
19	El Eden	14.49	1	Rectangular	2.90
20	Esperanza	10.44	1	Rectangular	2.09
21	First Past Corals WL	13.74	1	Rectangular	2.75
22	La Bahia	42.00	1	L-shaped	8.40
23	Las Casitas WL1(E)	351.79	2	Rectangular	70.36
24	Las Casitas WL2(W)	351.79	2	Rectangular	70.36
25	Luna Azul	67.35	1	Irregular	13.47
26	Nichte-Ha	25.75	1	L-shaped	5.15
27	Playa Blanca	43.87	2	Rectangular	8.77
28	Que Onda	47.10	2	Circular Polygonal	9.42
29	Sea Gate	19.79	1	Rectangular	3.96
30	Villas Flamingo	95.29	2	Rectangular	19.06
Minimum		**4.70**	**1.00**	**n.a.**	**0.94**
Maximum		**351.79**	**2.00**	**n.a.**	**70.36**
Average		**50.41**	**1.40**	**n.a.**	**10.08**
St. Dev.		**85.08**	**0.50**	**n.a.**	**17.02**

*Capacity is defined as per person per day based on 5 m^2 equivalency based on Danish EPA guidelines (1999)

n.a. = Not applicable

Distribution of wastewater to the constructed wetlands systems is a passive gravity fed process and white 4-inch PVC pipe is used as a spreader at the head or top cell of all systems investigated. Selected spreader pipes were excavated or were clearly visible in some systems (Fig. 4b). Spreader pipes were commonly drilled with 1 inch holes in rows the length of the pipe (Fig. 5). The water level usually stays at the level of spreader pipe, a few inches below the aggregate surface. However, in some instances, water was observed to collect above the aggregate surface which usually occurs due to pore occlusion (Fig. 4a). There is a great deal of variability in the inflow rates depending on the usage. There are fluxes in influent volumes depending on the pattern of daily usage as well as depending on seasonal variations based on the number of people actually using the facility. Since Akumal is a tourist destination, these systems get higher amounts of influent during the peak tourist seasons and at other times; there is a possibility that these may run dry while the buildings remain closed.

Control boxes in the systems provide hydraulic level control and are a critical access point for water sampling and maintenance. All systems except Casa Aurora, Corals wetland, 1st wetland past the corals wetland and Nicte-Ha systems have one or more control boxes. The control boxes in most of the wetlands are not easily accessible as some are deliberately sealed with concrete. Many others are overgrown with vegetation or are placed in unusual positions within the wetlands thereby making them inaccessible.

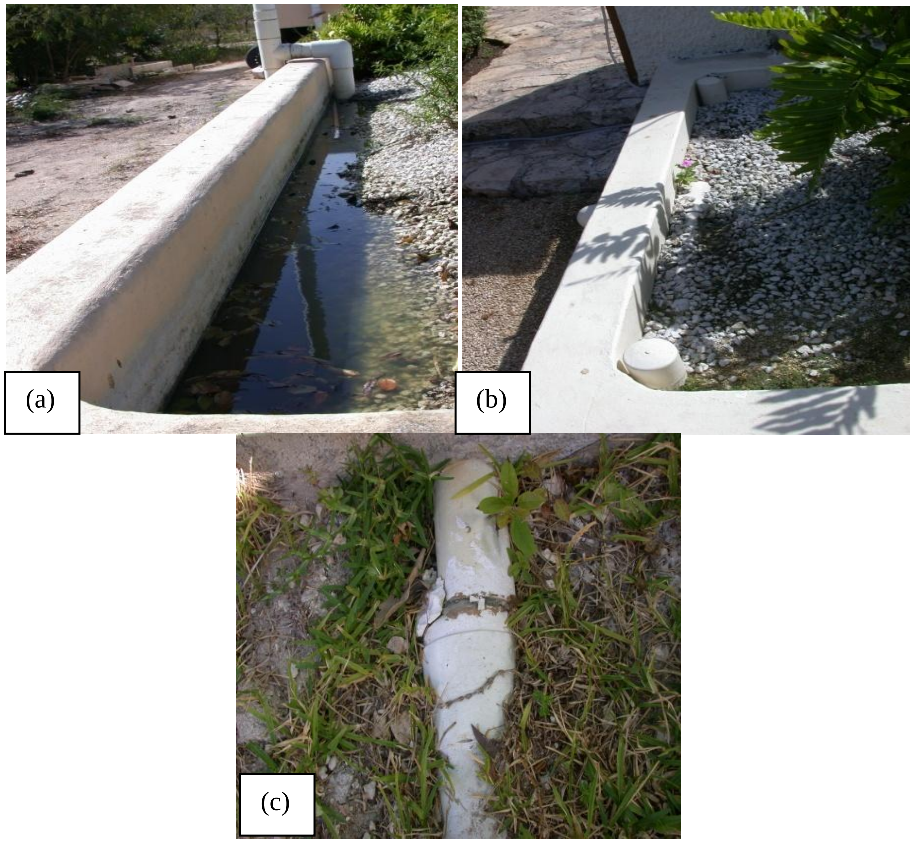


Figure 4: Examples of structural issues in Akumal Wetlands. (a) A partially exposed spreader pipe at Casa Caribe wetland. (b) Water above the aggregate surface in Las Casitas wetland. (c) A defective joint on an inlet pipe feeding into the influent control box at CEA Dive Shop wetland.

White 4 inch PVC pipes are used in all the systems in the control boxes and piping appears to be in good physical condition however some control boxes appear not to be designed well hydraulically and these are commonly dry or are simply piped incorrectly. For example, the Akumal Real Estate wetland is built at a higher elevation and the control box access is almost 5 feet above ground. The CEA Dive shop wetland inlet pipe that fed wastewater to the control box seemed to have a bad joint and might have a leak (Fig 4c).

Vegetation

Table 2 shows the estimated percentage of plant coverage in the wetlands and the percentage population of plant species present. Plant cover varies from 10 to 100%. The newly constructed or recently retrofitted wetlands had the least coverage as they were recently planted. In addition, lower plant coverage is observed in some older wetlands where the plants had died out in some specific areas or in wetlands that are planted with a few shrubs and/or tree species and no herbaceous species. Some of the older wetlands particularly some of the PCRF wetlands have 100% coverage.

The plant cover mainly consists of herbs, shrubs, ferns and trees. In all 38 plant species were recorded in the 30 investigated wetlands. 34 plants were identified and four remained unidentified (Table 2). Of these 38 species, only 4 species *Colocasia* spp. (taro), *Typha* spp. (cattail), *Acrostichum danaeifolium* (wetland fern) and *Cyperus lingularis* (sedge) are known to be conventionally used as wetland plants in constructed wetlands. Some wetlands had *Cocus nucifera* (coconut), *Cassia* spp. and palm trees of varying sizes. Many common ornamental garden plants (flowering as well as non flowering) that are aesthetically appealing are also used in the wetlands. The most common ones are palms, *Ixora*, *Hymenocallis* (spider lily), *Nerium* spp. (oleander), *Dracaena* spp., *Acalypha* spp., etc. Taro is the most commonly used wetland plant followed by wetland fern, palm and sedge. 26 (87%) of the wetlands had taro plants in them. Fruit plants were found in 43% (13) of the surveyed wetlands. Banana was the most common fruit bearing plant and was found in 9 wetlands. The Casa Redonda system had both its cells planted entirely with banana except single palm tree in each of the cell. The banana plants were planted 2-3 feet away from each other and the cells were not densely covered with vegetation. This system was completely shaded by the adjacent building and a high rise compound wall. Papaya plant was found only in the Nicte-Ha wetland along with taro, *Ixora*, spider lily and *Acalypha spp.* plants. Coconut plants were found in Dos Palamos and Las Casitas wetlands along with other vegetation like taro, spider lily etc. Cattail, a very commonly used wetland plant, is not very commonly used in Akumal systems and was found only in two wetlands, i.e. CEA Dive Shop and CEA New wetland.

Very dense growth and coverage was observed for plants like taro, sedge, wetland ferns and spider lily as these species propagate vegetatively and take up the entire area. The maintenance of plant cover varied greatly with wetlands having very well kept plants to wetlands that had very little to no maintenance of plants.

Table 2: Plant coverage and percentage population in each wetland

Wetland # *	Wetland Name*	Percent Cover	Shade Present	*Acalypha wilkesiana*	*Acrostichum danaeifolium*	*Colocasia spp.*	*Aloe vera*	*Caladium spp.*	*Canna spp.*
1	Akumal Real Estate	60	Yes						
2	Alam Ek	50	No		25.00	62.5			
3	Casa Aurora	95	Yes		6.25	25.00			
4	Casa Caribe	30	No		14.29				
5	Casa Christensen	100	No		7.69	76.92			
6	Casa Del Mar	90	No	8.33	2.78	13.89	33.33		16.67
7	Casa Del Sol	70	No			68.97			
8	Casa Malero	100	Yes		4.35	34.78			8.70
9	Casa Mayanah	50	No			90.00			
10	Casa Papagayo	50	Yes			72.00			
11	Casa Redonda	35	Yes						
12	Casa Zama	100	Yes			66.67			
13	CEA 1	100	Yes		0.95	76.19			
14	CEA 2	100	Yes		1.14	60.23			
15	CEA Dive Shop	60	Yes		10.81	5.41			
16	CEA New	10	No						13.64
17	Corals WL	60	Yes	2.27		70.45			
18	Dos Palamos	85	Yes	4.76	9.52	4.76			
19	El Eden	95	Yes			75.00			
20	Esperanza	90	Yes			50.00			
21	First past corals WL	90	Yes		45.83	54.17			
22	La Bahia	80	No			73.53			
23	Las Casitas (East)	50,90	No		50.79	22.22			
24	Las Casitas (West)	60,35	No		61.25	22.50			
25	Luna Azul	50	Yes			41.94			
26	Nicte-Ha	65	Yes	9.09		54.54			
27	Playa Blanca	10	Yes			8.51		10.64	
28	Que Onda	40	No			28.13			3.13
29	Sea Gate	60	No			92.06			
30	Villas Flamingo	10	No			29.25			2.83
Number of wetlands in which plant species occurs									
				4	13	26	1	1	5

Table 2 Contd.

Wetland # *	***Carica papaya***	***Cassia spp.***	***Cassia alata***	***Cestrum nocturnum***	***Chamaedorea spp.***	***Chrysalidocarpus lutescens***	***Cordia sebestena***	***Crinum spp.***	***Cocos nucifera***	***Cyperus lingularis***
1						12.12	3.03			
2						3.23				
3						12.50				
4						14.29				
5						3.85				
6								5.56		11.11
7			6.90					6.90		13.79
8								4.35		13.04
9						2.00		2.00		
10										28.00
11						11.76				
12			11.11							
13										
14				1.14	1.14	1.14				
15							2.70			5.41
16										
17										
18						4.76		14.29	38.1	
19						12.5				
20										50.00
21										
22						2.94				20.59
23		2.38							2.38	
24		1.25						5.00	2.50	
25								3.23		6.45
26	9.09							18.18		
27										
28						3.13	6.25			37.5
29						4.76		3.17		
30	0.94					3.77		1.89		
Number of wetlands in which plant species occurs										
	2	2	2	1	1	14	3	10	3	9

*refer to table 2 on page 24 for names of wetlands corresponding to the serial number.

Table 2 Contd.

Wetland # *	***Dieffenbachia spp.***	***Dracaena spp.***	***Epipremnum aureum***	***Ficus spp.***	***Hedera helix***	***Heliconia spp.***	***Hibiscus spp.***	***Hymenocallis littoralis***	***Ipomoea pes-carpae***	***Ixora spp.***
1			6.06					78.79		
2										6.25
3										56.25
4										
5					7.69					
6							2.78			
7										
8										34.78
9										
10										
11										
12										11.11
13	2.86		17.24		0.95	2.86		2.86	8.62	
14			22.73			7.95		7.95		
15										
16								22.73		
17		4.55								
18	4.76									
19										
20										
21										
22							2.94			
23				3.17				3.17		3.97
24										1.25
25								45.16		
26										9.09
27	27.66	23.4				29.79				
28			3.13					6.25		
29										
30			12.26					19.81		2.83
Number of wetlands in which plant species occurs										
	3	2	5	1	2	3	2	8	1	8

*refer to table 2 on page 24 for names of wetlands corresponding to the serial number.

Table 2 Contd.

Wetland # *	***Musa spp.***	***Nerium spp.***	***Philodendron spp.***	***Ravenala madagascariensis***	***Sansivera spp.***	***Thrinax radiata***	***Tradescantia spp.***	***Typha spp.***	**Unidentified Tree/Shrub**
1									
2									6.25
3									
4		42.86		14.29		14.29			
5	3.85								
6						5.56			
7	3.45								
8									
9	6.00								
10									
11	88.24								
12	11.11								
13	3.81						9.52		
14	3.41								14.77
15								70.27	5.41
16								63.64	
17	13.64				6.82	2.27			
18			4.76			14.29			
19			12.5						
20									
21									
22									
23		9.52							2.38
24		5.00				1.25			
25									
26									
27									
28		3.13					6.25		3.13
29									
30	6.6						19.81		
Number of wetlands in which plant species occurs									
	9	4	2	1	1	5	3	2	5

*refer to table 2 on page 24 for names of wetlands corresponding to the serial number.

Some of the poorly maintained wetlands had a very high organic content in their aggregate and plants with poor health. The 1st wetland after Corals Wetland was fully covered with wetland ferns and taro plants that seemed to be fairly old and had considerably thick base with roots covering almost the entire surface area. The aggregate in this wetland was covered with almost an inch thick organic matter and dead leaves. There was a considerable amount of soil like organic matter in the aggregate which had packed the aggregate tightly. The top few inches of the aggregate seemed drier as compared to other wetlands which indicated poor water flow. This might be attributed to compaction of aggregate, plant overgrowth and possibly blocked inflow for the system as the control box for this system was nonexistent altogether. Similarly, the Casa Papagayo wetland seemed to be poorly maintained with approximately 50% plant coverage. Almost half of the wetland surface was devoid of any plants. The taro and sedge plants in the Casa Papagayo wetlands had stunted growth with dry and patchy leaves in comparison to plants in other wetlands which had better conditions. The Las Casitas wetland showed a fairly old growth stand of wetland fern, taro, oleander, spider lily etc. However, in about 50% of the wetland area, the wetland ferns and other shrubs/trees had been recently pruned approximately 4-5 inches above ground very recently. Some plants might have been possibly removed from the wetland as there were considerable areas that were devoid of plants. Also, in comparison to the approximately 95% coverage reported by Krekeler *et al*. (2007), the CEA wetland had coverage of around 60% this time. Personal communications with a CEA volunteer revealed that they had undertaken pruning and cutting of plants for unexplained reasons.

The CEA New, Casa Redonda, Villas Flamingo and Playa Blanca wetlands were either recently constructed or refilled with new aggregate. The plants used in these wetlands were a mix of ornamental plants and commonly used wetland plants. Plants were more or less evenly placed about 2 feet apart from each other in rows that were around 2.5 feet apart. The plant species used in these wetlands consisted of taro, cattail and spider lily along with many other ornamental garden plant species (flowering as well as non-flowering). Almost around 50-55% of the surveyed wetlands were either partially or completely shaded by adjacent buildings or by trees for at least few hours a day depending on their orientation. Casa Caribe, Casa Redonda and Akumal real estate wetlands were the three wetlands which didn't have the conventional wetland plants such as wetland fern, cattail, taro or Cyperus.

Plant Diversity

Shannon diversity index was calculated for all the wetland systems to obtain an overview of overall diversity of vegetation in these wetlands (Table 3). All of the plants in the wetlands were counted as mentioned in the methods section. Weed plants were not counted in this part of the investigation. The minimum Shannon's diversity index was 0.33 (natural log) and 0.14 (base 10). The maximum Shannon's diversity index was 1.91 (natural log) and 1.35(base 10). The average was 1.10 (natural log) and 0.52 (base 10) with a standard deviation of 0.47 and 0.26 respectively (Table 3).

Table 3: Shannon's Diversity Index

No.	Wetland Name	Shannon's Diversity index (Natural log)	Shannon's Diversity index (Base 10)
1	Akumal Real Est.	0.72	0.31
2	Alam EK	0.99	0.43
3	Casa Aurora	1.10	1.35
4	Casa Caribe	1.48	0.64
5	Casa Christensen	0.65	0.37
6	Casa Del Mar	1.91	0.83
7	Casa Del Sol	1.01	0.44
8	Casa Malero	1.49	0.65
9	Casa Mayanah	0.34	0.18
10	Casa Papagayo	0.59	0.26
11	Casa Redonda	0.36	0.16
13	Casa Zama	1.00	0.44
14	CEA 1	1.44	0.63
15	CEA 2	1.24	0.69
16	CEA Dive Shop	0.90	0.39
17	CEA New	1.06	0.46
18	Corals WL	1.01	0.74
19	Dos Palamos	1.87	0.81
20	El Eden	0.74	0.32
21	Esperanza	0.69	0.3
22	First past corals WL	0.69	0.3
23	La Bahia	0.76	0.33
24	Las Casitas (east)*	1.50	0.65
25	Las Casitas (west)*	1.19	0.52
26	Luna Azul	1.12	0.49
27	Nicte-Ha	1.29	0.56
28	Playa Blanca	1.75	0.76
29	Que Onda	1.79	0.78
30	Sea Gate	0.33	0.14
31	Villa Flamingos	1.88	0.82
	Minimum / Maximum	0.33/1.91	0.14/1.35
	Average	1.10	0.52
	Standard Deviation	0.47	0.26

*East and west sections of the wetland counted separately

Geotechnical Properties

Figure 5: Larger aggregate at Villas Flamingo wetland. Spreader pipe exposed to show holes meant for dispersal of wastewater.

Figure 6: Smaller aggregate at Las Casitas wetland. The aggregate has been removed to expose water just a few centimeters below the surface.

All of the SFCWs in Akumal utilize limestone aggregate. The aggregate is sub-angular or angular. The longest and the shortest axes of the clasts were measured for each system.

The average short axis size ranged from 4.91 mm (Las Casitas (west)) to 24.26 mm (CEA 2) with a standard deviation of 3.96mm. The average long axis size ranged from 8.88mm (Las Casitas West) to 44 mm (CEA 2) with a standard deviation of 6.77mm. The uniformity coefficient ranged from a minimum of 1.29 to a maximum of 2.79 with an average of 1.52. The standard deviation was 0.32. The most common aggregate size ranged from 15 to 30 mm in diameter for most of the wetlands. However, some wetlands had smaller aggregate with diameter <1 cm (Fig. 6). Que Onda wetland, on the other hand, had aggregate ranging from 50 to 60 mm in the diameter which was the largest aggregate size observed.

The grain size analysis revealed unimodal and multimodal grain size distributions in the samples. Samples from 22 wetlands had multimodal grain size distributions and samples from 8 wetlands had unimodal grain size distribution. The modes ranged from 5.95 to 39.33 mm. (Table 4).

Table 4: Grain size parameters of aggregate

No.	Wetland Name	Range (mm) (long axis)	Modes (mm) (long axis)	St. dev. (long axis)	Aspect ratio (average)	Uni. coeff. (C_u)=d60/d10
1	Akumal real estate	15.54-41.72	20.02+	4.51	2.35	1.34
2	Alam Ek	4.50-20.90	8.76+	3.34	2.32	1.78
3	Casa Aurora	12.93-42.92	19.07+	5.97	2.13	1.43
4	Casa Caribe	15.99-37.11	19.72+	4.37	2.18	1.29
5	Casa Christensen	13.08-35.52	20.49	5.16	2.26	1.54
6	Casa Del Mar	5.80-28.07	14.25+	4.16	2.40	1.40
7	Casa Del Sol	10.31-37.92	18.40+	4.87	2.08	1.42
8	Casa Maleno	6.99-34.31	21.00	4.36	2.21	1.34
9	Casa Mayanah	13.42-37.82	18.82+	4.62	2.24	1.41
10	Casa Papagayo	15.67-33.3	20.55	3.75	2.54	1.31
11	Casa Redonda	10.2-33.79	15.78+	4.35	2.05	1.41
12	Casa Zama	15.35-32.78	19.11+	4.06	2.24	1.32
13	CEA 1	12.72-41.64	12.72+	5.64	2.32	1.43
14	CEA 2*	17.30-78.03	17.30+	16.69	1.86	1.40
15	CEA Dive Shop	7.11-43.80	17.26	7.37	2.38	1.77
16	CEA New	9.43-44.9	26.39+	6.27	2.14	1.43
17	Corals wetland	5.18-44.04	22.55	9.45	1.88	2.20
18	Dos Palamos	11.27-29.39	21.72	3.88	2.38	1.41
19	El Eden	13.53-55.8	25.90	8.59	2.38	1.45
20	Esperanza	10.86-36.94	21.81+	4.76	2.42	1.38
21	First Past Corals WL	10.93-33.77	13.17+	5.08	2.44	1.52
22	La Bahia	5.34-35.78	17.82+	6.48	2.35	2.07
23	Las Casitas WL1(E)	3.25-38.44	20.26+	7.61	2.33	2.79
24	Las Casitas WL2(W)	4.09-16.40	5.95+	2.74	1.96	1.67
25	Luna Azul	14.27-39.18	21.82+	4.88	2.21	1.34
26	Nichte-Ha	12.07-31.93	17.43	4.4	2.38	1.36
27	Playa Blanca	6.74-34.92	12.44+	4.72	2.40	1.37
28	Que Onda	25.68-70.03	39.33+	7.54	1.85	1.37
29	Sea Gate	15.48-36.27	20.38+	4.19	2.06	1.32
30	Villas Flamingo	7.42-30.05	15.71+	3.41	2.28	1.29
	Minimum / Maximum	**n.a.**	**5.95/39.33**	**2.74/16.69**	**1.85/2.54**	**1.29/2.79**
	Average	**n.a.**	**18.99**	**5.57**	**2.23**	**1.52**
	Standard Deviation	**n.a.**	**5.80**	**2.63**	**0.18**	**0.32**

*Only 44 clasts were measured, **+** multiple modes exist, smallest mode value is listed, na=not applicable

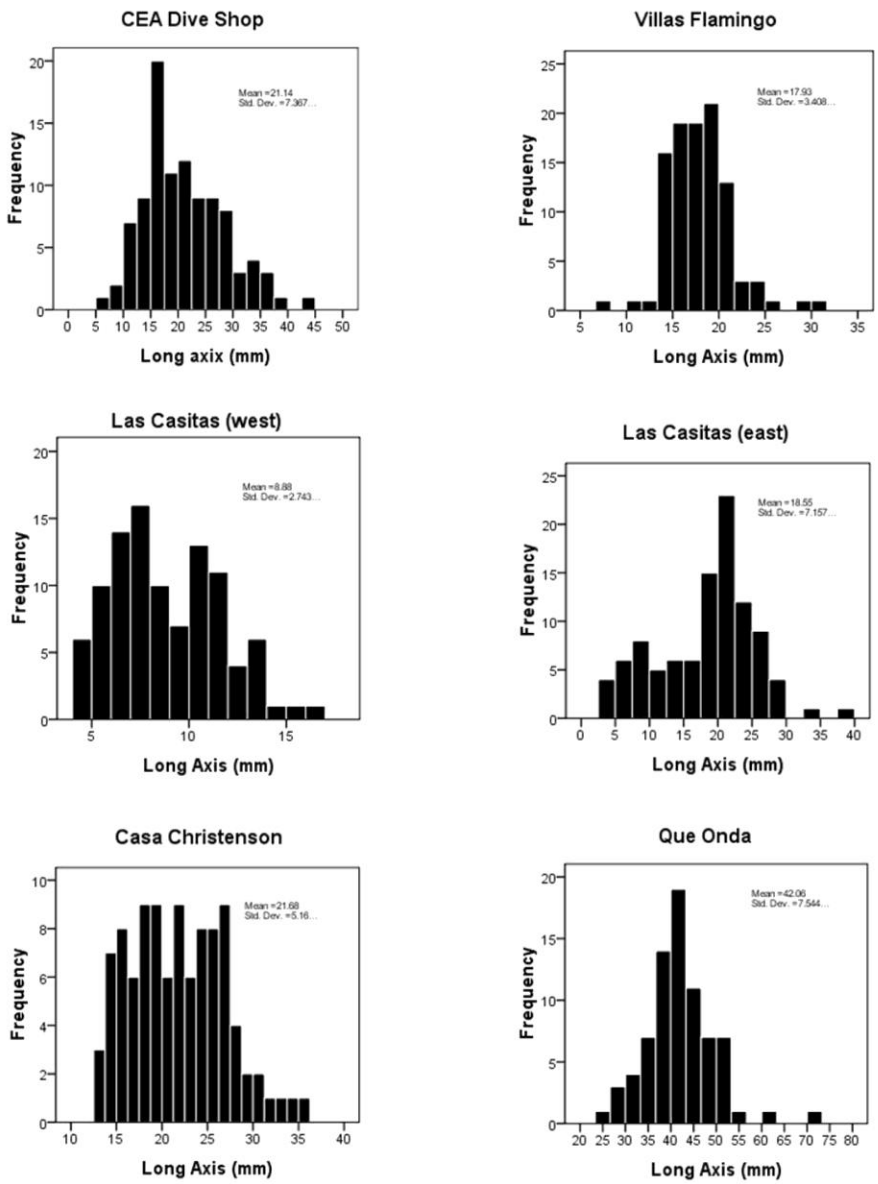


Figure 7: Representative histograms illustrating the observed variations in grain size distribution.

The representative frequency histograms for the long axis measurements (Fig. 7) clearly shows the variations observed in the size of the aggregate used. The histograms for the CEA Dive Shop, Las Casitas (East), Villas Flamingo and Casa Christenson show the most commonly occurring grain sizes found in all the studied wetlands dominated by grain sizes between 15-30mm. The CEA (West) wetland however had smaller aggregate sizes ranging from 5-15mm. On the other hand, the Que Onda wetland has maximum number of grain sizes falling between 30-50mm.

The scatter plot for measurements of long axis and short axis for all the 30 wetlands that were studied (Fig. 8) indicates that most of the aggregate samples, the long axis ranged from approximately 10-30 mm and the short axis ranged from 5-15 mm.

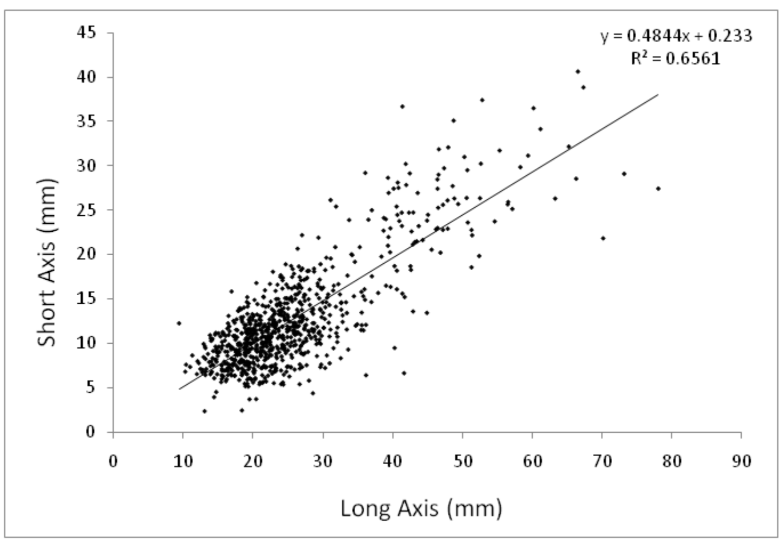


Figure 8: Scatter plot for measurements of long axis and short axis of aggregates from all 30 wetlands.

Table 5: Bulk properties and mineralogy of aggregate

No.	Wetland Name	Organic Matter %	Porosity	K value	Mineralogy
		(field estimate)	(Bulk %)	(cm/s)	(From X-Ray Diffraction analysis)
1	Akumal real estate	1	47	0.04731	Calcite
2	Alam Ek	5	38	0.02101	calcite, aragonite
3	Casa Aurora	5	42	0.05392	Calcite
4	Casa Caribe	10	34	0.04723	Calcite
5	Casa Christensen	1	46	0.05777	Calcite
6	Casa Del Mar	5	40	0.03048	calcite, aragonite
7	Casa Del Sol	1	47	0.04730	calcite, aragonite
8	Casa Maleno	5	52	0.03087	calcite, quartz, boehmite
9	Casa Mayanah	10	48	0.02804	calcite, quartz, boehmite
10	Casa Papagayo	10	40	0.04570	Calcite
11	Casa Redonda	4	44	0.03893	Calcite
12	Casa Zama	15	46	0.04030	Calcite
13	CEA 1	8	44	0.04260	Calcite
14	CEA 2	20	50	0.04830	Calcite
15	CEA Dive Shop	5	52	0.04797	calcite, aragonite
16	CEA New	1	42	0.06074	Calcite
17	Corals wetland	15	40	0.04022	Calcite
18	Dos Palamos	15	52	0.04775	Calcite
19	El Eden	10	50	0.03451	calcite, aragonite, quartz, boehmite
20	Esperanza	5	48	0.04065	calcite, quartz
21	First Past Corals WL	20	38	0.01900	calcite, aragonite
22	La Bahia	10	46	0.04145	calcite, aragonite
23	Las Casitas WL1(E)	15	42	0.03303	Calcite
24	Las Casitas WL2(W)	15	26	0.02525	calcite, quartz, boehmite
25	Luna Azul	5	38	0.04258	calcite, aragonite
26	Nichte-Ha	5	44	0.03397	calcite, quartz, boehmite
27	Playa Blanca	1	38	0.04371	Calcite
28	Que Onda	2	52	0.04517	Calcite
29	Sea Gate	10	48	0.04589	Calcite
30	Villas Flamingo	1	44	0.03928	calcite, quartz, boehmite
	Minimum	1.00	26	0.01900	n.a.
	Maximum	20.00	52	0.06074	n.a.
	Average	7.83	44	0.04070	n.a.
	Std. Dev.	5.80	6	0.00992	n.a.

n.a. = not applicable

The bulk properties of aggregate from all the wetlands and their mineralogy are listed in Table 5. Variations were observed in porosity, permeability and mineralogy of the aggregate samples from all the wetlands. The average porosity observed for samples collected from the wetlands was 43.89% and the minimum and maximum porosity was found to be 26% and 52% respectively. Hydraulic conductivity values (K) were measured and vary from 0.019 cm/s to 0.06 cm/s with an average of 0.041 cm/s. A statistically significant difference (P=0.001) was found using the two sample t-test when the average K of pure calcite aggregate was compared to the average K of other aggregate samples that were a mixture. Pure calcite aggregate, on an average, had 0.012cm/s higher permeability as compared to aggregate samples that are a mixture of calcite and other minerals. This difference however, might not only be as a result of difference in mineralogy. Other factors such as organic matter content, size of aggregate etc. might also be responsible for the difference. K was not found to be significantly correlated with aspect ratio or uniformity coefficient of the aggregate.

X-Ray Diffraction Analysis of Powdered Aggregate

X-ray diffraction of powdered aggregate samples indicates that the dominant minerals are calcite, aragonite, quartz and boehmite. Calcite was identified using PDF #047-1743. The (104) reflection for calcite is strongest at $d_{(104)}$ ~ 0.303 nm. Aragonite is identified using PDF #041-1475. The (111) reflection for aragonite is strongest at $d_{(111)}$ ~ 0.339 nm. Boehmite is identified using PDF#021-1307. The (020) reflection for boehmite is strongest at d $_{(020)}$ ~ 0.611 nm for oriented slides. For powder patterns the $d_{(120)}$ ~ 0.316 nm peak is prominent. The difference is attributed to orientation effects. Quartz is identified using PDF#046-1045. The (101) reflections for quartz was strongest at $d_{(101)}$ ~ 0.334 nm. For 16 wetland systems, aggregate comprised of pure calcite, 7 have a mixture of calcite and aragonite, 5 have a mixture of calcite, quartz and boehmite and only 1 wetland has all the four minerals (i.e., calcite, quartz, aragonite and boehmite) in its aggregate (Table 5). Representative X-ray patterns from selected samples can be seen in figures 9, 10 and 11. In addition, powder X-ray diffraction analysis was performed on insoluble residue from selected clasts which indicated the presence of chlorite along with boehmite (Fig. 12).

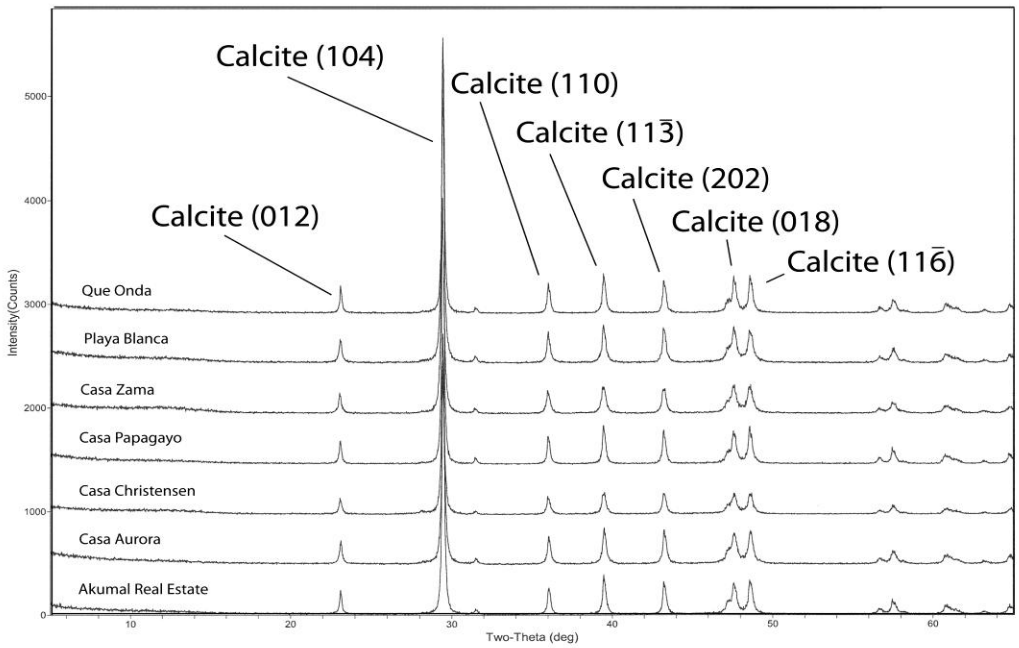


Figure 9: Representative powder X-ray diffraction patterns of aggregate with a mineralogy dominated by calcite. Major lines for calcite are labeled with their respective Miller indices.

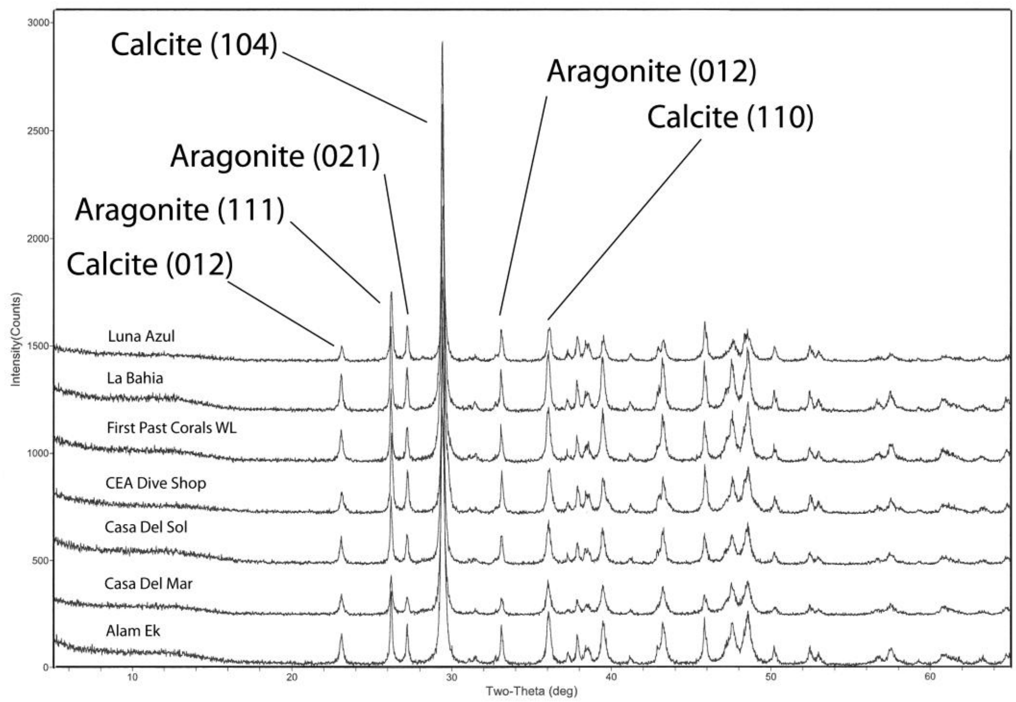


Figure 10: Representative powder X-ray diffraction patterns for aggregate samples with mineralogy dominated by calcite and aragonite. Major lines for minerals are labeled with their respective Miller indices.

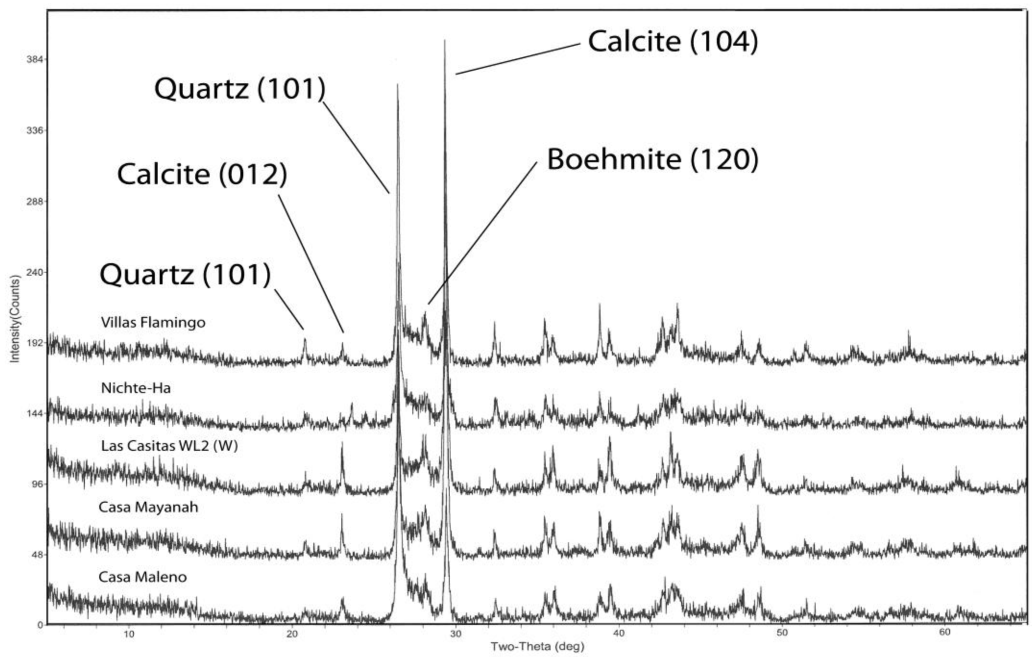


Figure 11: Representative powder X-ray diffraction patterns for mineralogy dominated by calcite and quartz. Selected major lines for calcite, aragonite and boehmite are labeled with their respective Miller indices. Notice the (120) of boehmite is a broad peak suggesting disorder in all samples.

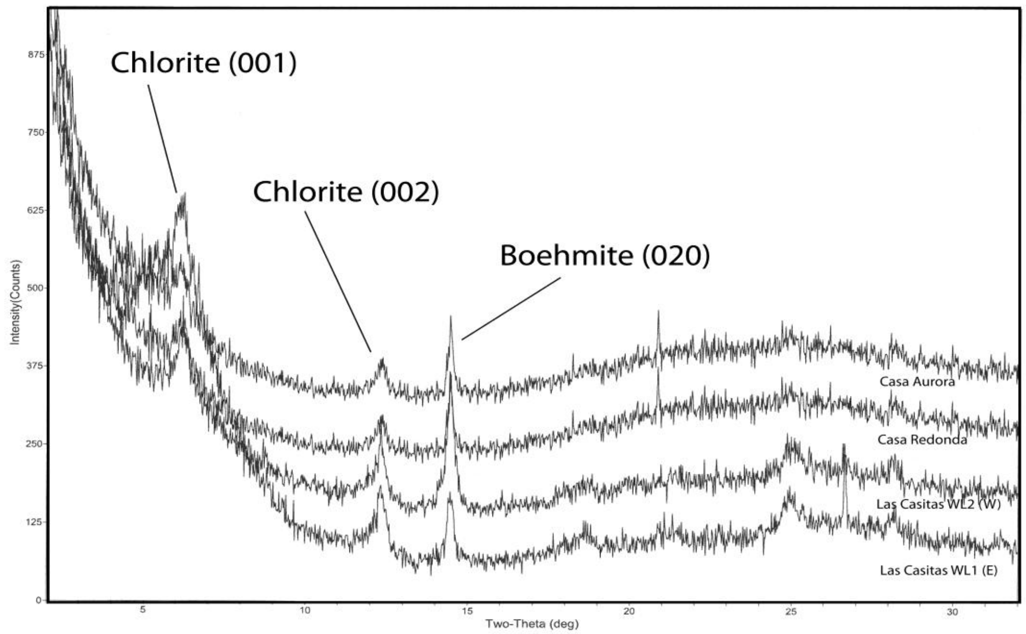


Figure 12: Powder X-ray diffraction patterns for insoluble residue form selected clasts in respective wetlands. Patterns show are under ethylene glycol treatment and do not deviate from air-dry treatments indicating no expanding minerals are present. The d(001) values of the chlorite are approximately 1.44 to 1.43 nm and d (002) values are approximately 0.72 nm. The strong (020) boehmite peak occurs in each sample.

Scanning Electron Microscopy (SEM) of Aggregate

Material from several SFCWs was investigated using a variety of SEM techniques to provide constraints on texture and mineralogy of the aggregate used in selected systems. SEM investigation indicates that a variety of surface and internal textures exist in the aggregate of the systems. The SEM analyses also indicate active dissolution and re-precipitation of calcite within the aggregate. Occurrence of cassiterite was found in aggregate sample from one of the 30 wetlands. The SEM/EDS analysis of selected samples of biofilm defines aspects of composition and structure for the first time for SFCWs in Akumal.

SEM analysis of clast samples from different wetlands (Casa Redonda, Casa Mayanah and Casa Aurora) revealed morphologies and textures that indicate presence of numerous pores within the aggregate as well as active dissolution and reprecipitation of calcite within the clasts. Low magnification images of clast surfaces (Fig.13) from show many distinct pores distributed over the surface. Higher magnification images (Fig.13) indicate that these pores are not superficial, but penetrate to inside the clasts. These pores are commonly circular to oval in shape and are lined with euhedral crystals of calcite of varying size and morphologies. The pores vary in diameter from approximately 20 to 40 μm in diameter. No organic matter was found within the pores or within the aggregate indicating that biofilm development was limited only to the aggregate surface. Different calcite grain textures are observed within the clasts ranging from well defined rhombs, euhedral and scalenohedral morphology and irregular shapes that seemed to be corroded due to dissolution. The sizes of calcite crystals range from approximately 1 µm to 25 µm and the crystals show varying morphology in different samples. Two distinct generations of calcite crystals are clearly observed in some of the samples which are indicative of dissolution and reprecipitation (Fig. 14, 15 and 16).

In Fig. 14, a representative SEM image of aggregate from Casa Redonda, is presented showing partially or completely corroded larger (8-9µm long) scalenohedral or "dogtooth" shaped calcite crystals indicate dissolution within the clast. The smaller (<1 µm in diameter) euhedral calcite crystals indicate re-precipitation. Multiple generations of calcite are observed in SEM images of sample material from Casa Aurora (Fig.15) where larger euhedral crystals (approx. 14-16 µm long) from the first generation surround smaller, elongated (4-5 µm long) calcite crystals which represent the second generation of calcite. These two distinct populations indicate that the system is actively undergoing re-precipitation of calcite. SEM images of clasts from Casa Mayanah (Fig. 16) show irregularly shaped calcite crystals which are also indicative of active dissolution of calcite which causes the crystals to become smaller and irregular shaped. The Casa Redonda system is a comparatively new system with new aggregate, while the Casa Aurora and Casa Mayanah are older systems. Specific age of these systems could not be found, however, looking at the amount of organic matter, color, biofilm development, it could be said that Casa Redonda had comparatively new aggregate.

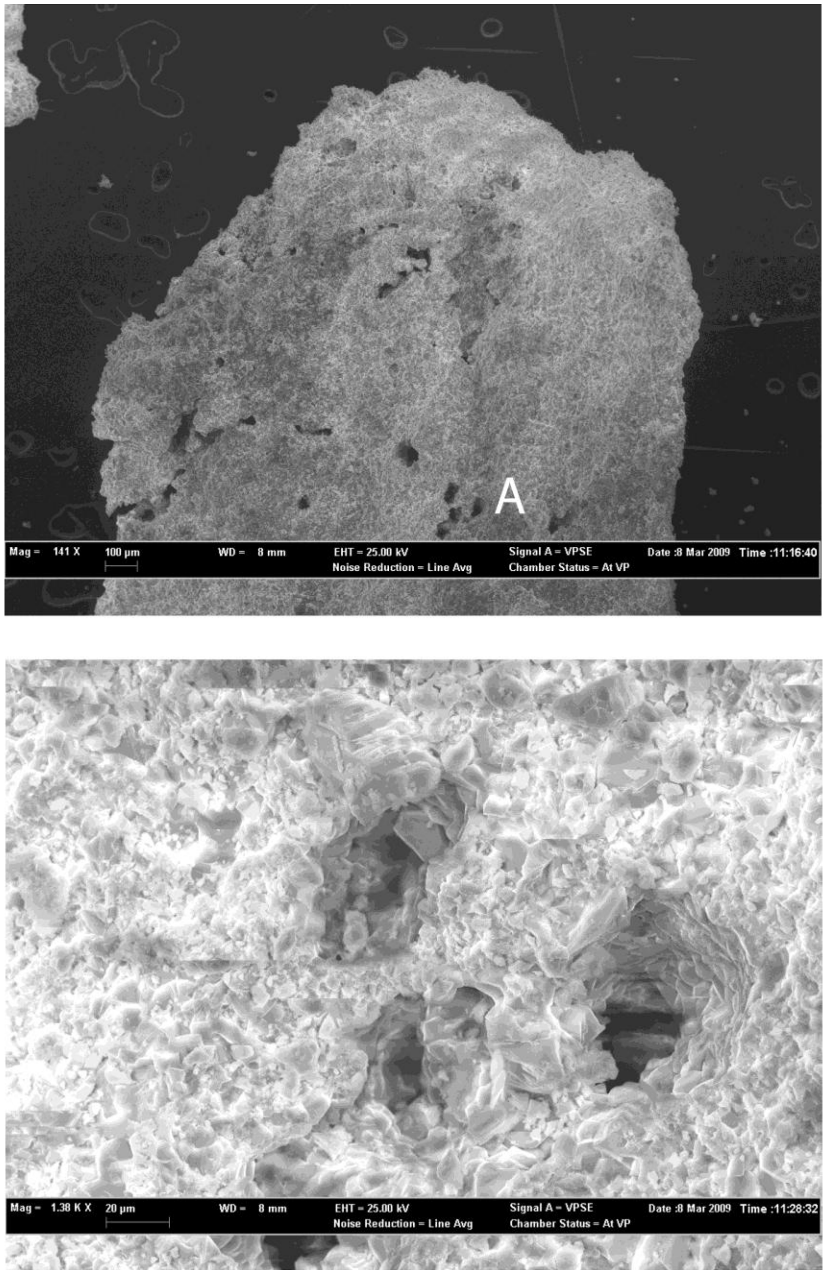
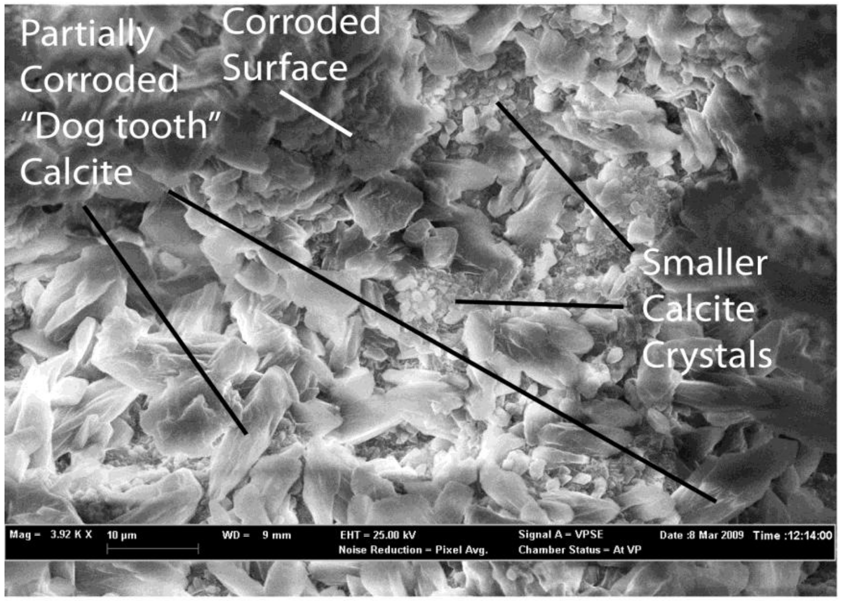


Figure 13: SEM images of clast from Casa Mayanah highlighting the nature of pores within the clast. The upper image shows a low magnification image of the surface. Pores of various sizes and shapes are visible all over the surface of the clast. The lower image shows a higher magnification image of the same piece near “A” in the above image. This image shows circular to oval pores approximately 20 to 40 μm wide surrounded by euhedral calcite crystals of varying sizes within the pores. No organic matter is observed.



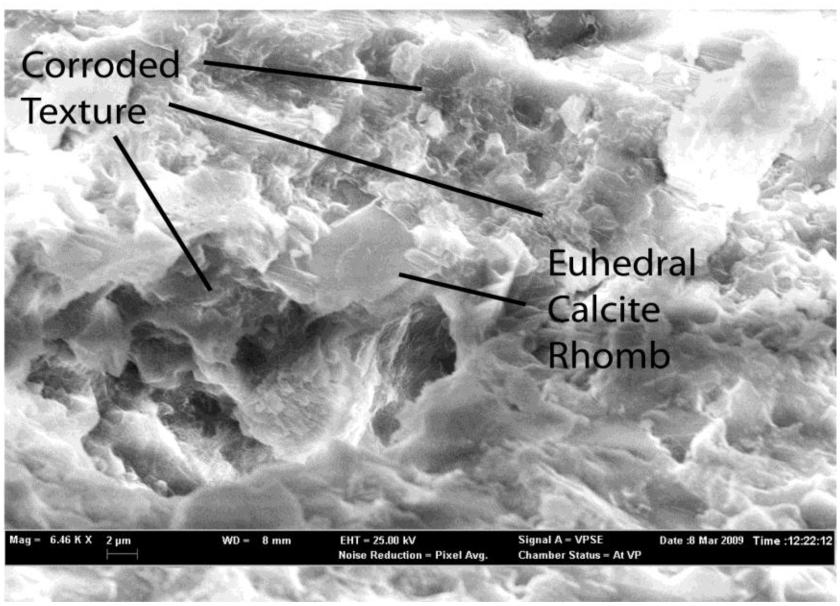
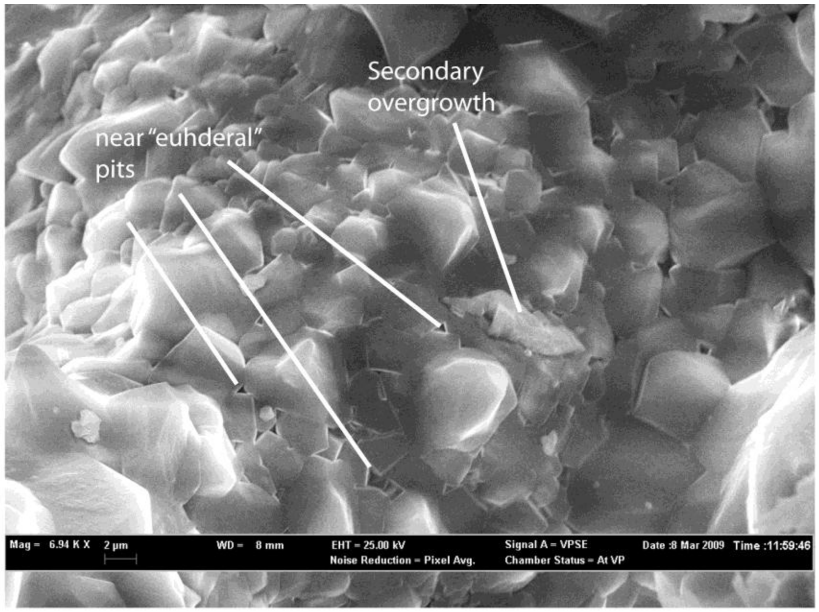


Figure 14: SEM images of clasts from Casa Redonda illustrating dissolution and reprecipitation textures. The upper image shows partially corroded "dogtooth" or scalenohedral calcite crystals along with clusters of small calcite crystals. Smaller crystals are interpreted to be a re-precipitation texture owing to the overlapping nature of the texture. The lower image shows a euhedral calcite rhomb surrounded by a corroded texture of calcite. The lack of dissolution texture on the rhomb is interpreted to be an effect of crystallinity and lower surface area.

Figure 15: SEM image of broken clast from Casa Aurora. This image shows two distinct generations of calcite. Larger calcite rhombs representing the first generation surround the smaller elongated calcite crystals that represent the secondary texture. The smaller crystals form as a result of calcite reprecipitation.



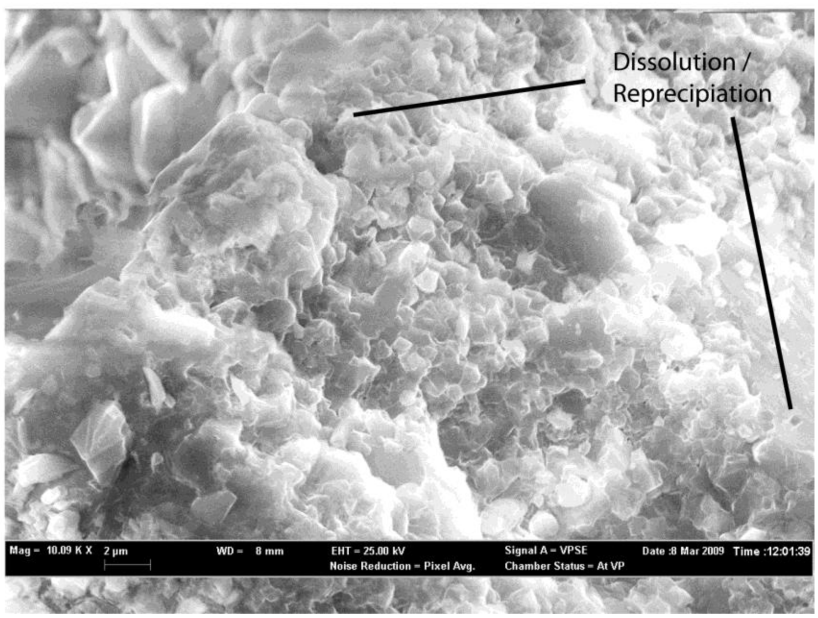


Figure 16: SEM images of clasts from Casa Mayanah illustrating dissolution and reprecipitation textures. The upper image shows several euhdral calcite crystals with a secondary calcite overgrowth in the center of the image. The inter-crystal space has euhedral pits which are interpreted to be a texture of petrological origin. The lower image shows irregularly shaped small calcite crystals with a corroded texture indicative of dissolution-reprecipitation.

Cassiterite

SEM investigation found only a single occurence of heavy metal bearing material. Several examples of cassiterite (SnO_2) were observed from a single clast of the Casa Aurora system. Cassiterite was detected by using BSE (backscattered electron mode) imaging and EDS spot analysis (Fig.17). The cassiterite particles are approximately 1-15μm in diameter and have a platy morphology. Most cassiterite particles are associated with pores which are approximately 20 to 40 μm in diameter. The cassiterite particles might be naturally occurring in the limestone aggregates as these particles were not found in all the aggregate samples.

Biofilm

Many systems were observed to have significant biofilm development. The biofilms were a dark green to black coating often less than an mm in thickness.The Villas Flamingo and the Casa Redonda system had aggregate that appeared relatively new with the aggregate surfaces being free of any biofilm. Selected samples of the CEA Dive Shop SFCW were investigated with SEM to assess mineralogical nature of the films.

Biofilm surface coatings of clasts from the CEA Dive Shop SFCW has a complex textures (Fig. 18). The biofilm is composed of an organic layer or mat that contains a variety of mineral material and has a distinct inorganic chemical composition. The biofilm development on the clasts are superficial and do not penetrate deep into the aggregate. The biofilm is composed of 50-70% organic matter and diatoms, clay minerals, iron sulfides, titanium dioxide and calcite crystals compose the reminder. Well preserved pinnate diatoms of approximately 7-10 µm are seen adhering to the organic matrix in several examples and they compose approximately 15% of the coatings. Aggregates of iron sulfide, approximately 0.8µm to 2µm in diameter, compose approximately 3-5% of the biofilm and are found dispersed throughout the organic matrix. Iron sulfide is likely pyrite based on morphology and instability of marcasite in freshwater systems. Calcite rhombs composed approximately 0.1 to 1.0% of the surface of organic matter and their size ranged from 7 to 8 µm long. Clay minerals consistent with size, texture and chemical composition of kaolinite occur locally and compose around 1-5% of the biofilm. Titanium oxide particles are euhedral, 150-180 nm in diameter, and compose approximately 1% of the coatings. The Ti oxide morphology is consistent with anatase.

P, Si, Al, Mg, Na, K, S and Cl compose the inorganic portion of the biofilms. Significant amounts of Fe and Ti are also found in many biofilms, however these elements were not found in all the biofilm coatings. The weight percentages were correlated to see if any relationship exists between any of the inorganic components. A correlation might suggest possible interaction/adsorption. A strong positive correlation between weight percentages of Na_2O and MgO with r^2=0.84 is observed (Fig. 18). A moderately positive correlation with r^2=0.58 and r^2=0.57 is observed between the weight percentages of sulfur (expressed as SO_3) and chlorine (expressed as Cl_2O) and K_2O and

SO_3 respectively (Fig. 18). Weight percentage of P (expressed as P_2O_5) showed a positive correlation with that of Al (expressed as Al_2O_3) with r^2=0.68 (Fig. 19).

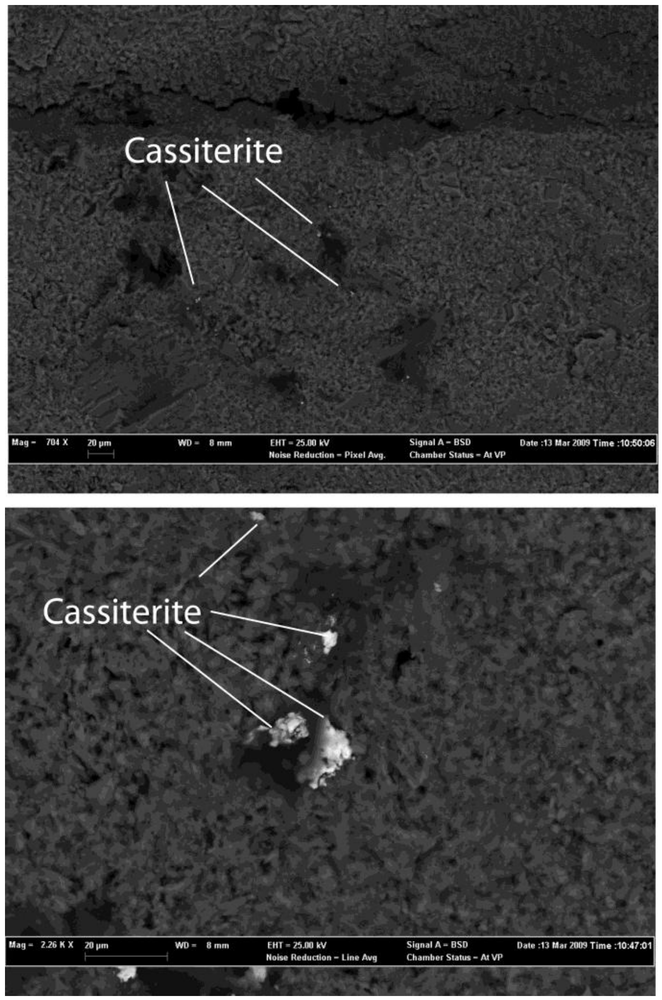


Figure 17: Back scatter electron image of cassiterite particles in a clast from Casa Aurora. The upper image is at a low magnification with bright high contrast white particles of cassiterite concentrated in pores against a dark background of calcite. The lower image is a higher magnification image of cassiterite particles showing a platy morphology with diameters between approximately 1 and 15 μms. Cassiterite particles are surrounded by fine grained calcite crystals.

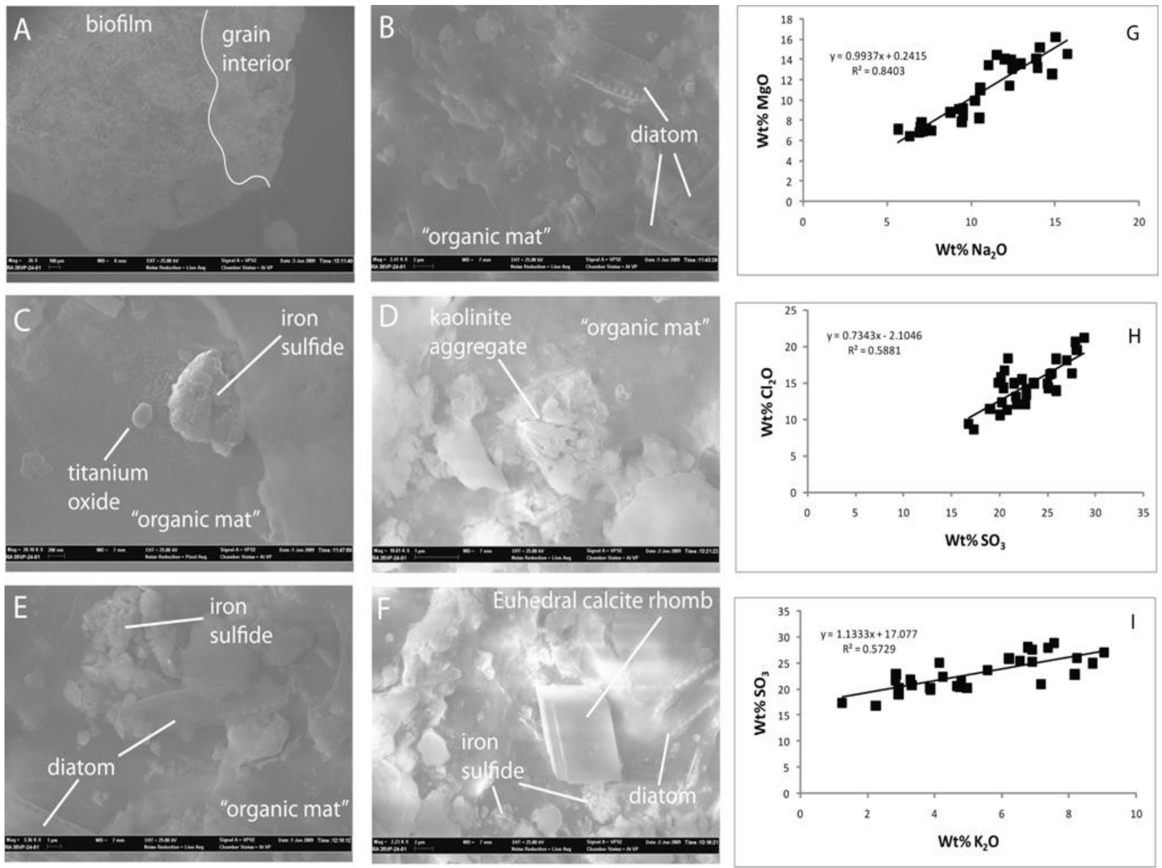


Figure 18: SEM and EDS data from biofilms from the CEA Dive Shop wetland A) Low magnification image of a broken clast showing both biofilm and grain interior. B) Biofilm with diatoms partially encapsulated by the surrounding organic mat C) Iron sulfide and titanium dioxide particles on the surface of organic mat. D.) Kaolinite aggregate on the surface of an organic matter E) An additional example of iron sulfide particles and diatoms on the surface of an organic mat. F) Eudehdral calcite crystal, iron sulfide particles and diatom on the surface of an organic mat. (G-J) Plots of EDS compositions of inorganic component of organic mats of biofilms.

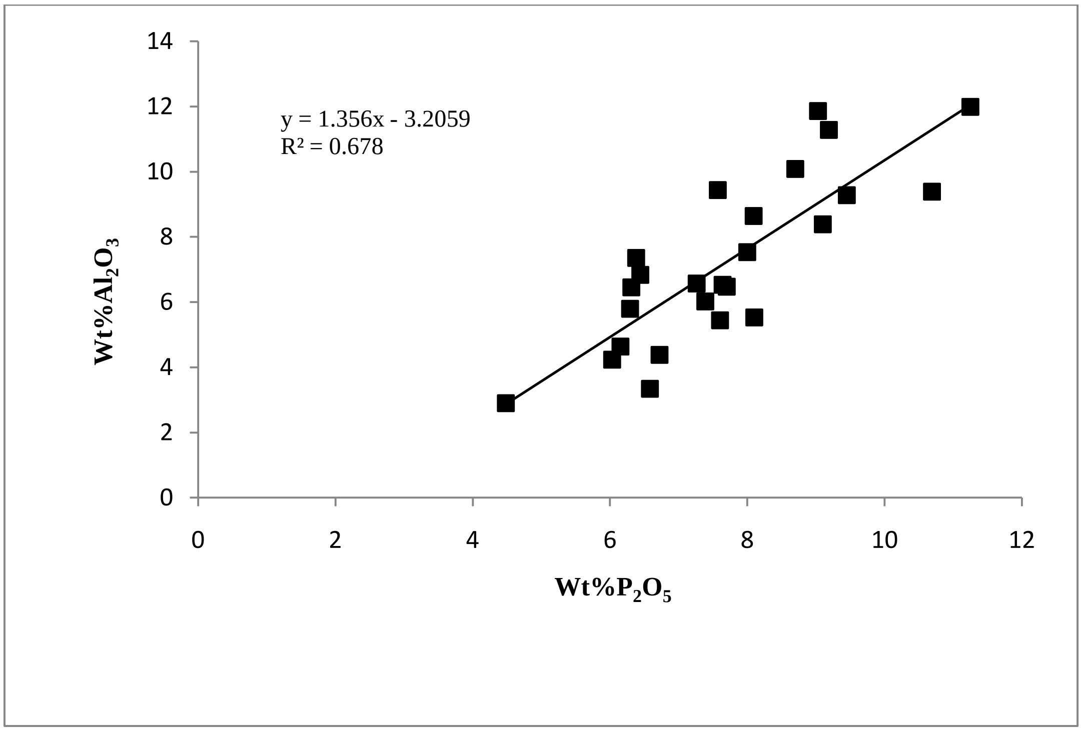


Figure 19: Plot showing a positive correlation between weight percentages of phosphate and aluminum from EDS analyses of biofilm.

Water Quality

Basic water quality parameters including temperature, dissolved oxygen, pH and conductivity were measured for influent and using a YSI datasonde (Table 6). The ammonia and phosphate concentrations were also measured for the wetlands that had accessible control boxes (Table7).

Table 6: Influent and effluent water quality parameters for selected wetlands

Wetland Name	Temperature (°C)		pH		Conductivity (mS/cm)		Dissolved Oxygen (mg/L)		Oxidation-Reduction Potential (mV)	
	In	Eff.+	In	Eff.	In	Eff.	In	Eff.	In	Eff.
Akumal Real Estate	*	25.81	*	7.05	*	6.916	*	0.96	*	-253.6
Casa Christenson	*	25.81	*	7.63	*	6.916	*	1.7	*	-312.0
Casa Maleno	*	25.42	*	7.56	*	6.384	*	0.82	*	-337.0
Casa Mayanah	*	25.48	*	7.05	*	6.916	*	0.96	*	-379.6
Casa Redonda	24.98	24.82	7.23	7.58	6.95	0.122	0.49	0.51	-384.0	-262.8
CEA 2	*	25.66	*	7.76	*	6.645	*	0.59	*	-364.2
CEA Dive Shop	23.99	24.63	7.65	7.59	6.979	10.37	6.47	0.49	-187.2	-330.4
Coral Wetland	*	26.49	*	6.93	*	8.508	*	0.02	*	-394.0
Las Casitas (East)	25.58	25.37	7.34	7.46	7.571	6.699	0.33	0.37	-311.7	-348.3
Las Casitas(West)	24.11	24.66	7.82	7.62	7.188	7.296	0.29	0.36	-251.4	-245.6
Que Onda	*	25.89	*	7.45	*	5.79	*	7.23	*	-98.8
Villas Flamingo	25.03	24.83	7.46	7.42	6.711	6.371	0.57	0.54	-392.6	-375.8

* indicates data not available
+ indicates Effluent

The basic water quality parameters measured with YSI data sonde show variations in parameters such as temperature, pH and conductivity and dissolved oxygen (Table 6). The temperatures for the influent vary minimally from 23.99 to 25.58˚C for all wetlands that were measured. The effluent also temperature also varied little, from 24.63 to 25.37˚C for all wetlands that were measured. The temperature change recorded for measured wetlands varied from a 0.21 ˚C reduction to a 0.64 ˚C increase. The dissolved oxygen ranged from 0.29 to 6.47 mg/l in the influent and 0.36 to 0.54 mg/l in the effluent. A maximum gain of 5.98 mg/l and the maximum reduction of 0.07 mg/l were observed in dissolved oxygen concentrations in the effluents when compared to respective influent which amounts to a 92 % gain and 24% reduction respectively. pH for 6 influents and 15 effluents was measured. The pH ranged from a minimum of 7.21 to a maximum of 7.82 with an average of 7.45 for the influent. The pH for effluent ranged from a minimum of 6.93 to a maximum of 7.76 with an average of 7.45 (Table 6). The conductivity ranged from a minimum of 6.71mS/cm to a maximum of 7.57 mS/cm with an average of 7.08 mS/cm for the 6 wetland influents measured. For effluents, the conductivity ranged from a minimum of 0.12mS/cm to a maximum of 10.37 mS/cm with an average of 6.25 mS/cm (Table 6). An increase in conductivity of 3.39 mS/cm to a decrease of 6.83 mS/cm was observed in effluents of 6 wetlands whose influent conductivity was also measured. The oxidation-reduction potential, (ORP) for the inflow ranged from -187.2 mV to -392.6 mV. For the outflow, the ORP ranged from -98.8 mV to -394.0 mV (Table 6).

Table 7: Influent and effluent Ammonia and Phosphate concentrations

Wetland Name	Ammonia (mg/L)		% Change ↑ or↓	Phosphate (mg/L)		%Change ↑ or↓
	Inflow	Outflow		Inflow	Outflow	
Akumal Real Estate	*	38.4	*	*	5.64	*
Casa Christenson	*	68.04	*	*	9.48	*
Casa Maleno	**26.4**	**4.8**	**81.81↓**	**7.52**	**1.2**	**84.04↓**
Casa Mayanah	*	107.52	*	*	20.9	*
Casa Redonda	**111.36**	**34.56**	**68.96↓**	**9.52**	**7.76**	**18.48↓**
CEA 2	*	96	*	*	9.08	
CEA DS	**0.32**	**1.39**	**334.38↑**	**0.8**	**2.8**	**250↑**
El Eden	*	19.2	*	*	7.24	*
Esperanza	*	25.2	*	*	5.84	*
Las Casitas(East)	**31.2**	**26.4**	**15.38↓**	**8.32**	**10.44**	**25.48↑**
Las Casitas(West)	**29.4**	**24**	**18.36↓**	**11.32**	**10.44**	**7.77↓**
Que Onda	*	0.36	*	*	1	*
Villa Flamingo	**55.2**	**1.92**	**96.52↓**	**10.24**	**0.83**	**91.89↓**
Cenote	*****	***1.2***		*****	***0.32***	*****
Average (For WLs)	**42.31**	**34.45**		**7.95**	**7.12**	
Minimum	**0.32**	**0.36**		**0.8**	**0.83**	
Maximum	**111.36**	**107.52**		**11.32**	**20.9**	

* = Data not available
↑ = Increase
↓ = Decrease

Variations were also observed in the ammonia and phosphate concentrations of influents and effluents (Table 7). The minimum observed concentration of ammonia in the measured influents (6 wetlands) was 0.37 mg/L while the maximum was 111.36 mg/L. The minimum observed concentration of ammonia in the measured effluent (13 wetlands) was 0.36 mg/L and the maximum was 107.52 mg/L. The minimum and maximum concentrations for phosphate in the measured influents were 0.8 mg/L and 11.32 mg/L respectively. The minimum and maximum concentrations for phosphate in the measured effluents were 0.83mg/L and 20.9 mg/L respectively. The minimum 96% reduction (Villa Flamingo) to a 350% gain (CEA Dive shop) was observed in ammonia concentration. 92% (Villa Flamingo) reduction to 250% gain (CEA Dive shop) was observed in phosphate concentrations in the 6 wetlands that had data from both influents and effluents. Measurements were also taken for a cenote near the Villas Flamingoes wetland. The ammonia concentration was 1.2 mg/L and phosphate concentration was 0.32 mg/L for the cenote near Las Casitas Wetland.

Comparative Parameters

Little variation was observed in temperature and pH of the sampled influents and effluents. No major temperature change was observed between influents and respective effluents. A reduction of up to 0.2 ˚C and an increase of 0.64 ˚C were observed. The temperatures of all the sampled influents and effluents lied between around 24 – 26 ˚C. The observed variation in pH when influents and respective effluents were compared was around 0.02 reductions to a 0.35 increase. No major pH fluctuations were observed in any of the systems. All the measured samples had their pH within the range of 7-8. Extreme values were not observed. Variations were observed in conductivity of influents as well as effluents that were measured. All the influents had conductivity between 6 mS/cm to 7.5mS/cm whereas the effluents showed a larger variation with conductivity ranging from 0.12mS/cm to 10.37mS/cm. This indicates a large variation in the conductivity of the effluents. Similarly, the dissolved oxygen content ranged between approximately 0.3 to 0.6mg/L for all the influents. CEA dive shop influent was one extreme outlier with the dissolved oxygen concentration of approximately 6.5mg/L. Minor changes were observed for the respective effluents except for the CEA dive shop effluent. A decrease of 0.03 mg/L to a gain of 0.07 mg/L was seen for all the effluents but for CEA dive shop the gain was 5.98 mg/L. The ORP readings for all the influents and effluents were found to be consistently in the negative range indicating a reducing environment. The CEA Dive Shop wetland also showed an increase of 334% and 250% in ammonia and phosphate in its effluent as compared to the influent. The two different sections of the Las Casitas wetland also showed different efficiencies in reduction of phosphate. The Las Casitas east wetland system showed a 25% gain in phosphate concentrations as compared to the respective influent. The Las Casitas west wetland on the other hand showed around 8% reduction in phosphate concentrations in its effluent. However, both the sections of Las Casitas wetlands i.e. east and west did show 15 and 18% reduction respectively in ammonia concentration. Villas Flamingo, which is the newest wetland with respect to aggregate media and plant cover, showed 96% and 92% reduction in ammonia and phosphate concentrations respectively.

Few parameters co-varied with water quality. The Shannon's diversity index (base 10) shows a statistically significant negative correlation with the phosphate concentration in the outflow ($P=0.07$, $R^2 = 0.26$). However, a very weak correlation was found between ammonia content in the outflow and plant diversity index (P=0.22, R^2 = 0.13). Many other confounding variables might have an effect on the phosphate and ammonia content in the outflow like the type of aggregate, retention time, inflow concentrations, loading, size of the wetlands, hydraulic properties of the wetland etc. No statistically significant correlations were found between mineralogy, K values and water quality parameters.

Chapter 4: Discussion

This investigation is the most extensive study of SFCWs in Akumal since the work of Nelson (1998). The present investigation is arguably more interdisciplinary in nature that other later investigations such as Krekeler *et al*. (2007) and Whitney *et al*. (2003). Although some aspects of this study are are exploratory, critical new insights are gained and the investigation provides baseline information that can be used for a variety of more detailed studies on specific aspects of the systems.

Aspects of Basic Construction

A variable amount of effort in engineering or design is evident from the field survey. Systems that are seemingly well designed (although not necessarily well functioning at the moment) include CEA 1, CEA 2, CEA Dive Shop, CEA new, and PCRF supported wetlands. Some of the commonly observed problems in basic construction of SFCWs were unusual shapes, under-sizing and inaccessible control boxes.

Shape

Unusual shapes like polygons, 8-shaped, L shaped or irregularly shaped systems will usually not be very efficient hydrologically because the wastewater will not evenly distribute to the whole system and there might be dry areas as well as overloaded areas within the same system resulting in poor performance and problems such as ponding of water and odor. This might also negatively affect the plant cover due to dry areas as well as water accumulation in other areas. Two celled rectangular or square systems are hydrologically better as it is less susceptible to flooding and allows more even distribution of wastewater, ample time for the wastewater to pass through the system and therefore better efficiency. Smaller, single celled systems might be more susceptible to overloading, flooding and poor performance. Another major problem observed in the investigated systems was inaccessible and sealed control boxes and the lack of access to standpipes of final effluent.

Capacity and Usage

The constructed wetlands in Akumal seem to be mostly built in accordance to the available space and therefore, most of them seemed to be undersized based on their calculated capacity. The capacity of these wetlands is much lower than the number of people using the facilities feeding into these SFCWs. Most of the wetlands are undersized and probably overloaded based on the 5 square meter wetland area per person requirement (Danish EPA 1999) since most of the properties that feed into the systems are huge buildings build to occupy larger number of people. 19 wetlands out of 30 were found to be less than 5 square meter in area. Since Akumal is a tourist destination and most of these SFCWs are located in the North Akumal, which is a tourist area, there might be fluctuations in the usage of the facilities based on seasonal influx of people. Undersized, poorly vegetated, improperly managed wetlands might give rise to the problem of odor. Odor might also be indicative of poor wetland performance. 40-45% of the wetlands might have this problem. The Las Casitas wetland, the largest in the area, seemed to be of appropriate size and capacity to support approximately 140 people based on the 5 m^2 requirement per person per day. The SFCW systems in the area need to be designed based on the maximum loading and some extra buffer capacity for unprecedented high usage.

Permeability and Porosity

Pore occlusion is a major process in many SFCWs and appears to occur commonly when there is smaller angular aggregate, high organic matter, or rapid increases or pulses of flow associated with high use periods. Generally, gravel media used in constructed wetlands initially get clogged with influent solids (Kadelec and Wallace, 2008). Higher organic matter accumulation occurs in upper layers of wetlands with plants due to the addition of dead plant matter to the surface. Higher organic matter accumulation has also been observed in the inflow zones of the wetlands owing to the fact that the plant roots tend to increase the rate of filtration and retention of solids that enter the system (Tanner and Sukias, 1995). The effect of clogging by organic and inorganic wastewater solids, microbial detritus (except plant litter) and the theoretical service life of a hypothetical gravel bed constructed wetland was calculated by Beauchamp *et al*. (1988) to be about 100 years. Reed and Brown (1992) estimated solids accumulation to be less than 1% of the available pore space of the gravel media in the first 18 months of use of the constructed wetland. A major reduction in substrate hydraulic conductivity at the head of the wetlands during first year of operation was observed in wetlands treating domestic wastewater at Richmond, Australia by Fisher (1990). However, no major reduction in permeability due to solids accumulation was observed over the 2 ½ years monitoring period along the length of the bed for these wetlands in Australia (Fisher, 1990).

Very high organic content in the aggregate was observed for some of the wetland systems in Akumal. The CEA 2 wetland and the First wetland after corals wetland had approximately 20% organic matter and this organic matter had the consistency of fine grained soil. Other systems like the Dos Palamos and the Corals wetland also had approximately 15% organic material. This organic matter consists mainly of leaf litter comingled with some finer particles formed due to breakdown and weathering or dissolution of the limestone aggregate. All this material occupies the space in between aggregate grains and can cause reduction of flow of water through the system. For example, an accumulation of water at the surface of aggregate was observed in the Las Casitas wetland. Pulses of high influent loading can also result in accumulation of water at the surface and cause problems with hydrology of the SFCWs.

A design modification may alleviate clogging of pores. It may be beneficial to have a smaller inlet cell in the two-celled wetlands and this small cell could be emptied out and replanted more frequently as required in order to minimize problems with clogging of media and poor hydraulics of the system. Ideally, a smaller inlet cell that has a control mechanism for adjusting hydraulic head may enable easier maintenance.

Vegetation

The selections of the plants in these SFCWs are more or less similar with choice of locally available garden plants (flowering or non-flowering) along with plants like taro, sedge and wetland fern and cattail which have traditionally been used in wetlands all around the world. Taro is the most commonly used plant and is present in 90% of the studied wetlands of which in about 55% wetlands, it makes up more than 50% of the total plant population. Other than taro, the use of plants in the wetlands was variable. None of the wetlands have all the 38 species present in it. About 66% of the studied wetlands had either one of the palm species (*Chrysalidocarpus lutescens*, *Thrinax radiata* or *Chamaedorea* spp.). The other more commonly used species included wetland ferns and spider lily which were present in about 43% and 30% of the studied wetlands respectively. *Colocasia* spp. (taro) has shown positive results in reduction of nitrate and phosphate content as well as removal of organic matter from domestic wastewater (Bindu *et al*., 2008). Some wetlands had xerophytic plants such as *Nerium* and *Aloea vera*.

Nerium and *Aloe vera* are morphologically adapted to lose minimum water through transpiration. Therefore, they might not be as efficient in reducing the wastewater volume as compared to other plants. Some of the wetlands also had tree species planted in them. If left unchecked, these trees have a potential to grow larger and cause damage to the structure of the wetland. The major risk is from the roots which might grow through the base or the side walls of the systems thereby causing seepage. Many large palm trees and cassia trees are planted near the wetland wall. As these trees grow older, they might pose a risk of exerting pressure and breaking or cracking the walls. Most of the wetlands in Akumal had overgrown plants that had been there probably since the wetlands were first built. Plants that are too old and overgrown tend to have very dense root systems thereby obstructing air circulation to the lower layers of the aggregate. Wetland fern, taro, sedge and other such plants that propagate vegetatively, tend to form dense clusters and that takes up all the available space. Dense vegetation can cause a variety of problems including reduction of dissolved oxygen concentrations consistently below 1.0mg/L (Kadelec and Knight, 2006) thereby hindering the process of nitrification which in turn can affect the functioning of microbes and macroinvertebrates involved in decomposition of dead plant matter (Vymazal, 1995, Thullen *et al*. 2005). In Akumal, non-wetland plants are used which might not be as efficient in diffusing oxygen to the lower layers of aggregate via their root systems. Anaerobic conditions in the aggregate would mean lesser or no nitrification at all. A dense plant growth would also mean more dead plant material that decomposes and re-releases the nutrients back into the system. Therefore proper management of these plants is necessary to avoid very dense growth that could inhibit air circulation in the aggregate media due to overgrown roots, offshoots and dead plant material.

Non-Wetland Plants

Aesthetic aspect of the plants used in these wetlands is an important factor. This can also be economically beneficial. Locally available garden plants are being used in Akumal wetlands. Studies in different parts of the world as well as in Mexico have indicated that these plants not only survive the conditions in the constructed wetlands but also remove pollutants (e.g., Konnerup *et al*., 2008; Zurita *et al*., 2009). However, their capability to transfer oxygen to the aggregate media through their root systems is not very well known. Flowering plant species like *Heliconia*, *Canna*, *Anthurium* along with other garden plants species when used in constructed wetlands, have shown considerable reduction in total suspended solids and chemical oxygen demand along with reduction in nitrogen and phosphorus (Konnerup *et al*., 2008; Zurita *et al*., 2009). Designs involving use of ornamental plants (flowering as well as non flowering) have been proposed so that the wetlands can be used in areas involving the service industry (Nyakang'O and Van Bruggen, 1999). Flowers and foliage plants that can be harvested for decorative purposes or can be sold in the market can be grown in these wetlands to make them look aesthetically appealing. Since Akumal is a rapidly growing tourist destination with many hotels and restaurants in the area, decorative foliage and flowers could be sold locally or used in-house for decoration. However, proper and dedicated management of plant cover is required to get this gain out of the wetlands.

Harvesting

Harvesting of plants in wetlands has long been considered as a way to remove pollutants, especially phosphorus and nitrogen (Kadelec and Wallace, 2008). Reed *et al*. (1995) positively correlated harvesting with phosphorus removal from wetland systems. However, it was suggested that phosphorus removal by harvesting is efficient only in systems which are lightly loaded around 1g/m^2/yr (Richardson and Craft 1993, Kim and Geary, 2001). In systems that receive higher loading rates, the major portion of phosphorus is removed by storage in the substrate media and not by plant biomass (Geary and Moore, 1999, Kim and Geary, 2001). Nitrogen removal to some extent can be gained in tropical environments with fast growing plants but even then, the potential is very limited (Kadelec and Wallace, 2008). Management of the harvested biomass is another issue that cannot be easily resolved as there are no economically viable methods available (Kadelec and Wallace, 2008). In Akumal, it was observed that plant pruning was being done at the Las Casitas wetlands. However, this was not being done in a planned manner. This wetland had problems such as water accumulating at the surface and aggregate reduction along with decreased vegetation and poor quality of plant health. All the pruned plants were totally devoid of leaves. Most of the wetland ferns were trimmed just a few inches above ground including their actively growing fronds in the center. Unplanned harvesting of plants in this manner would help little in nutrient removal or in plant health.

Diversity Index

Shannon's diversity index ranged from a minimum of 0.33 to a maximum of 1.99 (natural log). The Shannon's diversity index ranged from a minimum of 0.14 to a maximum of 1.35(base 10). This diversity index increases with the increase in the number of unique species and also increases with the increase in the evenness of the species. In an earlier study by Nelson, conducted in 1997, the Shannon's diversity indices were calculated for two PCRF wetlands that were constructed in August 1996. The diversity for the constructed wetlands was 1.35 and 1.36 respectively and their collective diversity was 1.42 which was found to be lower than the diversity of the natural tropical forest ecosystem near the study area with the diversity of 1.61. However, the mangrove ecosystems had a lower diversity at 0.45. A total of 70 species were reported to be found in those two wetland systems. In the current study 38 species were identified to be present in the 30 wetlands. However, none of the wetlands had all these 38 species present in them. The numbers in the current study might be low because only the plants that were planted intentionally in the wetlands were counted and the small weed species were not taken into consideration.

Aggregate Media

The aggregate used in all the wetlands is locally available limestone that comes from Carica Quarry. The grain size reveals unimodal as well as multimodal grain size distribution with the smallest modes ranging from 5.95 to 39.33 mm. The grain size of the media used in the wetlands play an important role in the hydraulics of the system as well as in providing ample surface area for processes like adsorption and bacterial reactions. The aggregate used in the wetlands in Akumal meets the uniformity coefficient (d_{60}/d_{10}) requirements as set by the Danish EPA (1999). However, it does not meet the d10 and the d60 requirements since these guidelines suggest that the media should have d10 between 0.25 and 1.2 mm and d60 between 1 and 4 mm (Brix *et al*., 2001; Brix, 2004; Brix *et al*., 2005). The aggregate used in Akumal wetlands is of much larger size as observed in this study. The average short axis size ranged from minimum 4.91 mm - 24.26 mm (±3.96 mm) and the average long axis size ranged from a minimum of 8.88mm - 44 mm (±6.77 mm). Larger aggregate size means reduced effective surface area to act upon the wastewater passing through the system. The Danish EPA guidelines are designed to effectively remove 95% BOD and also have 90% nitrification. Phosphate removal according to these guidelines can be achieved up to 90% by precipitation of phosphorus with aluminum polycholoride in the sedimentation tank (Brix, 2004). However, since the design and media used in Akumal is different from the Danish EPA guidelines, only extensive studies on nutrient removal efficiency of the aggregate can yield insight into the efficiency of the system design. Reductions in phosphate and nitrate levels observed in the newly constructed wetlands such as Casa Redonda and Villas Flamingo having new gravel media might be an indication of faster adsorption of nutrients by newer material as compared to older materials. This reduction can be attributed to the media as these wetlands do not have a high plant cover. Villa Flamingo was recently planted and the plants in this wetland were in their juvenile stage and had not yet started growing actively. Reductions were also observed in the Las Casitas wetland which is an older wetland but the reductions were not as large as those observed in the above mentioned wetlands. The actual permeability of media in the wetland might differ from the measured permeability owing to plant growth, organic matter and compaction of the media over a period of time. The actual permeability within the systems might be lower than what was measured during this study. Permeability

Porosity for the systems ranged from 26 to 52% with an average of 44%. The high porosity can be attributed to the angular nature of the aggregate thus creating more space between individual particles. The microscopic pores present on the surface of the aggregate might also contribute to higher porosity. Higher porosity is essential to hold air and water in between the aggregate for the nitrification process to be faster and more efficient. Pores within the aggregate samples studied under SEM might also play a vital role by increasing the reactive surface area thereby increasing the removal of phosphates from the wastewater.

No meaningful correlations between the bulk properties occur. This lack of correlation is attributed to the fact that the aggregate is crushed synthetic and not a natural sand or gravel. Because of the lack of such relationships a predictive model is not possible.

Pores

The exact cause of the size and distribution of the pores is not determined and without a specific geologic context such an assessment is not feasible. However, from the perspective of materials properties these pores increase the reactive surface of the aggregate thereby allowing more contact of the wastewater with the surface of the aggregate. A higher proportion of pore space is a favorable property; however the increase in surface area will enhance overall dissolution.

Mineralogy

The X-ray diffraction analysis revealed four distinct mineralogical compositions of the aggregate, i.e. 1) 15 wetlands with calcite 2) 7 wetlands with calcite and aragonite 3) 5 wetlands with calcite, quartz and boehmite and 4) 1 wetland with calcite, quartz, aragonite and boehmite. The geologic cause for the variation in their composition is unclear. Boehmite and chlorite found in this geologic material might be formed due to alteration of windblown volcanic ash from Caribbean or might be a part of soil deposition that occurred during the formation of the region.

It is known that boehmite and other minerals having Al-OH groups have a capability to adsorb phosphate on their surfaces and this property has been studied by many researchers. These minerals are said to have high phosphate sorption capacity owing to their small size and larger surface area (Watanabe *et al*., 2002). In a study conducted on synthetic aluminum oxide hydroxide consistent with structure of boehmite in lab, it was found that it selectively adsorbs phosphate from seawater and the adsorption was influenced by pH and anions present in the water (Tanada *et al*., 2003). Boehmite is therefore a desirable component of aggregate in general for SFCWs in Akumal. Furthermore the relation of P content and Al content observed in the biofilms is likely a function of P sorption on boehmite and suggests that boehmite is an important part of the functionality of the biofilms.

The aggregate source of all wetlands is the Calica quarry, however the sources of aggregate must not be form the same bed and therefore variations in mineralogical compositions are observed. Geologic causes for variation are unclear however; the result of this investigation suggests a petrological investigation of the Calica quarry is warranted to identify beds with high proportions of boehmite, a beneficial mineral for removal of phosphate.

Aggregate Dissolution and Reprecipitation

Several lines of evidence suggest that the aggregate is dissolving and reprecipitating in the system complicating and perhaps reducing retention of pollutants. There is a marked increase in conductivity of approximately 1.0 to 3.0 mS/cm in the effluents compared to the influent suggesting dissolution is occurring. Furthermore SEM investigation in the current study shows several textures indicative of dissolution. Prior studies (Krekeler *et al*., 2007) have also indicated that there is an active dissolution of aggregate happening in all the wetlands in the area which results in the drop of aggregate levels in the wetlands. Reduction in aggregate levels has a potential of negatively affecting the plant life as well as the overall reduction of pollutants due to reduced surface area. If the aggregate level drops below the feeder pipes, it will result in ponding of water. This was observed in Las Casitas wetland.

Dissolution and reprecipitation of calcite in the wetland systems is a critical process which has not been documented in detail. Dissolution of mineral aggregate might occur due to its interaction with water and also due to the effect of factors such as pH and presence of reactive components in the wastewater. Aggregate dissolution is a naturally occurring phenomenon in the region which is predominated by karst systems made up of calcite and aragonite minerals (Tulaczyk, 1993; Krekeler *et al*., 2007). However, presence of heavy metals such as Pb, Zn, Co and Cr has been reported in fresh aggregate samples (Krekeler *et al*., 2007) and the dissolution of aggregate in the wetland systems could release these heavy metals into the environment. Approximately 1.0 to 3.0 kg of heavy metals could be released from the systems according to a prior estimate (Krekeler *et al*., 2007). In addition, other adsorbed pollutants could be released back into the environment. Phosphate is adsorbed on the limestone surface and plays a major role in phosphate removal from wastewater. Due to dissolution of the aggregate, this adsorbed phosphate might be released back into the environment after some time and the aggregate would eventually lose its phosphate removal efficiency. Therefore it is very important to estimate the time frame within which the aggregate remains functional without discharging the pollutants back into the environment. Detailed modeling of aggregate dissolution would be beneficial for future study and should involve a combination of field and laboratory analysis. Such an undertaking is out of the scope of this thesis; however the results of the current study indicate dissolution-reprecipitation is a major process and the microscopy results are the first direct evidence of this process occurring at the micro-scale.

Biofilm

Biofilm developing in the root zones and on the aggregate surfaces have been recognized as an important factor in treatment of wastewater (Polprasert and Agarwalla, 1994; Larsen and Greenway, 2004; Gannon *et al*., 2007; Domozych and Domozych, 2008). This is the first attempt to look at the aggregate biofilm for wetlands in Akumal. Although, owing to the study of dry biofilm surface on aggregate from just one wetland in the region limits the scope of the study, it gives a valuable insight and new information on this aspect of the systems. The SEM investigation indicates a complex texture in the biofilms with it various organic and inorganic components. The biofilm was not found to have formed in the interior of aggregate although the aggregate used in the systems is highly porous. The inorganic composition of the biofilm consisting of Na, Mg, K, S and Cl can be attributed to interaction with sea water as these are major components of sea water. This CEA dive shop system does receive inflow from showers and therefore this chemical composition is consistent with the use of the system. Mineral identification for the biofilms is difficult owing to the uneven surface which makes it impossible to study using backscatter electron diffraction. Correlation between aluminum oxide and phosphorus oxide is consistent with the fact that aluminum oxides present in the media tend to adsorb phosphorus. This indicates that inorganic processes on the surface of the media are responsible for some of the phosphate sequestration in the systems. The occurrence of iron sulfide in the biofilms indicates a reducing environment and this was also found to be consistent with a negative (approx. -330) oxidation-reduction potential measurements of the effluent. The source of tin oxide and kaolinite might be sunscreen lotion being washed off into the sewage water.

The specific microbial community structure of these biofilms is not determined and the nature of their involvement in cycling of sulfur, phosphate and nitrate as well as other pollutants in wastewater is undetermined. An in-depth analysis of bacterial communities of the biofilm, their interaction with the inorganic and organic components of the biofilm as well as the surrounding wastewater and rhizosphere and their capability of removing pollutants will have to be studied in order to better understand their role within the system.

Cassiterite

Cassiterite (SnO_2) is the only heavy metal bearing mineral observed to occur in the wetland aggregate. Cassiterite occurs in placer deposits but such occurrences in low temperature limestones are not reported in the literature. Clay-sized cassiterite is uncommon in sedimentary materials as an authigenic phase. However, Krekeler *et al*. (2004) found cassiterite at a paleohydrologic redox boundary surface in palygorskite deposits in the Hawthorne Formation of southern Georgia using TEM. The origin of cassiterite in the SFCW aggregate is interpreted as diagenetic and is a feature original to the rock. The overall texture and close association with pores supports this interpretation. The environmental impacts of cassiterite are negligible owing to the low abundance of the material in the aggregate and the comparatively low solubility of the mineral. Heavy metals in minerals such as cassiterite do not decompose by the weathering process or by contact with aqueous oxidizing environment (Siegel, 2002). Tin in the form of organotin compounds are toxic to humans, animals and microorganisms (Winship, 1988, Heinz, 2003). Inorganic tin compounds have also been reported as being toxic (Hallas, *et al*. 1982). However, no toxicity has been reported for tin oxides owing to their low solubility and non-toxicity (Hallas, *et al*. 1982).

Water Quality

The minor variation in the pH of the wastewater flowing through the system could be attributed to the dissolution of calcite which is also a source of buffering many natural water bodies by contributing carbonate ions to the buffering system. However, detailed analysis of the dissolution rates within the system and the influent pH fluxes is necessary to determine the exact role that calcite dissolution plays as a buffering agent. For example the concentrations of Ca^{2+} and HCO_3^-, and CO_2 need to be determined in influent and effluent before a generalized model can be made. Higher conductivity of the effluent water is consistent with dissolution of calcite within the systems since dissolution gives out ions into the water thereby increasing its conductivity.

Dissolved oxygen (DO) level in the water is an important factor in the nitrification process wherein nitrifying bacteria convert ammonia into nitrates and nitrites which can either be assimilated by plants or released back as nitrogen into the atmosphere by the process of denitrification. Optimum DO levels are essential to maintain an active nitrifying bacterial community within the wetland system. Thus low DO levels within a wetland system could result into lower efficiency of nitrogen removal from the wastewater. DO levels in the Akumal systems were found to be consistently low indicating anaerobic conditions within the systems. This could be attributed to clogging of the media and also to improper plant selection resulting in very little oxygen being fixed into the media via the roots of the plants.

Negative oxidation reduction potential values indicate a reducing environment within the systems and are broadly consistent with the low dissolved oxygen levels. Reducing environment and anoxic condition is also consistent with formation of iron sulfide in the biofilm. Oxidation reduction conditions in the wetland systems are important to retain inorganic phosphorus within the systems (Szogi, *et al*. 2004). It has been suggested by researchers that in wetland soils with ORP values less than 120mV, the reduction of Fe^{3+} and Mn^{4+} into soluble Fe^{2+} and Mn^{2+} might happen which could subsequently result in the release of P associated with oxidized forms of iron and manganese (Gambrell and Patrick, 1978; Sahandeh *et al*., 2003; Szogi *et al*., 2004).

Nitrogen and phosphorus are important nutrients for terrestrial as well as aquatic biodiversity. However, an increase in the levels of nitrogen and phosphorus content in any ecosystem is detrimental. In the marine environment, excess nutrients cause eutrophication which in turn can cause problems like algal blooms and anoxic conditions within the marine environment. Excessive nutrients in the marine water also leads to detrimental effects on the corals which are usually adapted to oligotrophic (low nutrient) environment. For sensitive waters, United Nations Environmental Program (UNEP, 1998) recommends nitrogen levels below 5 mg/L (eg.Whitney *et al*., 2003). The local environmental authority in Mexico, The Secretariat of Environment and Natural Resources, in its official Mexican standards for establishing the maximum allowable limits of contaminants in wastewater discharges into national waters recommends the average monthly and daily levels of total nitrogen in estuaries to be below 15 mg/L and

25 mg/L respectively. The required average monthly and daily total phosphate concentrations for estuaries are recommended to be 5 mg/L and 10 mg/L respectively. However, as per the Quality Criteria for Water by US EPA (1986), for streams and reservoirs, the recommended phosphate levels is 0.05 mg/L and 0.25 mg/L respectively. In currently tested systems in Akumal, 6 out of 13 wetlands meet the Mexican standards for average daily nitrogen in effluent and 10 of them meet the requirements for phosphate concentrations. However, it is worth noting that the standards that have been set up are very high given the sensitivity of the area owing to the presence of coral reef system. For marine waters, nutrients, especially nitrogen and phosphate are a limiting factors and excess of these nutrients might give rise to eutrophication. The fate of the effluent after it is released into the environment is undetermined.

Chapter 5: Management Recommendations

Design

At present in Akumal, most the wetlands are smaller than the required capacity based on 5 m^2 wetland area per person. In the future, newer wetlands should be constructed based on the required capacity based on the estimated peak tourist season loading that the wetland is destined to receive. Having an extra buffer capacity will be helpful to accommodate increase in the number of people using the facilities in the future.

Rectangular wetlands with aspect ratio (L/W) greater than 1 are recommended for good hydraulic conductivity within the system. Shapes like figure 8, polygon, octagon or any irregular shape should be avoided as they might cause problem with the flow of water. The control boxes should be constructed at an accessible spot and should not be sealed off. This will help in keeping a check on water level, clogging and testing of water quality. Odor can be managed by maintaining healthy plant cover, by maintaining the water level few inches below the aggregate surface and preventing clogging.

CEA has started using liners in its new wetlands. Krekeler *et al*. (2007) suggested use of locally found Ca-montmorillonite clay bed in Reforma region as a suitable material for use as liner for the systems as the investigation revealed that the clay is environmentally safe for use and could function efficiently under the chemical conditions existing in the wetlands.

Use of corals to build the walls of wetlands might cause the system to leak wastewater and should be avoided. Conventional items such as bricks and mortar should be used as these are structurally more stable and leak resistant. Since there is reduction in the level of aggregate due to dissolution and compaction, the spreader pipe should be laid such that it doesn't get exposed and stays few inches below the aggregate surface. This will ensure that the water level stays below the surface and leaves some space for air circulation in the top layers of aggregate. Design modifications to increase air circulation or use of aeration system can be considered in order to decrease anoxic conditions and maximize nitrification within the systems.

Since drop in aggregate level was observed, more aggregate can be added on top to ensure that the spreader pipe remains few centimeters below the surface. Also, as more organic matter gets collected in the system near the inflow, it might be beneficial to have a smaller cell towards the inflow in which the aggregate and plants could be more frequently replaced. This option will be cheaper as compared to replacing the aggregate for the whole wetland and will also help in prevention of aggregate media clogging. Multi celled systems could also be an option wherein, the aggregate in the cells towards the inflow could be more frequently replaced to prevent clogging of aggregate media. In multi celled systems, the media for different cells can be replaced more periodically in order to get higher efficiency given the fact that newer systems with fresh aggregate show higher efficiency in nitrogen and phosphorus removal.

Aggregate

This study reveals that the limestone aggregate used in the wetlands dissolves. More in depth study is required to calculate the rate of dissolution and the maximum functional period for the material used in the systems. Dissolution of the aggregate might release the adsorbed pollutants back into the environment. Therefore, it is essential that the aggregate within the systems be changed every few years depending on the economic feasibility. The size distribution of the aggregate does not meet the Danish EPA requirements and is much larger in size. Use of smaller aggregate should be considered as this would also increase the reactive surface area. Using aggregate of lower solubility in the systems and the addition of granular palygorskite to the systems as a tertiary cell or treatment are suggested.

Since calcite and boehmite are better adsorbents of phosphates in a wetland system and calcite aggregate also has higher permeability, aggregate having higher quartz content should be avoided. Higher aragonite content might add to dissolution since aragonite is more soluble (Ksp = 8.22) as compared to calcite (Ksp = 8.35). Krekeler *et al*. (2007) also suggested that locally available dolomite might be a better choice of aggregate owing to its lower solubility (Ksp = 16.54 to 17.09) as compared to calcite and aragonite (Ksp values from Krauskopf, 1979).

Vegetation

A wide variety of garden plants are being used in Akumal. However, little is known about their efficiency in the systems and their capability to remove pollutants from the wastewater. The amount of oxygen that these plants are able to fix into the media via their roots is also unknown. Therefore, the use of these plants should be limited. More conventionally used wetland plants such as taro, sedge, wetland fern, cattails and other locally available wetland plants should be used. The ornamental garden plants can be planted towards the edges of the wetlands to make them aesthetically appealing. Plants with higher rates of growth such as taro and sedge should be used so that they can fix more nutrients in their biomass. Plants with slower growth rates such as *Nerium*, *Acalypha*, spider lily etc. might be less efficient as they would take up lower amounts of nutrients given their slower growth rate.

The use of tree species in the wetlands should be avoided. The tree species might pose a threat to the structural integrity of the systems as they grow older and larger in size. The roots of these trees can cause damage to the base and the walls of the systems thereby causing leakage of wastewater that could easily get to the underlying aquifers given the geology of the area. The tree canopy can also cause shading and reduce the loss of water through transpiration by other plants in the wetlands. The use of xerophytic plants should also be avoided in the systems as these plants are morphologically adapted to reduce loss of water from their leaves which in turn could reduce the reduction of total wastewater volume through evapotranspiration. If biomass harvesting is considered as a method to remove nutrients, it should be well designed and well managed. Haphazard harvesting of plants from the wetlands might result in a negative effect on their functioning. Entire removal of plant cover should be avoided other than when it is done to replace the old aggregate or plants.

Since vegetatively propagating plants such as taro, sedge, wetland ferns etc. are used in the wetlands, it is essential to manage these plants and not let them overgrow to the extent that their roots cover the entire surface of the wetland. Dense vegetation can cause consistent lower dissolved oxygen within the system which can reduce the rate of nitrification. Dense vegetation also adds to the leaf litter and organic matter which could again clog the aggregate at the surface and cause anoxic conditions. Most of the older wetlands in Akumal seem to have the plants that were originally planted and they are highly overgrown. This also means that they have the same original aggregate in these systems. Many of these wetlands also had very high organic matter and soil in their aggregate. This could mean poor hydraulic conductivity within the system. Removal of the old plants and aggregate once every few years might be beneficial in order to keep these systems functional and free of problems such as poor hydraulic flow, anoxic conditions in the aggregate, saturation of the aggregate and release of pollutants back into the environment due to aggregate dissolution.

Although the flow of the effluent into the environment could not be traced for every wetland, rather than directing the effluent directly out into the ocean or into bare ground, it should be directed towards the mangroves or any vegetated areas in the near vicinity. This might help in additional uptake of pollutants and nutrients by the plants in the environment before they get to the ocean or the aquifer. The fate of the effluent after it is released into the environment and how it interacts with the natural systems in the area is unknown at this point of time.

A proper construction, design, planting and maintenance regime is required to manage the wetlands in the area. Eco-friendly practices should be encouraged amongst the tourists as well as the locals in terms of use of chemicals, shampoos, soaps, detergents, cleaning agents etc. Property rental and hotel businesses in the area that use wetland systems in Akumal could participate in a self monitoring program wherein they could test the basic effluent water quality parameters at regular intervals of time to keep a check on the functioning of the system. However, the economic feasibility of this will have to be considered.

Chapter 6: Conclusion

The overall performance of the wetlands in reducing the level of pollutants and nutrients depends on a wide variety of parameters such as shape, size, media, vegetation cover, type of vegetation, loading rates, microbial activity etc. This study gives a snapshot on the performance of some of the wetlands in terms of phosphate and nitrogen removal as well as some of the important criteria affecting its performance such as vegetation, structure, size, shape, characteristics of aggregate.

The systems in Akumal had been set up following Nelson's initial designs. However, the initial prototypes are not being followed consistently and important factors such as shape, size, capacity, loading and overall treatment goals are not given prime importance. These wetlands have a greater potential to treat wastewater if some of the important aspects of construction and maintenance are followed.

There is a great deal of uniformity as far as the materials used and the style of construction. However, there is variability in terms of size and shapes of the wetlands. Variability was also observed in the use of plants in the systems as well as the management of the plant cover. This study gives a snapshot view of the conditions of the studied wetlands. However, very detailed comparisons of all the parameters are not possible owing to accessibility issues as well as logistical issues such as unavailability of a functional lab on site. The lack of the ability to sample from most wetland systems is a main problem hindering a detailed understanding of the systems.

At present there is no consistent policy for constructing new wetlands. Currently, no best comprehensive set of practices or recommendations exist for the systems that can be followed by the property owners or managers to get the best wastewater treatment efficiency out of these systems. Although CEA has some recommendations but they are not extensive and are also not necessarily scientifically accurate. The CEA is not liable for the construction and proper functioning of these systems and only provides general guidelines. These recommendations are very general and it is up to the owner of the property to decide aspects such as size, shape and maintenance of the wetlands. As mentioned earlier, there are several issues with regards to the maintenance of the systems that need to be addressed.

It can be said that there are distinct aggregate types in the systems based on the mineralogy and grain size. The effect of these variations in the aggregate on the wastewater treatment efficiency of the systems will require more detailed studies in the future. The implications of aggregate dissolution are another area of concern which will have to be studied. The role of the non-wetland plant species used in the systems is not well understood and in most of the cases, the vegetation is poorly managed. This study indicates that the vegetation being used in the systems is not appropriate and that better choice of plants and better choice of management practices can be made in the future. The study of biofilms from the CEA Dive Shop wetland reveals a complex structure and composition having significant mineralogical components which warrants further detailed study of the components of the biofilms and their specific role in wastewater treatment. A large range of variation was observed in the nutrient removal potential of the systems. A higher percentage of nitrogen and phosphate removal in wetlands with new aggregate and low plants cover is something that needs to be investigated in detail. At this stage, it is very difficult to pinpoint the reason for these variations owing to the limited data. However, this study does reveal the fact that the wetlands in the area might not be at their best required and expected functionality. Construction and management protocols are required to be designed for the wetlands in the area to get the desired results.

The effect of aggregate dissolution on pollutant retention, role of non-wetland plants in the system, the characterization and role of microbial communities in the biofilm, coliform bacteria removal efficiency and fate of effluent after release from these wetlands are some of the major areas which can be investigated in the future. This study reveals the fact that there is a great scope of improvement in the construction, plant management and overall long term management of the systems in order to obtain the desired wastewater treatment goals.

Appendix A – PDF Cards

PDF#041-1475 for Aragonite

PDF#041-1475: QM=Star(S); d=Diffractometer; I=Diffractometer | **PDF Card**

Aragonite (Aragonite)
$CaCO_3$

Radiation=CuKa1 Lambda=1.540598 Filter=
Calibration=Internal(Si) 2T=21.075-89.411 I/Ic(RIR)=1.0
Ref: Keller, L., Rask, J., Buseck, P., Arizona State Univ., Tempe, AZ, USA.
ICDD Grant-in-Aid (1989) CAS#:14791-73-2

Orthorhombic - Powder Diffraction, Pmcn (62) Z=4 mp=
CELL: 4.9623 x 7.968 x 5.7439 <90.0 x 90.0 x 90.0> P.S=oP20 (?)
Density(c)=2.927 Density(m)=2.950 Mwt=100.09 Vol=227.11 F(30)=217.4(.0041,34/0)
Ref: Jarosch, D., Heger, G.
Tschermaks Mineral. Petrogr. Mitt., v35 p127 (1986)

NOTE: Specimen from Sefrou, Morocco. Microprobe analyses (wt.%): major Ca, and trace Sr(<<1). To replace 5-453 and validated by calculated pattern 24-25. Optical data on specimen from Bilin, Bohemia, Czechoslovakia.
Color: Colorless

Strong Lines: 3.40/X 2.70/6 1.98/6 3.27/5 2.37/5 2.48/4 1.88/3 1.74/3

82 Lines, Wavelength to Compute Theta = 1.54059Å(Cu), I%-Type = (Unknown)

#	d(Å)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(Å)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	4.2120	3.0	1	1	0	21.075	10.538	0.1187	42	1.4040	3.0	3	3	0	66.548	33.274	0.3561
2	3.9840	1.0	0	2	0	22.296	11.148	0.1255	43	1.3804	0.0	0	4	3	67.838	33.919	0.3622
3	3.3970	100.0	1	1	1	26.212	13.106	0.1472	44	1.3663	2.0	2	4	2	68.635	34.318	0.3660
4	3.2740	50.0	0	2	1	27.216	13.608	0.1527	45	1.3639	2.0	3	3	1	68.773	34.387	0.3666
5	2.8720	6.0	0	0	2	31.115	15.558	0.1741	46	1.3592	5.0	1	1	4	69.045	34.522	0.3679
6	2.7330	9.0	1	2	1	32.741	16.371	0.1829	47	1.3507	2.0	0	2	4	69.541	34.771	0.3702
7	2.7020	60.0	0	1	2	33.128	16.564	0.1850	48	1.3487	3.0	3	2	2	69.659	34.830	0.3707
8	2.4810	40.0	2	0	0	36.176	18.088	0.2015	49	1.3416	2.0	1	5	2	70.082	35.041	0.3727
9	2.4110	14.0	0	3	1	37.264	18.632	0.2074	50	1.3290	1.0	0	6	0	70.846	35.423	0.3762
10	2.3730	45.0	1	1	2	37.884	18.942	0.2107	51	1.3290	1.0	1	4	3	70.846	35.423	0.3762
11	2.3420	25.0	1	3	0	38.405	19.202	0.2135	52	1.3058	1.0	2	5	1	72.300	36.150	0.3829
12	2.3300	25.0	0	2	2	38.610	19.305	0.2146	53	1.3035	1.0	1	2	4	72.448	36.224	0.3836
13	2.1900	12.0	2	1	1	41.187	20.593	0.2283	54	1.2615	5.0	3	3	2	75.268	37.634	0.3964
14	2.1680	2.0	1	3	1	41.624	20.812	0.2306	55	1.2521	1.0	1	6	1	75.933	37.967	0.3993
15	2.1080	20.0	1	2	2	42.866	21.433	0.2372	56	1.2427	3.0	3	4	1	76.611	38.306	0.4023
16	2.1080	20.0	2	2	0	42.866	21.433	0.2372	57	1.2427	3.0	2	0	4	76.611	38.306	0.4023
17	1.9774	55.0	2	2	1	45.853	22.926	0.2529	58	1.2406	4.0	4	0	0	76.765	38.382	0.4030
18	1.9500	1.0	0	3	2	46.535	23.267	0.2564	59	1.2365	6.0	3	1	3	77.066	38.533	0.4044
19	1.8821	25.0	0	4	1	48.318	24.159	0.2657	60	1.2245	3.0	0	5	3	77.963	38.981	0.4083
20	1.8775	25.0	2	0	2	48.444	24.222	0.2663	61	1.2245	3.0	1	3	4	77.963	38.981	0.4083
21	1.8616	2.0	0	1	3	48.885	24.443	0.2686	62	1.2149	2.0	2	5	2	78.698	39.349	0.4116
22	1.8275	4.0	2	1	2	49.859	24.929	0.2736	63	1.2059	4.0	2	4	3	79.401	39.700	0.4146
23	1.8149	20.0	1	3	2	50.229	25.114	0.2755	64	1.2059	4.0	0	6	2	79.401	39.700	0.4146
24	1.7598	3.0	1	4	1	51.917	25.958	0.2841	65	1.1890	3.0	1	5	3	80.760	40.380	0.4205
25	1.7430	25.0	1	1	3	52.455	26.227	0.2869	66	1.1864	2.0	2	2	4	80.973	40.487	0.4214
26	1.7290	12.0	2	3	1	52.913	26.456	0.2892	67	1.1711	3.0	2	6	0	82.258	41.129	0.4269
27	1.7257	16.0	0	2	3	53.022	26.511	0.2897	68	1.1711	3.0	1	6	2	82.258	41.129	0.4269
28	1.6984	2.0	2	2	2	53.942	26.971	0.2944	69	1.1642	1.0	0	4	4	82.852	41.426	0.4295
29	1.6369	3.0	0	4	2	56.144	28.072	0.3055	70	1.1642	1.0	3	4	2	82.852	41.426	0.4295
30	1.6300	1.0	1	2	3	56.403	28.201	0.3067	71	1.1600	2.0	4	2	1	83.219	41.609	0.4310
31	1.6198	2.0	3	1	0	56.790	28.395	0.3087	72	1.1389	1.0	4	0	2	85.118	42.559	0.4390
32	1.5588	4.0	3	1	1	59.229	29.614	0.3208	73	1.1370	0.0	0	1	5	85.294	42.647	0.4398
33	1.5357	2.0	0	5	1	60.211	30.105	0.3256	74	1.1323	1.0	3	3	3	85.733	42.866	0.4416
34	1.4993	4.0	2	4	1	61.831	30.915	0.3335	75	1.1274	1.0	4	1	2	86.196	43.098	0.4435
35	1.4891	1.0	2	1	3	62.301	31.151	0.3358	76	1.1256	2.0	3	5	1	86.368	43.184	0.4442
36	1.4764	2.0	3	2	1	62.898	31.449	0.3387	77	1.1256	2.0	2	3	4	86.368	43.184	0.4442
37	1.4672	4.0	1	5	1	63.338	31.669	0.3408	78	1.1089	2.0	1	7	0	87.998	43.999	0.4509
38	1.4360	1.0	0	0	4	64.880	32.440	0.3482	79	1.1089	2.0	1	1	5	87.998	43.999	0.4509
39	1.4167	1.0	2	2	3	65.875	32.938	0.3529	80	1.1035	1.0	4	3	1	88.541	44.271	0.4531
40	1.4132	3.0	0	1	4	66.059	33.030	0.3538	81	1.1035	1.0	0	2	5	88.541	44.271	0.4531
41	1.4107	4.0	3	1	2	66.191	33.096	0.3544	82	1.0950	0.0	4	2	2	89.411	44.706	0.4566

PDF#021-1307 for Boehmite

PDF#021-1307: QM=Indexed(I); d=Diffractometer; I=Diffractometer | **PDF Card**

Bohmite, syn
AlO(OH)

Radiation=CuKa1 | Lambda=1.54056 | Filter=Ni
Calibration= | 2T=14.485-147.377 | I/Ic(RIR)=
Ref: Natl. Bur. Stand. (U.S.), Circ. 539, v3 p38 (1954)

Orthorhombic - Powder Diffraction, Amam (63) | Z=4 | mp=
CELL: 3.7 x 12.227 x 2.868 <90.0 x 90.0 x 90.0> | P.S=oC16 (?)
Density(c)=3.070 | Density(m)=2.51A | Mwt=59.99 | Vol=129.75 | F(30)=15.4(0.034,57/0)
Ref: Ibid.

NOTE: This data was originally on 5-190 with the a and c reversed, and called "α". Intensities verified by calculated pattern. Sample from Aluminum Company of America. Spectroscopic analysis (wt.%): Ca, Mg, Si <0.1, Fe, Mn, Ni, Ti, <0.01, Cr, Cu <0.001. Pattern taken at 26 C. Lepidocrocite is the Fe analogue.

Strong Lines: 6.11/X 3.16/7 2.35/6 1.86/3 1.85/3 1.45/2 1.31/2 1.66/1

42 Lines, Wavelength to Compute Theta = 1.54059Å(Cu), I%-Type = (Unknown)

#	d(Å)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(Å)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	6.1100	100.0	0	2	0	14.485	7.243	0.0818	22	1.1609	4.0	1	10	0	83.140	41.570	0.4307
2	3.1640	65.0	1	2	0	28.181	14.091	0.1580	23	1.1337	6.0	2	0	2	85.602	42.801	0.4410
3	2.3460	55.0	0	3	1	38.337	19.168	0.2131	24	1.1152	2.0	2	2	2	87.375	43.687	0.4484
4	1.9800	6.0	1	3	1	45.789	22.895	0.2525	25	1.0917	2.0	3	3	1	89.755	44.877	0.4580
5	1.8600	30.0	0	5	1	48.930	24.465	0.2688	26	1.0459	2.0	0	8	2	94.867	47.433	0.4781
6	1.8500	25.0	2	0	0	49.212	24.606	0.2703	27	1.0281	2.0	3	5	1	97.049	48.525	0.4863
7	1.7700	6.0	2	2	0	51.595	25.798	0.2825	28	0.9903	2.0	2	6	2	102.126	51.063	0.5049
8	1.6620	14.0	1	5	1	55.223	27.612	0.3008	29	0.9818	2.0	1	12	0	103.363	51.681	0.5093
9	1.5270	6.0	0	8	0	60.590	30.295	0.3274	30	0.9506	2.0	3	7	1	108.255	54.128	0.5260
10	1.4530	16.0	2	3	1	64.030	32.015	0.3441	31	0.9310	2.0	0	3	3	111.662	55.831	0.5371
11	1.4340	10.0	0	0	2	64.982	32.491	0.3487	32	0.9247	2.0	4	0	0	112.821	56.410	0.5407
12	1.4120	2.0	1	8	0	66.122	33.061	0.3541	33	0.9105	2.0	2	8	2	115.561	57.781	0.5491
13	1.3960	2.0	0	2	2	66.979	33.490	0.3582	34	0.9023	2.0	1	10	2	117.233	58.617	0.5541
14	1.3830	6.0	1	7	1	67.694	33.847	0.3615	35	0.8937	2.0	0	13	1	119.065	59.532	0.5595
15	1.3690	2.0	2	6	0	68.481	34.241	0.3652	36	0.8907	2.0	0	5	3	119.724	59.862	0.5614
16	1.3120	16.0	2	5	1	71.905	35.953	0.3811	37	0.8660	2.0	1	5	3	125.617	62.809	0.5774
17	1.3030	4.0	1	2	2	72.480	36.240	0.3837	38	0.8607	2.0	4	3	1	127.007	63.504	0.5809
18	1.2240	2.0	1	4	2	78.001	39.000	0.4085	39	0.8316	2.0	2	3	3	135.725	67.862	0.6013
19	1.2090	2.0	3	2	0	79.157	39.578	0.4136	40	0.8286	4.0	4	5	1	136.756	68.378	0.6034
20	1.1780	4.0	2	8	0	81.673	40.836	0.4244	41	0.8180	2.0	1	7	3	140.672	70.336	0.6112
21	1.1711	2.0	0	6	2	82.258	41.129	0.4269	42	0.8026	2.0	2	5	3	147.377	73.689	0.6230

PDF#047-1743 for Calcite

PDF#047-1743: QM=Calculated(C); d=Calculated; I=Calculated	PDF Card

Calcite (Calcite)
$CaCO_3$

Radiation=CuKa1 Lambda=1.54056 Filter=
Calibration= 2T=23.054-135.725 I/Ic(RIR)=
Ref: Bernstein, L., Menlo Park, CA, USA.
Private Communication (1994)

Rhombohedral - Single Crystal, $R\bar{3}c$ (167) Z=6 mp=
CELL: 4.9896 x 4.9896 x 17.061 <90.0 x 90.0 x 120.0> P.S=hR10 (?)
Density(c)=2.711 Density(m)=2.37A Mwt=100.09 Vol=367.85 F(30)=999.9(.0003,33/0)
Ref: Effenberger, H. et al.
Z. Kristallogr., v156 p233 (1981)

NOTE: Pattern calculated using Lazy-Pulverix including anomalous dispersion corrections. Specimen from Iceland. R=0.022; Rw=0.023. Microprobe analysis (wt.%): Ca O 55.7, Mg O 0.2, Fe O 0.1 Data collected using MoK_{α}-radiation, graphite monochromator.

Strong Lines: 3.04/X 1.88/2 1.91/2 2.28/2 2.09/2 2.49/1 1.60/1 3.85/1

60 Lines, Wavelength to Compute Theta = 1.54059Å(Cu), I%-Type = Peak Area

#	d(Å)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(Å)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	3.8548	8.9	0	1	2	23.054	11.527	0.1297	31	1.0614	1.4	2	0	14	93.055	46.528	0.4711
2	3.0355	100.0	1	0	4	29.400	14.700	0.1647	32	1.0472	4.9	4	0	4	94.711	47.355	0.4775
3	2.8435	2.2	0	0	6	31.435	15.718	0.1758	33	1.0448	5.3	1	3	-8	95.000	47.500	0.4786
4	2.4948	14.7	1	1	0	35.969	17.985	0.2004	34	1.0352	2.5	1	0	16	96.158	48.079	0.4830
5	2.2846	20.2	1	1	-3	39.408	19.704	0.2189	35	1.0349	0.8	1	1	-15	96.200	48.100	0.4831
6	2.0944	16.1	2	0	2	43.158	21.579	0.2387	36	1.0230	0.6	1	2	-13	97.695	48.848	0.4887
7	1.9274	7.0	0	2	4	47.114	23.557	0.2594	37	1.0118	5.4	3	0	12	99.155	49.577	0.4941
8	1.9124	21.7	0	1	8	47.506	23.753	0.2615	38	0.9897	0.7	2	3	-1	102.218	51.109	0.5052
9	1.8753	23.2	1	1	-6	48.504	24.252	0.2666	39	0.9847	2.7	3	2	-2	102.936	51.468	0.5078
10	1.6258	4.2	1	2	-1	56.562	28.281	0.3075	40	0.9807	0.6	3	1	-10	103.528	51.764	0.5098
11	1.6041	11.8	1	2	2	57.398	28.699	0.3117	41	0.9767	2.4	2	1	-14	104.121	52.061	0.5119
12	1.5869	1.2	1	0	10	58.079	29.040	0.3151	42	0.9656	1.8	2	3	-4	105.830	52.915	0.5178
13	1.5252	6.6	1	2	-4	60.667	30.334	0.3278	43	0.9637	4.4	0	4	8	106.129	53.065	0.5188
14	1.5178	3.0	2	0	8	60.997	30.499	0.3294	44	0.9562	1.0	0	2	16	107.333	53.666	0.5229
15	1.5094	3.6	1	1	-9	61.374	30.687	0.3313	45	0.9520	0.6	3	2	-5	108.028	54.014	0.5252
16	1.4732	2.7	2	1	-5	63.052	31.526	0.3394	46	0.9429	4.2	4	1	0	109.552	54.776	0.5303
17	1.4404	8.4	3	0	0	64.659	32.330	0.3471	47	0.9377	1.9	2	2	-12	110.472	55.236	0.5332
18	1.4217	4.8	0	0	12	65.612	32.806	0.3517	48	0.9183	0.6	2	3	-7	114.037	57.018	0.5445
19	1.3568	1.9	1	2	-7	69.186	34.593	0.3685	49	0.8990	1.9	3	2	-8	117.936	58.968	0.5562
20	1.3390	3.1	0	2	10	70.240	35.120	0.3734	50	0.8950	1.8	4	1	-6	118.779	59.389	0.5586
21	1.2967	3.7	2	1	-8	72.891	36.446	0.3856	51	0.8929	2.2	1	2	-16	119.248	59.624	0.5600
22	1.2849	0.8	0	3	6	73.667	36.833	0.3891	52	0.8860	2.8	1	1	-18	120.770	60.385	0.5643
23	1.2474	1.5	2	2	0	76.271	38.135	0.4008	53	0.8598	0.6	5	0	2	127.243	63.621	0.5815
24	1.2352	2.8	1	1	-12	77.159	38.579	0.4048	54	0.8571	3.2	2	3	-10	127.970	63.985	0.5833
25	1.1868	0.8	1	3	-2	80.940	40.470	0.4213	55	0.8551	0.6	2	1	-17	128.545	64.272	0.5848
26	1.1798	3.7	1	2	-10	81.523	40.762	0.4238	56	0.8545	0.8	1	3	-14	128.704	64.352	0.5851
27	1.1729	0.5	0	1	14	82.105	41.052	0.4263	57	0.8470	2.5	0	5	4	130.852	65.426	0.5903
28	1.1538	6.8	1	3	4	83.768	41.884	0.4334	58	0.8369	3.1	0	1	20	133.975	66.987	0.5974
29	1.1423	3.5	2	2	-6	84.804	42.402	0.4377	59	0.8353	0.8	3	2	-11	134.496	67.248	0.5986
30	1.1247	0.9	2	1	-11	86.458	43.229	0.4446	60	0.8316	1.6	3	3	0	135.725	67.862	0.6013

PDF#046-1045 for Quartz

PDF#046-1045: QM=Star(S); d=Diffractometer; I=Diffractometer — **PDF Card**

Quartz, syn (Quartz)
SiO_2

Radiation=CuKa1 Lambda=1.5405981 Filter=Ge
Calibration=Internal(Si) 2T=20.860-144.117 I/Ic(RIR)=3.41
Ref: Kern, A., Eysel, W., Mineralogisch-Petrograph. Inst., Univ. Heidelberg, Germany.
ICDD Grant-in-Aid (1993)

Hexagonal - Powder Diffraction, $P3_221$ (154) Z=3 mp=
CELL: 4.91344 x 4.91344 x 5.40524 <90.0 x 90.0 x 120.0> P.S=hP9 (O2 Si)
Density(c)=2.650 Density(m)=2.660 Mwt=60.08 Vol=113.01 F(30)=538.7(.0018,31/0)
Ref: Z. Kristallogr., v198 p177 (1992)

NOTE: Pattern taken at 23(1) C. Low temperature quartz. 2υ determination based on profile fit method. To replace 33-1161.
Color: White

Strong Lines: 3.34/X 4.25/2 1.82/1 1.54/1 2.46/1 2.28/1 1.37/1 2.13/1

58 Lines, Wavelength to Compute Theta = 1.54059Å(Cu), I%-Type = Peak Area

#	d(Å)	I(f)	h	k	l	2-Theta	Theta	1/(2d)	#	d(Å)	I(f)	h	k	l	2-Theta	Theta	1/(2d)
1	4.2550	16.0	1	0	0	20.860	10.430	0.1175	30	1.0638	0.0	4	0	0	92.788	46.394	0.4700
2	3.3435	100.0	1	0	1	26.640	13.320	0.1495	31	1.0477	1.0	1	0	5	94.650	47.325	0.4772
3	2.4569	9.0	1	1	0	36.544	18.272	0.2035	32	1.0438	0.0	4	0	1	95.118	47.559	0.4790
4	2.2815	8.0	1	0	2	39.465	19.732	0.2192	33	1.0346	1.0	2	1	4	96.237	48.118	0.4833
5	2.2361	4.0	1	1	1	40.300	20.150	0.2236	34	1.0149	1.0	2	2	3	98.750	49.375	0.4927
6	2.1277	6.0	2	0	0	42.450	21.225	0.2350	35	0.9896	0.0	1	1	5	102.230	51.115	0.5053
7	1.9799	4.0	2	0	1	45.793	22.896	0.2525	36	0.9872	0.0	3	1	3	102.566	51.283	0.5065
8	1.8180	13.0	1	1	2	50.139	25.069	0.2750	37	0.9783	0.0	3	0	4	103.876	51.938	0.5111
9	1.8017	0.0	0	0	3	50.622	25.311	0.2775	38	0.9762	0.0	3	2	0	104.202	52.101	0.5122
10	1.6717	4.0	2	0	2	54.875	27.437	0.2991	39	0.9608	0.0	3	2	1	106.592	53.296	0.5204
11	1.6592	2.0	1	0	3	55.325	27.662	0.3014	40	0.9285	0.0	4	1	0	112.113	56.057	0.5385
12	1.6083	0.0	2	1	0	57.235	28.617	0.3109	41	0.9182	0.0	3	2	2	114.060	57.030	0.5446
13	1.5415	9.0	2	1	1	59.960	29.980	0.3244	42	0.9161	2.0	4	0	3	114.466	57.233	0.5458
14	1.4529	2.0	1	1	3	64.035	32.018	0.3441	43	0.9152	2.0	4	1	1	114.638	57.319	0.5463
15	1.4184	0.0	3	0	0	65.786	32.893	0.3525	44	0.9089	0.0	2	2	4	115.884	57.942	0.5501
16	1.3821	6.0	2	1	2	67.744	33.872	0.3618	45	0.9009	0.0	0	0	6	117.536	58.768	0.5550
17	1.3750	7.0	2	0	3	68.144	34.072	0.3636	46	0.8972	0.0	2	1	5	118.312	59.156	0.5573
18	1.3719	5.0	3	0	1	68.318	34.159	0.3645	47	0.8889	1.0	3	1	4	120.123	60.061	0.5625
19	1.2879	2.0	1	0	4	73.467	36.734	0.3882	48	0.8814	0.0	1	0	6	121.852	60.926	0.5673
20	1.2559	3.0	3	0	2	75.659	37.830	0.3981	49	0.8782	0.0	4	1	2	122.604	61.302	0.5694
21	1.2283	1.0	2	2	0	77.675	38.837	0.4071	50	0.8598	0.0	3	0	5	127.250	63.625	0.5815
22	1.1998	2.0	2	1	3	79.884	39.942	0.4167	51	0.8458	0.0	1	1	6	131.202	65.601	0.5911
23	1.1978	0.0	2	2	1	80.046	40.023	0.4174	52	0.8407	0.0	5	0	1	132.755	66.377	0.5947
24	1.1840	2.0	1	1	4	81.173	40.586	0.4223	53	0.8359	0.0	4	0	4	134.292	67.146	0.5981
25	1.1802	2.0	3	1	0	81.491	40.745	0.4237	54	0.8296	1.0	2	0	6	136.422	68.211	0.6027
26	1.1530	1.0	3	1	1	83.840	41.920	0.4337	55	0.8254	2.0	4	1	3	137.893	68.947	0.6058
27	1.1407	0.0	2	0	4	84.957	42.478	0.4383	56	0.8189	0.0	3	3	0	140.316	70.158	0.6106
28	1.1145	0.0	3	0	3	87.439	43.719	0.4486	57	0.8117	3.0	5	0	2	143.249	71.624	0.6160
29	1.0816	2.0	3	1	2	90.831	45.415	0.4623	58	0.8097	0.0	3	3	1	144.117	72.058	0.6175

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Curriculum Vitae

Sheela Varma was born and brought up in Baroda, India. She graduated from Basil High School, Baroda in 1997. She received her Bachelor of Science and Master of Science degrees in Botany from The Maharaja Sayajirao University of Baroda in 2000 and 2002 respectively. She was employed with a business process outsourcing company and a leading job portal in the same city for two years before coming to USA in fall of 2007 as an international graduate student at George Mason University.