Assessment of the Water Quality, Some Trace Elements Content of *Heritierafomes* Fruits and *Pneumatophores* of Sundari After Oil Spill in Shela River at Sundarban, Bangladesh

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Abstract: To assessment the effects on the ecosystem of Sundarbans a Mangrove Forest (SMF) in Bangladesh after oil spillages on 9th December 2014 into the shela river of Sundarbans, mainly focus on to determine the water quality and some trace elements content of Sundari (*Heritierafomes*) fruit and the aerial roots (pneumatophores) of Sundari. The water quality parameters viz, alkalinity, dissolved oxygen, hardness, pH, EC, ORP, salinity, nitrite and chloride contents were determine by using pH meter, DO meter, electroconductivity meter, Salinitimeter during high tide time and downstream. The nitrite and chloride contents of water and the trace elements contents of sundari fruits and roots were analyzed in the laboratory by using atomic absorption spectrophotometer. After oil spillage the alkalinity, dissolved oxygen (DO), hardness, EC, ORP, nitrite and chloride contents of water during high tide time and downstream were slightly decrease but the salinity of water decrease remarkable. The Fe and Zn contents in Heritierafomes fruits and pneumatophores of Heritierafomes were increased significantly but the Cu, Cd, Pb and Ni contents were remain constant. After analyzing the results, in this study, it is clearly indicated that the criteria needed for the good quality of water and the some micro-nutrient contents of Heritierafomes fruits and pneumatophores of Heritierafomes are remarkable change due to the oil spill into the shela river of Sundarban as compare to before oil spillage. This study also represent that the Fe and Zn contents of Sundari fruits and roots are significantly increasing due to the massive changing of water quality of Shela river of Sundarbans. Finally, this study would helpful to measure the threaten affect on aquatic animals, others wild animal and different tree spices of the mangrove forest as well as the ecosystem of Sudarban.

Keywords: Water Quality, Oil Spillage, Shela River, Sundari Fruits, Sundarbans Mangrove Forest (SRF)

1. Introduction

Sundarban is one of the largest mangrove forest in the world and it has been considered a highly productive ecosystem, which provides a wide range of valuable forest products, maintains water, play a vital role for the nursery grounds for many commercially important sea species. The Sundarban mangroves develops a variety of means to adjust with the extreme environment. In addition to water, mangrove require adequate supply of mineral nutrients such as nitrogen and phosphorus in the form of inorganic nitrate and phosphate [1, 2]. Rainfall, fresh water from rivers or as run off from the land, tide- borne soluble or particle bound nutrients are essential for the sustaining varieties of life in the Sundarban. Salinity is considered to be the obvious criteria for a gradient determining species distribution because of its known effects on individual trees. The Sundarban provide ecological services as an essential habitant for wide variety of flora and funna, nutrient producer, water purifier, nutrient and sediment trap, storm barriers, shore stabilizer, aesthetic

attraction and energy storage unit [3]. Thus Sundarban forest is vital for healthy coastal ecosystems. The forest detritus consisting mainly of fallen leaves and branches provides nutrient for the marine environment and supports varieties of sea life in intricate food webs associated directly through detritus or indirectly through the planktonic and epiphytic algal food chains [4]. The shallow intertidal reaches that characterize the mangrove wetlands which provide refuge and nursery grounds for juvenile fish, crabs, shrimps and mollusks. Fruits of *Heritierafomes* are mainly utilized as a major sources of foods by different spices of animals in Sundarban for their survival [5]. Beside these, good quality of water is essential to survive the fishes and others aquatic animals in Sundarban. The Sundarbans mangrove Forest (SMF), the single largest chunk of productive mangrove forest in the world, plays an important role in the economy of the south western region of Bangladesh as well as in the national economy [6]. Population growth and economic development have brought immense pressure on mangrove resources and its ecosystem.

The extensive shipping of crude oil over the world's oceans has increased concern about the effects of accidental spillage of petroleum in the marine environment. As Sundarban is one of the major route of transportation of crude oil and others goods for Mongla Port in Bangladesh. So, accidental oil spillage into the rivers of sundarban could be dangerous for this mangrove forest because monitoring and surveillance facilities are not available in Sundarbans to quantify the extent of oil pollution. No facilities exist for any clean up operation after an oil spill.

On 9th December 2014, the oil spillage affect on the Sundarban's ecosystem. The spillage oil cover nearly 3,900 square miles of the Sundarban, the world's largest Mangrove forest. As a result this may impact on long term chronic poisoning of mangrove plants and associated fauna by the toxic components of the retained oil. About 56-60% of the spilled oil over water surface is lost by evaporation depending on the type of oils [7]. The light molecular weight fraction of oil gets dissolved in water and thus a dilute oil water suspension is formed, from which emulsification starts [8]. The water content of the emulsion is about 8-20%. It forms frothy mass. The consequent effect on water quality parameters include reduction of visibility (turbidity), reduction of photosynthesis, reduction in dissolved oxygen (imbalance in respiration and production), higher demands on nutrients (imbalance in nutrient budget), increase in the organic carbon content, and increase in oil and grease content (tainting effects on biota). In addition to this well accepted fate of oil spilling, there are also effects on the regulation of the chemical composition of water [7, 9]. In shela river, where the oil tanker reportedly sank, along with the Pashur, another affected place, are home of several species, including the plants, rare plants, Irrawaddy and Ganges dolphins. This catastrophe is unprecedented in the Sundarbans and its long term impact on vast populations of small fishes, dolphins, plankton, algae, fungi, plants, animals as well as Mangrove ecology. Due to oil spill the water quality is changed. The

polluted water uptake by the plant root. So the plant essential trace elements could be changed. As pneumatophores of Heritierafomes is an important route of water uptake and fruits of Heritierafomes are the major sources of food for different spices of animal in Sundarban for their survival [10, 11]. Beside these, good quality of water is essential to survive the fishes and others aquatic animals in Sundarban. So, this study mainly focused on to assessment of water quality and measurement of some trace elements like Fe, Zn, Cu, Cd, Pb and Ni contents in *Heritierafomes* fruits and *pneumatophores* of *Heritierafomes*. As Zn and Fe plays an important role as a structural component of several proteins, function as an intra-cellular signaling, stabilized RNA and DNA structure and required for RNA polymerase activity [12]. Beside these Zn may also beneficial effect for the treatment of kidney disease, asthma, eczema etc [13]. So, appropriate amount of Zn and Fe containing *Heritierafomes* fruits is essential for the good health of mangrove animals as well as human.

As a result the medicinal quality of the fruit of *Heritierafomes* will be lost due to contain abnormal amount of (less/high) trace elements. By eating grasses and plant's leaves and fruits animal will be affected. Many plants, fishes and others aquatic animals survival capacity could be hampered. Thus wildlife in Sundarbans an ecological hotspot straddling southwestern Bangladesh and eastern India is under serious threat after oil spill. Maintenance of ecological balance is unique but fragile ecosystem is therefore absolute necessary by way of reduction in biotic interference and conservation of the flora and fauna.

Keeping the abovementioned information in mind, an oil dispersion experiment was conducted at Jessore University of Science and Technology (JUST) lab March 2015. As a consequence of oil spillage, we hypothesize that there is effect on the ions regulation between water-sediment interfaces that were not possible to study at field levels because of large sensitive aquatic ecosystem. Therefore, this present study mainly focused on the assessment of water quality and the trace elements contents of *Heritioerafomes* fruit and *pneumatophores* of *Heritierafomes*.

2. Materials and Methods

2.1. Sampling and Analytical Techniques

Water samples were collected in November 2014 and March 2015 from Dangmari station of SMF located adjacent to the Mongla Port, Khulna (Fig. 1 and 2a). The samples of the study were collected by using a country boat. Water from 10-25 cm depth was collected for physicochemical analyses [14]. A standard Secchi disc was used to measure the transparency of water while for water temperature a digital thermometer was used (Model No. 950).

Salinity and pH of the water were measured *in situ* by Salinity Meter (Atago-Refractometer) and Hanna-pH meter, respectively. Alkalinity and dissolved oxygen (DO) were measured by digital alkaliometer and DO meter respectively.

Water samples were transported into the Centre for Sophisticated Instrumentation and Research Laboratory, Jessore University of Science and Technology, Jessore. University for analyzing different parameters.

Figure 1. *Water quality and mangrove forest tree before oil spillage into the Shela river of Sundarban.*

(a)

(b)

Figure 2. *(a) Water quality and mangrove forest tree after oil spillage into the Shela river of Sundarban. (b)Affected pneumatophores of Heritirefomes afteroilspillage into the Shela river of Sundarban.*

2.2. Collection of Plant Materials and Preparation of Samples

The *Heritierafomes* fruit and *pneumatophores* tuber were collected from shela river at oil spilling area of Sundarban,

Bangladesh. Authentication was confirmed by DEPARTMENT OF BOTANY, RAJSHAHI UNIVERSITY, BANGLADESH. The fruits and tuber were washed with distill water and then chopping by a sharp knife and dry into the oven at 55°C temperature. After drying it's crushing into a mortar by pestleand makes it into powder for ethanol extraction.

Preparation of Ethanol Extract for plant materials

Each of the 15 gm of *Heritierafomes* fruit and *pneumatophores* tuber dried powders were placed in the Soxhlet thimble and extracted with 200ml of respective solvents continuously for 30-40 hours. The solution thus extracted was filtered through muslin layer, centrifuged and the collected filtrate was evaporated to dryness on hot plate at constant temperature of 60°C. The clumpy dry residue obtained was scraped by knife, made into fine powder form and stored in air tight plastic vials for Atomic Absorption Spectrophotometric analysis.

2.3. Analysis of Sample by AAS (Atomic Absorption Spectrophotometer)

For the estimation of Cu, Fe, Cd, Pb, Zn and Ni contents in the water and Heritierafomes fruit and pneumatophores tuber of Sundarban by using Atomic Absorption Spectrophotometer

The following procedures were used for analysis the samples:

2.3.1. Sample Digestion Procedures

To ensure the removal of organic impurities from the samples and thus prevent the interference in analysis, the samples were digested with concentrated Nitric acid. 5 mL of conc. HNO_3 was added to 100 mL of sampling water into the 250 mL conical flask then heated on a hot plate and evaporated till 20 mL was left. After cooling the flask again 5 mL of conc. HNO_3 was added and heated the flask on the hot plate. The digestion was continued till 10 mL was left and finally filtered and diluted with distilled water into 100 mL of volumetric flask and stored in the refrigerator.

2.3.2. Standard Preparation

The stock solution of Copper, Iron, Cadmium, Lead, Zinc and Nicol were prepared by dissolving 1000 mg of Copper, Iron, Cadmium, Lead, Zinc and Nicol powder into the one liter volumetric with 68% of nitric acid. The mixture was shaken and the flask made up to the 1 L mark with the nitric acid for each metal. Calibration solutions of the target metal ions were prepared from the standard stock by serial dilution.

2.3.3. Sample Analysis

The digested water samples were analyzed for the presence of Copper, Zinc and Lead using the Thermo scientific ICE 3000 series Atomic Absorption Spectrophotometer. The calibration plot methods were used for analysis. The air acetylene the flame used and hallow cathode lamp of the corresponding elements were the resonance. Line source, the

wave length for the determination of six elements were 324.8, 248.3, 228.8, 217.0, 213.9 and 232.0 nm for Copper, Iron, Cadmium, Lead, Zinc and Nicol respectively. The digested samples were analyzed in triplicates with the average concentration of metals being displayed in mg/L by the instruments after extrapolation from the standard curve.

2.3.4. Measuring Conditions for AAS

The analyses of Fe, Cd, Cu, Pb, Zn and Ni were carried out using the atomic absorption spectrometer (Thermo scientific ICE 3000 series) which operates in two modes: single-beam and double-beam. The operating conditions are given in Table 1.

Table 1. *The operating parameters for the atomic absorption spectrometer.*

Elements	Wavelengt(nm)	standard(mg/L)	Band pass (nm)	HCL Current (mA)	Flame /Lamp
Cu	324.8	1000	0.5	4.0	Air/acetylene
Fe	248.3	1000	0.2	4.0	Air/acetylene
Cd	228.8	1000	0.5	4.0	Air/acetylene
Pb	217.0	1000			Air/acetylene
Zn	213.9	1000	0.2	4.0	Air/acetylene
Ni	232.0	1000	0.2	4.0	Air/acetylene

3. Results

In this study, the figure 1, 2a and 2b represent the oil contaminated area of Shela river before and after oil spill at Shela river in Sundarban. The physico-chemical conditions of water of the oil contaminated area of Sundrabans were studied and data are presented in tables 2. Table 2 show the pH, alkalinity, DO (dissolved oxygen), hardness, and the chloride content of water of the oil contaminated area of the Shela river of Sundarban during high tide time and downstream were 8.14, 68.3mg/L, 4.08mg/L, 855mg/L,1860mg/L and 7.55, 34.2mg/L, 4.34mgL, 752.4mg/L, 1650mg/L respectively. Before oil spill the pH, alkalinity, DO (dissolved oxygen), hardness, and chloride content of the fresh water (before oil spill) of the Shela river during high tide time and downstream were 7.6, 69mg/L, 6.1mg/L, 890mg/L,1900mg/L and 7.4, 40mg/L, 6.19mg/L, 801mg/L, 1700mg/L respectively. Beside these table 2 also indicated that the salinity, ORP, EC and nitrite of oil spill contaminated water during high tide time and downstream were 43ppm/salt, 341mV,7.24μS/cm,21.45mg/L and 233ppm/salt, 282mV, 7.03μS/cm and 15.5mg/L respectively. The salinity, ORP, EC and nitrite contents of the water before the oil contaminated area of the Shela river of the Sundarban during high tide time and downstream were 52ppm/salt, 344mV, 7.34μS/cm, 25mg/L and 260ppm/salt, 285mV, 7.12μS/cm and 18mg/L respectively.
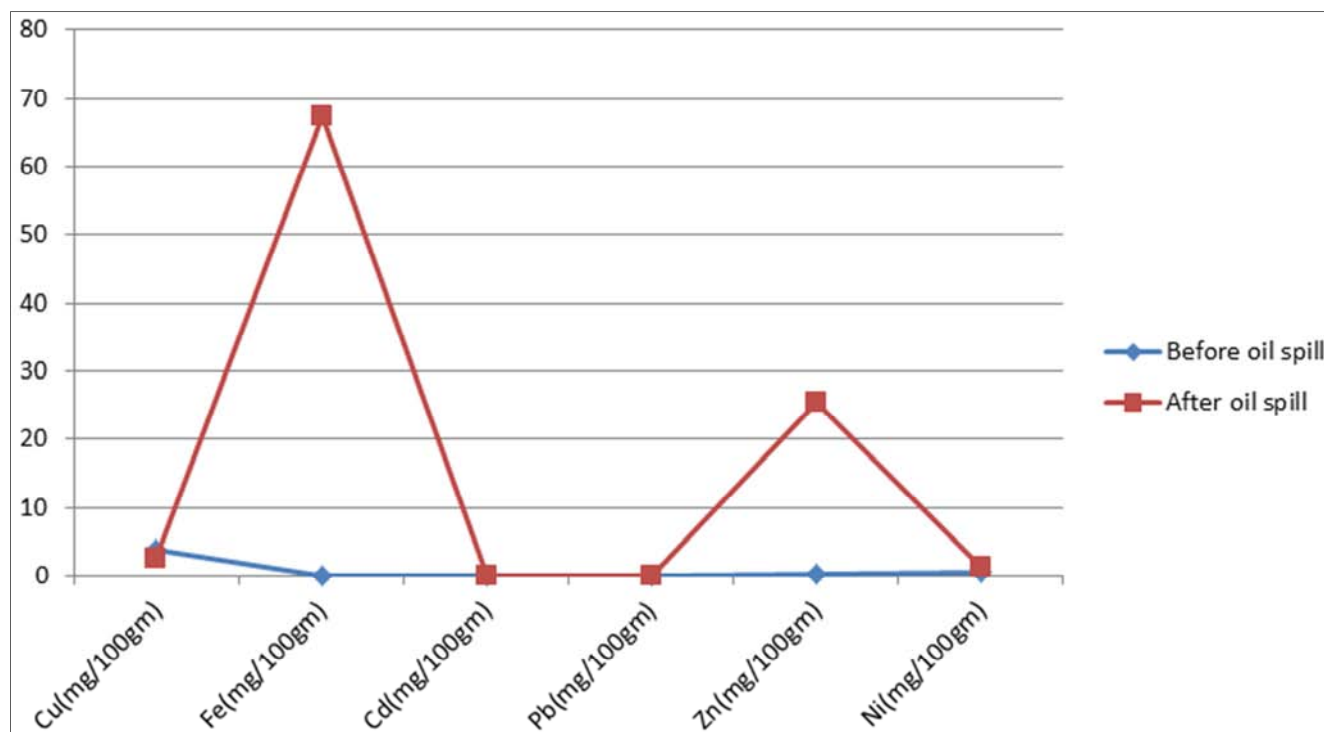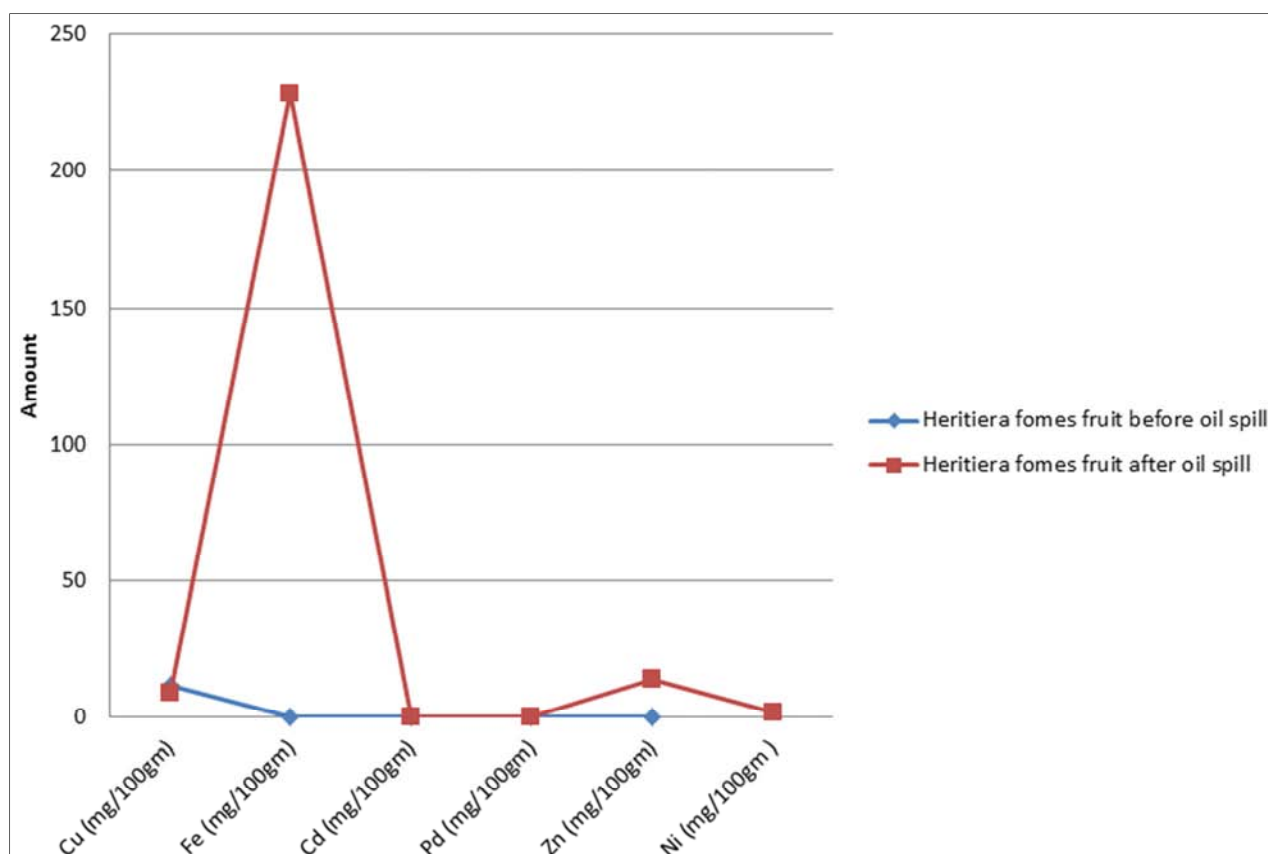

Figure 3. *Plot of concentration versus sample six metal present in Heritirefomes fruits before and after oil spillage.*

***Table 2.** Determination of water quality by using different parameters before and after oil spill in the ShelariverSundarban.*

| Parameters | Before oil spillage | | | | After oil spillage | | | |
| | DH | | DD | | DH | | DD | |
	Amount	SD	Amount	SD	Amount	SD	Amount	SD
pH	7.6	0.18	7.4	0.2	8.14	0.2	7.55	0.23
ORP(mV)	344	1.2	285	1.5	341	0.2	282	1.00
DO(mg/L)	6.1	0.2	6.19	0.18	4.08	0.3	4.34	0.12
EC(µS/cm)	7.34	0.09	7.12	0.07	7.24	0.09	7.03	0.07
Salinity(ppm/salt)	52	1.8	260	3.5	43	3.5	233	2.3
Alkalinity(mg/L)	69	2.12	40	2.05	68.3	2.98	34.2	3.12
Chloride(mg/L)	1900	4.30	1700	3.80	1860	2.5	1650	2.2
Nitrite(mg/L)	25	0.32	18	0.28	21.45	0.25	15.5	0.21
Hardness	890	4.89	801	5.02	855	5	752.4	5.88

DH-During high tide time, DD-During downstream, SD-Standard deviation.

***Figure 4.** Plot of concentration versus sample six metal present in pneumatophores of Heritirefomes before and after oil spillage.*

This study also compare the various micronutrient (Cu, Fe, Zn, Ni, Cd and Pb) contents of *pneumatophores* of *Heritierafomes and Heritierafome*s fruit before and after oil spill into the shela river at Sundarban are shown and figure 3 and figure 4 respectively. From these figure (Fig. 3 and 4) it is clearly indicated that the Fe and Zn contents in both the *pneumatophores* of *Heritierafomes* and *Heritirefomes* fruit are remarkable increase as compare to before oil spillage. But no changed observed the contents of Cu, Zn, Ni, Cd and Pb. From figure 3, it observed that after oil spillit *Heritirefomes* fruit contains Cu, Fe, Zn, Ni, Cd and Pb were 9.124mg%, 228.606mg%, 13.949mg, 1.554gm%, 0.00mg% and 0.00mg% respectively but before oil spillage the Cu, Fe, Zn, Ni, Cd and Pb contents were 11.91mg%, 0.16mg%, 0.15mg%, 0.78mg%, 0.00mg% and 0.00mg% respectively.

In case of pneumatophores of Heritierafomes after oil spillage, Cu, Fe, Zn, Ni, Cd and Pb contents were 2.616gm%, 67.421mg%, 25.455mg%, 1.213gm%, 0.00mg% and 0.00mg% respectively. But before oil spillage Cu, Fe, Zn, Ni, Cd and Pb contents were 3.87mg%, 0.11mg%, 0.37mg%, 0.57mg%, 0.00mg% and 0.00mg% respectively (shown in figure 3 and 4).

4. Discussion

To assessment the physico-chemical conditions of water and some trace elements content of *Heritierafomes* fruits and pneumatophores of Sundari of the oil contaminated area of the Sundrabans were studied and data are presented in tables

and figures.

During the periods of study high oil content, TSS, Chemical Oxygen Demand (COD) and total hardness; low transparency, poor productivity, poordiversity and abundance of phytoplankton and zooplankton, and high content of oil in soil indicate that the water and soil of the study areas of the Sundarbans have become polluted by the oil contamination (shown in figure 2a and 2b). Internationally highest 10 mg /L oil contamination is tolerance level of aquatic biodiversity. More than 10 mg/l of oil creates lethal conditions for the aquatic lives. Chowdhury et al. [7] reported that in Bangladesh, oil contamination is responsible for high TSS, COD, hardness etc. and low transparency, lower rate of productivity and poor plankton populations.

On the basis of present conditions of the study areas like physico-chemical conditions of water and soil; floral and faunal status it can be concluded that the intertidal zones and the forest floor besides the river Shela and connected canals, creeks of the Sundarbans have been contaminated by the furnace oil, earlier this areas were free from this type of oil pollution (shown in figure 1). Floral and faunal statuses are indicating that primary producer, consumer and some aquatic animals and some plants and their habitats have already been affected by the oil pollution (shown in figure 2b).

In this study from table 1, it is indicated that the pH, EC, alkalinity, chloride nitrite and hardness are slightly increase during high tide time as compared to down stream but dissolved oxygen (DO), salinity are slightly decrease during the high tide time as compare to the down stream. Therefore, from table 1 it is clearly observed that most of the parameters that have been done for the determination of water quality are slightly increasing after oil spilling but only the dissolved oxygen [15] and salinity are decreased as compared to before oil spillage. These changes may be due to hydrocarbon present in the spill oil. The impact of a given oil discharge is determined very much by the nature of the hydrocarbons in the oil. Other factors including weather conditions and the distance of the discharge from shore also play an important role in determining the extent of ecological damage [16, 17].

In this study, we also observed that dissolved oxygen (DO) decreased after oil spillage, this may be due to less chance to incorporate the atmospheric oxygen into water and hence DO can be reduced. Eills et al. [9] reported that that when oil is spilled onto the water surface, natural processes such as evaporation, dissolution and biodegradation are affected and ultimate impact on the aquatic system. Getter et al. [18] also reported that degradation rates depend on great many factors, including the characteristics of the oil, temperature, availability of nutrients, degree of physical mixing and so forth. Therefore, the changed of the normal characteristics of water obtained from this study (table-2) may effect on the aquatic system of Sundarban.

In this study, we measurement the Cu, Fe, Cd, Pd, Zn and Ni contents in the pneumatophores of Heritierafomes and Heritierafomes fruits. From figure 3 and 4 it is clearly indicated that Cu, Cd, Pd and Ni contents remain unchanged as compare to the uncontaminated water (before oil spillage

water) but the Fe and Zn contents of *Heritierafomes* fruits and *pneumatophores* of *Heritierafomes* remarkably high. Halder *et al*. [19] reported that *Heritierafomes* fruits content little amount of Fe and Zn. But it has been reported that the addition of organic compounds into water may increase or decrease the biological activity, presumably because of increased or decrease rates of metal ion uptake by organisms [19, 20]. In this present study, we observed that the Fe and Zn contents of the *Heritierafomes* fruits and *pneumatophores* were remarkably increased due to presence of organic compound in the contaminated water. So this result consistent with Halder *et al*. [19] that organic compounds into water may increase or decrease the rates of metal ion uptake by organisms. From figure 2a and 2b, it is observed that due to the deposition of oil on mangrove roots, and thus pneumatophores (Breathing roots - special rooting systems of the mangroves plants) of the different woody plants including Sundari (*Heritierafomes*– a major tree species of the forest), Keora (*Sonneratiaapetata*– leaf is the main food of the spotted dear), Gewa (*Excoecariaagallocha*), etc have been affected. This may be causes due to penetrating in the soil and hampered the biological process of many plant or may be highly contents Zn and Fe toxic effects.

5. Conclusions

After investigation of the oil spill contaminated water of Shelariver in Sundarban, it is observed that the water quality is changed due to changing different parameters of water. As a result it may be threat many aquatic species for their survive. Therefore, it is necessary to monitor the changes in water quality status associated with oil spills. Moreover, to sustain the productivity of the natural environment, strategic plans need to be developed for the protection of the water environment from the harmful effects of any oil spills. Besides these some trace element contents of *Heritierafomes* fruit and *pneumatophores* were also changed specially Fe and Zn content were very high but detectable amount of Cd and Pb were not found in *Heritierafomes* fruits and *pneumatophore*s. Finally, this study would helpful to measure the threaten affect on aquatic animals and different tree spices of the mangrove forest. The present study also open a door for further research to assessment the affect of high iron and zinc containing Sundari fruits dependent respective animals as well as the ecosystem of Sudarban.

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