CHAPTER 4

CONCLUSIONS FROM THE STUDY
4.1 Conclusions from the study on soil quality damages due to oil field activities

1. The results of the present investigation reveal some important observations of soil physicochemical parameters.
2. The results have shown that all the soil parameters determined in the present study are affected by the contamination of produced water and crude oil.
3. The results have indicated that the pollutants released by the oil field operations have spread into considerable distance affecting the soil quality.
4. The uncontaminated soils of Rudrasagar and Lakowa are acidic in nature. It is seen that soil pH decreases with increase in distances from GGSs. Thus the soils near the GGS’s are either less acidic or alkaline in nature. The normally acidic soils of the agricultural fields turn alkaline near the GGSs due to discharge of alkaline effluent (pH of produced water=7.5) from the oilfield operations.
5. The soil pH depends on the presence of acidic or basic components supplied by the effluents. The rates of penetration of different components into soil are different. Due to the different rate of infiltration of different components the pH values are found to be different in different depths. The surface soils are directly affected by the produced water and hence they have a tendency to become more alkaline than the other soils. The present study reveals that in a particular location the pH value of the surface soil is greater than the middle soil as well as the bottom soil. The bottom soil shows the least value as compared to the surface and middle soil.
6. The present study reveals that redox potential has a tendency to turn negative or much less near the GGS. The redox potential value of produced water is found to be negative (-) 0.068mV. Discharge of produced water to the nearby areas of the GGSs is responsible for the negative or less redox potential of soils near the GGSs.
Thus the extent of pollution can be measured directly by using negative redox potential \((-\text{E}_h\))). The depth wise variation of \((-\text{E}_h\)) values is also similar to that of \(p^H\) values. In general, the \((-\text{E}_h\)) value of surface soil is found to be greater than the middle soil as well as the bottom soil. The least value is obtained for the bottom soil.

7. It is observed that the values of soil parameters at 500m distance from the GGSs are either equal or nearly equal to the Control soil values. After 500m the probability of pollution due to the horizontal spreading of effluents from the GGSs becomes negligible. Thus, the horizontal spreading of the effluents is most effective up to a distance of about 500m.

8. Generally, the soils near the GGSs have higher electrical conductivity than those away. Due to the discharge of ionically rich produced water (EC, 3.20mS/cm), the soils near the GGSs contain high amount of ions. This results in the high value of electrical conductivity. This is in accordance with the results obtained for \(p^H\) and \((-\text{E}_h\)) as discussed earlier.

9. The depth wise variation of electrical conductivity reveals that in a particular location the electrical conductivity value of the surface soil is generally greater than the middle soil as well as the bottom soil. The bottom soil shows the least value as compared to the surface and middle soil. This type of variation was also found in case of \(p^H\) values. Any soil parameter not only depends on the infiltration of the effluent but it also depends on the different rates of infiltration of different constituent salts of the effluent. Electrical conductivity is related to total amount of ions or salts but \(p^H\) depends on whether the salt accumulated is acidic or alkaline. Due to this reason, in some cases the depth wise variations obtained for the \(p^H\) of the soils were found to be different from the variations observed for the electrical conductivity values.

10. Crude oil is hydrophobic in nature. Due to considerable input of hydrophobic organic substances into soils from spillage of crude oil (TPH=47.22%) the soils near the GGSs have less tendency to hold water. The present study shows that water holding capacity (WHC) values of the soils near the GGSs are less than the values obtained for the soils away from the GGSs. From the comparative
discussions of WHC and TPH it is seen that the results obtained for WHC can be explained mainly in terms of the impact of spillage of crude oil.

11. For the depth wise variation of WHC, it is necessary to consider both the factors, i.e., contamination of soil by crude oil as well as the presence of naturally occurring humic substances. In most of the cases the bottom soils show least WHC values. This is due to the less amount of humic substances at the bottom soils. In many cases surface soils show lesser WHC value than the middle soils. This may be due to the presence of more hydrophobic substances at the surface.

12. The soil texture results indicate loam type nature of uncontaminated oil field soils. The results also imply a considerable input of sand particles from oil field activities. Five major types of textural classes were detected in the soil samples of contaminated sites. These are: loam, sandy loam, sandy clay loam, silty loam and loamy sand. Distance wise as well as depth wise variation of soil texture is not very clear from the obtained results.

13. The crude oil contains substantial amount of carbon (28.08%, Walkley and Black method) and this contributes to the TOC content of the soil. The present study reveals that the TOC contents of oil-contaminated soils are high. The increase in TOC due to the presence of crude oil is not beneficial for plant growth as it alters the carbon – nitrogen ratio in the soil. Most of the trends are indicative of decrease in TOC content with respect to increase in distance. It is interesting to note that variation of TOC with respect to distance in majority of the cases is opposite to that of variation of WHC with respect to distance. This means that in contaminated sites WHC decreases with increase in TOC (mainly due to the presence of hydrophobic crude oil).

14. The carbon content in different depths depends on different factors like rate of infiltration of crude oil, evaporation of crude oil, biodegradation of crude oil in the different depths etc. In most of the cases the surface soils show higher value of TOC than the other soils while the TOC content of a bottom soil in majority of the cases is generally smaller than the other soils. This may be attributed to the presence of more hydrocarbons at the surface and less at the bottom.

15. TPH is the most important parameter to evaluate the pollution status of a site. In uncontaminated sites there is no petroleum hydrocarbon in the unpolluted soils
which is clear from the fact that the value of TPH (%) value in the uncontaminated sites is zero. So a non-zero TPH value will directly indicate the polluted nature of the soil. But it is also to be remembered that due to the natural degradation of crude oil a polluted soil after some time may not show the presence of petroleum hydrocarbons.

16. In general, WHC decreases with the increase in TPH content of soil. On the other hand, TOC increases with the increase in TPH. Present study reveals significant negative correlation between WHC and TPH while the correlation between TPH and TOC was found to be significantly positive. The relations of TPH content with TOC and WHC are very important to study the oil polluted soils.

17. The results suggest decrease in TPH content with respect to increase in distance. In most of the cases the least TPH value is observed for the bottom soil while the surface soil shows maximum TPH content.

18. The present study reveals the presence of large amount of anions in the oil field soils. This may be attributed to the contamination of soils by produced water which is very rich in soluble salts of anions like chloride, sulphate and phosphate.

19. In the present study the second batch of soil samples shows that in most of the distances the chloride contents are same and hence no variation is observed with respect to distance. This may be due to the high rate of horizontal flow of chloride ions which makes the chloride contents equal in different distances. Chloride ions may also penetrate to the deeper depth easily and after a long time the chloride content at surface soil will become optimum with respect to the soil characteristics. This will give rise to an equal value of surface soil chloride contents in different distances. But generally chloride content decreases with increasing distances from the GGS’s as shown by the results obtained from the first and second batch of soil samples. This may be due to the fresh discharge of produced water at the time of sample collection.

20. The other anion contents, ie, sulphate content and phosphate content show clear trend of variation with respect to distance. In these cases the amount of an anion decreases with increasing distances from the GGSs.

21. The study reveals that in a particular location the ionic content of the surface soil is generally larger than the middle soil as well as the bottom soil while the bottom

226
soil in majority of the cases shows the least value as compared to the other soils. Some exceptions were also observed which may be attributed to the infiltration capacities of various salt components of the produced water.

22. Produced water is very rich in cations like sodium and potassium. The soils of the agricultural field near the GGS have tendency to contain high amount of sodium and potassium due to the discharge of produced water during oil field operation.

23. The results obtained from the analysis of the soil samples of all the batches reveal that the sodium and potassium contents, similar to pH values, decrease gradually with increasing distances from the GGSs. This reveals that concentrations of sodium and potassium depend on the accumulation of produced water near the oil field soil. This indicates that the main source of these ions is produced water.

24. Iron is a very abundant element of earth’s crust. Also, crude oil is a rich source of iron content. Due to these reasons the oil field soils contain large amounts of iron. The study reveals that the soils of the agricultural field near the GGSs contain high iron content due to the spillage of crude oil during the oil field operations.

25. It is seen that aluminium contents of contaminated soils as well as uncontaminated control soils are very high. It is due to the fact that aluminium is the second most abundant element in the earth’s crust followed by Si. From the results obtained from crude oil analysis it was found that crude oil is a rich source of aluminium. Due to the spillage of crude oil during the oil field operations the oil field soils contain large amounts of aluminium.

26. The soils of the agricultural field near the GGS contain appreciable amounts of cadmium. The analysis of the collected crude oil sample suggests that crude oil is a rich source of cadmium. During the oil field operations the crude oil may accidentally enter the soils of the agricultural field near the GGS and increases the cadmium content. Similarly, crude oil also contains an appreciable amount of cobalt. The study reveals that crude oil polluted soils of the agricultural field near the GGS contain cobalt in high amount as compared to the control soils.

27. Many of the solid materials generated during the oil field activities include chromium. The study reveals that crude oil also contains a high amount of chromium. The present study reveals elevated amount of chromium in the
contaminated sites due to the contamination of soils by chromium containing pollutants.

28. Crude oil analysis shows that crude oil is a rich source of copper. It is seen that the oil-polluted soils of the agricultural fields near the GGSs contain appreciable amounts of copper. In all the fields, the soils of the control sites, recorded the minimum copper content. Similarly, the soils of the agricultural fields near the GGSs are found to have high manganese content due to the spillage of manganese-containing crude oil.

29. The present study reveals that the nickel contents of uncontaminated control soils are below the detection limit the contaminated soils contain appreciable amount of nickel. This indicates considerable input of nickel from crude oil or the waste materials generated during the oil field activities.

30. Crude oil contains lead in an appreciable amount. The present study indicates that lead is not only present in the oil-contaminated soil but it also present in the control soil samples where no impact of crude oil is expected. The lead content in control soils may be due to the contamination of soils by Pb present in automobile exhaust or Pb-containing paints.

31. Presence of an appreciable amount of zinc in crude oil was observed during the analysis of crude oil. Present study reveals that uncontaminated as well as contaminated soils contain appreciable amount of zinc. Oil-polluted soils of the agricultural field near the GGS, in general, contain higher amounts of zinc than the control soils. The contamination of soils by crude oil results in the increase of zinc content of soils.

32. Crude oil as well as the waste materials generated during the drilling activities in an oil field contains mercury. The present study reveals the presence of mercury in the contaminated soils. In case of uncontaminated soils the mercury content is found to be below the detection limit.

33. The results of the present study revealed that in a particular location the metal content of the surface soil, in general, is greater than the middle soil as well as the bottom soil. The bottom soil shows the least value as compared to the surface and middle soil. The metal content of a middle soil is generally smaller than the surface soil but greater than the bottom soil.
34. On the basis of the above facts it is clear that soil pH, (-)Eh, EC; concentrations of major anions like chloride, sulphate and phosphate; and cations like sodium and potassium depend on the extent of pollution of soil by the accumulation of produced water.

35. The present study also reveals that WHC, TOC and the amount of metals like Fe, Al, Cd, Co, Cr, Cu, Mn, Ni, Pb, Zn and Hg in soils depend on the TPH values. The present study clearly indicates the presence of appreciable amount of these metals in crude oil. Thus the main source of these ions is crude oil.

36. From the available results of first batch of soil samples it is clear that within a GGS different directions are polluted to different extent. The present study determines the spots within a GGS showing the maximum (minimum in case of WHC) values of parameters. Direction wise variation becomes more complicated with the inclusion of different depths but it becomes less complicated if the average of the three values (i.e., surface soil value, middle soil value and bottom soil value) in a particular location is considered. With a few exceptions, the maximum values of pH, (-)Eh, EC, Cl\(^-\), SO\(_4^{2-}\), PO\(_4^{3-}\), Na and K within a GGS are obtained in the same spot. Similarly, the maximum values of other metals (except Na and K), TOC, TPH and minimum values of WHC within a GGS are obtained in a same spot.

4.2 Conclusions from the study on accumulations of metals in plants grown in crude oil contaminated sites

1. The present study indicates presence of seven heavy metals (Cd, Cu, Zn, Fe, Mn, Ni and V) in rice grains, rice husks, papaya fruits, tea leaves, banana, *Ziziphus jujuba* Lamk., *Brassica juncea*, Hk. F. & Th., and brinjal in varying amount.

2. The results obtained from the analysis of rice grains and rice husks revealed that different parts of a plant contain an element in different concentrations. The results also indicate that the distribution pattern of metals in different plant parts varied depending on the metal.

3. Results revealed that in most of the cases Fe, Mn and V content are in appreciable amount.
4. The results revealed that rice grain and rice husk contain Fe and Mn in high abundance. Fe is the most abundant element in rice grains for all the sites. In case of rice husks collected from contaminated sites the most abundant element is manganese whereas iron is the most abundant element in rice husks collected from uncontaminated sites. Cd is the least abundant element for rice grains whereas Ni is the least abundant element for rice husks. The presence of high amount of iron and manganese in rice husks is of special importance.

5. Tea leaves also contain Fe and Mn in high abundance. Fe is the most abundant element in the uncontaminated samples of tea leaves but in contaminated samples Mn becomes more abundant. Tea leaves are also important sources of V, Zn, Cu, and Ni but they are not major sources of Cd. Accumulation of Cd in tea leaves as well as in *Brassica juncea, Hk. F. &Th.* leaves is less though Cd is considered to be absorbed effectively by leaf system. In general, Cd is the least abundant element in most of the plant samples.

6. An interesting fact is that papaya fruits contain all the elements in good amounts. It is observed that in case of papaya Zn accumulation becomes more prominent with the increase in contamination of soil by crude oil. Uptake of nickel by banana in the contaminated soils is of special interest as this reverses the usual trend of Zn to Ni concentration in uncontaminated samples. It is important to note that vanadium is found in very poor amount in *Ziziphus jujuba Lamk.* and brinjal. *Brassica juncea, Hk. F. &Th.* leaves are very rich source of iron and manganese.

7. Accumulation of seven heavy metals (Cd, Cu, Zn, Fe, Mn, Ni, and V) in plants varied depending on the growth site. It was observed that metal concentrations in plants were increased with the increase in contamination of growth soil by crude oil. Extent of increasing concentration varied with the type of element and also with the type of plant tissue.

8. The results obtained from the present study indicate that the consumption of rice and other edible plant parts collected from contaminated area may pose a serious risk to human health due to toxic concentration of metals like cadmium.
4.3 Conclusions from the study on the effects of pH and N-P-K fertilizer on degradation of petroleum hydrocarbons in oil contaminated soil

1. The results obtained from the remediation experiment revealed that the degradation of crude oil was very good at pH 4.5 and showed identical TPH degradation (enhanced degradation) pattern similar to the 'Control soil' with pH 5.0 (original pH). This may be due to the fact that biological activity in the soil is less affected by small pH variation. As the 'Control soil' is acidic in nature these observations may be attributed to the members of the indigenous microbial community.

2. The soil samples whose pH was adjusted to 5.5 and 6.5 showed enhanced degradation at lowest TPH content (initial TPH=0.3%) and decreased degradation at other higher TPH contents (initial TPH=1.5, 3.0 and 5.5%) as compared to the degradations at original pH. The enhanced degradation at lowest initial TPH concentration may perhaps be due to the favorable evaporation of PH's or use of the PH's in other physical processes. At other higher 'TPH's these processes are not predominant due to high initial TPH. The soil sample whose pH was adjusted to 8.5 showed identical TPH degradation as above.

3. The soil pH between pH 5.5 and 8.5 encourage microbial activity.

4. The soil sample whose pH was adjusted to 3.5 showed less TPH degradation at all initial TPH concentrations. This may be due to the decreased microbial activities at very low pH 3.5 as compared to original pH 5.0.

5. The study conducted at different pH's showed that the remediation was the highest at pH 7.5. This may be due to the fact that microbial activity is greater at or near neutral pH, which enhances degradation processes, mineralization, and nitrogen transformations (e.g., nitrogen fixation and nitrification).

6. The common order of degradation (Dph) (measured as total percentage loss in TPH) at each TPH (except at TPH 0.3%) according to pH variation is as follows:
   \[ D_7 > D_4 > D_{ORIGINAl} > D_5 > D_6 > D_8 > D_3 \]
   At TPH% 0.3% the order is slightly different:
   \[ D_7 > D_4 > D_5 > D_6 > D_8 > D_{ORIGINAl} > D_3 \]
   The less degradation at
original pH may be due to the non-treatment condition i.e., absence of pH controlling reagents.

7. The degradation continued to improve with time up to 180 days. Thus, the pH factor affected total petroleum hydrocarbons (TPH) degradation.

8. The present study reveals significant degradation of petroleum hydrocarbons with the addition of N-P-K fertilizer. The common order of degradation ($D_{\text{pH/NPK\%}}$) (at initial TPH 3.0%) according to N-P-K variation after six months of experimentation is as follows: $D_{7.5/90\%} > D_{7.5/60\%} > D_{7.5/30\%} > D_{7.5/0\%} > D_{\text{ORIGINAL}/0\%}$ The results suggest improved degradation with increase in concentration of N-P-K fertilizer. Soil responded most positively to 90% more N-P-K fertilizer.

9. The study reveals that both factors (that is optimum pH and N-P-K fertilizer) in combination increased the total petroleum hydrocarbons (TPH) degradation. This will, ultimately, help in preparing a suitable strategy for remediation of petroleum hydrocarbon contaminated soil.