

EFFECT OF CHEMICAL REMEDIATION OF CRUDE-OIL-POLLUTED AGRICULTURAL LAND ON SOIL PROPERTIES AND CROP PERFORMANCE

O. E. ESSIEN

Department of Agricultural and Food Engineering, University of Uyo, Uyo, Nigeria. Email: tobessien@yahoo.com

ABSTRACT

Chemical degreaser with detergent was used to wash crude-oil-polluted agricultural soil and restore it to 83% -93% of the unpolluted soil's status for sustainable productivity. Comparison of reclaimed soil's properties with unpolluted soil sample of the same area indicated no significant differences ($p=0.05$) between their values for soil moisture content, soil pH, evapotranspiration, root elongation and soil fertility. Root elongation at 1.1cm/day in the reclaimed soil compared with 1.29 cm/day in unpolluted soil indicated 83% recovery. Saturated hydraulic conductivity also had 83% recovery. However, infiltration rate showed a low recovery of 30%, perhaps, due to the wetness of the reclaimed soil's surface prior to the reclamation process. The soil macro/microspores were unblocked by the degreaser enabling the root pores to overcome the osmotic problem caused by oil-molecules' blockade and conduct moisture through to the phloem and leaves to sustain evapotranspiration, leaves turgidity and plant health. The chemical reclamation by degreaser with detergent is highly recommended for short-duration in-situ remediation of crude-oil-polluted agricultural land.

Keywords: *crude-oil degradation soil, agricultural land, chemical remediation, degreaser/detergent, crop performance.*

1.0 INTRODUCTION

Crude-oil spillage is one environmental cause of hazards eroding sustainable productivity of natural resources on the immediate and surrounding areas of its contact (Henry and Heinke, 2005). Its various hazardous effects have been indicated on agricultural soils and crops (Udo and Fayemi, 1975; Amadi et al., 1996; Roberts, 1997; Daniel-Kalio and Braide, 2004; Atubi and Onakala, 2006). These scenarios result in undevelopment of agricultural land, and a loss of farmers' equity and production efficiency because they affect the

interdependent socio-economic and environmental linchpins and their cultural matrices (Atubi and Onakala, 2006; Hugon, 2008). The loss by farmers of the ultimate and equitable goal of sustainable agricultural land development due to the conspiracy of oil-spillage degradation of the previously precious land has ignited community protests that consume millions of GNP to diffuse and for gross environmental improvement yet with little or without equitable attention to mitigating the causal situation (Aghalino, 2000).

In order to restore capacity and hope to continue in rightful exploitation of agricultural land resources to farmers, scaled but sometimes slipshod reclamation have been undertaken. However, remediation that drags on for many agonizing years to restore capacity often does not address the consonance of the immediate needs of the eager farmers to recapture their land for re-development and productivity. Reclaiming oil-polluted lands be immediate to avoid further damage to soil, water and aquatic resources amongst others (De Wrachien and Chisci, 1999). Therefore, a need arises to shortcut the long-duration remediation processes, like bio-remediation and natural restoration, by using quicker and, possibly, participatory-farmers process. One way of achieving this is by the chemical reclamation process that loosens the adhesive bonds of the large hydrocarbon oil molecules, breaks up and degrades them for flushing out of the soil in a matter of days, (not months not years as in bio-remediation and natural restoration) for a return of the soil to production. The effectiveness of such chemical remediation on restoring productive soil properties and crop performance within a short duration is the object of this investigation.

2.0 METHOD

2.1 Site Location

This experimentation was carried out on the crude-oil-polluted field located at the periphery of an area of oil leaks at Okorete in Eastern Obolo L.G.A, Akwa Ibom State, Nigeria. The field was planted with fruit trees quava and citrus. However, the trial crop was okra (*Abelmoschus esculentum Moench. L*)

2.2 Experimental Design

An incomplete randomized block design was used. Square portions of 4m x 4m were cleared in two locations in the farmland.. One plot was the crude- oil polluted area which was to be restored to original soil, while the other was original, unpolluted soil. Three replicates were made. The seeds were planted both in sample boxes with the representative soils augered into them, as well as in-place on the field. This allowed the soil samples to be manipulated easily and characteristics compared in sample and field plots.

2.3 Chemical Material/Application

The chemical for reclaiming the polluted soil was a degreaser/ detergent. The degreaser was sodium lauryl benzene sulfonate (SO_3Na). Into a bowl of water were added droplets of hydrophobic oil. In a short time, the very polar water molecules, and the oil then coalesced and floated to the top. When emulsion agent, such as detergent, was added, a suitable emulsion resulted, having a specific gravity of 0.86, an average molecular weight of 250g, and a normal alkylbenzene weight percentage of 94% (Whitten et al, 1985). These detergents of sodium of large chemical molecules are fatty-acids having a polar head and non-polar hydrocarbon tail. When they were added to an oil-water mixture in soil and the mixture vigorously shaken, a true emulsion was formed, which was then flushed out as in Whitten et al, (1985). The chemical was prepared by a contract chemist.

One liter of the degreaser chemical and a liter of ordinary detergent solution (in this case, OMO detergent) were poured into the oil-polluted soil through the double ring infiltrometer cylinder and allowed two hours to break the bonds that had trended to block the soil micro and macro pores.

2.4 Other Experimental Data

Other data collected by measurements were: moisture content, evapotranspiration, water deficit in plant leaves, and root elongation (the later two indicating crop response to soil water availability). Soil tests were carried out also to determine the following: engineering properties including permeability coefficient, infiltration rate, and soil fertility status including total nitrogen, total carbon and total phosphorus. From these data, the effect of chemical reclamation of the crude-oil-polluted agricultural field was evaluated. Some data on the initially crude-oil-polluted soil was obtained before reclamation process commenced.

For moisture content determination, soil samples were augered at different spots at depths of 15-20cm. They were taken in black poly bags (that prevented evaporation) to Agricultural Engineering Laboratory of University of Uyo, Uyo within few hours where they were weighed fresh, and then dried in an oven at 103°C for 24 hours. From oven, the split samples were brought out into desiccators and weighed again after cooling. The moisture content in % (dry basis) was obtained as:

$$\bar{O}_{ab} = (W_f - W_d) 100 / W_d \quad 1$$

where, \bar{O}_{ab} is moisture constant dry basis,

W_f and W_d are sample's fresh and dry weight, respectively (mg). The same process was used for both reclaimed and unpolluted soils. Evapotranspiration was obtained from representative samples of two soils by weighing the samples. A weighed empty container was filled to three-quarters of its volume with sample of the reclaimed soil. The same process was used for the control soil sample. The two containers were planted with okra seeds (*Abelmoschus esculentum*) and allowed five days to germinate. Equal volume of water was added to each container and weighed. The weights of the containers were measured daily and additional volume of water replenished as the need for replenishment arose in any of them. Root elongation was determined on representative soil samples. After the seeds had germinated in the two containers, they were allowed three days to stabilize before taking measurement of growth parameters. The seedlings in each container were carefully uprooted to avoid breaking, and their root-lengths were measured and average taken. The soil attached to the root hairs was shaken off and used to determine soil moisture. The exercise went on for eight consecutive days. Also, the weight of fresh leaves was measured concurrently while the oven dry weight was obtained the following day.

Infiltration rate was measured and computed using the double ring method (Reddy, 2006; Raghunath, 2008). Hydraulic conductivity (saturated) was obtained using variable head permeameter (Lui and Evett, 2000; Bhattacharya and Michael, 2003).

Soil fertility test involved the determination of values of pH, total organic matter content, total carbon, available phosphorus and total nitrogen. Soil pH was read from the pH meter with electrode inserted into the settled suspension. Available phosphorus was determined using Bousch and Lamb supertonic 70 electrophotocolorimeter (Wolf and Beagle, 1995). Total nitrogen was determined by the use of Kjeldahl digestion flask containing boiling chips (Bremmer, 1996). Soil organic carbon was obtained by mixing ground and sieved samples in 125ml Erlenmeyer flask and titrating the solution with 0.5N Ferrous Sulphate solution (Nelson and Sommers, 1996).

Statistical analysis: Parametric values of the reclaimed soil were compared with those of the unpolluted soil to estimate the levels of restoration using t-statistics, and ANOVA.

3.0 RESULT AND DISCUSSION

Soil moisture content (m.c.) and pH are compared in Fig.1. Chemical degreaser/detergent reclaimed the polluted soil from average mc of , as the t-test indicated no significant differences ($p=0.05$) for m.c. $7.1\%_{db}$ in initially crude- oil polluted soil to $9.4\%_{db}$ in reclaimed soil compared to $11.7\%_{db}$ in the unpolluted soil (Fig.1). This gave moisture holding capacity of 32.4% above the level in the polluted soil and a capacity restoration of 80.3% of the original level. This is very satisfactory as the t- test indicated no significant difference ($p = 0.05$) for m.c .between the reclaimed and the original soil samples.

The original (unpolluted) soil was already acidic at pH of 4.5, and chemical reclamation restored the polluted soil from its slightly weak acid level (pH = 5.7) to same strong acid (pH = 4.8) as the original (Fig 1). The t-test showed no significant difference ($p=0.05$)

between the unpolluted and the reclaimed soils. Bulk and dry densities for the unpolluted and reclaimed soils were 2.081 and 1.873 g/cm^3 and 2.81 and 1.870 g/cm^3 respectively, indicating no significant difference at $p=0.05$.

3.1 Evapotranspiration and Water Deficit in Plants

The evapotranspiration or loss of soil/plant water to the environment had distinctive profile in the reclaimed and unpolluted soils. While the original soil sample started off on 25th of September with 7.61 ml and ended on 20th of October with 7.49ml, the reclaimed soil sample started off with 7.78 ml and ended up with 7.71ml on the respective dates. These gave a consumptive use rate of 7.62 ml/ day on the reclaimed soil which showed no significant difference at $p=0.01$ on F-ratio test (Fig. 1). This shows that, although evapotranspiration was not below 7.5 ml/day in the control soil, the reclaimed soil may have had more wetness by its reclamation process to warrant a fractional excess of 24% above the average value of the control soil. Otherwise the restoration within 21 days to the original status was thorough and fast perhaps faster than the long duration process of bioremediation and natural restoration (compared Ayotamuno et al, 2005).

The moisture deficit in plant and its mass percentage are given in Table 1. Water deficit was, in this case, caused by osmotic failure due to soil pores and root pores blockage (CIGR, 1999). It varied in the replicates, but the overall average loss of mass of water in leaves were 71.1%_{wb} in the unpolluted soil sample and 68.9% in the reclaimed soil sample, which was only a marginal (not significant) mean difference (Table 1). However, the recovery by chemical reclamation restored full evapotranspiration functions to the crops on the soil so remediated. That means the blockade of the of the soil pores and plant roots pores were degreased and washed clean so that roots were able to absorb moisture from the soil and conduct same upwards through the xylem and phloem to the leaves to sustain evapotranspiration, plants or leaves turgidity and health (Michael, 1978; Abii and Nwosu, 2009).

3.2 Soil Nutrients and Soil Fertility Bola

The degreaser-and-detergent reclaimed soil showed no significant difference ($p = 0.01$) in its nutrient values compared to the original data except for phosphorus (Fig. 2). There was a remarkable recovery of total nitrogen at 0.25 mg/l back to the unpolluted soil's value of 0.24 mg/l. Same remarkable recovery was observed in total carbon at 0.22 m/l more than its original value of 0.15 mg/l, while mean available phosphorus at 0.63 mg/l recovered back to the 90% of original soil's value of 0.9 mg/l (Fig. 2).

This recovery was very significant at 0.01 when it is noted that in the crude-oil fouled soil these nutrient values were initially increased to 67% - 100% above the control soil's values (Abii and Nwosu, 2009; Essien and John, 2009).

However, since household detergent and some industrial wastes contain boron, which is a micronutrient that is essential for plant growth at low concentration (CIGR, 1999), the soil should be tested for it to avoid excess accumulation in the reclamation process with degreaser/detergent emulsion. Also, use of municipal waste water should be avoided.

3.3 Root elongation (plant Growth Index)

Root elongation in unpolluted soil went from 6.40cm in day 1 (25th September) to 22.00 cm on 12th day (6th October), giving a mean lengthening of 13.47 ± 6.35 cm; while it went from 6.38 cm on day 1 to 19.50 cm on the 12th day with a mean lengthening of $11.13 \text{ cm} \pm 4.77$ cm in the reclaimed soil. Root elongation versus time curve (Fig.3) in the unpolluted soil showed temporal variation in the rate of root movement. In the first five days root lengthened at the rate 0.79 cm/day; in the next ten days, root had a growth rate of 1.66cm/day, showing rapid elongation. Thereafter, it dropped to about 1cm/day giving average growth rate of 1.20 cm /day. The profile of elongation versus time (days) as shown in Fig.3 indicates a third degree mathematical relationship.

Root elongation rate in the reclaimed soil also had a temporal variation. In first five days, root grew at the reduced rate of 0.41 cm/day, followed by a smoother elongation in the next ten days at the rate of 1.60cm/day, giving average elongation rate of 1.1cm/day or 16% less than the rate in unpolluted soil, which means 84% restoration in the reclaimed soil. No significant difference was observed in the t-test (@ p = 0.05) between elongation rate in both soils. The mathematical relationship for the reclaimed soil was in the form:

$$Re = e^{at} \quad 2$$

with a slope line given by the equation

$$Y = 1.5144X + 2.8007, R^2 = 0.924 \quad 3$$

where Re is root nominal elongation (cm), t is time (days) and a = (ln Re)/t or is obtainable from the graph plot; and Y = line of slope and X = daily root elongation (Fig.3) The root elongation for the unpolluted soil was in the form of a third degree curve, and its slope line was given by the equation:

$$Y = 2.0431X + 2.23, R^2 = 0.94 \quad 4$$

3.4 Infiltration Rate and Hydraulic Conductivity

Infiltration measurement carried out at the onset of the experiment showed that the unpolluted soil infiltrated at a mean constant rate of 9.7cm/hr while that of the degreaser/detergent-reclaimed soil was considerable reduced to

2.5cm/hr indicating about 26% recovery. This low level may be attributed to the already wet nature of the reclaimed soil's surface. The value was higher than the 0.3 cm/hr for the fouled soil degreaser/detergent, causing increase in the infiltration from the abysmally low value of the polluted soil (0.3 cm/hr for the fouled soil. (Essien and John, 2009) showing that the pores of the soil were now opened by the degreaser/detergent, causing increasing increase in the infiltration rate from the abysmally low value of the polluted soil (0.3 cm/hr).

Table 2 compares the saturated hydraulic conductivity for the unpolluted and the reclaimed soil samples. It was observed that no significant difference (p = 0.05%) existed between the values for the polluted soils. The recovery was 83.4% on the average.

4.0 CONCLUSION AND RECOMMENDATIONS

Chemical reclamation of the crude-oil-polluted agricultural land was experimented with. It recovered 83 93% of the soil properties status, fertility and plant growth indices. Root elongation and water deficit recovered by 83% with elongation rate of 1.1 c/day in the reclaimed compared to 1.20 cm/day in the unpolluted soil. For soil fertility nutrients, there was a remarkable recovery back to original soil nutrient values. Evapotranspiration process was normal with no significant difference between the consumptive use value of 7.63 ml/day on the control soil and 7.72 ml/day on the reclaimed soil.

The soil macro/micro pores were unblocked enabling root pores to overcome the osmotic problem previously caused by the blocking oil molecules and to conduct moisture through to phloem and leaves to sustain evapotranspiration, turgidity and plant health. However, soil infiltration recovered substantially at 30% of the unpolluted soil perhaps because of the wetness of the reclaimed soil during the reclamation period. However, saturated hydraulic conductivity, which recovered 83.4%, and soil pH were not significantly less than the original soil status. Since boron is usually in household detergent and municipal/industrial waste waters, it should be tested for in the soil after using chemical degreaser/ detergent. Similarly, municipal waste water should be avoided in applying irrigation to the reclaimed soil. Chemical reclamation by degreaser and detergent is highly recommended for short-term reclamation of crude-oil polluted agricultural land.

REFERENCES

Abii, T. A. and Nwosu, P. C. (2009). The Effect of Oil-Spillage on the Soil of Eleme in Rivers State of the Niger Delta Area of Nigeria. *Research Journal of Environmental Sciences* 3(3): 316-320.

Aghalino, S. O. (2000). Petroleum Exploration and Agitation for Compensation by oil Mineral Producing Communicaties in Nigeria. *J. Environ. Policy Issues* (1): 11.

Amadi, A., Abbey, S. A. and Nma, A. (1996). Chronic Effect of oil Pollution on Soil Properties and Microflora of a Rainforest Ecosystem in Nigeria. *Water, Air and Soil Pollution* 86:1-11.

Atubi, A. O. and Onakala, P. C. (2006). The Socio-Economic Effects of oil Spillage on Agriculture in the Niger Delta. *J. Environ. Stud.*, 2:50-56.

Ayotamuno, M. J., Kogbara, R. B. (2005) Bioremediation of a Crude-Oil Polluted Agricultural Soil in Port Harcourt, Nigeria, using different levels of Nutrients Application. Proceedings of the 6th International Conference and 27th AGM of the Nigerian Institution of Agricultural Engineers (NIAE), December 12-15th, 2005, Yenagoa. Vol. 27 pp 352- 360.

Bhattacharya, A. K. and Michael, A. M. (2003). *Land Drainage: Principles, Methods and Applications*. Konark Publishers Pvt. Ltd., Delhi 110092.

Bremmer J. M. (1996). Nitrogen Total. In D. L. Sparks (Editor). *Methods of Soil Analysis, Part 3, Chemical Methods*. Soil Science Society of America Book Series. Number 5 pp 961-1010.

CIGR (1999) *Handbook of Agricultural Engineering, Volume 1, Land and Water Engineering* (van Lier, H. N. and L. S. Pereira, Editors) p 113-520.

Daniel-Kalio, L. A. and Braide, S. A. (2004). The Effect of Oil Spill on a Cultivated Wetland Area of the Niger Delta. *J. Nig. Environ Soc.* 2(2): 153-158.

De Wrachien, D., and Chisci, G. (1999). *Land Reclamation and Conservation (soil reclamation)*. In CIGR Handbook of Agricultural Engineering Vol. 1 pp 113-520.

Essien, O. E. and John, I. A. (2009). The Effect of Oil-Spillage Pollution and Chemical Remediation on Agricultural Soil Properties and Crop Growth. *Journal of Applied Sciences, Engineering and Technology* (in press).

Henry, J. G. and Heinke, G. W. (2005). *Environmental Science and Engineering*, 2nd Edition. Prentice-Hall of India, New Delhi 110001. pp 1 137.

Hugon, P. (2008). Sustainable Development Issues in Africa. In *Africa Geopolitics, Africa and Sustainable Development*. No. 29 (Jan-March): 63-76.

Lui, C. and Evett, J. B. (2000). *Soil Properties: Testing, Measurement and Evaluation*, 4th Edition. Prentice-Hall, New Jersey.

Michael, A. M. (1978). *Irrigation: Theory and Practice*. Vikas Publishing House, New Delhi, 801p.

Nelson, O.W. and Sommers, L.E. (1996). Total Carbon, Organic Carbon and Organic Matter. In D.L. Sparks (Editor). *Methods of Soil Analysis, Part 3, Chemical Methods*. Soil Science Society of America Book Series, No.5 pp 961-1010

Raghunath, H. M. 2008 *Hydrology: Principles, Analysis and Design*, Rev. 2nd Edition. New Age International Publishers, New Delhi.

Reddy, P. J. R. (2006). *A Textbook of Hydrology*: Laximi Publications, New Delhi.

Roberts, H. J. (1997). Oil Contaminated Soil and Some Reclamation, *J. Soil Sci.* 24:231-245.

Udo, E. J. and Fayemi, A. A. (1975). The Effects of Oil Pollution of Soil on Germination, Growth and Nutrient Uptake of Corn. *J. Environ Quality* 4(4): 534-540.

Whitten, K. W., Gailey, K. D., Davis, R. E. (1985). *General Chemistry*, 3rd Edition. Saunders Holder Sunburst Series.

Wolf, A. M. and Beagle, D. B. (1995). Recommended Soil Tests for Micronutrients Phosphorus, Potassium, Calcium and Magnesium. In Thomas Sims and A. Wolf (Editors), *Recommended Soil Testing Procedure for Northeastern United State*. Northeast Regional Bulletin No.493, Agricultural Experiment Station, University of Delaware, Newark, DE, Pp 25-34.

Table 1: Moisture deficit in plant (ml) and percentage loss by mass of leafweight.

Replicates	Control Soil			Reclaimed Soil		
	Ww	Wd	Dw	%Loss wb	Wd	Dw
1	4.40	1.80	2.60	58.60	1.80	58.60
2	6.40	1.82	4.78	74.70	1.82	74.70
3	6.40	1.84	4.78	74.40	1.84	74.40
4	5.60	1.52	4.08	72.90	1.52	72.90
Avg.		4.05	70.15		3.54	68.40
Sd		±1.02	27.74		±0.63	25.77

Note: Ww = wet weight, Wd = weight, Dw: moist deficit weight, %Loss wb = percentage moisture loss (wet basis). Scale: 1ml = 1gm of water, 1-cal = 1, 0.6108 = 1.433, implying no significant mean difference at p = 0.100

Table 2: Saturated hydraulic conductivity for Control and Reclaimed Soil

Replicates	Time, sec	K _{sat} Control Soil, cm/sec.	K _{sat} Reclaimed Soil, cm/sec.	t-test/ significance	Recovery
1	61	0.025	0.023	ns, p=0.01	88.5
2	50	0.024	0.018	ns, p=0.05	67.0
3	40	0.023	0.018	ns, p=0.05	71.0
4	30	0.022	0.20	ns, p=0.01	91.0
5	20	0.022	0.022	ns, p=0.01	100
Gen.					
Average		0.023	0.018		

Note: K_{sat} = Saturated hydraulic conductivity, ns=not significant at P= 0.05, Recovery, % = $\{1 - (K_{reclaimed}/K_{satcontrol})\} \times 100$

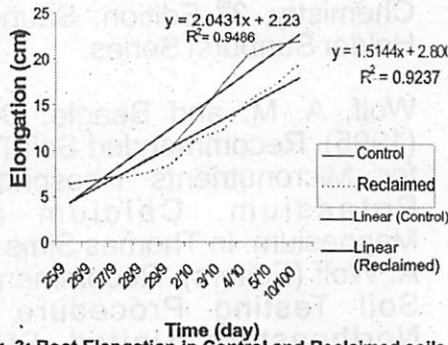


Fig. 3: Root Elongation in Control and Reclaimed soils

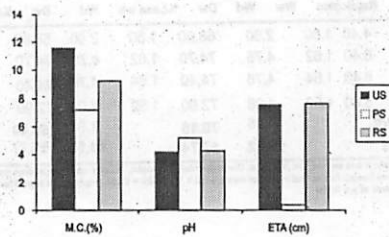


Fig. 1: Comparative Bar charts of Moisture content (m.c. db), pH and Evapotranspiration (ETA) for Control (US), Polluted (PS) and Reclaimed (RS) soils.

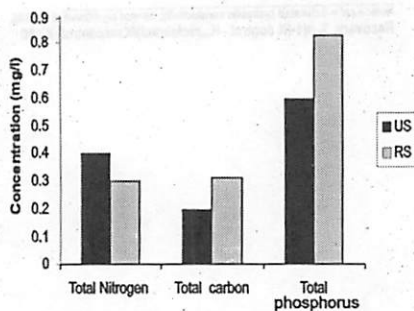


Fig. 2: Bar chart for component Nutrient composition in Control (US) and Reclaimed (RS) soils