

Composition of the Water Soluble Fraction (WSF) of Amukpe Well-Head Crude Oil Before and after Exposure to *Pistia stratiotes* L.

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Abstract: The composition of the water soluble fraction of Amukpe well-head sample of crude oil before and after exposure to *Pistia stratiotes* was investigated. Ionic contents, heavy metals and physical characteristics were determined before and after exposure. The *Pistia* sp. was exposed to (full-strength), 100, 50 and 25%, WSF water (control, %WSF) for 5 days. The composition of the WSF changed during the experimental period. The following ionic components of WSF increased in concentration (Cl^- , NO_3^- , HCO_3^- , SO_4^{2-} , Na^+ , K^+ and Ca^{++}), heavy metals (Mn and Zn) and physical characteristics (TDS and EC). Heavy metals (Cu on the other hand and Fe) ions (Mg^{2+} and Fe^{2+}) and physical characteristics (pH) were found to decrease after exposure to the *Pistia*. The statistical analysis showed significant difference between control and WSF treatments.

Key words: *Pistia stratiotes*, water soluble fraction, crude oil, Amukpe well-head and composition

INTRODUCTION

Nigeria is an oil producing country and over 90% of her earnings come from oil. Delta State is a major oil producing area in the Niger Delta Region. Therefore, oil pollution effects are of interest to the Niger Delta. As long as the exploration and exportation continue in Nigeria, the incidence of oil spills and of hydrocarbon pollution will continue to be anticipated and studied.

The oil producing areas have been continually battered by the activities of oil companies (Ogri, 2001). Oil spillage takes place ever so frequently and this has serious implications for terrestrial and aquatic ecosystem. Therefore, the study of the effect of the Water Soluble Fraction (WSF) of crude oil is important in order to understand and possibly prevent their undesirable effects.

Crude oil contains a very small water soluble portion referred to as the Water Soluble Fraction (WSF) (Kavanu, 1964). Water soluble fraction is produced during a long period of oil water contact (Baker, 1970). When there is delay in clean up action for any reason, after spillage has occurred, the water soluble components of crude oil are given time to get well into the aquatic ecosystem. The components of crude oil that go into solution make up the WSF. Concawe (1979) reported that pure hydrocarbons yield 4.2 mg L^{-1} of WSF.

Water lettuce (*Pistia stratiotes*) belongs to the family Araceae and the order Arales (Akobundu and Agyakwa, 1998). It is commonly found floating in conglomerate in

stagnant or slow flowing water (Morton, 1961). The young plant is attached to the parent by a connecting stem which grows out of the stem. It may grow up as the young plant grows large, to render it independent. *Pistia stratiotes*, a free floating macrophyte, is separated by numerous spongy cells in the lower parts of the leaves, stems and roots. It is characterized by excessive proliferation which renders it a threat to water users. It is a macroscopic primary producer in the aquatic ecosystem. When sudden depletion of macrophytes occurs the ecosystem, an oligotrophic situation results (Camougis, 1981). In the short term, this directly affects the (flora and fauna) at the consumer level of the ecosystem. Indirectly and in the long term, the inhabitants and the environment are affected.

Edema and Okoloko (1997) reported the inhibitory effect of the water soluble fraction (WSF) of Escravos light and Odidi well crude oil on the growth and mitotic cell division of *Allium cepa*. Anoliefo and Okoloko (2000a) observed that the WSF of crude oil reduced seedling vigour and vine length and yield of *cucumeropsis manni* and affected the respiratory metabolism (Anoliefo and Okoloko, 2000b) of the same plant. Vwioko and Okoloko (2004) also reported growth depression in *Allium cepa*. Harris and Davidson (2002) stated that macrophytes take up elements in their ionic forms.

This study looks at the composition of the water soluble fraction of Amukpe well-head crude oil before and after exposure to *Pistia stratiotes* with a view of providing information on the impact and toxic level of the WSF.

MATERIALS AND METHODS

Sample area: Crude oil sample was collected from Amukpe in Sapele Local Government Area of Delta State. The crude oil was collected from Amukpe flow station (Well No 25) owned by Shell Petroleum Development Company of Nigeria Limited, while the experimental plant was collected from River Ethiope in Sapele Local Government Area of Delta State. The plant species is common in the area and enough quantity was obtained for the study. These 2 locations are situated between latitude $5^{\circ}5'$ and $6^{\circ}3'$ N, longitude $5^{\circ}5'$ and $6^{\circ}15'$ E of the equator.

Plant collection: The plants were collected by hand. They were gathered into and carried in plastic bags into the laboratory (Wood, 1975) and transferred to an aquarium for 7 days for culturing to acclimatize before use. Before use, the plant samples were washed with tap water to remove debris and then rinsed in deionized water (Harris and Davidson, 2002).

Preparation of Water Soluble Fraction (WSF): The WSF was prepared according to the method of Anderson *et al.* (1974). A sample of crude oil (500 mL) was slowly mixed in equal volumes of deionized water in 2 L screw cap conical flask. A Gallenkamp tabletop magnetic bar was used for mixing. Stirring was done for 20 h at room temperature ($28 \pm 1^{\circ}\text{C}$). The oil water mixture was allowed to stand overnight in a separating funnel. The lower phase was collected and used as stock or 100% WSF and diluted with water to give 50 and 25% strength WSF which were stored in screw-cap bottles prior to use.

Treatment: Control (deionized water) and 3 levels of treatments (25, 50 and 100%) were used. Each treatment, including control was in 5 replicates.

Growth medium analysis: The growth medium was analysed for heavy metals and ionic contents in WSF using the atomic absorption spectrophotometer (Model UNICAM, 969) and standard methods by APHA (1998). The pH values were measured by using a pH meter. Electrical conductivity (EC) values were measured with a conductivity meter (Model DDS-30). Total dissolved solids (TDS) is half of electrical conductivity value as described by Ademoroti (1996). Three replicates per treatment were analysed.

Statistical analysis: One-way analysis of variance was employed for this study.

RESULTS AND DISCUSSION

The results in Table 1 shows that the WSF of Amukpe well-head crude oil may be considered saline, as it contains the major ions that constitute the total salinity of water. The concentrations of the 4 major cations Ca^{++} , Mg^{+} , Na^{+} and K^{+} and 4 major anions, HCO_3^{-} , CO_3^{-} , SO_4^{2-} and Cl^{-} usually constitute the total ionic salinity of water for all practical purposes (Wetzel, 2001). Concentrations of ionized components of other elements such as N, P and Fe and numerous minor elements are of immense biological importance but are usually minor contributors to total salinity (Wetzel, 2001). The sum of all ionic concentrations is the basis for salinity measurement (Covich, 1993). Total dissolved solids and ionic conductivity of water are the generally used measurements (Covich, 1993).

The values of ions increased with increase in concentrations of the WSF prior to exposure. Also, there was increase in Cl^{-} , NO_3^{-} , HCO_3^{-} , SO_4^{2-} , Na^{+} , K^{+} and Ca^{++} values after exposure to *Pistia stratiotes*. This is in agreement with the report of McOliver (1981) that when there is an oil spillage more salts are released into the river. Thus, the amount of salts contained in the aquatic ecosystem increased. These increases could be due to leakage of the cells brought about by salt (Ionic) stress and associated oxidative damage (Burdon *et al.*, 1996). Salt stress refers to an excess of ions and is not limited to Na^{+} and Cl^{-} ions (Hopkins, 1999). The sum of ions in the WSF of Amukpe well-head crude oil had higher values than river waters of Africa as reported by Wetzel (2001). Salts influence the activities of aquatic plants resulting in the death of aquatic plants. Salt stress has been reported by Concawe (1979) to reverse the condition that could make essential nutrient available to plants thereby resulting in mitochondria damage (Cowell, 1977). The presence of ions in plants may block the oxidation of pyruvate for energy production (Anoliefo, 1991).

Decrease in the amount of Mg^{2+} and Fe^{2+} as presented in Table 1 indicates absorption or uptake of the ions by the plant cells. Macrophytes take up ions in their ionic forms (Harris and Davidson, 2002). This depends on the selective nature of the cell and the ions it can accommodate or sequester (Flowers and Hajibagheri, 2001).

The heavy metals detected before and after exposure to the aquatic macrophyte at the different levels of WSF treatments were Fe, Cu, Mn, Cr, Pb, V and Zn (Table 2). Botkin and Keller (1998) stated that Pb, Cr and V are among metals that pose hazard to living organisms. Heavy metals are non-biodegradable and toxic under certain conditions (Rana, 2005). The results in Table 2 shows reduction in values of Fe, Cu, Cr and V (100% WSF) after

Table 1: The ionic contents (ppm) of the wsf of Amukpe well-head crude oil before (BE) and after (AE) exposure to *P. Stratiotes* (values are mean and standard error in parentheses)

WSF	Chloride Ion (Cl ⁻)		Nitrate Ion (NO ₃ ⁻)		Sulphate Ion (SO ₄ ²⁻)		Hydrogen Carbonate Ion (HCO ₃ ⁻)		Sodium Ion (Na ⁺)		Potassium Ion (K ⁺)		Calcium Ion (Ca ²⁺)		Magnesium Ion (Mg ²⁺)		Iron II Ion (Fe ²⁺)		Sum	
	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE
25	15.9 0.00	49.53 2.38	0.16 0.00	0.34 0.01	1.68 0.01	0.14 0.02	61.00 0.00	151.83 0.38	29.00 0.06	28.10 1.15	11.80 0.01	16.13 1.13	1.94 0.01	1.94 0.01	1.61 0.01	0.51 0.01	0.24 0.00	0.01 0.00	123.33	245.5
50	20.26 0.00	49.90 2.04	0.19 0.00	0.39 0.01	1.97 0.00	0.18 0.01	81.00 1.00	153.50 0.44	30.30 0.00	37.57 1.20	12.8 0.06	18.57 1.02	2.8 0.03	2.8 0.03	1.7 0.01	0.81 0.01	0.25 0.01	0.02 0.00	151.27	263.7
100	25.50 0.29	50.34 1.87	0.19 0.00	0.54 0.00	2.73 0.01	0.29 0.00	122.4 0.21	255.30 0.59	33.00 0.00	49.27 0.33	11.8 0.01	16.13 1.13	4.29 0.00	0.96 0.00	2.06 0.05	1.57 0.16	0.29 0.00	0.21 0.01	206.26	385.8

Table 2: Heavy metal content (ppm) of the WSF of Amukpe Well-Head crude oil before (BE) and After (AE) exposure to *P. stratiotes* (values are mean and standard error in parentheses)

WSF of crude oil	Iron		Copper		Manganese		Chromium		Lead		Vanadium		Zinc	
	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE	BE	AE
25	0.24 0.02	0.01 0.00	0.08 0.01	0.01 0.00	nd 0.00	0.01 0.00	0.02 0.00	0.01 0.00	nd nd	nd nd	nd nd	nd nd	0.03 0.00	0.01 0.00
50	0.25 0.01	0.01 0.00	0.09 0.00	0.02 0.00	0.01 0.00	0.01 0.00	0.03 0.00	0.01 0.00	nd nd	nd nd	nd nd	nd nd	0.03 0.00	0.02 0.00
100	0.29 0.00	0.21 0.00	0.11 0.00	0.02 0.00	0.02 0.00	0.02 0.00	0.04 0.00	0.03 0.00	0.01 0.00	0.01 0.00	nd nd	0.01 0.00	0.03 0.00	0.04 0.00

Table 3: Physical Characteristics of (WSF) of Amukpe Well-Head Crude Oil Before (BE) and After (AE) Exposure to *P. stratiotes* (Values are mean and standard error in parentheses)

WSF	pH		Electrical conductivity (µScm ⁻¹)		Total Dissolved Solids (mg ⁻¹)		Sum (EC + TDS)	
	BE	AE	BE	AE	BE	AE	BE	AE
25	7.85 0.67	7.40 0.00	142.33 1.20	159.00 4.53	3.50 0.21	32.10 0.06	145.83	191.10
50	8.70 0.12	7.40 0.00	161.00 0.57	182.00 1.15	7.62 0.15	81.47 0.89	167.62	263.40
100	8.84 0.18	7.40 0.00	205.33 1.76	245.67 1.20	15.02 0.01	128.93 0.18	220.35	374.56

ND: Not Detected

exposure, while Mn and Zn showed increases in values. The reduction indicates uptake of the metals. Some amounts of these metals are essential for plant growth as micronutrients (Hopkins, 1999; Hoagland, 1972).

Table 3 shows the physical characteristics of Amukpe WSF before and after exposure to *Pistia* sp. The pH for Amukpe changed to about neutral level following exposure to *Pistia* sp. Also, following exposure to the aquatic macrophyte, the total dissolved solids increased remarkably in the well-head WSF source. Lowering of the WSF pH by aquatic macrophyte indicates that cations were taken up more than anions. The uptake of excess anions raises the soil pH (Wild, 1996). Low metal availability may be favoured by pH 7-7.5 (Wild, 1996). The pH values recorded were within the maximum permissible level for portable water 6.5-9.8 values of WHO (1995). The increase in electrical conductivity with the experimental plants is a sign of pollution. The higher the pollution level and related ionic concentration is, the higher is the electrical conductivity values because the

ability of an aqueous solution to carry on electric current depends on the presence of ions, their concentrations, mobility and valence (Ademoroti, 1996).

In all, the results in Table 1-3 show that the ionic, heavy metals and physical characteristics are within the maximum permissible limits of the WHO values by extension, therefore, the effect of growing *Pistia* in a water body polluted. By crude oil would include lowering of pH and a little uptake of some heavy metals. On the whole, however, it cannot be recommended as a pollution-remediating agent based on the results of this exercise.

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