

Identification of Hydrocarbon Microseepage Using Trace Metal Indicators in Petroliferous Region of South Cambay Basin, Gujarat, India

M. A. Rasheed*, P. L. Srinivasa Rao., Anand Patil., Harshit Patel, Shubhangi Kala, Annapurna Boruah., Syed Zaheer Hasan., P.H. Rao, T.Harinarayana

Petroleum Research Wing,
Gujarat Energy Research and Management Institute (GERMI),
Gandhinagar, Gujarat, India

*abdul@germi.res.in

Abstract: *The concentrations of trace elements have been used as indirect proxy for detection of hydrocarbon microseepage. The long-term seepage of hydrocarbons, either as macro or micro-seepage, can set up near-surface oxidation reduction zone that favors the development of a diverse array of chemical and mineralogical changes. Under the reducing environment the hydrocarbon seepage, the solubility of trace elements increases that transports, due to hydrodynamic flow in the soil leading to the movement of soluble elements towards the reducing area. This study compares the trace element concentrations with adsorbed soil gaseous hydrocarbons and explains the trace elements concentrations pertaining to the hydrocarbon micro seepages. Total 81 numbers of soil samples were collected from the depth range of 1-2.5 meters below the ground level from Southern part of the Cambay Basin.*

The trace metals such as Chromium (Cr), Copper (Cu), Arsenic (As), Selenium (Se) and Antimony (Sb) in the soil samples were analyzed using Atomic Absorption Spectrometer. The analytical results show the varying range of concentrations as Cr (0 to 76ppm), Cu (59 to 168ppm), as (63 to 155ppm), Se (72 to 182ppm) and Sb (6 to 19ppm). It has been observed that the concentrations of these elements are more when they are compared with their normal concentrations in the soils. The analyses of adsorbed soil gases show the presence of high concentrations of methane (CH₄) ranged between 2 to 290 ppb, and sum of concentrations of ΣC_{2+} (C₂H₆, C₃H₈ and n-C₄H₁₀) ranged between 7 to 118 ppb. The integrated approach of trace elements over adsorbed light gaseous hydrocarbon (ΣC_{2+}) anomalies showed better understanding. The increased concentrations of trace metals, suggest a soil chemical change to a reducing environment, presumably due to the influence of hydrocarbon microseepage. This methodology could further integrated with other geo-scientific studies such as 3D Seismic studies which may evolve with the holistic picture of identification of hydrocarbon bearing formations within the exploration blocks and the frontier areas.

Keywords: *Hydrocarbon; Microseepage; Trace metals; Adsorbed soil gas, Cambay Basin.*

1. INTRODUCTION

The surface geochemical methods are based on the premise that the hydrocarbons gases, CH₄, C₂H₆, C₃H₈, C₄H₁₀ and C₅H₁₂ tends to migrate to the surface from the sub-surface regions through faults and fractures with different mechanisms as diffusion, effusion, buoyancy and advection etc. These gases get adsorbed near surface soil matrix, which on further quantification draws the hydrocarbon potential of an area (Price, 1986; Tedesco, 1995; Schumacher and Abrams, 1996). These gaseous hydrocarbons may be detected either directly through adsorbed soil gas or free gas and indirectly using microbial indicators and trace element behavior geochemistry through the geochemical changes they induce with an anomaly at the surface. The long-term seepage whether macro or microseepage can set up a near-surface oxidation reduction zone that favors the development of a diverse array of chemical and mineralogical changes (Donovan, 1974; Petrovic et al, 2008, Khan and Jacobson, 2008). The bacterial oxidation of light hydrocarbons can further bring significant changes in the pH and Eh of the surrounding environment, thereby changing the stability fields of the different mineral species present in the said environment.

The anomalies in the concentration of trace metals as chromium (Cr), manganese (Mn), selenium (Se), antimony (Sb), copper (Cu), bromide (Br), and zinc (Zn) are related to the hydrocarbon reservoirs (Clark et al., 2003). Since, a boundary is formed between the reducing and oxidizing zones

by the deposition of carbonate oxide and sulphide minerals, several metals are mobilized in soils and accumulated around the hydrocarbon accumulation zones (Nissenbaum and Swaine, 1976). Trace metal associations forming organo-metallic compounds have been found as “haloes” or concentrated over or around the underlying hydrocarbon reservoirs (Duchscherer, 1983; Schumacher, 1996). Geochemical haloes for vanadium (V), chromium (Cr), manganese (Mn), nickel (Ni), cobalt (Co), copper (Cu), molybdenum (Mo), uranium (U), iron (Fe) and zinc (Zn) have been worked out by Duchscherer (1984) in the oil fields of Texas and Montana, USA. Manganese (Mn), vanadium (V), nickel (Ni), and copper (Cu) trace elements, as well as the radioactive elements like uranium (U) and radium (Ra), were found to be adsorbed to a greater extent around the periphery of Kyurov-Dag Oil Field in the Azerbaijan field (Alekseev et al. 1961).

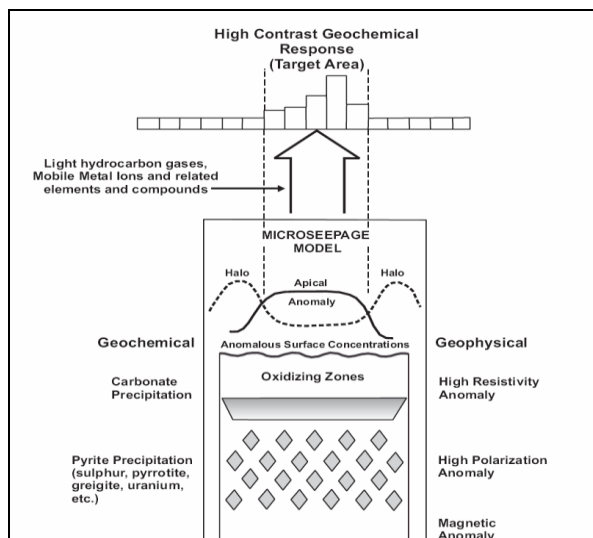


Fig1. Diagrammatic view showing the Vertical migration of elements and compounds, mineralogical haloes and geophysical responses over a hydrocarbon reservoir (modified after Schumacher, 1996).

Anomalous amounts of vanadium, chromium, nickel, cobalt, manganese mercury, copper, molybdenum, uranium, zinc, lead and zirconium are positive indicators of petroleum deposits (Duchscherer, 1984). Trace elements concentrations have been used as indirect indicator for hydrocarbon microseepage (Schumacher, 1996; Madhavi et al, 2011; Rasheed et al., 2012). The present study is aim on the role of trace elements as indicators in locating the hydrocarbon microseepage in the study area of South Cambay Basin, Gujarat, India, with the objective to appraise the usefulness of analytical data by integrating with adsorbed soil gas data as an elementary tool in deciphering the zone of hydrocarbon accumulation.

2. GEOLOGY OF THE STUDY AREA

The Cambay basin is an intracratonic graben bounded on the both sides by basin-margin faults covering an area around 59,000 sq km. The Geological location map of the study area in Cambay Basin in figure 2. The detailed stratigraphy, geology and tectonics have been reported by Raju (1969), Bhandari and Choudhary (1975), Biswas (1982, 1987), Biswas et al. (1994), and Kundu et al. (1997). The graben is divided into four blocks, ranging from north to south as Ahmedabad-Mehsana, Tarapur, Broach-Jambusar and Narmada (Mathur et al. 1968) The basin is further divided into two parts as North Cambay basin and South Cambay basin being separated by the Mahi River (Mayor, S. et. al., 2004). The study area falls in the Northern part of the Ankleswar oil field, which is an important part of the Narmada-Tapti block of South Cambay basin (Dhar and Bhattacharya, 1993).

The Ankleshwar oil field lies in the western part of the Cambay Basin. The field is marked by a doubly plunging anticline, trending ENE–WSW having multi-layered sandstone reservoir of deltaic origin. The Ankleshwar formation, which was deposited during the marine regression phase during the Upper to Middle Eocene (Holloway et al., 2007) is the major stratigraphic unit. The formation consists of four sub-litho logical units. Telwa shale acting as an effective seal, Ardol, Kanwa shale and Hazad members from top to bottom. The Hazad is an important reservoir sandstone; however, it contains shale laminae. The Ardol section comprises sand-shale alterations (Bhanja, et. al., 2011; Vadapalli, et. al., 2014). The Ankles war formation is overlain by the Dadhar formation and underlain

Identification of Hydrocarbon Microseepage Using Trace Metal Indicators in Petroliferous Region of South Cambay Basin, Gujarat, India

by Cambay shale, the source rock. (Vadapalli, et. al., 2014). The generalized stratigraphy of Cambay Basin is shown in Figure 3.

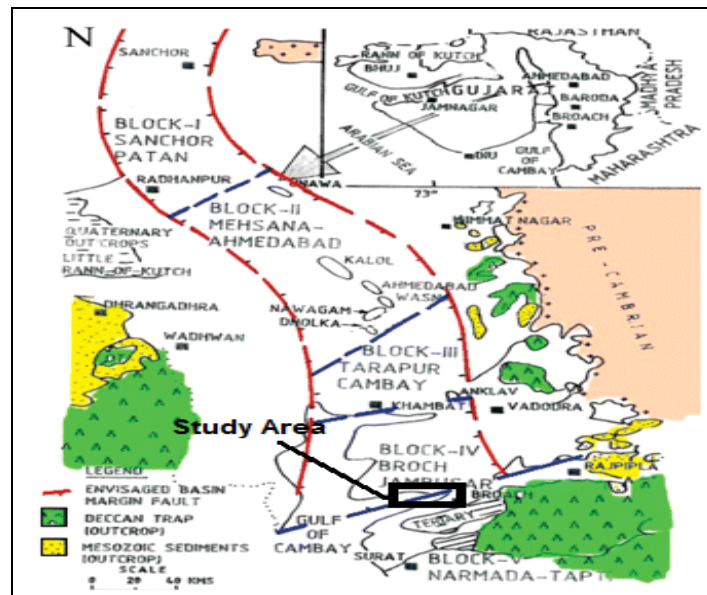


Fig2. Geological location map of the study area in Cambay Basin.

| Formations | Thickness (ft) | Lithology | Lithological Description | Age |
|-----------------|----------------|-----------|---|----------------|
| GUJ. ALLUVIUM | 50 - 100 | | Yellow and grey sandy clays | RECENT |
| JAMBUSAR | 300 | | Yellow and grey clays, sands, gravel and kankar | PLEISTOCENE |
| BROACH | 300 | | Chocolate brown and red brown claystone, sandy claystone and sandstone | PLIOCENE |
| JHAGADIA | 200 | | White and grey calcareous and micaceous sandstone, grey, shaly sandstone and sands | UPPER MIOCENE |
| KAND | 200 | | Grey clay and claytons with occasional sandstone and conglomerate | MIDDLE MIOCENE |
| BABAGURU | 300 | | Ferruginous sandstone conglomerate and grey clays-claystone | LOWER MIOCENE |
| TARAKHSHWAR | 150 | | Varegated and mottled claystone and sandstone Carbonaceous silty shale | OLIGOCENE |
| TARAPUR SHALE | 200 - 300 | | Greenish grey to dark grey shales, silty and sandy shales and argillaceous sandstones south of Mahisagar river, sandstones, dark grey, greenish grey shales, coaly shales and coals | UPPER EOCENE |
| BANDHUPUR SHALE | 200 - 300 | | Sandstone, calcareous silty shales and siltstone, silty claystones, dark grey shales, coaly shales and coals | MIDDLE EOCENE |
| THARAD SHALE | 500 - 750 | | Dark grey to grey shale, moderately hard, massive sands, sandstone, Carbonaceous dark grey shales and coals | LOWER EOCENE |
| CAMBAY SHALE | 500 - 750 | | Dark grey to black fossiliferous shales, hard and rich in contained organic matter, intertonguing with Olpad formation | PALAEOCENE |
| OLPAD | 20 - 1500 | | Volcanic conglomerates, sandstones, silty clay, claystones and clays of light grey to reddish brown and flaming red color. The matrix is clayey and chloritic locally carbonate enriched zones are also present | PALAEOCENE |

Fig3. Generalised stratigraphy of Cambay basin (after Raju and Srinivasan, 1993)

3. MATERIALS AND METHODS

3.1. Sample Collection

Towards and accuracy in the analytical trends the area under study has been divided into 1km x 1km interval grid from where the samples were collected. In total 81 sampling locations have been identified and the core samples were collected from the depth range of 1- 2 m using manual hammering of hollow metal pipe. For this purpose 500 g of core soil samples were collected and wrapped in aluminum foil and sealed in poly-metal packs used for analysis of adsorbed soil gases and trace element concentrations. The samples were sealed in plastic bags marked with the sample number code along with the location using the global positioning system (GPS) (Rasheed et al, 2008).

3.2. Methodology Adopted for Gas Chromatograph

The light gaseous hydrocarbons were extracted from the soil samples using a gas extraction system (Horvitz, 1981). 1 gm of 63 μ particle size soil sample was used to extract light gaseous hydrocarbons

after acid treatment in glass degasification apparatus and subsequent analyses on gas chromatograph (GC) and gas chromatograph–combustion–isotope ratio mass spectrometer (GC–C–IRMS) analysis for samples that had higher concentrations of hydrocarbons. During acid treatment, the dominant gas released was CO₂ which was trapped in KOH solution. The light gaseous hydrocarbons were collected by water displacement in a graduated tube fitted with rubber septa. The volume of desorbed gas was recorded and 500 µl of desorbed gas sample was injected into gas chromatograph (Varian CP 3380) fitted with a Porapak Q column, equipped with a flame ionization detector. The gas chromatographs were calibrated using external standards with known concentrations. The quantitative estimation of light gaseous hydrocarbon constituents in each sample was made using peak area measurements and a correction for moisture content on a wet basis was also applied. The hydrocarbon concentration values of individual hydrocarbons from methane through pentane are expressed in parts per billion (µg/kg).

3.3. Atomic Absorption Spectrometer

Atomic absorption occurs when a ground state atom absorbs energy in the form of light of a specific wavelength and is elevated to an excited state. The amount of light energy absorbed at this wavelength will increase as the number of atoms of the selected element in the light path increases. The relationship between the amount of light absorbed and the concentration of analytes present in known standards can be used to determine unknown sample concentrations by measuring the amount of light they absorb. The analysis of trace metals in the soil samples was carried out using AAS (Perkin-Elmer AAnalyst-400) at the Petroleum Research Lab, GERMI, Gandhinagar. Photo multiplier tube detector has been used to determine the concentration of trace metals. Five trace metals of 81 samples were analyzed by using the AAS.

3.4. Sample Processing

100 gm of soil sample was taken in 250 ml of distilled water and soaked it for overnight. The soaked soil sample was mixed by using constant speed mixture (500 RPM). The complete mixed soil sample sieved with 63 micro sieve using Electro lab Sieve shaker for 20 minutes. The 63 micron sieved sample was kept for drying in Petri dishes. Dried soil sample powdered in an agate mortar and filled into the plastic vial.

3.5. Sample Digestion

0.3 gm of powdered soil sample was taken in Teflon vessels and 6 ml of conc. Nitric acid (HNO₃) and 1ml of Hydrofluoric acid (HF) mixture was added to sample. This mixture was digested for approximately 45 minutes at 40 bar pressure and 175 °C temperature in microwave digester (Perkin Elmer TITAN-MPS).

4. RESULTS AND DISCUSSIONS

4.1. Trace Element Geochemistry

Trace element concentrations in soil samples of the study area are given in Table 1. The trace metals such as Chromium (Cr), Copper (Cu), Arsenic (As), Selenium (Se) and Antimony (Sb) have been considered for the study. The concentration of each of the trace elements is found as Cr (0 to 76ppm), Cu (59 to 168ppm), as (63 to 155ppm), Se (72 to 182ppm) and Sb (6 to 19ppm) respectively. The Descriptive statistics of trace elements in soil samples of the study area is given in Table 1. The concentrations of trace elements in normal soils are as taken as Cr (70ppm), Cu (30ppm) (Bowen, 1979). It has been observed that the concentration of trace elements is tremendously increased when compared with normal concentrations in soils. The trace element concentration distribution maps of the study area are shown in Figures 4-9 indicate that this anomalous concentration of these trace elements is found in South Western part of the study area. This increased concentration of trace metals, suggests the chemical change that the soil has gone to a reducing environment, presumably due to the influence of hydrocarbon microseepage (Tedesco, 1995). The concentration of trace elements in the study area need to confirm by integrating with adsorbed light gaseous hydrocarbons.

Table1. Descriptive statistics of trace elements in soil samples of the study area.

| Elements | Minimum | Maximum | Mean | Standard Deviation |
|----------|---------|---------|------|--------------------|
| Cu | 59* | 168 | 106 | 24 |
| Cr | 0 | 76 | 21.3 | 14.8 |
| Se | 72 | 182 | 115 | 26.3 |
| Sb | 6 | 19 | 14.9 | 2.8 |
| As | 63 | 155 | 102 | 18.4 |

Identification of Hydrocarbon Microseepage Using Trace Metal Indicators in Petroliferous Region of South Cambay Basin, Gujarat, India

*ppm: parts per million

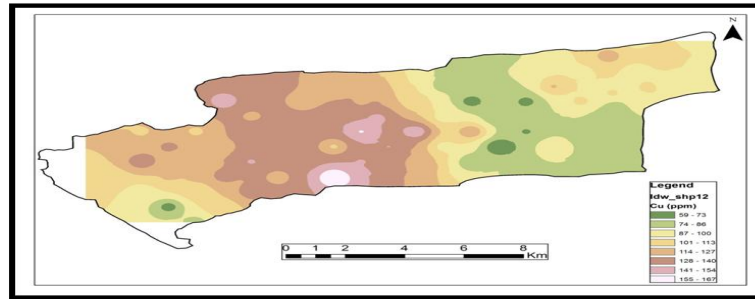


Fig4. Concentration Distribution Map of Copper (Cu).

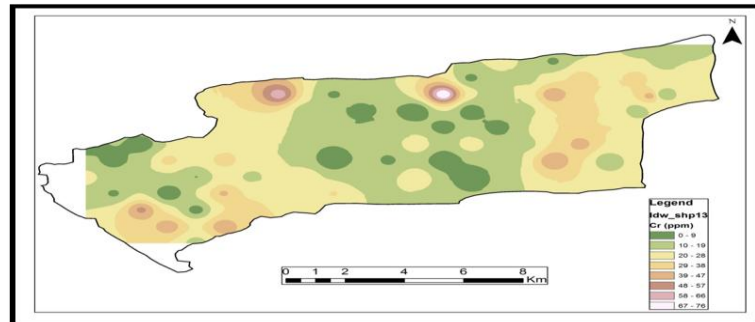


Fig5. Concentration Distribution Map of Chromium (Cr).

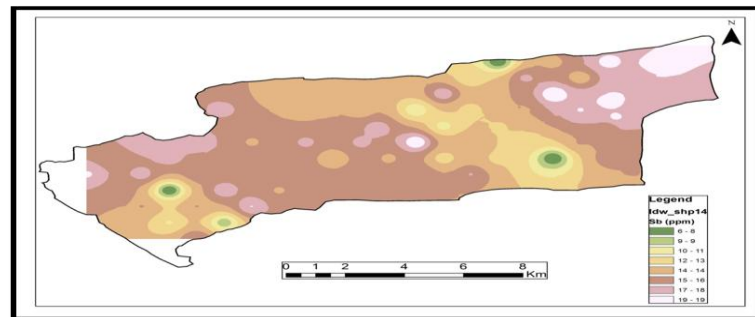


Fig6. Concentration distribution map of antimony (sb).

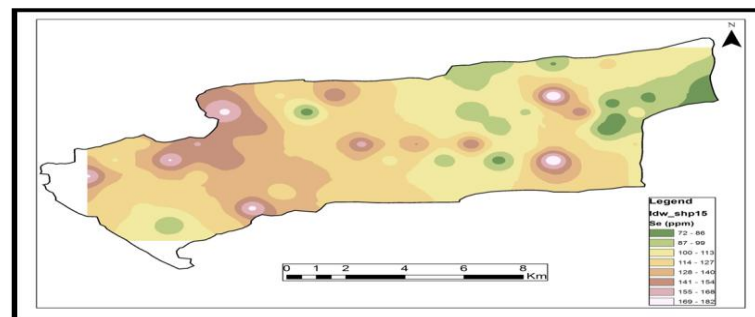


Fig7. Concentration distribution map of selenium (Se).

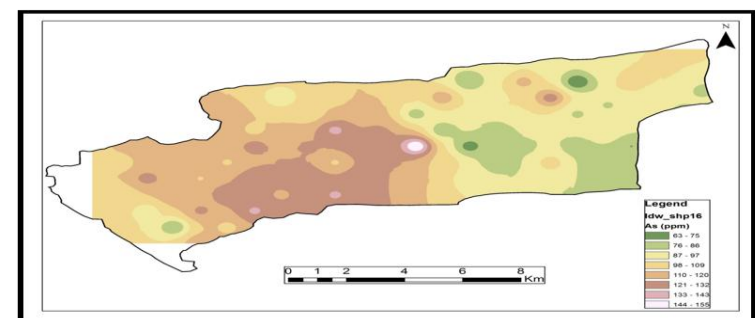


Fig8. Concentration distribution map of arsenic (As).

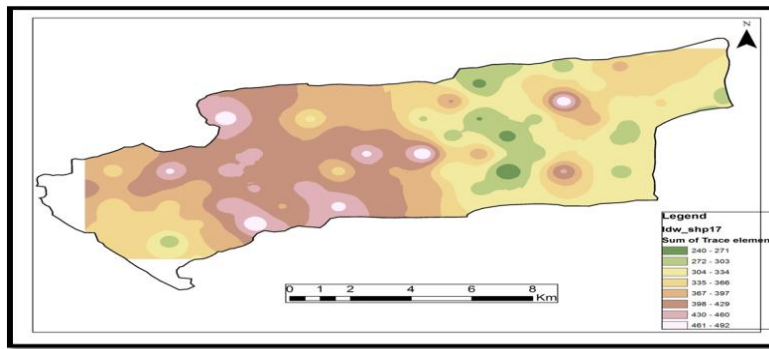


Fig9. Sum of all trace elements concentration distribution map.

4.2. Trace Metals Verses Adsorbed Soil Gases

This study compares the trace elements with direct detection of adsorbed light hydrocarbon soil gas concentrations and explains how the trace elements concentrations vary near hydrocarbon anomalies. The compositional correlation is fundamental to understanding the link between trace element concentrations and hydrocarbon anomalies. The adsorbed soil gas analysis showed the presence of methane (C_2H_4) ranged between 2 to 290 ppb, and sum of concentrations of ΣC_{2+} (C_2H_6 , C_3H_8 and $n-C_4H_{10}$) ranged between 7 to 118 ppb. The integrated map of adsorbed light hydrocarbon gases with sum of trace elements are represented in Figure 10. The anomaly for adsorbed soil gas and sum of trace metal were observed in the SW part of the study area. The long term seepage of light gaseous hydrocarbon a reducing environment is created due to the bacterial oxidation of light hydrocarbons, which can directly or indirectly bring about significant changes in the pH and Eh (Oxidation-Reduction potential) of the surrounding environment, thereby also changing the stability fields of the different mineral species present in that environment. In the reducing environment, solubility of trace elements increases and transport occurs, due to hydrodynamic flow in the soil, the soluble elements move towards the reducing area. Sum of the trace metals concentrations were observed near the hydrocarbon anomalies (Fig. 10).

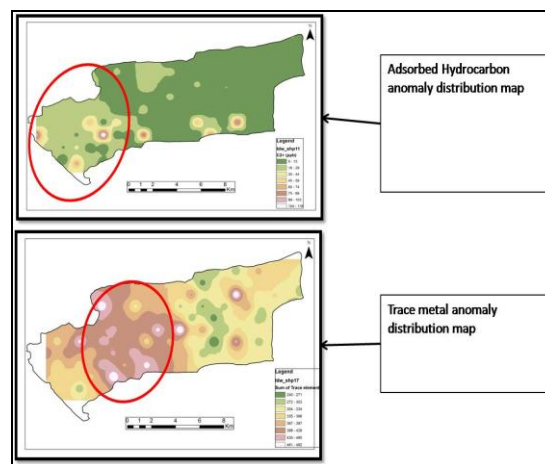


Fig10. Integration of adsorbed soil gases and Trace metal anomaly. The trace element studies in correlation with adsorbed soil gas studies confirmed the Halo type relation between the direct (adsorbed soil gases) and indirect (trace metals) methods.

4.3. Halo Anomaly

Integrated map of trace elements over adsorbed light gaseous hydrocarbons (ΣC_{2+}) anomalies showed good correlation (Fig. 10). The adsorbed soil gas anomalies were seen in the SW and also adjacent to the trace metal anomalies. Thereby observing the composite maps of hydrocarbons and trace elements, clearly indicate that trace elements are accumulated around the hydrocarbon anomalies, creating a halo pattern. The study shows that most of the trace elements follow a halo pattern encircling an apical pattern of hydrocarbon seepage. The composite maps of hydrocarbons and trace elements, clearly indicate that trace elements are accumulated around the hydrocarbon anomalies, creating a halo pattern. Trace elements occur as a near surface 'halos' which will be pathfinders or otherwise important in the search for hydrocarbon anomalies (Siegel, 1974). Duchscherer (1983)

reported that trace element associations form organometallic compounds, are found “haloed” or concentrated over or around underlying hydrocarbon reservoirs. Enrichment of trace elements seen around the hydrocarbon anomaly helps verify the correlation between microseepage and trace elements concentrations. That enrichment of trace elements around the hydrocarbon anomalies can suggest that trace elements can be a pathfinder for hydrocarbon microseepage paths.

5. CONCLUSIONS

Adsorbed light gaseous hydrocarbon and trace metal anomalies are found in SW part of the study area. The increased concentration of trace metals suggests a soil chemical change presumably happened due to the influence of hydrocarbon microseepage. The composite anomaly maps of ΣC_{2+} and the trace elements when correlated clearly indicate the possible hydrocarbon seepage in the study area. This methodology could further integrated with other geo-scientific studies such as 3D Seismic studies which may evolve with the holistic picture of identification of hydrocarbon bearing formations within the exploration blocks and the frontier areas.

ACKNOWLEDGEMENTS

The authors are thankful to the Managing Director and Director Exploration of Gujarat State Corporation Limited for granting permission for carrying out the field work from the study area and for other technical support. Thanks are due to the Director, Gujarat Energy Research and Management Institute for moral support for the successful completion of this research work as part of students internship programme.

REFERENCES

- Bhandari, L.L. and Choudhary, L.R. (1975) Stratigraphic Analysis of Kadi and Kalol Formations, Cambay Basin, India. *Amer. Assoc. Petrol. Geol. Bull.*, v.59, pp.856-871.
- Bhanja, A.K., Rajesh Chandra, Saikia, B.K. and Asim Samanta (2011) Identification of Promising zones within non archie reservoirs of a Brown Field in Ankleswar, Gujarat, India, based on newly developed Log Overlays Technique and Reverse Modelling, SPWLA-INDIA 3rd Annual Logging Symposium, Mumbai, India, pp.1-6.
- Biswas, S.K., Rangaraju, M.K., Thomas, J. and Bhattacharya, S.K. (1994) Cambay – Hazad Petroleum System in South Cambay Basin, India. *In: L.B. Magoon and W.G. Dow (Eds.), Petroleum System from Source to trap. Amer. Assoc. Petrol. Geol.*, v.60, pp.615-624.
- Bowen H J M. *The Environmental Chemistry of the Elements.* Academic Press, London, New York. 1979
- Dhar, P.C and Bhattacharya, S.K. (1993) Status of exploration in the Cambay basin. *In: Biswas, S.K., Dave, A, Garg, P., Pandey, J., Maithani, A. and Thomas, N.J. (eds.), Proceedings Second Seminar on Petroliferous basins of India, vol.2, Indian Petroleum Publishers, Dehra Dun, India, pp. 1-32.*
- Donovan T J. Petroleum microseepage at Cement, Oklahoma Evidence and mechanisms. *American Association of Petroleum Geologists Bulletin.* 1974. 58: 429–446
- Duchscherer Jr. W. Geochemical hydrocarbon exploration—a new/old exploration tool. *In: Proceedings of the 9th International Geochemical Exploration Symposium. Journal of Geochemical Exploration, 1983.19: 335–336*
- Holloway, S., Garg, A., Kapshe, M., Pracha, A. S., Khan, S. R., Mahmood, M. A., Singh, T. N., Kirk, K. L., Applequist, L. R., Deshpande, A., Evans, D. J., Garg, Y., Vincent, C. J., and Williams, J. D. O.: A regional assessment of the potential for CO₂ storage in the Indian subcontinent, Sustainable and Renewable Energy Programme Commissioned Report CR/07/198 by British Geological Survey (BGS), NERC, 2007.
- Rasheed, M. A., Lakshmi M, Rao P L S, Kalpana M S and Dayal A M. (2013). Geochemical evidences of trace metal anomalies for finding hydrocarbon microseepage in the petroliferous regions of Tatipaka and Pasarlapudi areas of Krishna Godavari Basin, India. *Petroleum Science Journal*, 10: 19 - 29.
- Madhavi T, Kalpana M S, Patil D J, et al. Evidence for a relationship between hydrocarbon microseepage and trace metal anomalies: an implication for petroleum exploration. *Geosciences Journal.* 2011. 15(2): 121-224

- Mathur, L.P., Rao, K.L.N. and Chaube, A.N. (1968) Tectonic framework of Cambay Basin, India. ONGC Bull., v.5, pp.7-28.
- Mayor S, Sawkar SS, Das AK, Ram G, Randhava DS and Painuly SP (2004). Identification of Preferred Reservoir Development In Olpad Formation For The Exploration of Deeper Prospects Broach Block, Cambay Basin, in 5th Conference and Exposition on Petroleum Geophysics, Hyderabad, India 388-395.
- Nissenbaum A and Swaine D J. Organic matter-metal interactions in recent sediments, the role of humic substances. *Geochemica et Cosmochemica Acta*. 1976. 40: 809-816
- Petrovic A, Khan S D and Chafetz H S. Remote detection and geochemical studies for finding hydrocarbon- induced alterations in Lisbon Valley, Utah. *Marine and Petroleum Geology*. 2008. 25: 696–705
- Price L C. A critical overview and proposed working model of surface geochemical exploration. In: Davidson M J (ed.), *Unconventional Methods in Exploration for Petroleum and Natural Gas*, Symposium IV. Dallas: Southern Methodist University Press. 1986. 245-304
- Raju, A.T.R. and Srinivasan, S. (1993) Cambay basin – Petroleum habitat. In Biswas, S.K., Dave, A, Garg, P., Pandey, J., Maithani, A. and Thomas, N.J. (eds.), *Proceedings Second Seminar on Petroliferous basins of India*, vol.2, Indian Petroleum Publishers, Dehra Dun, India, pp. 33-78.
- Rasheed, M.A., Veena Prasanna, M., Satish Kumar, T., Patil, D.J. and Dayal, A.M. (2008). Geo-microbial prospecting method for Hydrocarbon Exploration in Vengannapalli village, Cuddapah Basin, India. *Current Science*, vol.95, no.3, p. 361 – 366.
- Schumacher D and Abrams M A. Hydrocarbon Migration and its Near-Surface Expression. AAPG Memoir. 1996. 66: 71-89
- Siegel F R. *Applied Geochemistry*. John Wiley & Sons. 1974. 139-141
- Tedesco S A. *Surface Geochemistry in Petroleum Exploration*. New York: Chapman & Hall. 1995. 256.
- Vadapalli, U., Srivastava, R. P., Vedanti, N., and Dimri V. P. (2014) Estimation of Permeability of a sandstone reservoir by fractal and Monte Carlo simulation approach: a case study, *Non elinear Processes in Geophysics*, v. 21, pp. 9-18.