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TRACE METALS AND TOTAL HYDROCARBON LEVELS IN SOIL AND BIOTA OF A SEASONAL WETLAND DRAINED BY MUNICIPAL RUNOFF FROM CALABAR, CROSS RIVER STATE, NIGERIA.

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ABSTRACT

Samples of soil and biota were collected from a seasonal wetland drained by municipal runoff near Calabar and analyzed for trace metals, total hydrocarbon (THC) and some related physicochemical parameters, to determine pollution levels, if any, of this wetland. Trace metals and THC in soil samples showed elevated mean levels of Fe (2149.25 ± 173.16µg/g), Pb (1.34 ± 0.44 µg/g), Cu (196.6 ± 78.0µg/g), Cd (0.949 ± 0.45µg/g), Ni (0.62 ± 0.57µg/g) and THC (283.5 ± 47.78µg/g). Fe, Cu and THC levels were higher than acceptable limits recommended by the Federal Environmental Protection Agency (FEPA), the Department of Petroleum Resources (DPR) of Nigeria and EPA. Results also indicated point source pollution from the municipality. Evidence of serious impact of these pollutants was observed. The observed high levels of some trace metal and THC and bioaccumulation factor, indicate that the seasonal wetland is not suitable for fishing and other ecological benefits.

KEYWORDS: Trace metal, THC contamination, municipal-runoff, bioaccumulation, wetland.

INTRODUCTION

Normal environmental conditions are altered when heavy metals and hydrocarbons pollute land and water (Giddings, 1973; Clark *et al*, 1997). Ogezi (1992) indicated that heavy metals were very significant in the environment because unlike the hydrocarbon pollutants they are not eliminated by natural processes such as biodegradation. Moreover, most trace metals are concentrated and released in food webs and may have the potential to cause adverse effects on humans through bioaccumulation (Ogezi, 1992; Clark *et al*, 1997).

Trace metals and hydrocarbon from sewage and industrial effluents are transported through runoff to drainage system and may be partitioned into water, sediments and biota on entering the wetland and aquatic environment (Wagner, 1974; ICES, 1991). It has been noted (Giddings, 1973; UNEP, 1992) that trace metals and hydrocarbon owe their source mainly to emission from fossil fuel combustion in power generation as well as industrial plants, refuse incineration, domestic sewage and agro-chemicals from nearby farms which are characteristic of municipal wastes that are transported by runoff into aquatic environments (Berry and Horton, 1974). Murray *et al* (1995) indicated that the much wider range of hydrocarbons found in marine plankton suggests that some of them may be of exogenous origin and this points to the anthropogenic nature of most hydrocarbons in aquatic environment (Clark *et al*, 1997). Urban runoffs carry wastewater drained from many parts of the municipality (Berry and Horton, 1974, Montgomery, 2000) and may transport such wastes into the aquatic environment.

A wetland is an area that is regularly saturated with surface or ground water and is characterized by prevalence of vegetation that is adapted to an aquatic environment of water-saturated soil condition (FEPA, 1991). Wetlands are ecologically important as they provide natural resources such as timber, wildlife with fishing grounds and serve as one of the sources of ecological control by generating O_2 and absorbing CO and CO_2. The latter process controls air pollution in adjoining urban areas (Raufu, 2000).

Rapid urbanization has a devastating impact on the environment of the wetlands of Nigeria whose area extent is about 3 million hectares (NEST, 1991). Cross River State of Nigeria alone has about 95,000 hectares of coastal saline or estuarine wetlands classified as flood plains (NEST, 1991). This could be badly polluted (GESAMP, 1997). The aim of this study, therefore, was to determine if the wetland adjoining Calabar Municipality where most of the runoffs drain into is contaminated by trace metal and hydrocarbons. The result for the study would be useful for municipal planning for environmental quality and resource control of this wetland as in fishing and extensive dry season farming. It will also provide baseline data for future environmental monitoring of this ecosystem.

MATERIALS AND METHODS

Study area

The study area is a seasonal wetland drained by municipal runoff, situated at the south eastern part of the ancient city of Calabar, (within latitude 4.5°N and longitude 8.22°E)(Fig. 1). It covers an area of about 5.77 km^2 and is situated near the Great Kwa River estuary in proximity of the Atlantic Coast. It is dry but with muddy soil during the dry season months of November to March. Calabar is a growing industrial and commercial city and the seat of State government but it is characterized by relatively low industrial activities but high population density. The main drainage channel runs from Municipality directly into this wetland often carrying indiscriminately disposed and untreated wastes that could be estimated at several metric tonnes per week with great potential for environmental hazards.

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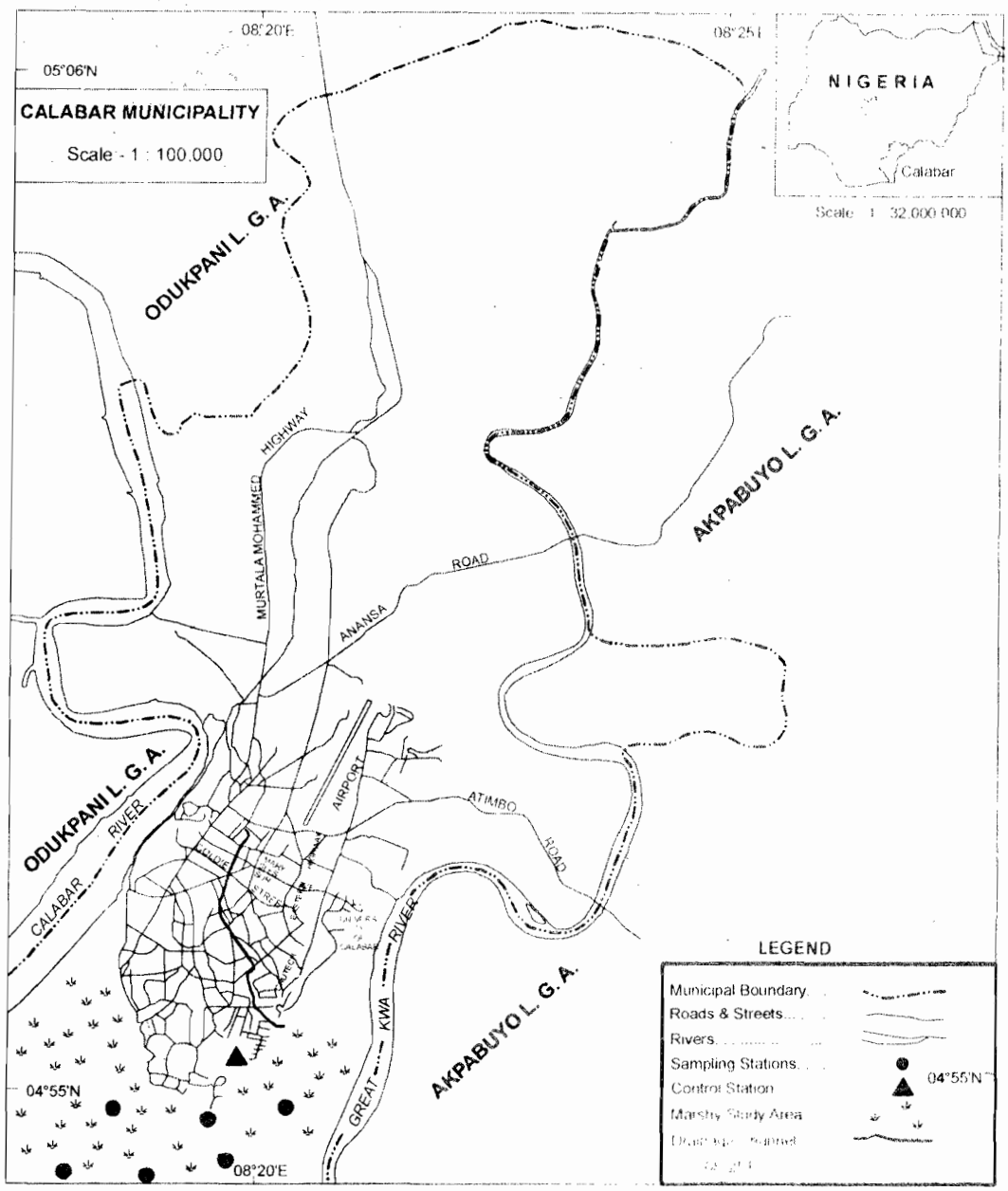

Fig. 1 Sampling stations at CRUTECH wetland area, Calabar Municipality

Sampling

Soil samples were collected at six (6) selected locations in a rectangular grid using soil tube and rammer (Rump and Krist, 1988) in the study area. Four stations were sampled from a location outside the study area not directly affected by municipal runoff and used for control. Composite samples from each station were taken in polyethelene bags to the laboratory for analysis.

Some samples were pretreated by drying at room temperature for three days, pulverized and sieved through 63µm mesh using a nylon sieve. These were then acid-digested using a mixture of 40% conc. Hydrofluoric (HF) acid and 70% aqua regia (HNO_3 – HCL (1:3 $^{v}/_{v}$)) to release the metal content into solution (Loring and Rantala, 1992). The pretreated samples were then analyzed for trace metals using a computerized HACH spectrophotometer, DREL 3000, at various wavelengths after colour development using various reagents (HACH, 1990). These are based on the principle of colorimetry (Skoog *et al*, 1988).

THC was determined by extracting it with a mixture of methanol and dichloromethane (60:40 $^{v}/_{v}$) and then analyzed using a HACH spectrophotometer DREL 3000 at a wavelength of 430 nm.

Particle grain sizes were determined by the hydrometer method (Bouyoucos, 1951) as modified by Gee and Bauder (1986).

The pH was determined using pretreated soil samples mixed with distilled water in ratio of 1:2 ($^{w}/_{v}$) by a Coring pH meter model 5 (Rhykard *et al*, 1995).

Total organic carbon (TOC) was estimated by the Walkley Black wet oxidation method using 1 gram of pretreated sample and converted (1.7 x C) to percentage organic matter (Agboola, 1986; Tack *et al*, 1996).

Biological specimens of snails (*Gastropoda* species), periwinkles (*Tympanotonus fuscatus*) and ferns (Cinnamon fern) were collected randomly in the study area and carried in plastic containers to the laboratories for analysis (ASTM, 1990; ICES, 1991).

Samples were washed thoroughly with distilled water to remove soil and other particles. The shells of the periwinkles were crushed to remove the soft tissues which were then washed and rinsed in distilled water. The soft tissue (5g) was homogenized using a steel blender. The homogenase was digested for hydrocarbon extraction by refluxing in 20ml of alcoholic KOH and 5ml of brine solution (ICES, 1991). Fern plant tissues were treated similarly. The digested tissue samples were then extracted for hydrocarbon by solvent extraction using a mixture of methanol/dichloromethane in the ratio 60:40 ($^{v}/_{v}$) (ICES, 1991). The biota were also acid-digested for trace metal analysis after drying in the oven for 6 hours at 105°C (Breder, 1982).

Bioaccumulation factor (BAF), the increase in concentration of toxicant in an organism relative to the concentration in the environment (Hardman *et al*, 1994) was calculated for organisms in this study on dry weight (dw) basis relative to soil sample.

Statistics

To find out if there existed significant relationship between trace metals and THC in the area, the data was subjected to Pearson product moment correlation between each of the metals and THC computation (Kerlinger and Peelhazur, 1973; Bowerman and O'Connell, 1977) and tested for significance using student t-test.

RESULTS AND DISCUSSION

Results of the analysis of soil samples for some trace metals and THC from various sampling sites are presented in Table 1. Table 2 shows the measurements from control area. Figure 2 shows the spatial variation in the levels of trace metals and THC in the study area. The comparative mean level for trace metals and THC measured in the study area with those from the control site are depicted in Figure 3.

The mean levels of most trace metals and THC in the study area were higher than those from control site (Tables 2 and 3), indicating that the study area has been contaminated by runoff water from this municipality. The control station does not receive direct runoff from this source. The observed high levels in soil of Fe (2015.0 – 2464.0 µg/g), Cu (65.0 – 282.0 µg/g) and their mean 2149.25 ± 173.16µg/g and 196.6 ± 78.03µg/g respectively, are higher than the acceptable limits of 300 and 25µg/g for Fe and Cu respectively (FEPA, 1991). The various locations had varying trace metal concentrations with Fe and Cu being the highest (Table 1). The order of accumulation of metals was Fe > Cu > Pb > Cd > Ni. Thus, Cd and Ni had the least measurements while V was not detected (ND). The presence of V in any environment is an indication of petroleum hydrocarbon contamination (NRC, 1985: Asuquo et al, 1999). Therefore this ecosystem may not have been seriously contaminated by petroleum hydrocarbon at the time of this study.

There was a significant difference ($p \leq 0.05$) between Pb and TOC although a negative correlation (Table 6) between the two. This may be due to chelation of Pb (Huheey, 1978) by the organic compounds in this wetland environment. The averagely high levels of some trace metals observed in this study could be generally associated with the wear and tear of equipment used for industrial processes besides some industrial activities such as the road side mechanic activities and metal works (FEPA, 1991). The runoff through piles of solid wastes from various sources including petrol stations and rusts from mechanic workshops are considered important sources. Automobile mechanic workshop is considered as the major source of metals in this municipality beside the artisan metal works dotting all over the city.

Table1: Mean levels of trace metals and THC concentrations from each station in the study area.

STN	Metals in µg/g						
	Fe	Cu	Pb	Cd	Ni	V	THC
1	2464.0	65.0	1.724	1.28	0.81	ND	208.2
2	2048.0	194.0	1.426	1.06	0.67	ND	275.2
3	2059.0	188.0	1.441	1.071	0.51	ND	[illegible]
4	2070.0	282.0	1.445	1.07	0.68	ND	309.0
5	2239.0	269.4	1.567	1.164	0.38	ND	280.0
6	2015.0	175.0	0.461	1.05	0.66	ND	353.8
$\bar{X}$	2149.25	196.6	1.34	0.949	0.618	ND	283.5
SD	173.16	78.04	0.45	0.45	0.57	ND	47.78

Table 2: Trace metals and THC concentrations from control station, showing mean and S.D.

STN	Metals in µg/g						
	Fe	Cu	Pb	Cd	Ni	V	THC
1	1750.0	173.0	0.422	0.90	0.056	ND	100.1
2	1752.0	172.6	0.421	0.89	0.058	ND	99.3
3	1753.2	172.8	0.422	0.91	0.057	ND	99.1
4	1752.5	173.1	0.421	0.92	0.058	ND	99.0
$\bar{x}$	1752.0	172.8	0.4215	0.905	0.0573	ND	99.13
SD	1.19	0.16	0.0005	0.01	8.29×10^{-4}	ND	0.7496

S.D. = Standard deviation
ND = Not detected

Table 3: Overall mean concentrations (µg/g) of each trace metal and THC in the study and control site.

	Fe	Cu	Pb	Cd	Ni	V	THC
Study area	2149.25 ± 173.16	196.6 ± 78.04	1.34 ± 0.45	0.949 ± 0.45	0.618 ± 0.57	ND	283.5 ± 47.78
Control Site	1752.0 ± 1.19	172.8 ± 0.16	0.421 ± 0.0005	0.91 ± 0.01	0.0573 ± 8.29×10^{-4}	ND	99.2 ± 0.7496

ND = Not detected

Table 4: Trace metal and THC levels in Biota in µg/g

Biota	Fe	Cu	Pb	Cd	Ni	V	THC
Periwinkle	83.5	51.50	0.07	0.05	0.055	ND	414.0
Snail	36.65	ND	ND	0.20	ND	ND	136.6
Fern	90.25	14.5	0.63	0.45	0.45	ND	1407.0

ND = Not detected

Table 5: Correlation between trace metals and THC levels in the study area

Metal	Correlation	t-value	Remarks
Fe	-0.8187*	3.188	Significant
Cu	-0.5583	1.505	Not significant
Pb	-0.8639*	3.836	Significant
Cd	-0.3417	0.813	Not significant
Ni	-0.2391	0.551	Not significant

* Significant $p \leq 0.05$

Table 6: Mean, S.D. and multiple correlation coefficient between trace metals and physicochemical parameters.

Metal	Fe	Cu	Pb	Cd	Ni	V	THC	$\bar{x}$	S.D.
PCP									
TOC	-0.3114	0.3047	-0.7258*	-0.2903	-0.4863	ND	0.7110	23.8	8.66
pH	0.2776	0.5108	-0.1689	-0.2453	-0.5960	ND	0.4175	5.53	0.25
%Clay	-0.7074*	0.1347	-0.4571	-0.7091*	0.1874	ND	0.5252	16.6	8.79
%Silt	-0.5345	0.0835	0.1394	-0.5477	0.0563	ND	-0.0099	28.67	3.59
%Sand	0.7599*	-0.7062*	0.0379	0.7358*	0.6374	ND	-0.5342	50.73	7.97
Mean	2149.25	196.6	1.34	0.949	0.618	ND	283.5	-	-
S.D.	173.16	18.04	0.45	0.45	0.57	ND	47.18	-	-

* Significant at 0.05 level, d.f. = 5, Critical r = 0.669
S.D. = Standard deviation

Table 7: Bioaccumulation factor (BCF) calculated relative to dry weight of soil sample

Biota	Fe	Cu	Pb	Cd	Ni	V	THC
Periwinkle	0.039	0.26	0.05	0.05	0.089	-	1.46
Snail	0.012	-	-	0.210	-	-	0.482
Fern	0.042	0.74	0.468	0.474	0.728	-	4.96

$$BCF_w = \frac{C_{org}}{C_w}$$

$$BCF_s = \frac{C_{org} \times Ka}{C_{sed} \times r}$$

Where BCF = bioaccumulation factor
C_{org} = THC level in biota
C_w = THC level in water
C_{sed} = THC level in sediment
Ka = the soil partition coefficient = ratio of THC in soil (sediment) to that in water
r = 2 for organics, empirically determined ratio of suspended matter (Mc Eldowney et al, 1994)

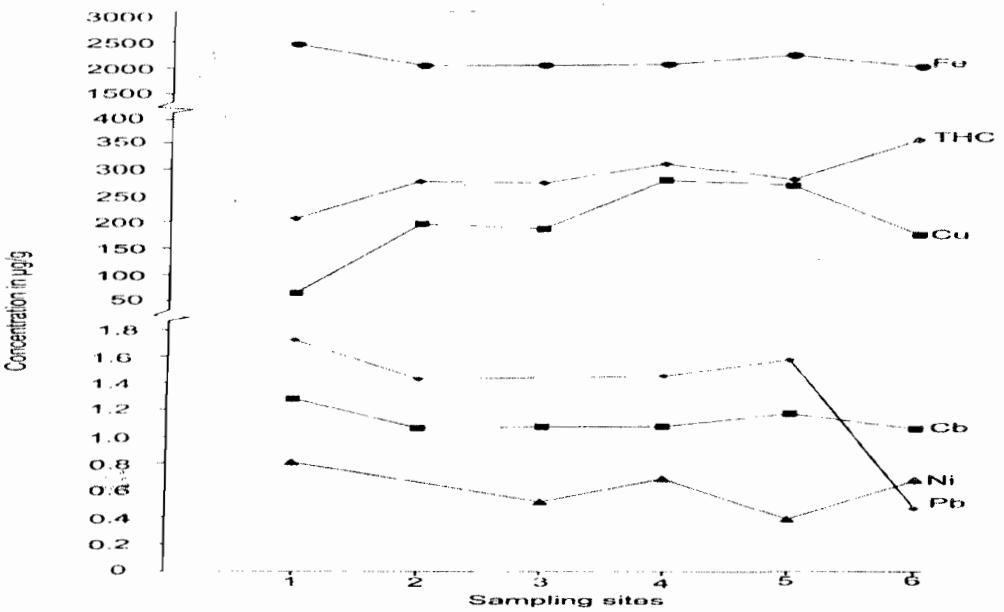

Fig. 2 Spatial variation of trace metals and THC in the study area

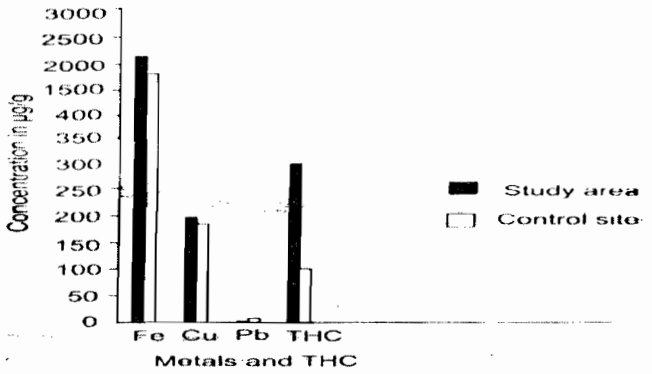

Fig. 3 Comparative mean level of trace metals and THC in the study area and control site (levels of other metals Cd, Ni and V were negligible in both locations

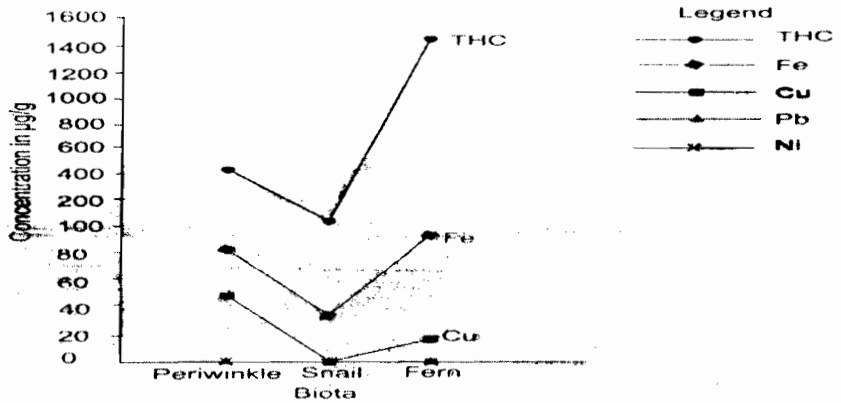

Fig. 4 Comparative plot of trace metals and THC level in each biota

Though Calabar city has relatively few industries whose metal contributions to this wetland may be minimal, atmospheric routes through fallout are possible (Parry *et al*, 1981; Clark *et al*, 1997). Indiscriminate burning of combustible wastes and forest fires are common in this geographical area coupled with gas flaring from nearby offshore petroleum wells.

THC level was very high in this environment. It varied between 99.0 – 353.8 µg/g with an average level of 283.5 ± 47.98µg/g in the study area. This is much higher than the limit (30mg/kg) set by DPR (1991). The level of THC in the study area is also higher than in the control site (Table 3). From Table 5 it is observed that all the metals (except Cu) correlate negatively with THC in the study area, again suggesting the absence of petroleum hydrocarbon or that petroleum as major source of hydrocarbon is neither present nor constitute a significant source of metal in this wetland. Normally, petroleum (especially crude oil) is a major source of trace metals in aquatic environments (NRC, 1985; GESAMP, 1993). Though Cu correlated positively with THC, the correlation coefficient is not significant (Table 6). The results also show that only Fe and Pb show significant ($P \leq 0.05$) correlation with THC. Apparently, runoff input carrying petroleum product such as the carelessly discarded waste engine oil from automobile workshops could have been responsible for the high level of THC (Odu, 1981) coupled with, perhaps, hydrocarbons from the swamp environment (Tissot and Welte, 1984; GESAMP, 1993).

The observed anomalously high levels of THC in soil (208.2 – 353.8 µg/g) and in biota (1407.0 µg/g) in fern, 136.6 µg/g in snail and 414.0 µg/g in periwinkle were all beyond the permissible levels of 100 mg/kg for sediments (Chemical Society of Britain, 1985) and 25 mg/kg for organisms (GESAMP, 1993).

The mean THC level in study area vary slightly from site to site (Table 1, Figure 2), with sites 4 and 6 having the highest concentrations of 309.0 µg/g and 353.8 µg/g respectively. The least polluted was site 1 with concentration of 208.2µg/g of soil sample. This may be due to its proximity to the municipality (dry land area) and an earlier contact with municipal runoff may not allow for much accumulation in soil compared to the down stream areas of the wetland where settlement is better enhanced due to accumulation of debris and sedimentation of denser particles (Loring and Rantala, 1992). Both trace metal and THC levels in this study are relatively higher than those of some industrialized areas of the world such as Japan with an average level of 27.5 µg/g of THC and much lower concentration for trace metals in similar studies (Chen et al, 1997). This is perhaps due to better waste treatment facilities and better regulatory control than in this country where there is indiscriminate discharge of untreated waste into the environment.

Accumulation of trace metal and THC in biota appears to be higher than in the soil samples (Table 1 and 4), though THC concentrations were anomalously high for both soil and biota. However, bioaccumulation factor (BAF) – the increase in concentration of toxicant in organisms relative to the environment (soil/sediments) (Hardman et al, 1994) calculated for this study (Table 7) suggests moderate contamination of trace metal but high for THC. BAF calculated on dry weight (dw) basis relative to soil sample suggest that fern had the highest value while snail had the least. BAF for all organisms except snail were unusually high (above a unit). This agrees with the unusually high level of THC in this ecosystem. Higher bioaccumulation factor suggests that the organism is more prone to high contamination, (Hardman et al, 1994). The order of bioaccumulation for the three organisms studied was Fern > Periwinkle > Snail suggesting also that the accumulations of contaminants and the potential for their pollution is in this order.

From the results and ongoing discussion it could be deduced that this wetland is contaminated with trace metals but definitely polluted with THC, implying that the organisms here are being polluted by THC. The results also indicate that municipal runoff is the major source of pollution in this wetland. In **conclusion,** this wetland is highly contaminated with trace metals and THC from the municipality through runoff and perhaps other sources (atmospheric fallout) (Sell, 1981). While the soil is highly contaminated with trace metal, it is polluted with THC. There is a strong evidence of bioaccumulation especially by aquatic plants as exemplified by the high level of contaminants (in fern plants) studied. This is a possible bioindicator of pollution in this study.

This wetland ecosystem appears to be more contaminated compared to some other regions of the world (especially most developed areas of the world). Therefore, effective control through environmental monitoring and improvement of waste treatment facilities is recommended for the Municipality.

RECOMMENDATION

This being the first study of its kind in this area, it is **recommended** that periodical pollution monitoring studies be carried out using results from this study as baseline data and relate their results to the pollution level of the Municipality to enable appropriate planning for environmental quality controls. Most especially, waste treatment should be encouraged before discharge into the drainage system of the municipality.

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