

*Summary
&
Conclusion*

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The Gulf of Suez has been and still subjected to severe oil pollution especially due to the massive ship movements in the Suez Canal and the different petroleum activities concentrated in this area. Environmental assessment of petroleum contamination with special emphasis to polynuclear aromatic hydrocarbons taking place in Tamsah Lake, Suez Canal and Suez Gulf to identify the origin and sources of hydrocarbon contaminants as well as the levels and sources of PAHs present has been studied. This study is a part of a long monitoring programme put by the Egyptian Petroleum Research Institute.

The first step in assessing the environmental pollution study is to determine the magnitude and the concentration of oil content. For Suez Canal, data obtained show that oil contents are ranging between 33.6 and 65.6 mg/l for water samples and 110.5- 587.5 mg/kg of dry weight for sediment samples. For Tamsah Lake, oil contents results ranges between 2.80 and 103.3mg/l for water samples, and 135.73 -634.61mg/kg dry weight for sediment samples. Oil content values for the collected fish samples are 138.6, 101.9, 133 and 128.8mg/Kg. Gulf of Suez, oil contents are ranging between 36-230 mg/L for water samples from 160 to 360 mg/kg of dry weight for sediment samples. Generally the oil contents for water, sediment and fish samples are high enough to affect the aquatic life in one way or another. Directly or indirectly the presence of the pollutants in fish tissues may be a risk for their potential bioaccumulation in some tissues of the consumer's bodies

The second step is to identify the source and type of pollution using gas chromatographic technique. For Suez Canal, water samples are contaminated by mixed petrogenic with biogenic hydrocarbons while it is mainly petrogenic for sediment samples. Based on the concept that each type of hydrocarbon pollutants has its own feature (fingerprint), gas chromatographic fingerprint of the studied samples reveal that the type of contaminations can be attributed to crude oil, lubricating oil and/or mixed crude oil. Regarding the weathering degree, both weathered and severely weathered profiles are present indicating continuous petroleum inputs in the studied area. Different

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GC parameters were applied in order to identify the origins, sources and degrees of weathering and also to detect the discrepancies in the results obtained by these parameters if present.

For Temsah Lake the gas chromatographic profiles indicate that the source of contamination is pure petrogenic for water samples and either petrogenic or mixed petrogenic with biogenic hydrocarbons for sediment samples. The types of contaminations are crude oils, lubricating oils and fuel oils. Concerning the weathering degrees, all types of weathering are present indicating continuous petroleum inputs.

For Gulf of Suez, the gas chromatographic profiles show that the source of contamination is either petrogenic or mixed petrogenic with biogenic for both water and sediment samples. The sources of contamination is either petrogenic or mixed petrogenic with biogenic. Crude oil and lubricating oils are the main source of contamination. All samples were subjected to weathering in different degrees. The presence of crude oil pollutants of different weathering degrees indicates the continuous petroleum inputs.

The gas chromatographic information provides strong evidence that the hydrocarbons contaminating the environment are mainly due to petroleum inputs. However, it is generally advisable to support gas chromatographic evidence by data from alternative methods of analysis. This confirmation is provided by the UV absorption technique. UV spectroscopic technique fails to give more informations regarding the individual PAHs present, so the distribution of individual PAHs were further investigated using high performance liquid chromatography (HPLC). Investigation of individual PAHs in the extracted oil from water and sediment samples is a very important part of environmental quality assessment

The third step is to identify the distribution and the origin of the listed reference US Environmental Protection Agency (EPA) priority pollutants; 16 polycyclic aromatic hydrocarbons (PAHs). Investigation has been done using high performance liquid chromatography (HPLC). Quantitative determination of PAHs in case of Suez Canal shows that their concentration

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ranged from 212.34 to 348.33 $\mu\text{g/l}$, 231.76 and 3099.82 $\mu\text{g/kg}$ for water and sediment, respectively. For Temsah Lake between 52.46–3393 $\mu\text{g/l}$, 585.9–8592.8 $\mu\text{g/kg}$ and 1696.4–4785.7 $\mu\text{g/kg}$ for water, sediment and fish samples, respectively. Gulf of Suez showed the concentrations ranging from 81.15–4441.88 $\mu\text{g/l}$, 763.5 to 6741 $\mu\text{g/kg}$ for water and sediments, respectively. Different HPLC parameters (Phe./Ant. and Flu./Pyr.) were applied in order to identify the origin of PAHs in collected samples. Data show that the origin is either petrogenic, pyrogenic or mixed petrogenic and pyrogenic.

Biostimulation treatment show the best results in biotreatment techniques of oil polluted sediments regardless to the type of hydrocarbons and their concentrations, indicating that biostimulation treatment accelerates the biodegradation process, as compared to *Staphylococcus gallinarum* NSH37 and bioaugmentation treatments, for biostimulation treatment, the degree of TPH removal reaches 77%, 53% and 74% for S21, S22 and S23, respectively. For treatment with NSH37, the degree of TPH removal reaches 50%, 41% and 47% for S21, S22 and S23, respectively. For bioaugmentation treatment, the degree of TPH removal reaches 38%, 21% and 36% for S21, S22 and S23, respectively. Biostimulation expresses the highest rate in the 16-PAHs removal followed by treatment with *Staphylococcus gallinarum* NSH37 while bioaugmentation treatment shows the lowest efficiency.

The results of this work showed that *Staphylococcus gallinarum* NSH37 has potential application in bioremediation of oil polluted sediment samples on the lab scale and it is recommended to be applied in the treatment of oil polluted environments.

In conclusion the oil contents in the Gulf of Suez environment are shown to be high enough to affect the aquatic life specially the food chain. Bioremediation is a proven alternative treatment tool that can be used in certain oil contaminated environments. Typically, it can be used as a polishing step after conventional mechanical clean up options have been applied. Repeated environmental assessments are still needed in order to update the baseline information for future conservation programs.

References

REFERENCES

REFERENCES

- Abalos, A.; Vinas, M.; Sabate, J.; Manresa, M.; and Solanas, A.; *Biodegradation*, **15**(4), 249-260(2004).
- Abbondanzi, F.; Bruzzi, L.; Campisi, T.; Frezzati, A.; Guerra, R.; and Iacondini, A.; *International Biodeterioration & Biodegradation*; **57**, 214-221 (2006).
- Abu-Elgheit, M.A.; and Ijam, M.J.; *Prep.-Amer. Chem. Soc. Pet. Chem.*; **25**(3), 429-433(1980).
- Adlard, E.R.; *J. Institute Petroleum*, **58**, 560-563(1972).
- Ahmed, M.T.; Moustafa, G.A.; Al Rasbi, S.A.;and Askar A. ; *J. Chemosphere*; **36**(6), 1391-1403 (1998).
- Ahmed, M.T.; Nagla, L.; El Shiekh, E.; Mosleh, Y.;Abdel Moniem, I.; *J. Aquatic Ecosystem Health and Management*; **4**, 165-173 (2001).
- Aichberger, H.; Loibner, A.P.; Celis, R.; Braun, R.; Ottner, F.; and Rost, H.; *Soil & Sediment Contamination*; **15**, 73-85 (2006).
- Aitken, M.D.; Chen, S.H.; Kazunga, C.; and Marx, R.B.; "Bacterial biodegradation of high molecular weight polaromatic hydrocarbon" ESE notes feature article, Published by the Department of Environmental Sciences & Engineering at the University of the North Carolina at Chapel Hill.(2005).
- Albaiges, J.;and Albrecht, P.; *International J. of Environmental Analytical Chemistry*; **6**, 171-190(1979).
- Aldrett, S.; Bonner, J.S.; Mills, M.A.; Autenrieth, R.L.; and Stephens, F.L.; *Water Res.*; **31**, 2840-2848 (1997).
- Alexander, M; "Biodegradation and Bioremediation"; second ed. Academic Press, San Diego, USA, 239(1999).

REFERENCES

- Al-Yakoob, S.; and Al-Hashash, H.; "Identification of Hazard associated with polyaromatic hydrocarbons in edible fish from oil. Impacted Areas after the Gulf War" Scientific Workshop on Results of the R/V MT. Mitchell Cruise, Kuwait, 24-28 (1993).
- Alzaga, R.; Montuori, P.; Ortiz, L.; Bayona, J.; and Albaiges, J.; *J. of Chromatography A*; **1025**, 133-138(2004).
- Ambrose, D.; Ellender, J.H.; Sprake, C.H.S.; and Townsend, R.; *Journal of the Chemical Society*; **71**, 35-41 (1975).
- Anderlini, V.C.; Al-Harmi, L.; Delappe, B.W.; Risebrough, R.W.; Walker, W.; Simoneit, B.T.; and Newton, A.; "Distribution of hydrocarbons in the Oyaster, Pinctada Margaritifera, along the Coast of Kuwait." 57-62 (1981).
- Annual Book of ASTM standards; vol. **11.01** and **11.02**, Am. Soc. Test. Mater. Philadelphia (1992).
- Anyakora, C.; Ogbeche, A.; Palmer, P.; Coker, H.; Ukpo, G.; and Ogah, C.; *Chemosphere*; **60**(7), 990-997(2005).
- Atlas, R.M.; and Bartha, R.; *Biotechnol. & Bioeng.*; **14**,309-318(1972).
- Atlas, R.M.; *J. Chem. Tech. Biotechnol.*; **52**,149-156(1994).
- Atlas, R.M.; *Microbial Rev.*; **45**, 180-209 (1981).
- Bacaud, R.; Rouleau, L.; *J. Chromatography A*; **750**(1,2), 97-104(1996).
- Balkas, T.I.; Salihoglu, I.; Gaines, A.F.; Sunay, M.; and Mathews, P.H.; *Marine Pollution Bulletin*; **13**(3),202-209(1982).
- Barakat, A.O.; Mostafa, A.R.; Qian, Y.; and Kennicutt, M.C.; *Spill Science & Technology Bulletin*; **7**(5,6), 229-239(2002).
- Barakat, M.A.K.; Shimy, Th.M.; and Moustafa, Y.M.; *Energy Source*; **18**(7), 755(1996).
- Baumard, P.; Budzinski, H.; and Garrigues, P.; *Environmental Toxicology and Chemistry*; **17**, 765-776 (1998).

REFERENCES

- Beckles, D.M.; Ward, C.H.; Hughes, J.B.; Environ. Toxicol. Chem.; **17**(7), 1246-1251 (1998).
- Benka-Coker, M.O.; Olumagin, A.; Bioresour. Technol.; **53**, 211-215 (1995).
- Bento, F.M.; Camargo, F.A.O.; Okeke, B.C.; and Frankenberger, W.T.; Bioresource Technology; **86**, 171-175 (2004).
- Berger, B.D.; and Anderson, K.E.; "Modern petroleum, a basic primer of the industry", Penn Well Books(1978).
- Bernard, D.; Pascalin, H.; and Jeremie, J.; Marine Pollution Bulletin; **32**(10), 734-739(1996).
- Berrut, J.B.; and Jonathan, D.; Institute French Petroleum, **40**,400-409(1984).
- Bharrut, S.; Patience, R.; Mills, N.; and Hanes, T.; Organic Geochemistry; **26**(1,2), 49-57(1997).
- Boehm, P.D.; Douglas, G.S.; Burns, W.A.; Mankiewicz, P.J.; Page, D.S.; and Bence, A.E.; Marine Pollution Bulletin; **34**(8), 599-613(1997).
- Boonyatumanond, R.; Wattayakorn, G.; Togo, A.; and Takada, H.; Marine Pollution Bulletin; **52**, 942-956(2006).
- Cerniglia, C.E.; Biodegradation; **3**, 351-368 (1992).
- Chaillan, F.; Le Fleche, A.; and Bury, E.; Res. In Microbiol.; **55**, 587-595 (2004).
- Chaîneau, C.H.; Rougeux, G.; Yéprémian, C.; and Oudot, J.; Soil Biology & Biochemistry; **37**, 1490-1497(2005).
- Chebotarev "Metamorphism of natural waters in the crust of weathering" Geochim.Et Cosmochimica. Acta 8, part I, 22-48, part II, 137-170, and part III, 198-212(1955).
- Chiou, C.T.; McGroddy, S.E.; and Kile, D.E.; Environmental Science and Technology; **32**, 264-269 (1998).

REFERENCES

- Choiseul, V.; Wilson, J.G.; and Nixon, E.; *Biology and Environmental: proceedings of the Royal Irish Academy*; **98B** (2), 75-86 (1998).
- Chosson P., Lanau C., Cannan P. and Dessort D., *Nature*, **351**, 640-642(1991).
- Chou, C.L.; Haya, K.; Paon, L.A.; and Moffatt, J.D.; *Marine Pollution Bulletin* ;**49**(4-5),465-472(2004).
- Clark,R.C.; and Brown, D.W.;"Petroleum properties and analysis in biotic and abiotic systems", In D.C. Mlins, ed. *Effects of petroleum on arctic and subarctic, Marine Environments and Organisms*"vol. 1. *Nature and fate of petroleum* Academic Press, New York, p.1-89(1977).
- Clemente, A.R.; and Durrant, L.R.; " Biodegradation of PAHs in soil by two deuteromycete fungi" *contaminated soils, sediments & water: Science in the Real World* ,9, Edited by Calabrese, E.J.; KostECKI, P.T.; and Dragun, J. 13-20 (2005).
- Cocchieri, R.A.; Areense, A.; and Minicucci, A.M.;*Marine Pollution Bulletin*; **28**(2), 89-95 (1990).
- Coleman, W.; Munch, J.; Streicher, R.; Ringhand, H.; Paul, K.; and Frederick, C.; *Arch. Environ. Contam. Toxicol.*; **13** (2),171-178 (1984).
- Collins, A.G." *Geochemical classification of formation waters for use in hydrocarbon exploration and production*"; M.Sc. thesis, University of Tulsa, Tulsa, Ok.(1972).
- Collins, W.D.; *Industrial and Engineering Chemistry*; **15**,394(1923).
- Colombo, J.C.; Barreda, A.; Bilos, C.; Cappettetti, N.; Demichelis, S.; Lombardi, P.; Migoya, M.C.; Skorupka, C.; and Suarez, G.;*Environmental Pollution*; **134**, 277-289(2005).
- Corgie, S.; Beguiristain, T.; and Leyval, C.; "Biodegradation of phenanthrene and microbial community structure in the rhizosphere of ryegrass as a function of distance to roots" *geophysical Research abstracts* **6**, 76-93(2004).

REFERENCES

- Correns, C.W.;"The Geochemistry of the halogens in physics and chemistry of the earth" Edited by L.A. Ahrens et al.Mc.Graw-Hill, London.181 (1956).
- Coulon, F.; Pettetier, E.; Stlouis, R.; Gourhant, L.; and Delille, D.; Environ. Toxicol. Chem.; **23**, 1893-1901 (2004).
- Cyr, N.; Mac. Intyre, D.D.; Toth, G.; and Strausz, O.P.; fuel; **66**, 1709-1714(1987).
- Daling, P.S.; and Faksness, L.G.;Environmental Forensics; **3**, 263-278(2002).
- Damste, J.S.S.; and De Leeuw, J.W.; Org. Geochem.; **16**(4-6), 1077-111(1990).
- Davis, S.N.; and De Wiest, R.J.M.;"Hydrogeology" John Willy and Sons, Inc.New York (1966).
- De Luca, G.; Furesi, A.; Micera, G.;Panzanelli, A.;Piu, P.C.; Pilo, M.I.; Spano, N.; Sanna, G.;Marine Pollution Bulletin; **50**(11), 1223-1232, (2005).
- De Oteysa, T.G.; and Grimalt, J.O.; Environmental Pollution;**139**, 523-531(2006).
- Dean-Ross, D.; Moody, J.; and Cerniglia C.E.; FEMS Microbiology, Ecology; **41**,1-7(2002).
- Delille, D.; Delille, B.;and Pelletier, E.; Microb. Ecol.; **44**, 118-126 (2002).
- Devinny, J.; and Chang, S.H.;"Bioaugmentation for soil bioremediation. In: Wise, D.L.; Trantolo, D.J. (Eds.); Bioremediation of contaminated soils, Marcel Dekker, New York, 465-488(2000).
- Doong, R.-an.; and Lin, Y.-t.; Water Research; **38**, 1733-1744(2004).
- Dorn, P.B.; and Salanitro, J.P.; Chemosphere; **40**, 419-426(2000).
- Egaas, E.; and Varanis, A.; Bio. Chem. Pharm.; **31**(4), 561-566 (1982).

REFERENCES

- Elbassiouny, A.E.; "Contribution to study of waste water obtained in the Nile Delta gas field and its treatment"; Athesis of Ph.D., Ain Shams University,(1998).
- El-Gendy, N.Sh.;" Biodesulfurization potentials of crude oil by bacteria isolated from hydrocarbon polluted environments in Egypt"; A thesis of Ph.D., Cairo University,(2004).
- El-Moselhy, K.M.; and Gabal, M.N.; Journal of Marine Systems; **46**, 39-46 (2004).
- El-Sabah, M.I.; and Beltagy, A.I.; Bull. Inst. Oceanogr. Fish., ARE; **9**, 78-82 (1983).
- El-Samra, M.E.; and El-Deeb, K.Z.; Marine Pollution Bulletin;**19**(1), 14-18(1998).
- El-Serehy, H.A.H.; and Sleight, M.A.; Estuarine, Coastal and Shelf Science;**34**(2),127-139(1992).
- El-Tokhi, M.M.; and Moustafa, Y.M.; Petroleum Science and Technology; **19**(5,6), 481-494 (2001).
- Fernandes, M.B.; Sicre, M.A.; Boireau, A.; and Tronczynski, J.;Marine Pollution Bulletin; **34**(11),857-867 (1997).
- Floodgate, G.D.; Aquat. Microb. Ecol.; **9**,3-11(1995).
- Flores, G.P.; and Howard, A.M.M.; Revista Latinoamericana de Microbiolog; **43**(3), 143-150(2001).
- Frank, U.; Statnken, D.; and Gruenfeld, M.;" Methods for the source identification and quantification of oil pollution" Proceedings of the 1979 Oil Spill Conference, Edision, New Jersy, 323(1979).
- Frankenberger, W.T.; "The need for laboratory feasibility studies in bioremediation of petroleum hydrocarbons. In: Calabrese E, Kostechi P, eds. Hydrocarbon contaminated soils and groundwater"; **2**, Chelsea, MI: Lewis Publishers, 237-293 (1992).

REFERENCES

- Gaskin, S. ;and Bentham, R.; Int. Biodeterioration and Biodegradation; **56**, 80-85(2005).
- George, G.N.; Gorbaty, M.L.; and Kelemen, S.R.; ACS Symp. Serier, No.429,220(1990).
- Gigliotti, C.L.; Brunciak, P.A.; Dachs, J.; Glenn IV, T.R.; Nelson, E.D.; Totten, L.A.; and Eisenreich, S.J.; Environmental Toxicology and Chemistry; **21**(2), 235-244 (2002).
- Glober, C.J.; and Bullin, J.A.; Journal of Environmental Science Health; **24A**, 57-75(1989).
- Guillen, M.D.; Sopelana, P.; Partearroyo, M.A.; J. Agriculture. Food Chemistry; **48**, 126-131(2000).
- Guo, C.L.; Zhou, H.W.; Wong, Y.S.; and Tam, N.F.Y.; Marine Pollution Bulletin; **51**, 1054-1061 (2005).
- Gustafsson, O.; Haghseta, F.; Chan, C.; Macfarlane, J.; and Gschwend, P.M.; Environmental Science and Technology; **31**, 203-209 (1997).
- Hamed, M.A.F.;"Seawater quality at the northern part of the Gulf of Suez and the nearby area of the Suez Canal"; M.Sc. a thesis, faculty of science, El-Mansoura University,(1992).
- Hatch, A.C.; and Burton, GA.; Environmental Pollution; **106**, 157-167 (1999).
- Hem, J.D."Study and interpretation of the chemical characteristics of natural water",U.S.Geol.Surv. Water-Supply Pap. 2254(1992).
- Hem, J.D.; "Study and interpretation of the chemical characteristic of natural water" U.S. Geological survey, water supply, third edition (1989).
- Hennig, H.F.; Marine Pollution Bulletine; **10**,234-239(1979).
- Huang, H.; Bowler, B.F.J.; Oldenburg, T.B.P.; and Larter, S.R.; Organic Geochemistry; **35**, 1619-1634 (2004).

REFERENCES

- Hwang, H.M.; and Foster, G.D.; *Environmental Pollution*; **140**, 416-426 (2006).
- Ibrahim, M.B.M.; *Marine Pollution Bulletin*; **49**(4), 356-360(2004).
- Ignasiak, T.; Kemp-Jones, A.V.; and Strausz, O.P.; *J.Org.Chem.*; **42**,312-320(1977).
- Ilyina, A.; Castillo, S.M.I.; Villarreal S.J.A.; Ramirez E.G.; and Candelas, R.J.; *Bulletin of Moscow Uni.; series 2, Chem.*; **44**(1), 88-91 (2003).
- IP, "Standard Methods for Analysis and testing of petroleum and Related Product" The Institute of Petroleum, London, UK, (1995).
- Ivanov, V.V.; Baranov, L.N.; and Plotnikova, G.N.;" The main genetic type of mineral waters in the earth crust and their distribution in the USSR";, in Malkovesky M. and Kacura G., eds. Report to the 23rd I.G.C., session 1 on Genesis of mineral and thermal waters,33 pp. Prague.(1968).
- Jacobs, F-S.; and Filby, R.H.; *Fuel*; **62**, 1186-1192(1983).
- Jeng, W.L.; and Huch, C.A.; *Estuarine, Coastal and Shelf Science*; **66**, 217-224(2006).
- Johnsen, A.R.; Wick, L.Y. and Harms, H.; *Environmental Pollution*; **133**, 71-84 (2005).
- Jordan, R.E.; and Payne, J.R.; " Fate and weathering of petroleum spills in the marine environment: A literature review and synopsis. Ann Arbor, MI.:Ann Arbor Science Publications.174(1980).
- Kaplan, C.W; and Kitts, C.L; *Appl. Environ. Microbiol.*; **70**,1777-1786 (2004).
- Kathryn, A.B.; *Marine Pollution Bulletin*; **20**(2), 68-72(1993).
- Kazunga, C.; and Aitken, M.D.; *Appl. Environ. Microbiol.*; **66**, 1917-1922 (2000).

REFERENCES

- Ke, L.; Teresa, W.Y.; Wong, Y.S.; and Nora, F.Y.; *Marine Pollution Bulletin*; **45**, 339-347 (2002).
- King, A.J.; Readman, J.W.; and Zhou, J.L.; *Marine Pollution Bulletin*; **48** (3,4), 229-239 (2004).
- Kirimura, K.; Furuya, T.; Nishii, Y.; Yoshitaka, I.; Kino, K.; and Usami, S.; *J. Biosci. Bioeng.*; **91**(3), 262-266(2001).
- Lal, B.; and Khanna, S.; *J. Applied Bacteriology*; **81**, 355-362(1996).
- Launen, L.A.; Buggs, V.H.; Eastep M.E.; Enriquez, R.C.; Leonard, J.W.; Blaylock, M.J.; Huang, J.W.; and Häggblom, M.M.; *Bioremediation Journal*; **6**(2), 125-141(2002).
- Law, R.J.; *Mar. Poll. Bull.*; **9**(11), 293 (1978).
- Laws, E.A.; *Aquatic pollution*, John Wiley and Sons., New York. (1993).
- Leahy, J.G.; and Cowell R.R.; *Microbiol. Rev.*; **54**, 305-315 (1990).
- Lee, H.K.; Wright, G.J.; and Swallow, W.H.; *Environmental Pollution*; **49**, 167-175(1988).
- Lee, M.K.; and Saunders, J.A.; "Effects of pH on metals precipitation and sorption: field bioremediation and geochemical modeling approaches" *Vadose Zone J.*; **2**, 177-185(2003).
- Lei, L.; Khodadoust, A.P.; Suidan, M.T.; and Tabak, H.H.; *Water Research*; **39**, 349-361 (2005).
- Levy, E.M.; *Marine Pollution Bulletin*; **11**, 51-56(1980).
- Lewis, A.; and Aurand, D.; "Putting dispersants to work: overcoming obstacles. An Issue paper prepared for the 1997 oil spill conference. API: Washington, DC " 80(1997).
- Lin, Q.; and Mendelsohn, I.A.; *ecological engineering*; **10**, 263-274(1998).
- Luo, X.-J.; Chen, S.-J.; Mai, B.-X.; Yang, Q.-S.; Sheng, G.-Y.; and Fu, J.-M.; *Environmental Pollution*; **139**, 9-20 (2006).

REFERENCES

- Mackay, D.; Shiu, W.Y.; and Ma, K.C.; Illustrated handbook of physical-chemical properties and environmental fate for organic chemicals, vol. II. Lewis Publishers, Chelsea, MI.(1992).
- Macnaughton, S.J.; Stephen, J.R.; Venosa, A.D.; Davis, G.A.; Chang, Y.; and White, D.C.; Appl. Environ. Microbiol.; **65**(8), 3566-3574 (1999).
- Magi, E.; Bianco, R.; Ianni, C.; and Di Carro, M.; Environmental Pollution; **119**, 91-98 (2002).
- Mansfield, C.T.; Barman, B.N.; Thomas, J.V.; Mehrotra, A.K.; and McCann, J.M.; Analytical Chemistry; **71**(12), 81R-107R (1999).
- Maskai, K.; Zhou, J.L.; Hong, H.S.; and Zhang, Z.L.; Environmental Pollution; **118**, 109-122 (2002).
- Masters, C.D.; and Root, D.H.; " World resources of crude oil, natural gas ,natural bitumen and shale oil" Twelfth World Petroleum Congress, chichester, England Jhon Wiley & Sons, Topic 5,(1987).
- May, W.E.; Chesler, S.N.; Hertz, H.S.; and Wise, S.A.; Int .J. Environmental Analytical Chemistry; **2**, 259-75 (1982).
- McNally, D.L.; Mihelcic, J.R.; Lueking, D.R.; Environ. Soci. Technol.; **32**, 2633-2639 (1998).
- Medeiros, P.M.; and Bicego, M.C.; Marine Pollution Bulletin; **49**, 892-899(2004).
- Medeiros, P.M.; Bicego, M.C.; Castelao, R.M.; Rosso, C.D.; Fillmann, G.; and Zamboni, A.J.; Environmental International; **31**, 77-87(2005).
- Meisler, H.; and Becher, A.E.; "Hydrogeologic significance of calcium-magnesium ratios in groundwater from carbonate rocks in the lancaster Quadrangle, south eastern Pennsylvania", in Geological Survey research 1967, Chap.C,U.S. Geological Survey Professional Paper 575-C, C232-C235(1967).
- Méndez, E.M; España, M.S.A; and Montelongo, F.J.G.; Environmental Pollution; **111**(2), 177-187 (2001).

REFERENCES

- Meshal, A.H.; Bull. Inst. Oceanogr. Fish., Egypt, **1**, 463-473 (1970).
- Metwally, M.; Al-Mu Zaini, S.; Jacob, P.G.; and Bahloul, M.; Environment International; **23**(1), 115-121(1997).
- Metwaly, G.M.; Environmental pollution and hydrochemical studies at Qarun Lake; Athesis of M.Sc.,Zagazig University,(2004).
- Middleditch, B.; Basile, B.; and Chang, E; Chromatography; **142**, 777-785(1977).
- Mishra, S.; Sarma, P.M.; and Lal,B.; FEMS Microbiology Letters; **235**, 323-331 (2004).
- Moller T.H., Dicks B. and Goodman C.N."Fisheries and mariculture affected by oil spills".Proceedings 1989 International Oil Spill Conference, San Antonio, Tx. Amer.Petrol.Inst., Washington, DC., API Public ,4479,389-394(1989).
- Moustafa, Y.M.; Abdallah, R.I.; and Abd El Naby, I.M.; Journal of the faculty of Education; Ain Shams University; **22**, 705-716(1997).
- Moustafa, Y.M.;Abd El-Hakem, M.;Abdallah, R.I.;Barakat, M.A.K.; J.Egypt.J.Petrol.;**14**(1),85-93 (2005).
- Moustafa^a, Y.M. ;Biosciences, Biotech. Research Asia; **2**(1), 15-24 (2004).
- Moustafa^b, Y.M.; Oriental Journal of chemistry;**20**(2), 219-226 (2004).
- Mrayyan, B.; and Battikhi, M.N.; Journal of Hazardous Materials ;B120, 127-134 (2005).
- Murgich, J.; Abanero, A.J.; and Strausz, P.O.; Energy Fuel; **13**(2), 278-286 (1999).
- Neff, J.M.; and Anderson, J.W.; Bulletin Environmental Contamination Toxicology; **14**,122-128(1975).
- Nnubia, C.; and Okpokwasili, G.C.; Environmental Pollution; **82**, 153-156(1993).

REFERENCES

- Nouwen, J.; Borburgh, A.; and Vanermen, G.; *Environmental Studies*; **10**, 431-439 (2004).
- Nweke, C.O.; and Okpokwasili, G.C.; *African Journal of Biotechnology*; **2**(9), 293-295 (2003).
- Ojumu, T.V.; Bello, O. O.; sonibare, J. A. ;And solomon, B. O.; *African Journal of Biotechnology*; **4**(1), 31-35 (2005).
- Okpokwasili, G.C.; and Nnubia, C.; *J. Sci. Engr. Technol.*; **6**, 1420-1428 (1999).
- Olaniran, A.O.; Pillay, D.; and Pillay, B.; *Chemosphere*; **63**, 600-608 (2006).
- Palmer, C.;" The geochemical interpretation of water analyses"; *J.S. Geological Survey Bulletin*; **479**, 31(1911).
- Pelet, R.; Behar, F.; and Monin, J.C.; *Org. Geochem*; **10**(1,3), 481-498(1986).
- Pelletier, E.; Delille, D.; and Delille, B.; *Mar. Environ. Res.*; **57**, 311-327(2003).
- Perera, F.P.; Hemninki, K.; and Young, T.L.; *Cancer Research*; **48**, 2288-2291(1988).
- Peters, K.E.; and Moldowan, J.W.; *The Biomarker Guide: Interpreting Molecular Fossils in Petroleum and Ancient Sediments*. Prentice-Hall, New Jersey (1993).
- Piddington, C.S.; Kovacevich, B.R.; and Rambosek, J.; *Appl. Environ. Microbiol.*; **61**(2), 468-475(1995).
- Pilli, I.; Ritchie, L.; Heywood, R.; Wilson, G.; Pahlavanpour, B.; Setford, S.; and Saini, S.; *J of Chromatography A*; **1064**, 205-212(2005).
- Piper, A.M.; *American Geophysical Union Transactions*; **55**, 914-923(1944).
- Qiao, M.; Wang, C.; Huang, S.; Wang, D.; and Wang, Z.; *Environment International*; **32**, 28-33(2006).

REFERENCES

- Quintero, S.; and Diaz, C.; *Marine Pollution Bulletin*; **28**(1), 44-49(1994).
- Rahman, K.S.M.; Rahman, T.J.; Kourkoutas, Y.; Petsas, I.; Marchant, R.; and Banat, I.M.; *Bioresource Technology*; **90**,159-168 (2003).
- Ramsay, M.A.; Swannell, R.P.J.; Shipton, W.A.; Duke, N.C.; and Hill, R.T.; *Marine Pollution Bulletin*; **41**, 413-9 (2000).
- Raoux, J.M.; Bayona, J.C.; Miquel, J.L.; Teyssie, S.W.; Fowler and J. Albaigés ;*Estuarine, Coastal Shelf Science*; **48**, 605-616(1999).
- Ravelet, C.; Krivobok, S.; Sage, L.; and Steiman, R.;*Chemosphere*;**40**,557-563(2000).
- Readman, J.W.; Fillmann, G.; Tolosa, I.; , Bartocci, J.; Villeneuve, I.P.; Catinni, C.; and Mee, L.D. ;*Marine Pollution Bulletin*; **44**, 48-62(2002).
- Rodríguez, J.J.; and Padrón, S.C.;" Fluorescence techniques for the determination of polycyclic aromatic hydrocarbons in maine environment: an overview"; *Luminescence Spectroscopy, Faculty of Marine Sciences, University of Las Palmas de G.C., 35017 Las Palmas de G.C., Spain.*(2000)
- Roling, W.F.M.; Milner, M.G.; Jones, D.M.; Fratepietro, F.; Swannell, R.P.J.; Daniel, F.; and Head, I.M.;*Appl. Environ. Microbiol.*; **70**(5), 2603-2613(2004).
- Russ, J.C.; *Adv. X-Ray Anal.*, **29**, 413-422(1985).
- Sabaté, J.; Viñas, M.; and Solanas, A.M.; *Chemosphere*; **63**, 1648-1659 (2005).
- Said, T.; and Agroudy, N.; *Chemistry and Ecology*; **22**(15), 159-173 (2006).
- Samanta, S.; Singh, O.V.; and Jain, R.K.; *Trends in Biotechnology*; **20**(6), 243-248(2002).
- Sandrin, T.R.; and Maier, R.M.; *Environmental Health Perspectives*; **111**(8), 1093-1101(2003).
- Saponaro, S.;and Bonomo, L.; *Water Air Soil Pollution*; **135**, 219-36 (2002).

REFERENCES

- Sarkar, D.; Ferguson, M.; Datta, R.; and Birnbaum, S.; *Environmental Pollution*; **136**(1), 187-195 (2005).
- Schoket, B.; Doty, W.A.; and Vincze, I.; *Cancer Epidemiol. Biomarker prevention*; **2**, 349-353(1993).
- Scholz, D.K.; Kucklick, J.H.; Pond, R.; Walker, A.H.; Bostrom, A.; and Fischbeck, P.; "Fate of spilled oil in marine waters: Where does it go? What does it do? How do dispersants affect it? An Information Booklet for Decision-Markers. American Petroleum Institute, (1999).
- Seiple, K.M.; Cyr, N.; Fedorak, P.M.; and Westlake, D.W.S.; *Can.J.Chem.*; **68**,1092-1099(1990).
- Shi, Z.; Tao, S.; Pan, B.; Fan, W.; He, X.C.; Zuo, Q.; Wu, S.P.; Li, B.G.; Cao, J.; Liu, W.X.; Xu, F.L.; Wang, X.J.; Shen, W.R.; and Wong, P.K.; *Environmental Pollution*; **134**,97-111 (2005).
- Shirokoff, W.J.; Siddiqui, N.M.; and Ali, F.M.; *Energy Fuel*; **11**(3),561-565(1997).
- Shiu, W.Y.; and Mackay, D.; *Journal of Chemical & Engineering Data*; **42**, 27-30 (1997).
- Shouming, O.; Jianhau, Z.; Jinshu, Z.; Lamp, B. R.; *Chemosphere*; **56**(2),107-112(2004).
- Shriadah, M.A.; *Marine Pollution Bulletin*; **36**(11),862-863(1998).
- Smith M.J.E. and Sultan Bowman M.T. "Note on the destruction of alkali carbonates by organic acids in the groundwater of oilfields" *Congre's International des Mines, Metallurgie et Geologie Appliquee*, section Geoloia, VI.section, 259-261(1930).
- Soclo, H.H.; Garrigues, P.; Ewald, M.; *Marine Pollution Bulletin*; **40**, 387-396 (2000).
- Soliman, G.F.; *Simulation of water circulation in the Suez Bay and its hydrographic features during winter and summer. The 6th Conf. of the Envi. Prot. Is a Must. Nat. Oceanogr. And Fish., Euro-Arab Cooperation Center, Inter. Sci. Asso. And Soci. Fund for Development*, 400-433 (1996).

REFERENCES

- Speer, K.; Steeg, E.; Horsetmann, P.; Kuhn, Th.; Montang, A.; J. High Resolution Chromatography; **13**, 104-111(1990).
- Speight, J.G. ;and Moschepoids, S.E.;"On the molecular nature of petroleum asphaltenes"; In Bunger J.W. and Li N.C. (eds).Chemistry of asphaltenes American Chemical Society, Washington D.C., 1-15 (1981).
- Speight, J.G.; Fuel; **49**, 76-90(1970).
- Stephanie, G.M.; and Stephen, A.W.;Analytical Chemistry; **71**, 58-69(1999).
- Stout, S.A.; Uhler, A.D.; and Emsbo-Mattingly, S.D.; Environmental Science and Technology; **38**, 2987-2994 (2004).
- Stout, S.A.; Uhler, A.D.; and McCarthy, K.J.; Environ. Forens.; **2**,87-98(2001).
- Strausz, P.O.; Mojelsky, W.T.; Faraji, F.; Lown, M.E.; and Peng, P.; Energy Fuel;**13**,207-227(1999).
- Sulin, V.A.;Condition of formation principals of classification and constituents of natural water, particularly water of petroleum accumulation; Academy of Science, Moscow, Leningrad.(1948).
- Sun, W.H.; Io, J.B.; Robert, F.M.; Ray, C.; and Tang, C.S.; Environ. Sci. Pollut. Res. Int.; **11**(4), 260-266(2004).
- Tfouni,S.A.V.; Machado, R.M.D; Camargo, M.C.R.; Vitorino, S.H.P.; Eduardo, V.; and Toledo, M.C.F.; Food Chemistry; **101**, 334-338(2007).
- Thourya, M. S.; Contribution to the study of pollution by oil on the Gulf of Suez", Ph.D thesis, faculty of science, Ain Shams University,(1986).
- Todd, G.D.; Chessin, R.L.; and Colman, J.; "Toxicological profile for Total Petroleum Hydrocarbons (TPH), U.S. department of health and human services public health service, agency for toxic substances and disease registry" (1999).
- Tolosa, I.; De Mora, S.J.; Fowler, S.W.; Villeneuve, J.P.; Bartocci, J.; and Cattini, C.; Marine Pollution Bulletin; **50**, 1619-1633 (2005).

REFERENCES

- Tolosa, I.; Mora, S.; Sheikholeslami, M.; Villeneuve, J.; Bartocci, J.; and Cattini, C.; *Marine Pollution Bulletin*; **48**(1-2), 44-60 (2004).
- Trabelsi, S.; and Driss, M.; *Marine Pollution Bulletin*; **50**,344-359(2005).
- Trinidad, P.V.O.; Sobral, L.G.; Rizzo, A.C.L.; Leite, S.G.F.; and Soriano, A.V.; *Chemosphere*; **58**, 515-522 (2005).
- Tundo, P.; Raccanelli, S.; Reda, L.; Ahmed, M.T.; *Chemistry and Ecology*; **20**, 257-265 (2004).
- Tundo, P.; Reda, L.A.; Mosleh, Y; Ahmed, M.T.; *J. Toxicological & Environmental Chemistry*; **87**(1), 21-30 (2005).
- Van Der Have J.H. and Venner C.G." Petroleum and its products", 4-25(1975).
- Van-Hamme, J.D.; *Microbiol. Mol. Rev.*; **7**, 503-549 (2003).
- Varanasi U., Stein J.E. and Nishimoto M. "Biotransformation and deposition of polycyclic aromatic hydrocarbons (PAHs) in Fish. In metabolism of polycyclic aromatic hydrocarbons in the Aquatic environment" (U.Varanasi,ed.), Boca Raton, FL: CRC press. 93-149 (1989).
- Vidali, M.; *Pure App. Chem.*; **73**(7):1163-1172(2001).
- Viguri, J.;Verde, J.; and Irabien, A. *Chemosphere*; **48**, 157-165 (2002).
- Vogel, T.M.; *Current Opinion and Biotechnology*; **7**, 311-316 (1996).
- Waldo, G.S.;Carison, R.M.K.; Moldowan, J.M.; Peters, K.E.; and Penner-Hahn, J.E.; *Geochim Cosmochim Acta*, **55**(3),801-814 (1991).
- Wang, X.C.; Sun, S.; Ma, H.Q.; Liu, Y.; *Marine Pollution Bulletin*; **52**,129-138 (2006).
- Wang, Z.; and Fingas, M.F.; *Marine Pollution Bulletin*; **47**, 423-452(2003).
- Wang, Z.; Fingas, M.; and David, P.; *J.of chromatography A*; **843**,369-411(1999).

REFERENCES

- Wang, Z.; Fingas, M.; Owens, E.H.; Sigouin, L.; and Brown, C.E.; *J. of Chromatography A*; **926**, 275-290(2001).
- Wang, Z.D.; Fingas, M.; and Sergy, G.; *Environmental Science and Technology*; **29**, 2622-2631(1995).
- Wang, Z.D.; Fingas, M.; Lambert, P.; Zeng, G.; Yang, C.; and Hollebhone, B.; *J. of Chromatography A*; **1038**, 201-214(2004).
- Whittaker, M.; and Pollard, S.J.; *J. Planar, Chromatography*; **7**, 354-361(1994).
- Wu, Z., Zhang, J. and Zhijian, Z.; *Marine Pollution Bulletin*; **46**(5), 619-625 (2003).
- Xia, X.H.; Yu, H.; Yang, Z.F.; and Huang, G.H.; *Chemosphere*; **65**, 457-466(2006).
- Xu, B.X.; Fang, Y.Z.; *Talanta*; **35** (11), 891-894(1988).
- Yu, K.S.H.; Wong, A.H.Y.; Yau, K.W.Y.; Wong, Y.S.; and Tam, N.F.Y.; *Marine Pollution Bulletin*; **51**, 1071-1077 (2005).
- Zakaria, M.P.; Okuda, T.; and Takada, H.; *Marine Pollution Bulletin*; **142**(12), 1357-1366 (2001).
- Zakaria, M.P.; Takada, H.; Tsutsumi, S.; Ohno, K.; Yamada, J.; Kouno, E.; and Kumata, H.; *Environmental Science and Technology*; **36**, 1907-1918 (2002).
- ZoBell, C.E.; *Adv. Water Poll. Research*; **3**, 85-1118(1946).

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ANNEX-I

On 19 December 1972-OMAN - After a collision of Brazilian tanker Horta Barbosa with the South Korean Tanker Sea Star spilled about 840,000 barrels of crude into the Gulf of Oman.

On 15 December 1976-USA - The Argo Merchant ran a ground off Nantucket spilling 183,000 barrels of oil and causing a slick 160 km (100 miles) long and 97 km wide.

On 25 February 1977-PACIFIC - The Liberian-registered Hawaiian Patriot caught fire in the Northern Pacific spilling 723,000 barrels.

On 16 March 1978-FRANCE - About 1.6 million barrels of crude spilled after the Amoco Cadiz ran aground near Portsall in France's worst ever tanker accident. The resulting slick eventually covered 125 miles of Breton coast.

On 3 June 1979- MEXICO - An estimated 140 million gallons of oil spilled from an exploratory well in the Gulf of Mexico, 80 km NW of Ciudad del Carmen, Campeche.

On 19 July 1979-TRINIDAD & TOBAGO - About 2.2 million barrels of crude spilled after a collision off Tobago between the Atlantic Empress and the Aegean Captain.

On 6 August 1983- SOUTH AFRICA - Fire broke out on the Spanish tanker Castillo de Bellver and 1.8 million barrels of light crude burnt off the coast at Cape Town.

On 24 March 1989-USA - the Exxon Valdez hit rocks in Prince William Sound spilling 240,000 barrels of crude oil onto Alaskan shores.

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On 19 December 1989 - MOROCCO - After explosions and a fire Iranian tanker Kharg-5 was abandoned spilling 70,000 tonnes of crude oil, endangering the coast and oyster beds at Oualidia.

On 7 February 1990- USA - The tanker, American Trader, leaked 300,000 gallons of crude from a gash in the hull causing an oil slick 22 km long polluting Bosa Chica, one of southern California's biggest nature reserves.

On 26 January 1991-KUWAIT - An estimated 240 million gallons of oil were spilled from terminals, tankers and oil wells during the final phase of the Iraqi invasion of Kuwait. The fate of crude oil spilled into the Arabian Gulf after the 1991 war (6-8 million barrels) has been a question of major concern in recent years.

On 28 May 1991-ANGOLA/LIBERIA - A Liberian-registered supertanker, ABT Summer, leaked oil after an explosion off Angola causing an oil slick 17 nautical miles by three.

On 2 March 1992-UZBEKISTAN - An estimated 88 million gallons of oil spilled from an oil well at Fergana Valley.

On 19 September 1992 - INDONESIA - Liberian-registered tanker Nagasaki Spirit collided with container Ocean Blessing in the Malacca Straits spilling some 12,000 tonnes of crude.

On 5 January 1993--UNITED KINGDOM - Oil poured on to the coast of northern Scotland's Shetland Islands after the 89,000-ton Liberian-registered Braer hit rocks in heavy seas. The tanker carried 84,500 tons of crude oil.

On 21 January 1993-- SINGAPORE / INDONESIA / MALAYSIA - The 255,312-ton Singapore-registered tanker Maersk Navigator collided with the empty tanker Sanko Honour in the Andaman Sea en route from Oman to Japan. It was carrying a cargo of nearly 2 million barrels of oil. Its ruptured

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port side leaked burning oil and spread a slick up to 35 miles (56 km) long off Sumatra drifting towards India's Nicobar Islands.

On 11 February 1993--NETHERLANDS - Up to 30,000 seabirds were feared killed by a paraffin oil slick thought to have been discharged by a passing ship.

On 9 March 1993--GERMANY/POLAND - The wreck of the Jan Heweliusz, a Polish ferry which sank in the Baltic off Germany on January 14, leaked oil. The ship was estimated to have up to 80 tons of fuel on board.

On 3 June 1993--BELGIUM / UNITED KINGDOM - The tanker was loaded with 24,000 tons of petrol, which poured out of a hole in the port bow.

On 15 October 1993--GREECE - Oil leaked from the Greek tanker Iliad killed wildlife and destroyed fish farms .oil slick was caused when the tanker ran aground off the island of Spaktiria on October 9.

On 7 January 1994--PUERTO RICO - 750,000 gallons of heavy fuel oil had been spilled and had spread to cover a six-mile (9.6 km) stretch of shore. Conado Beach, the Conado lagoon and San Juan Bay were all polluted.

On 6 March 1994--THAILAND - About 105,670 gallons of diesel fuel spilled into the sea

On 31 March 1994--UNITED ARAB EMIRATES - 15,900 tons of crude oil leaked into the Arabian Sea

On 8 May 1994--VIETNAM - About 200 tons spilled into the river from the Vietnamese ship causing a 200-ton oil slick, which killed fish and other wildlife.

On 14 June 1994-- INDIA - Indian authorities began siphoning off 700 tons of oil from the Sea Transporter, a 6,000-ton Greek cargo ship which

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had been anchored off Aguada after it ran aground following a cyclone on June 5.

On 23 June 1994-- SOUTH AFRICA - An oil slick washing ashore on Dassen Island threatened a colony of endangered Jackass penguins and polluted mainland beaches.

On 11 August 1994-- UNITED STATES - The Columbus Iselin, a ship conducting oil spill research, ran aground in the Looe Key National Marine Sanctuary off the Florida Keys and was leaking fuel.

On 2 October 1994 -- PORTUGAL - A Panamanian registered tanker, Cercal, spilled about 2,000 tons of crude into the sea after striking a rock on its way into Leixoes harbor.

On 17 October 1994 -- CHINA - 1,000 meters of beaches and reefs at Dongshan, were polluted by an oil spill blamed on the Huahai Number Two tanker, owned by the state-run Huahai Company of Beijing.

5 June 1995 -- SINGAPORE - About 100 tons of fuel oil leaked from a bunker fuel barge.

11 July 1995-- AUSTRALIA - spilling more than 500 tons of fuel oil and causing a major pollution. Thousands of fairy penguins were fouled with oil.

25 July 1995-- SOUTH KOREA - A ship was loaded with 83,000 tons of crude oil. It was drifting toward the country's best known sea resort. 700 tons of fuel oil estimated to have been leaked.

15 February 1996 -- UNITED KINGDOM - The coast guard called a full environmental alert when the 147,000 deadweight ton Liberian-registered Sea Empress with a crew of 28 Russians hit rocks near the port of Milford Haven, Wales. The tanker, operated by Acomarit, had been carrying 130,000 tons of light crude oil. On February 20 an estimated 40,000 tons of crude oil spilled -- a third of its cargo -- creating a four-mile oil slick.

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19 March 1996--UNITED STATES - A barge operated by Buffalo Marine Services Inc. and loaded with about 210,000 gallons of fuel oil ruptured as it sailed through the Houston Ship Channel. About 4,200 gallons of oil spilled into Galveston Bay, causing a five-mile-long (eight km) oil slick.

On 7 January 1997-- JAPAN - Coastal fishing villages in northwestern Japan braced for economic and environmental catastrophe as oil slicks from sunken Russian tanker Nakhodka coated beaches and threatened prized shellfish beds. The spill from the ruptured tanker leaked 5,200 tons of heavy fuel oil.

On 2 July 1997--JAPAN - A supertanker struck a shallow reef in Tokyo Bay, a famed fishing ground, leaking an estimated 1500 tons of crude oil.

On 15 October 1997 -- SINGAPORE - More than 25,000 tonnes of oil leaked out from the vessel, and despite huge amounts of dispersant chemicals being applied both from the air and from vessels, the beaches of several smaller islands off Singapore are covered with greasy sludge.

On 12 January 1998 -- NIGERIA - 40,000 barrels of oil spilled from a ruptured pipeline. The spill is considered the largest ever in Nigeria.

On 12 December 1999 - FRANCE - The Maltese-registered tanker Erika broken up in stormy seas, and an estimated 15,000 tonnes of oil were drifting towards France's Atlantic shore with disastrous consequences for fishing and tourism.

On 27 December 1999-TURKEY - A Maltese-registered tanker carrying 45,753 tons of oil ran aground at the mouth of the Bosphorus strait across Istanbul, the largest city in Turkey, the Turkish Daily News reported. Murat Zafer Cetintas, head of the Organization of Eco-Warriors and the Environment, was quoted as saying that if necessary precautions are not taken, the city would face serious problems.

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On 27 December 1999 - ANGOLA - An offshore oil spill is approaching the Angolan coast, posing a threat to the fishing industry. Radio Ecclesia said the spill, which occurred in the Atlantic Ocean oil fields off Cabinda province, was advancing towards the coast.

On 4 January 2000 - TURKEY - About 900 tons of fuel oil had spilled and oil could be seen along five kilometers of the coast. Some 200 accidents over the last decade in the strait have caused oil spills and fires that sometimes shut down the strait.

On 18 January 2000 - BRASIL - At least 130,000 gallons of crude oil spewed out of a broken pipeline, polluting beaches and endangered plant and animal life

On 24 January 2000 - UNITED ARAB EMIRATES - The Honduran-flagged cargo vessel Al Jazyza 1 sank 4 miles east of Abu Dhabi's coast, laden with 980 tons of fuel oil. The tanker sank in bad weather leaving an oil spill.

On 2 February 2000-BOLIVIA - A flash flood broke a crude oil pipeline, spilling hundreds of barrels of oil into the Desaguadero River that flows into Lake Poopo.

On 2 February 2000-PHILIPPINES -A spill was said to have destroyed 2,700 metres of coral reefs and other marine resources.

On 7 February 2000-BRAZIL - Brazilian authorities scrambled to avert an environmental disaster in the Amazon jungle, after a barge holding nearly 500,000 gallons of oil sunk to the bottom of the world's largest river network.

On 1 April 2000 - INDONESIA - About 160.000 kilolitres of crude oil leaked out from the tanker "King Fisher".

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On 7 April 2000 - UNITED STATES - 111,000 gallons of oil spilled near Pepco's Chalk Point Generating Station, affecting shorelines of the Patuxent River in southern Maryland.

On 23 June 2000 - SOUTH AFRICA - The oil spill began when the bulk carrier Treasure carrying some 1,400 tonnes of oil sank off the coast of Cape Town. The spill washed straight into Robben Island.

On 6 July 2000 - UNITED STATES - 14,000 gallons of oil has spilled when 828-thousand gallons spilled, killing more than ten million lobsters and prompting a ban on fishing for five months.

On 16 July 2000-BRAZIL - more than 1 million gallons of crude leaked from a refinery into a river near the southern city of Curitiba. Television images showed a completely blackened river winding through the countryside.

On 25 July 2000 - BRAZIL - A large oil slick again spread over Rio's postcard-famous Guanabara Bay on Tuesday. The slick was broken up in patches across an area of more than 20 square miles.

On 1 August 2000 - CANADA - estimated 264,600 gallons of crude oil spilled in a pipeline. The heavy oil had also begun killing some of the river's fish.

On 8 August 2000-UNITED STATES - U.S. Coast Guard investigators boarded ships in Miami and Port Everglades, trying to determine which crew dumped oil off the South Florida coast, creating the area's worst oil spill in at least a decade. The oil contaminated 15 miles of beach, and all beaches along the 15-mile stretch were closed when the oil was discovered.

On 2 September 2000 - MALAYSIA - A major cleanup is underway following an oil spill from a sunken Chinese cargo ship at Tanjung Po anchorage point at the Sarawak River mouth. The ill-fated 5,000 ton Kingston registered vessel Double Brave was loaded with about 116 tons of

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diesel oil when it sank after a collision with a barge being towed by a tugboat.

On 4 September 2000 - GREECE - Miles of coastline was threatened by a spill, which came from the Cambodian-registered cement carrier Eurobulker X. It was the second spill within a week, following a smaller spill from a grounded freighter off the island of Kythira.

On 14 September 2000 - UNITED STATES - Wind and high waves spread a 30,000-gallon oil spill across Sandy Hook Bay, efforts to contain and clean up the mess.

On 4 October 2000 - INDONESIA - An estimated 7,000 tons of oil has been spilled in Indonesian waters off the Batu Berhanti Beacon, after a Panama registered tanker, Natuna Sea, ran aground damaging 4 of its cargo tanks.

On 4 November 2000 - BRAZIL - 13,200 gallons of crude near a popular beach resort area. The accident caused a slick measuring 492 feet, and posed a risk for the region's bustling beach resorts nearby.

On 14 November 2000 - HONG KONG - 230 cubic metres of heavy oil leaked into the sea north of Hongkong's Lantau Island,

On 28 November 2000 - UNITED STATES - A tanker spilled half a million gallons of crude oil into the Mississippi River, closing a busy shipping route for 26 miles and threatening wildlife.

On 14 January 2001- TAIWAN - Some 1,150 tonnes of fuel oil gushed out of a Greece-registered ship carrying 60,000 tonnes of iron ore, after it ran aground off the Kenting National Park. Marine mammals in the area, such as dolphins, were highly endangered by the spill.

On 15 January 2001- NORWAY - 750 tons of sludge had leaked from Norcem's facilities at Brevik. By the afternoon, some 100 tons had been

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recovered within the containment area around the tank, whilst another 190 tons had been recovered from the sea.

On 16 February 2001- INDONESIA - 800 tonnes of sump oil had leaked from a ship and reached the shore.

On 20 March 2001- BRAZIL - Up to 316,000 gallons of diesel had leaked. A huge diesel slick appeared on the surface when the platform sank to bottom of the ocean floor, almost a mile down. This was just another in a series of oil spills that have plagued the state owned Petrobras.

On 25 March 2001- DENMARK - More than 764,000 gallons of oil spilled. A slick about 9.3 miles long and 161/2-feet wide slipped into the narrow Groensund strait between the Danish islands of Moen, Bogoe and Falster, while the bulk of the oil remained in the Baltic Sea off southern Denmark.

On 6 April 2001- UNITED ARAB EMIRATES - The spill was caused by the Iraqi fuel tanker Zainab, suspected of smuggling around 1,300 tonnes of fuel oil from Iraq.

On 24 May 2001-BRAZIL - Petrobras, infamous for a series of spills over the previous two years, There were two oil slicks some 90 km off the coast, one of approximately 110,000 liters and another of some 10,000 liters of crude.

On 25 May 2001-CHILE - An oil tanker that ran aground in a remote southern Chilean fjord has spilled some 350,528 litres of crude, leaving an oil slick 70 miles (112 km) long and damaging wildlife

On 28 May 2001- MALAYSIA - An oil tanker with some 67 tonnes of fuel, including diesel and 1,500 tonnes of bitumen, sunk after it was crashed from behind by a super tanker about 7.5 nautical miles off Pulau Undan, near Malacca.

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On 30 May 2001- BRAZIL- Oil giant Petrobras said a break in its Paulinia pipeline dumped 220,000 liters of fuel oil in a residential neighborhood. The spill, which occurred 30 kilometers from the city of Sao Paulo, follows two unexplained and unclaimed oil spills in the Campos Basin off the coast of Rio de Janeiro state.

On 10 June 2001- PHILIPPINES -an oil spill has already affected a six-kilometer stretch of Carmona-Biñan River, just a few kilometers away from the Laguna Bay.

On 13 June 2001- MALAYSIA - The 533 ton MV Endah Lestari was on its way to East Kalimantan in Indonesia with some 600 tonnes of the poisonous industrial chemical phenol, and 18 tonnes of diesel. Newspaper reports said the toxic spill had killed thousands of fish and Singapore authorities have warned its citizens to stay away from nearby waters.

On 4 August 2001- USA - about 35,000 gallons (133,000 liters) of diesel fuel when it struck a rock and sank in the northern part of the sound about 40 miles (65 km) southwest of the port of Valdez.

On 10 August 2001 - MICRONESIA - A sunken World War II ship has been gushing 300 to 500 gallons of oil per hour into the Ulithi Atoll lagoon. The cause of the spill is the USS Mississinewa, a 553-foot Navy oiler sunk in 1944 by a one-man Japanese suicide submarine.

On 22 September 2001- USA - The fuel oil spill occurred at Barbour's Cut in La Porte, Texas, and some 860 barrels of fuel oil leaked into the channel. About 18,000 feet of boom were set up to contain the oil, and skimmers removed it.

On 4 October 2001- USA - Crews were slowed by explosive vapors as they tried to plug a leak in the trans-Alaska Oil Pipeline that spewed nearly 300,000 gallons of oil into the wilderness.

On 18 October 2001- BRAZIL - State oil giant Petrobras, which owns the tanker, said about 103,000 gallons (392,000 litres) of naphtha, an

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oil product lighter than gasoline, spilled into the Paranagua port area, about 380 miles (600 km) southwest of Rio.

On 21 November 2001 - GERMANY - Almost 2,000 tonnes of nitric acid has spilled into the Rhine River.

On 11 December 2001 - FINLAND - Oil from a spill off the country's west coast has washed ashore on some 1.24 miles of Ruissalo Island's coastline.

On 22 January 2002- THAILAND - Some 100,000 litres of oil had spilled from the Panama-registered tanker Eastern Fortitude when it hit a rock in Rayong Bay a week earlier.

On 8 February 2002 - UNITED STATES - A ship that sank nearly 50 years ago was to blame for a mystery oil spill that had killed more than 1,300 birds since November 2001.

On 9 February 2002- NEW ZEALAND - more than 700 tonnes of fuel ran aground a few hundred metres from the north island port of Gisborne. Already, several tonnes of thick black oil has drifted 400 metres to shore, polluting nearby rivers, beaches and coastline and sending noxious fumes over dozens of houses.

On 4 April 2002- JAPAN - The 10-kilometer (6.2-mile) long spill had been slowly moving towards the coast since it bubbled to the surface from a Belize-registered cargo ship that sank four days earlier, after colliding with a fishing boat.

On 6 April 2002- USA - a 90,000-gallon crude oil spill off the southeast Louisiana coast.

On 12 June 2002- SINGAPORE - about 450 tonnes of marine fuel oil to spill into the south-eastern waters of Singapore.

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On 31 July 2002- ROMANIA - Tons of oil gushed into a river in southern Romania after torrential rains damaged a pipeline. The spill occurred in the Prahova River

On 12 September 2002-SOUTH AFRICA - Salvage teams and ecologists battled to contain a spill of oil and chemicals from a blazing cargo vessel, and to prevent tides from pushing the spill into the pristine Saint Lucia wetlands, a wildlife sanctuary nearby. Wildlife officials warned that a serious oil spill could pollute the Umfolozi River and a nearby estuary, and damage mangroves, crocodiles, hippos and a turtle nesting area in the park.

On 13 November 2002-SPAIN - Four tugs failed in their attempts to rescue a leaking oil tanker with 77,000 tonnes of fuel aboard, which later broke in two and sank off the northwestern coast of Spain. The Prestige, Greek-owned and registered in the Bahamas, leaked most of its cargo, and the oil washed up on the Galician shores and approaching the coastlines of Portugal and France. All fishing activities had been banned in the area, and the incident was fast becoming one of the worst ecological disasters ever to happen.

On 23 November 2002-CHINA - A Chinese ship has collided with a Maltese-registered oil tanker, spreading an oil slick 2.5 miles by 1.4 miles across the Bohai Sea.

On 5 December 2002-SINGAPORE - A potentially disastrous crude oil spill in Singapore waters was contained to just 350 tonnes when a small general cargo vessel collided with a heavily-laden single-hulled tanker in the middle of the Singapore Straits.

On 14 February 2003-USA - Clean up operations are underway at Midway Atoll National Wildlife Refuge after an underground corroded pipeline fitting released as many as 100,000 gallons of fuel in the fuel farm area

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On 18 March 2003- AUSTRALIA - A large oil spill was threatening to pollute the Brisbane River, where up to 1.5 million litres of crude oil had leaked from a ruptured pipeline at the Santos terminal.

On 20 March 2003- VIETNAM - Thousands of acres of clam and shrimp farms were in danger after a ship carrying 600 tonnes of fuel oil sank in the river in Ho Chi Minh City.

On 31 May 2003- SWEDEN - 100 tonnes of oil had already leaked out into the water, and a large oil slick gushing from the vessel had hit Sweden's popular southeastern coast.

On 12 June 2003-SINGAPORE - The MV APL Emerald, a 40,077 ton container ship, spilled about 150 tonnes of fuel oil when it ran aground near Horsburgh Lighthouse, in the eastern approaches of the Singapore Straits.

On 12 July 2003-RUSSIA - More than two tonnes of fuel had leaked in the past few days from the Takeo Maru. The leaked oil is floating in the Tatar strait and heading for the coast.

On 13 August 2003- PAKISTAN - An oil tanker had broken up off Pakistan's Arabian Sea port, Karachi, after spilling nearly 10,000 tonnes of oil.

On 19 January 2004- PHILIPPINES - An oil spill coming from a diving boat that ran aground at the Apo Manor Reef in December, Residents of Barangay Siblayan in Occidental Mindoro, a nearby coastal town, said that the M/V Island Explorer had started to leak bunker fuel, endangering the reef which serves as a fish nursery .

On 20 January 2004- NORWAY - A large oil spill had started spreading from the capsized cargo vessel "Rocknes", that spilled several thousand litres of oil and bunker fuel along the coastline near the city of Bergen.

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On 4 March 2004- CHINA - Nearly one million people in southwestern Sichuan province were without water for drinking and bathing, after chemicals spilled from a factory into an important Yangtze river tributary.

On 2 October 2004 - INDONESIA - Oil began leaking in the region known as the Thousand Islands, and government officials said the spill may have been caused by leaking oil pipes operated nearby by China National Offshore Oil Corp, or by a mishap loading oil onto tankers.

On 14 October 2004 - USA - Emergency crews scrambled to control a massive south Sound oil spill that spoiled portions of Tacoma's Commencement Bay and stretched for miles in a bluish-black sheen, threatening pristine beaches and wildlife on Maury and Vashon islands.

On 18 November 2004- BRAZIL - oil slick spread from a cargo ship that exploded and broke in half at a port in southern Brazil. Workers found dead fish and dolphins in the toxic slick of fuel oil, diesel fuel and methanol that leaked from the ship. The slick, which blackened rocks and beaches, stretched for more than 20 kilometres from the port of Paranagua.

On 21 November 2004- CANADA - Scientists warn the 44,000 gallon oil spill at an oil platform off Canada's Newfoundland province could kill up to 100,000 seabirds. The spill coming at a bad time for the birds.

On 26 November 2004 - USA - A tanker has spilled what was initially estimated as appr. 30,000 gallons of crude oil into the Delaware River between Philadelphia and southern New Jersey, immediately creating a 20-mile slick that threatened fish and birds.

On 7 December 2004 - CHINA - Nearly 450 tonnes had been spilled. Oil was mainly leaking from the fuel tanks of the MSC Ilona that caused a slick about 17 kilometers long and up to several hundred meters wide.

On 10 December 2004- USA - Thousands of gallons of fuel oil spilling out of a Malaysian freighter that snapped in two off the US state of Alaska put the Aleutian islands' fragile ecosystem in jeopardy, fueling fears

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of an environmental crisis 15 years after the Exxon Valdez disaster. The Selendang Ayu's 480,000-gallon (1.8 million-litre) stock of thick fuel was leaking into the water off Unalaska Island, killing cormorants and marine life and leaving a thick and dark coating on beaches. Wildlife in the area includes endangered or threatened species such as Steller sea lions and Steller's eiders as well as western Alaska sea otters, the population of which is dwindling.

On 20 December 2004-EGYPT - An oil slick in the Suez Canal was threatening to reach the Mediterranean, port sources said. The spill was caused by a leak in a Kuwaiti tanker carrying 160,000 tonnes of crude, after it collided with a dredger further south on December 14. The slick had tripled in size over a week several aquatic species were threatened by the contamination, and foreign officials charge that the Egyptian authorities have no adequate strategy to face such environmental threats and lack means to combat them.

On Monday 27 February 2006-Suez Canal: Liberian tanker leaks 3,000 heavy fuels in Suez Canal.

Annex II

ANNEX-II

Hydrochemistry of water

Complete chemical analysis of the collected water samples show in Table (1) including PH, EC, TDS major cations and major anions were carried out using standard methods for the Examination of water and waste water. The results of these analyses are expressed in ppm, epm and epm % and presented in Table (1) the chemical characteristics of water in the study area are discussed using the following parameters:

- 1- Total dissolved solids (TDS)
- 2- Frequency distribution of major ions
- 3- Ion ratios
- 4- Hypothetical ion combinations
- 5- Hydrochemical facies and genetic classifications
 - A- A-sulin diagram
 - B- B-piper diagram

Total dissolved solids

Total dissolved solids content of water is the chemically determined residue on evaporation, which is determined by evaporating to dryness a known volume of water at specified temperature usually 180°C. TDS also may be estimated from the conductivity because TDS in mg/l is proportional to the conductivity in micromhos:

$$\text{TDS (mg/L)} = A * \text{Conductivity } (\mu\text{mhos})$$

Where A=0.54-0.96 (usually 0.64)

In the study area, the TDS values of the water samples ranges between 11451 and 52080 mg/L

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Table (1): Chemical composition of water samples

S.N.	pH	EC	TDS mg/L	Temp °C	Unit	Major Cations				T.C	Major Anions			T.A
						Na	K	Ca	Mg		Cl	HCO ₃	SO ₄	
1	8.6	38.5	36561	28.4	ppm	11763.0	244.5	415.2	1036.3	624.83	19870.0	134.0	2987.0	624.14
					epm	511.43	6.27	20.76	86.36		559.72	2.20	62.23	
					epm%	81.9	1.0	3.3	13.8		89.7	0.4	10.0	
2	8.6	37.9	35987	28.4	ppm	10919.0	284.0	414.0	1356.0	615.72	19887.0	134.2	2772.0	620.15
					epm	474.74	7.28	20.70	113.00		560.20	2.20	57.75	
					epm %	77.1	1.2	3.4	18.4		90.3	0.4	9.3	
3	8.5	36.8	34972	28.1	ppm	10919.0	282.5	443.0	1222.0	605.96	19026.0	135.1	2670.0	593.78
					epm	474.74	7.24	22.15	101.83		535.94	2.21	55.63	
					epm %	78.3	1.2	3.7	16.8		90.3	0.4	9.4	
4	8.8	30.5	28989	27.9	ppm	8671.0	231.1	401.5	1031.0	488.92	15822.0	140.2	2173.0	493.26
					epm	377.00	5.93	20.08	85.92		445.69	2.30	45.27	
					epm %	77.1	1.2	4.1	17.6		90.4	0.5	9.2	
5	8.6	32.2	30617	29.3	ppm	10035.0	201.0	351.0	817.0	527.09	17084.0	130.0	1949.0	523.97
					epm	436.30	5.15	17.55	68.08		481.24	2.13	40.60	
					epm %	82.8	1.0	3.3	12.9		91.8	0.4	7.7	
6	8.7	26.5	25198	29.3	ppm	8365.0	170.0	267.0	587.0	430.32	13581.0	140.0	1840.0	423.19
					epm	363.70	4.36	13.35	48.92		382.56	2.30	38.33	
					epm %	84.5	1.0	3.1	11.4		90.4	0.5	9.1	
7	8.6	42.6	40460	29.3	ppm	12622.0	338.0	475.2	1449.0	701.96	22850.0	110.0	2367.0	694.78
					epm	548.78	8.67	23.76	120.75		643.66	1.80	49.31	
					epm %	78.2	1.2	3.4	17.2		92.6	0.3	7.1	
8	8.5	31.9	30371	26.8	ppm	9857.0	169.0	345.0	871.0	522.73	16814.0	146.0	2062.7	519.00
					epm	428.57	4.33	17.25	72.58		473.63	2.39	42.97	
					epm %	82.0	0.8	3.3	13.9		91.3	0.5	8.3	
9	8.6	23.8	22658	26.9	ppm	5750.0	403.0	756.1	1195.0	397.72	12426.0	150.0	1743.0	388.80
					epm	250.00	10.33	37.81	99.58		350.03	2.46	36.31	
					epm %	62.9	2.6	9.5	25.0		90.0	0.6	9.3	
10	8.7	33.9	32257	29.1	ppm	11187.0	279.0	423.0	1106.0	606.9	19537.0	140.5	2274.0	600.02
					epm	486.4	7.2	21.2	92.2		550.3	2.3	47.4	
					epm %	80.1	1.2	3.5	15.2		91.7	0.4	7.9	
11	8.7	36.9	35124	28.2	ppm	10785.0	264.5	472.0	1214.4	600.50	19222.0	122.5	2577.0	597.16
					epm	468.91	6.78	23.60	101.20		541.46	2.01	53.69	
					epm %	78.1	1.1	3.9	16.9		90.7	0.3	9.0	

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Con. Table (1): Chemical composition of water samples

S.N.	pH	EC	TDS mg/L	Temp °C	Unit	Major Cations				T.C	Major Anions			T.A
						Na	K	Ca	Mg		Cl	HCO ₃	SO ₄	
12	8.5	12	11451	25.8	ppm	3093.0	110.3	184.2	434.6		5605.4	199.5	913.9	
					epm	134.48	2.83	9.21	36.22	182.74	157.90	3.27	19.04	180.21
					epm %	73.6	1.5	5.0	19.8		87.6	1.8	10.6	
13	8.4	17.4	16522	25.8	ppm	4478.0	186.0	286.0	759.0		8656.0	211.1	1266.3	
					epm	194.70	4.77	14.30	63.25	277.01	243.83	3.46	26.38	273.67
					epm %	70.3	1.7	5.2	22.8		89.1	1.3	9.6	
14	8.5	21.1	20121	25.8	ppm	5889.9	179.0	346.0	738.3		10528.1	231.9	1648.0	
					epm	256.08	4.59	17.30	61.52	339.49	296.57	3.80	34.33	334.70
					epm %	75.4	1.4	5.1	18.1		88.6	1.1	10.3	
15	5.3	42.2	40154	25.7	ppm	11958.0	429.2	611.8	1602.0		21770.0	137.3	3519.9	
					epm	519.91	11.00	30.59	133.50	695.01	613.24	2.25	73.33	688.82
					epm %	74.8	1.6	4.4	19.2		89.0	0.3	10.6	
16	8.4	46.9	44642	25.7	ppm	14119.0	400.5	624.0	1271.0		23927.0	197.7	3430.0	
					epm	613.87	10.27	31.20	105.92	761.26	674.00	3.24	71.46	748.70
					epm %	80.6	1.3	4.1	13.9		90.0	0.4	9.5	
17	8.3	44.5	42251	26	ppm	11238.0	608.0	1045.0	2031.0		23278.0	1372.9	1699.0	
					epm	488.61	15.59	52.25	169.25	725.70	655.72	22.51	35.40	713.62
					epm %	67.3	2.1	7.2	23.3		91.9	3.2	5.0	
18	8.4	45.8	43579	25.6	ppm	13280.3	402.3	608.3	1589.0		23742.0	122.0	3592.0	
					epm	577.40	10.32	30.41	132.42	750.55	668.79	2.00	74.83	745.62
					epm %	76.9	1.4	4.1	17.6		89.7	0.3	10.0	
19	8.3	46.6	44288	25.8	ppm	13349.0	420.0	587.0	1680.0		24478.0	103.7	3397.0	
					epm	580.39	10.77	29.35	140.00	760.51	689.52	1.70	70.77	761.99
					epm %	76.3	1.4	3.9	18.4		90.5	0.2	9.3	
20	8.4	47	44651	25.7	ppm	14291.0	389.0	593.0	1284.0		24356.0	131.8	3399.9	
					epm	621.35	9.97	29.65	107.00	767.97	686.08	2.16	70.83	759.07
					epm %	80.9	1.3	3.9	13.9		90.4	0.3	9.3	
21	8.3	45.5	43246	26	ppm	13568.0	382.0	664.0	1361.0		24247.0	67.1	2869.0	
					epm	589.9	9.8	33.2	113.4	746.3	683.0	1.1	59.8	743.88
					epm %	79.04	1.31	4.45	15.20		91.82	0.15	8.03	
22	7.6	54.8	52080	17.6	ppm	14961.00	509.50	572.00	1867.00		27068.00	189.20	3992.80	
					epm	650.80	13.03	28.54	153.64	846.02	763.59	3.10	83.13	849.82
					epm %	76.93	1.54	3.37	18.16		89.85	0.36	9.78	
23	7.5	53	50194.8	25	ppm	15321.00	1751.00	473.00	1055.00		28243.00	177.00	1760.80	
					epm	666.46	44.79	23.60	86.80	821.65	796.70	2.90	36.66	836.26
					epm %	81.11	5.45	2.87	10.56		95.27	0.35	4.38	

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Frequency distribution of major Ions

The frequency distribution of cations ($\text{Na}^+ + \text{k}^+$, Ca^{++} , Mg^{++}) and anions (Cl^- , HCO_3^- , SO_4^{--}) and TDS in the water samples collected from the study areas is given in the form of histograms Figs.(1 and 2) Where the following notes could be deduced:

Table (2): The min, max and mean values of major ions for water samples.

Parameters	Min	Max	Mean
Na+K	3203	15470	2708.6
Ca	184	1045	494.7
Mg	435	2031	1204.6
Cl	5605	27068	18807.9
HCO3	67.1	1372.9	202.1
SO4	913.8	3992.8	2506.5

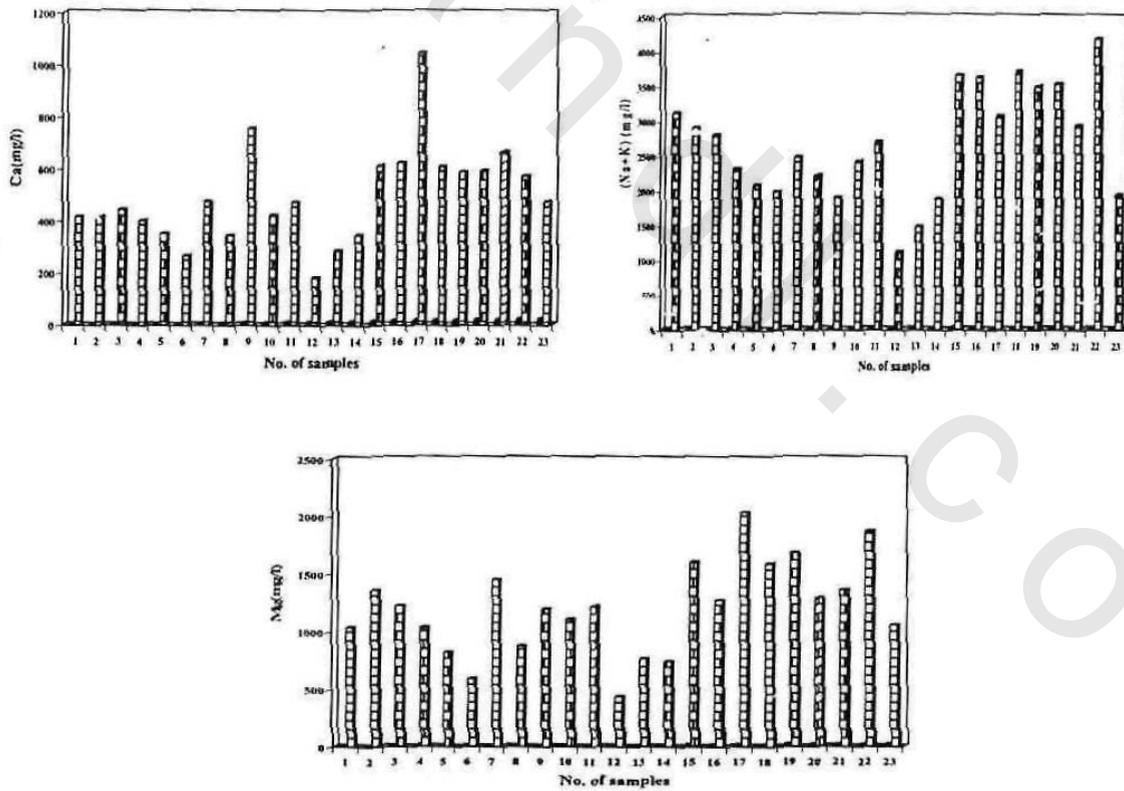


Fig.(1): Frequency distribution of major cation for water samples.

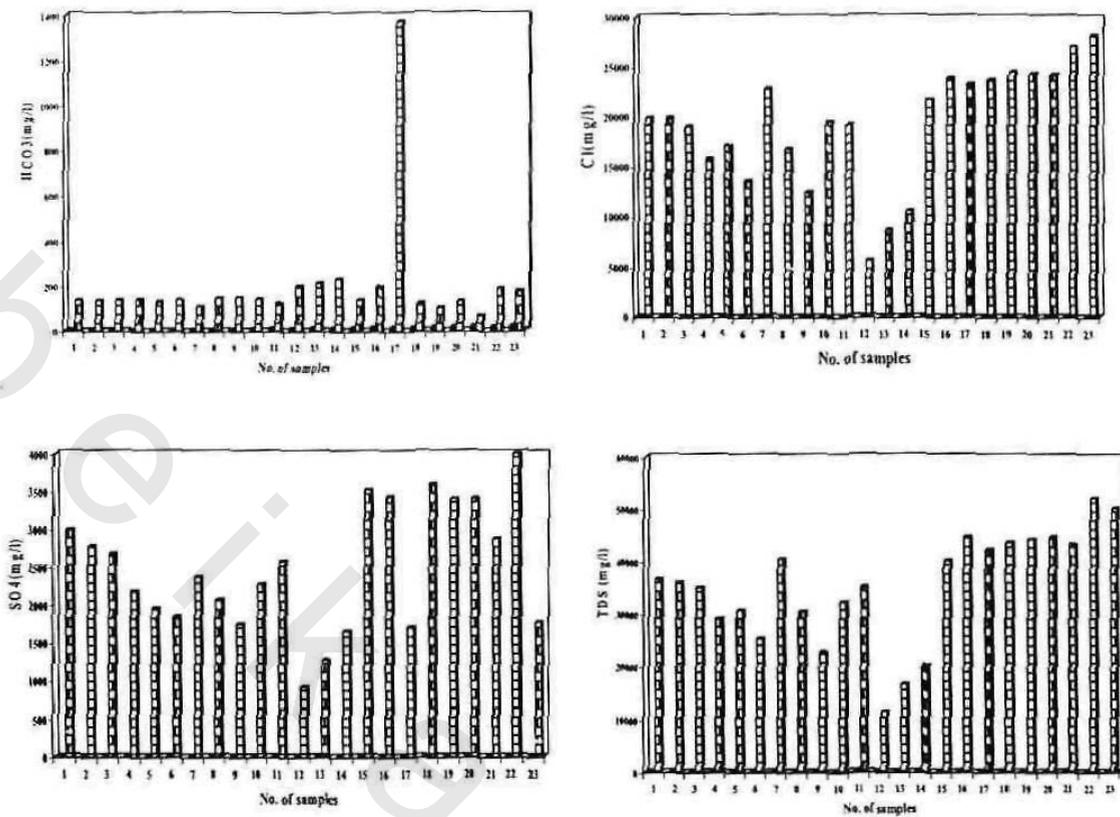


Fig.(2): Frequency distribution of major anion and TDS for water samples.

Ion ratios

Expression of the relationships among ions, or of one constituent to the total concentration in terms of mathematical ion ratios, is often helpful in making resemblances and differences among water types. Ion ratios are also very useful criteria used to detect the mineralization sources in the analyzed water sample. For example, the ratio of calcium to magnesium may be useful in studying water from limestone and dolomite and may help in tracing sea water contamination. The ratio of sodium to total cations is useful in areas of natural cation exchange, while the ratio of chloride to another ion also may be useful in studies of water contaminated with common salt (sodium-chloride) the following ion ratios are chosen for the studied area see Table (3).

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Table (3): Ion ratio of water samples collected from the studied area

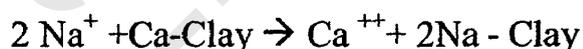
S.N	Na ⁺ /Cl ⁻	(Cl ⁻ -Na ⁺)/Cl ⁻	Ca ²⁺ /Mg ²⁺	SO ₄ ²⁻ /Cl ⁻	Cl ⁻ /HCO ₃ ⁻	Ca ²⁺ /Cl ⁻	Mg ²⁺ /Cl ⁻	Ca ²⁺ /SO ₄ ²⁻	Ca ²⁺ /HCO ₃ ⁻	Mg ²⁺ /HCO ₃ ⁻	(Cl ⁻ -Na ⁺)/Mg ²⁺	(Na ⁺ -Cl ⁻)/SO ₄ ²⁻
1	0.91	0.09	0.24	0.11	255.25	0.04	0.15	0.33	9.44	38.83	0.57	-0.79
2	0.85	0.15	0.19	0.10	255.01	0.04	0.20	0.36	9.39	50.72	0.77	-1.49
3	0.88	0.12	0.22	0.10	242.42	0.04	0.19	0.40	9.98	45.42	0.61	-1.11
4	0.85	0.15	0.24	0.10	194.23	0.04	0.19	0.44	8.72	36.92	0.82	-1.53
5	0.91	0.09	0.26	0.08	226.16	0.04	0.14	0.43	8.22	31.55	0.68	-1.12
6	0.95	0.05	0.28	0.10	166.94	0.03	0.13	0.35	5.81	21.05	0.40	-0.50
7	0.85	0.15	0.20	0.08	357.51	0.04	0.18	0.48	13.15	66.13	0.80	-1.94
8	0.90	0.10	0.24	0.09	198.21	0.04	0.15	0.40	7.19	29.95	0.64	-1.06
9	0.71	0.29	0.38	0.10	142.55	0.11	0.28	1.04	15.34	39.99	1.02	-2.77
10	0.88	0.12	0.23	0.09	239.31	0.04	0.17	0.45	9.17	39.52	0.71	-1.36
11	0.87	0.13	0.24	0.10	270.05	0.04	0.18	0.44	11.73	49.77	0.73	-1.36
12	0.85	0.15	0.26	0.12	48.36	0.06	0.23	0.48	2.81	10.94	0.66	-1.24
13	0.80	0.20	0.23	0.11	70.57	0.06	0.26	0.54	4.12	18.05	0.79	-1.87
14	0.86	0.14	0.28	0.12	78.14	0.06	0.20	0.50	4.54	15.98	0.67	-1.19
15	0.85	0.15	0.23	0.12	272.95	0.05	0.21	0.42	13.57	58.59	0.71	-1.28
16	0.91	0.09	0.30	0.11	208.33	0.05	0.15	0.44	9.61	32.28	0.58	-0.85
17	0.74	0.26	0.31	0.05	29.18	0.08	0.25	1.47	2.32	7.43	1.00	-4.74
18	0.86	0.14	0.23	0.11	334.88	0.05	0.20	0.41	15.18	65.38	0.70	-1.23
19	0.84	0.16	0.21	0.10	406.19	0.04	0.20	0.41	17.23	81.32	0.79	-1.55
20	0.90	0.10	0.28	0.10	318.09	0.04	0.15	0.42	13.70	48.92	0.62	-0.92
21	0.86	0.14	0.30	0.09	621.83	0.05	0.16	0.55	30.12	101.82	0.84	-1.57
22	0.85	0.15	0.19	0.11	246.24	0.04	0.20	0.34	9.20	49.54	0.73	-1.36
23	0.84	0.16	0.27	0.05	274.72	0.03	0.11	0.64	8.14	29.93	1.50	-3.55

Na⁺/Cl⁻ Ratio

The Na⁺/Cl⁻ ratio is a good indication for the chemical contamination of the natural water. The values of this ratio are always higher than unity in fresh and meteoric water, while it is less than unity in sea water.

Na⁺=Cl⁻ indicates halite dissolution

Na⁺< Cl⁻ indicates reverse softening (brine or sea water)



Na⁺> Cl⁻ indicates a Na source other than halite or natural softening.



Fig (3) shows the relation between Na⁺+ K⁺ (epm) vs. Cl⁻(epm) of the water samples. It is noted that all samples of the studied area have

Na⁺ /Cl⁻ values lower than unity suggesting that mineralization of these samples is due to marine chloride salts (MgCl₂ and CaCl₂).

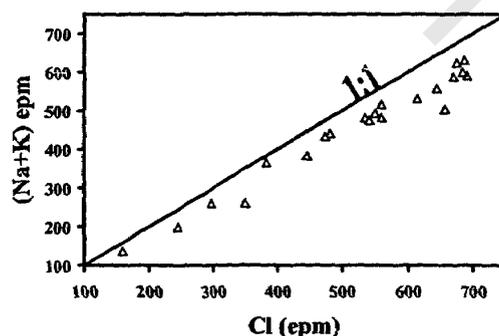


Fig.(3): Relation between (Na+K) vs. Cl.

Ca⁺⁺/Mg⁺⁺ Ratio

This ratio is useful in studding the different origins of the two ions. Carbonate rocks and dolomite contain mainly both Ca⁺⁺ and Mg⁺⁺ ions. Base

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Exchange process of Mg^{++} Ion against Na^+ or Ca^{++} is another source of magnesium ion.

In sedimentary rocks the lowest Ca^{++}/Mg^{++} will occur with dissolution of dolomite where Ca^{++} will be approximately equal to Mg^{++} (Meisler and Becher, 1967) This is suggested by a moderate TDS of about 500 mg/l. however, Ca^{++}/Mg approaches once it is very likely that Ca^{++} has been removed from the solution this process is commonly called dedolomitization if Mg^{++} is greater than Ca^{++} there are two common possibilities. The first is the dissolution of ferromagnesian minerals from mafic or ultramafic rocks where the TDS will be low about 100-200 mg/l. the second would be sea water intrusion where the TDS would be high- probably greater than 500 mg/l.

Fig (4) shows the relation between Ca^{++} vs. Mg^{++} for the studied area, the Ca^{++}/Mg^{++} ratio is found to be less than unity for the analyzed water.

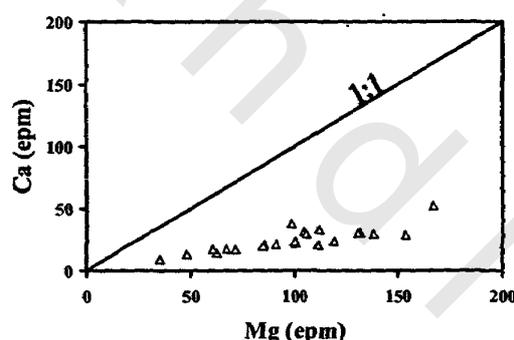


Fig.(4): Relation between Ca vs. Mg.

SO_4^-/Cl^- Ratio

This ratio is useful in detecting the influence of halite, gypsum, or anhydrite Collins (1972) found that generally the epm SO_4^-/Cl^- ratio ranged from 0-0.34, although usually it was <0.17 Hem (1992) suggests that sulphate in ionic proportions similar to sea water may indicate salt water intrusion the value of SO_4^-/Cl^- in sea water is 0.405 (meq/l).

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In the studied area, all water samples have SO_4^- ion concentration less than the Cl^- ion, which may be due to a higher content of halite salts within the aquifer deposits leading to an excess of Cl^- ion content the average value of $\text{SO}_4^-/\text{Cl}^-$ is 0.1.

$\text{Cl}^-/\text{HCO}_3^-$ Ratio

The $\text{Cl}^-/\text{HCO}_3^-$ ratio is low in case of water samples with low salinity due to the mixing with surface water and irrigation water. Dissolution of carbonate rocks dolomite and limestone are another source of bicarbonate ion content. In the studied area, $\text{Cl}^-/\text{HCO}_3^-$ ratio is found to be more than unity the average value is 230 with high TDS values, In general, the higher the salinity the higher the $\text{Cl}^-/\text{HCO}_3^-$ ratio of water.

$\text{Ca}^{++}/\text{Cl}^-$ and $\text{Mg}^{++}/\text{Cl}^-$ Ratios

These ratios, which represent a relative relationship between the less abundance ions (Ca^{++} & Mg^{++}) and the conservative ion (Cl^-), are helpful in studying the modification of water composition due to leaching action of different salts. In studied area, the average values for these ratio is 0.05 for $\text{Ca}^{++}/\text{Cl}^-$ ratio and 0.19 for $\text{Mg}^{++}/\text{Cl}^-$ ratio Fig.(5) shows the relation between Mg^{++} vs Cl^- for the analyzed water. This plot is an indication for the degree of mixing between marine and fresh water the location of the points around the 1:4 line (sea water composition).

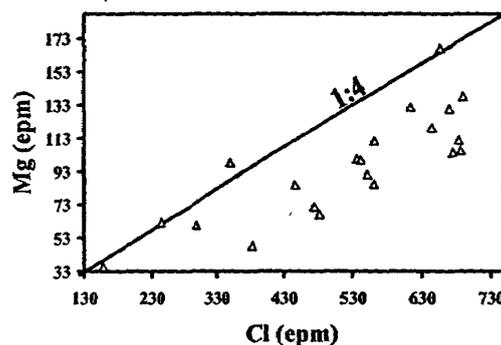


Fig.(5): Relation between Mg vs. Cl.

Ca⁺⁺/SO₄⁻⁻ Ratio

Generally, sulphate is the result of direct dissolution of gypsum (or anhydrite) or the neutralization of acid waters by limestone or dolomite

Ca⁺⁺=SO₄⁻⁻ indicates gypsum

Ca⁺⁺<SO₄⁻⁻ indicates pyrite oxidation, or Ca⁺⁺ removal, Such as calcite precipitation, or natural softening.

Ca⁺⁺>SO₄⁻⁻ indicates a Ca⁺⁺ source other than gypsum, such as calcite/dolomite or silicates.

Fig.(6) shows the relation between Ca⁺⁺ vs. SO₄⁻⁻ for the investigated water samples. In the studied area have the Ca⁺⁺/SO₄⁻⁻ ratio less than unity except sample no. 9.

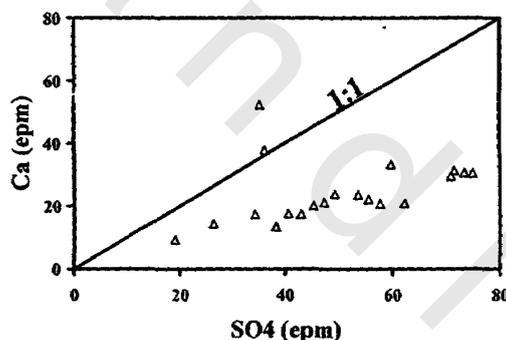


Fig.(6): Relation between Ca vs. SO₄.

Ca⁺⁺/HCO₃⁻ and Mg⁺⁺/HCO₃⁻ Ratios

These ratios, which represent a relative relationship between the less abundance ions (Ca⁺⁺ & Mg⁺⁺) and the conservative ion (HCO₃⁻), are helpful in studying the modification of water composition due to leaching action of different salts. Fig.(7) shows the relation between (Ca⁺⁺ + Mg⁺⁺) vs HCO₃⁻ for the analyzed water.

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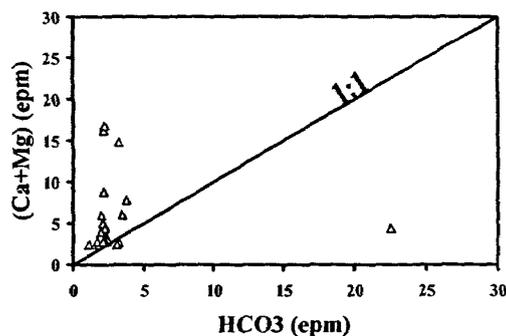


Fig.(7): Relation between (Ca+Mg) vs. HCO₃.

Hypothetical ion combinations

Hypothetically, the ions of strong acid (Cl⁻ & SO₄⁻) from chemical combinations with the alkalis (Na⁺ & K⁺) and the rest of acid radicals give combination with the alkali earths (Ca⁺⁺ & Mg⁺⁺) if the later are in surplus in water, they will combine with weak acids (CO₃⁻ & HCO₃⁻). The relationships between the equivalent cations & anions percentage in the study area can be illustrated in the form of ionic concentration bar graph (Collins, 1923) in this method, the concentration of the dissolved cat ions and anions, expressed in epm% are represented by vertical bar graph, the height of which is equivalent to the concentration percentage of anions (on the right half) or cations (on the left half). According to palmer method (Palmer, 1911) the deduced hypothetical ion combinations for each sample are given in a vertical segment between the two vertical halves. In general, the chemical composition of water reflects either primary marine or meteoric water origins. The gradual removal, mixing and dilution of the original marine water between rock pores by the invading meteoric water could be traced from one zone to another by determining its chemical composition. According to Ivanov et.al. 1968, water of "marine origin" is classified as magnesium chloride type and is characterized by the major chemical components:



Fig.(8) show that there are three different marine salt combination groups are represented as follows

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Group1 KCl, NaCl, MgCl₂, MgSO₄, CaSO₄.

For 43.5% of water samples (1, 7, 11, 15, 16, 18, 19, 20, 21, 22)

Group2 KCl, NaCl, MgCl₂, MgSO₄, CaSO₄, Ca (HCO₃)₂.

For 52.2% of water samples (2,3,4,5,6,8,10,12,13,14,17,23)

Group3 KCl, NaCl, MgCl₂, CaSO₄, Ca (HCO₃)₂.

For 4.3% of water sample (9)

These groups characterized by MgCl₂ salt, may indicate leaching of marine facies, the presence of calcium and magnesium sulphate may be the result of dissolution of evaporites containing sulphate group.

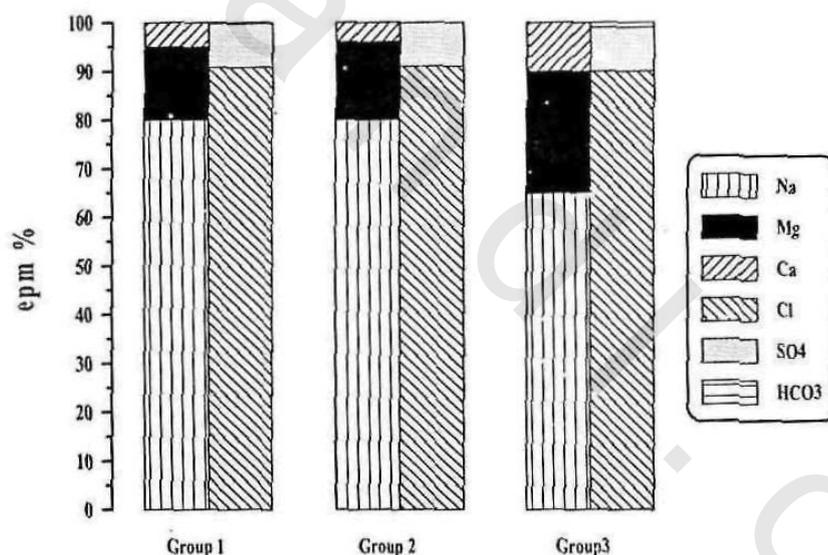


Fig.(8): Bar graph for Studied area.

Hydrochemical Facies and Genetic Classifications

Different methods of graphical representation of analysis have been proposed to detect and identify mixing of waters of different composition and to identify some of the chemical processes that may take place as natural

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water circulates. Two of the graphical techniques are used here for the classification of the waters in the study area.

Sulin Diagram

Sulin diagram of genetic classification (Sulin, 1948) Consists of two equal quadrants connected together at a central point where $(Na^+ + K^+)/Cl = 1$. the first one genesis where $(Na^+ + K^+)/Cl < 1$ this quadrant is divided into two equal triangles, the upper one represents $CaCl_2$ water type where $Cl^- - (Na^+ + K^+)/Mg^{++} > 1$, while the lower triangle represents $MgCl_2$ water type where $Cl^- - (Na^+ + K^+)/Mg^{++} < 1$ the second quadrant occupies the lower left side of the central point and indicates water of meteoric genesis when $(Na^+ + K^+)/Cl > 1$. similarly ,this quadrant is divided into two equal triangles, the lower one represents $NaHCO_3$ water type where $(Na^+ + K^+) - Cl / SO_4^{-} > 1$, while the upper triangle represents Na_2SO_4 water type where $(Na^+ + K^+) - Cl / SO_4^{-} < 1$. In the study area, the genetic salts are marine origin which represented by 100% $MgCl_2$ Fig. (9).

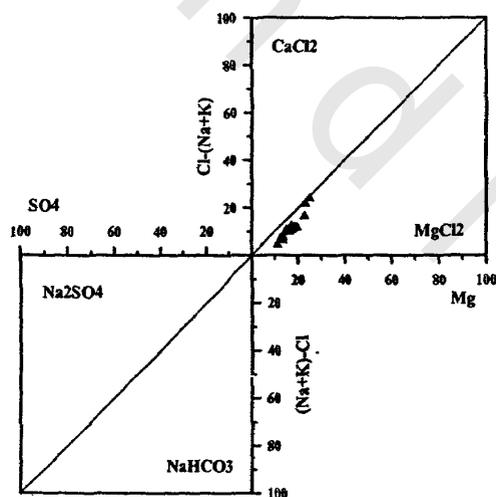


Fig.(9): Sulin diagram for Studied area.

Piper diagram

Piper diagrams (piper, 1944) are a combination anion and cation triangles that lie on a common baseline adjacent sides of the two triangles are then 60° apart. A diamond shape between them is plotted on a piper diagram

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can be used to make a tentative conclusion as to the origin of the water represented by the analysis. The diamond part of a piper diagram may be used to characterize different water types. Piper divided waters into four basic types according to their placement near the four corners of the diamond. Water that plots at the top of the diamond is high $\text{Ca}^{++} + \text{Mg}^{++}$ and $\text{Cl}^- + \text{SO}_4^-$, which results in an area of permanent hardness. The water that plots near the left corner is rich in $\text{Ca}^{++} + \text{Mg}^{++}$ and HCO_3^- and is the region of water of temporary hardness. Water plotted at the lower corner of water lying near the right-hand side of the diamond may be considered saline ($\text{Na}^+ + \text{K}^+$ and $\text{Cl}^- + \text{SO}_4^-$). In the studied area, the plotted data on the diamond shape Fig (10) occupies the upper right hand side of the diamond shape and this is dominantly characterized water of marine origin (sea water composition).

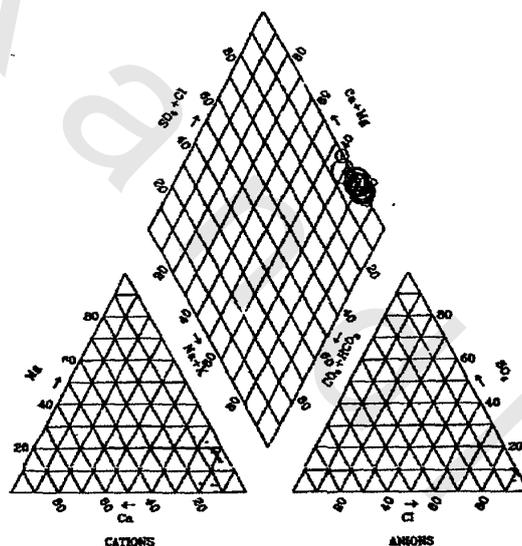


Fig. (10): Piper diagram for studied area.

Arabic Summary



تقييم الملوثات البترولية فى منطقة خليج السويس مع التركيز
على المركبات الهيدروكربونية العطرية عديدة الحلقة

رسالة مقدمة

كجزء متمم لنيل درجة الماجستير فى الكيمياء العضوية

مقدمة من

هاجر ربيع محمد على

بكالوريوس علوم - ٢٠٠١

قسم الكيمياء

كلية العلوم - جامعة حلوان

٢٠٠٧



**تقييم الملوثات البترولية فى منطقة خليج السويس مع التركيز
على المركبات الهيدروكربونية العطرية عديدة الحلقة**

رسالة ماجستير

التوقيع

أسماء السادة المشرفين

أ. و. جلال الدين حمزة الجميلى

أ. و. سامية رضوان العزباوى

أ. و. محمد إبراهيم رشى

أ. و. ياسر محمد محمود مصطفى

المخلص العربى

واكتملت الرسالة بدراسة بعض طرق معالجه التلوث البترولى بيولوجيا باستخدام الكائنات الدقيقة سواء المتواجدة أصلا فى البيئة أو المضافة إليها حيث وجد أن انسب الطرق وأكفأها هى تنميه الكائنات المتواجدة أصلا فى مكان التلوث المعالج وتمت هذه المعالجة على ثلاثة عينات من التربة الملوثة بدرجات مختلفة وخلصت الدراسة على ضرورة انجاز الرصد المتكرر من أن لآخر للملوثات البيئية فى المنطقة بهدف مساعده متخذى القرار على المتابعة ووضع الضوابط اللازمة لحماية المنطقة و الحفاظ على سلامتها بيئيا.

المخلص العربي

تتعرض منطقة خليج السويس بصفه مستمره إلى التلوث البترولى نتيجة للأنشطة البترولية المختلفة المتواجده به وبشواطئه.

وتشمل الدراسة رصد بيئى للتلوث البترولى المتواجد فى بعض مكونات البيئة المذكورة (مياه-رواسب-اسماك) و التى تشمل قناة السويس وبحيرة التمساح وخليج السويس بهدف التعيين الكيفى والكمى للملوثات وكل من مكوناتها على التركيز على المركبات العطرية عديدة الحلقة لما لها من تأثير ضار على البيئة والصحة.

وقدمت الدراسة فى ثلاثة اتجاهات أولها التعيين الكمى للملوثات ككل حيث أوضحت النتائج وجود تلوث بأحمال قد تعرض البيئة البحرية لآثار ضاره بما فى ذلك السلسلة الغذائية أما الاتجاه الثانى فقد تمثل فى تعيين المركبات البرافينية ذات السلسلة المستقيمة والمتفرعة وكذلك المركبات العطرية والبرافينية الحلقية ككل وذلك باستخدام جهاز كروماتوجرافيا الغازات حيث وجد أن الملوثات فى مجملها إما ناتجة من أصل بترولى أو بترولى مضاف إليه بعض المركبات البرافينية الناتجة من أصل حيوى كما ثبت وجود ملوثات حديثه أو متقدمة بدرجات مختلفة مما يدل على أن التسرب البترولى فى المنطقة متواصل (متكرر).

وللتعرف على نوعيه المركبات العطرية عديدة الحلقة تم استخدام جهاز كروماتوجرافيا السوائل ذو الأداء العالى حيث تم التعرف على العديد من المركبات ذات السمية العالية والمسرطنه.