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Integrated Geo-Microbial and Trace Metal Anomalies for Detection of Hydrocarbon Microseepage in Ahmedabad Block of Cambay Basin, India

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Abstract: The aim of the present work is to define the geo-microbial signatures along with trace metals, and to investigate whether the geo-microbial anomalies have correlation with trace metal anomalies in Ahmedabad block of Cambay basin. The surface geochemical techniques are based on seepage of light hydrocarbon gases from the oil and gas pools to the shallow surface and can bring up near-surface oxidation reduction zones that favor the development of a diverse array of chemical and mineralogical changes. The paper reports the role of hydrocarbon microseepage in surface alterations of trace metal concentrations and hydrocarbon oxidizing bacteria and its interrelationship. For the purpose a total of 90 soil samples are collected in grid pattern of 2 x 2 km interval. The paper reports the chemical alterations associated with trace metals in soils that are related to hydrocarbon microseepages above some of the major oil and gas fields of this petroliferous region. The concentrations of V (0 to149 ppm), Cr (2 to 192 ppm), Cu (4 to 171 ppm), Se (98 to 440 ppm), Zn (56 to 1215 ppm) are obtained. It is observed that the concentrations of trace elements are tremendously increased when they are compared with their normal concentrations in soils. In this study the hydrocarbon oxidizing bacterial counts ranged between 1.0×10^3 and 1.59×10^6 cfu/g of soil sample respectively. The attempt has made for the first time, which revealed good correlation as both these anomalies are found as apical in relation. Integrated studies between trace elements and hydrocarbon oxidizing bacterial anomalies showed positive correlation with existing oil and gas wells in the study area.

Keywords: Hydrocarbons, Microseepage, Hydrocarbon oxidizing bacteria, Cambay basin, Gujarat.

INTRODUCTION

The long-term seepage of hydrocarbons, either as macroseepage or microseepage, can set up near-surface oxidation reduction zones that favor the development of a diverse array of chemical and mineralogic changes (Donovan, 1974; Petrovic et al., 2008; Khan and Jacobson, 2008). It is also believed that hydrocarbons along with inorganic components associated with oil are continuously migrating to the surface which forms the basis for surface petroleum investigations with regard to trace metals (Petrovic et al., 2008). These light gaseous hydrocarbons may be detected either directly (adsorbed soil gas or free gas) or indirectly (microbial indicators, trace element geochemistry) through the geochemical changes they induce and an anomaly at the surface can be reliably related to petroleum accumulation at a deeper level. Some bacteria utilize hydrocarbon gases as their sole source of food and are found to be enriched in the near surface soils/ sediments above oil and gas reservoirs, hence the bacteria are used as indicators for finding oil and gas reservoirs (Rasheed et al., 2011). Microbial anomalies have been proved to be reliable indicators of oil and gas in the sub-surface (Pareja, 1994). The direct and positive relationships between the microbial population and the hydrocarbon concentration in the soil have been observed in various producing reservoirs worldwide (Tedesco, 1995; Sealy, 1974; Pareja, 1994; Wagner et al. 2002). The microbial prospecting method has been used to prioritize the drilling locations and to evaluate the hydrocarbon prospects of an area (Pareja, 1994). The success of microbial prospection for oil and gas has been reported to be around 90% (Wagner et al. 2002).

The trace element content of petroleum, natural gas, associated brines, coal and their host rocks has been established using sophisticated analytical procedures by hydrocarbon explorers/producers and the academic community. These trace element contents or "fingerprints" can be used to differentiate and characterize hydrocarbon geological environments globally. In effect, hydrocarbon reservoirs represent "metal-sources" comprising variable amounts of trace elements and compounds. The alterations occur because leaking of hydrocarbon. Anomalous amounts of vanadium, chromium, nickel, cobalt, manganese, mercury, copper, molybdenum, uranium, zinc, lead and zirconium are positive indicators of petroleum deposits. The migrating hydrocarbons create a reducing environment in the soil and sub-surface, which increases the solubility of many trace and major elements. The vertical migration of elements and compounds, mineralogical haloes and geophysical responses over a hydrocarbon reservoir (Schumacher, 1996) is shown in Fig.1.

The aim of the present work is to define the geo-microbial signatures along with trace metals, and to investigate whether the geo-microbial anomalies have correlation with trace metal anomalies in the study area of Ahmedabad block, Cambay basin and to obtain an independent evidence of upward migration of hydrocarbons from the deep sub-surface source as basis for further application of microbial prospecting study in the frontier basins.

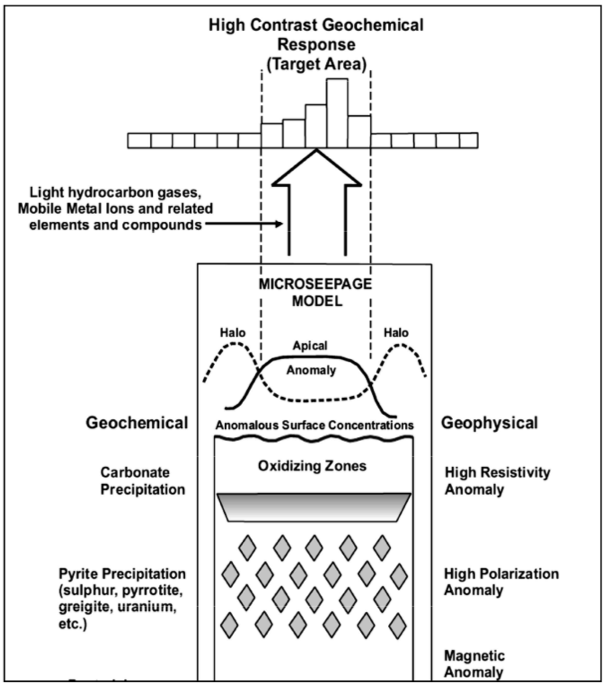


Fig.1. Vertical migration of elements and compounds, mineralogical haloes and geophysical responses over a hydrocarbon reservoir (modified after Schumacher, 1996).

GEOLOGICAL SETTING

The Cambay basin in Gujarat state lie predominantly onshore, with only the south western corner on the offshore in the Gulf of Cambay. The basin is rich petroleum province with active exploration history. The Cambay basin is a narrow elongated intra-cratonic rift basin of late Cretaceous age that contains different sub-basins with varying sediment fills. The basin is a north-south trending graben with an average width of 50 km and 450 km length with a maximum depth of about 7 km. The maximum depth of the basin may exceed 11 km if Deccan trap lava flows is also included as a part of the basin. The basin has more than 40 years of active hydrocarbon exploration history, covering an area of 53,500 sq km including 6,880 sq km in the shallow waters of Gulf of Cambay. It extends between the latitudes 21°00' and 25°00' N and longitudes 71°30' and 73°30' E (Fig.2). The origin of the Cambay and other basins on the western margin of India are related to the breakup of Gondwana supercontinent in the late-Triassic to early-Jurassic (215 Ma). As India drifted away

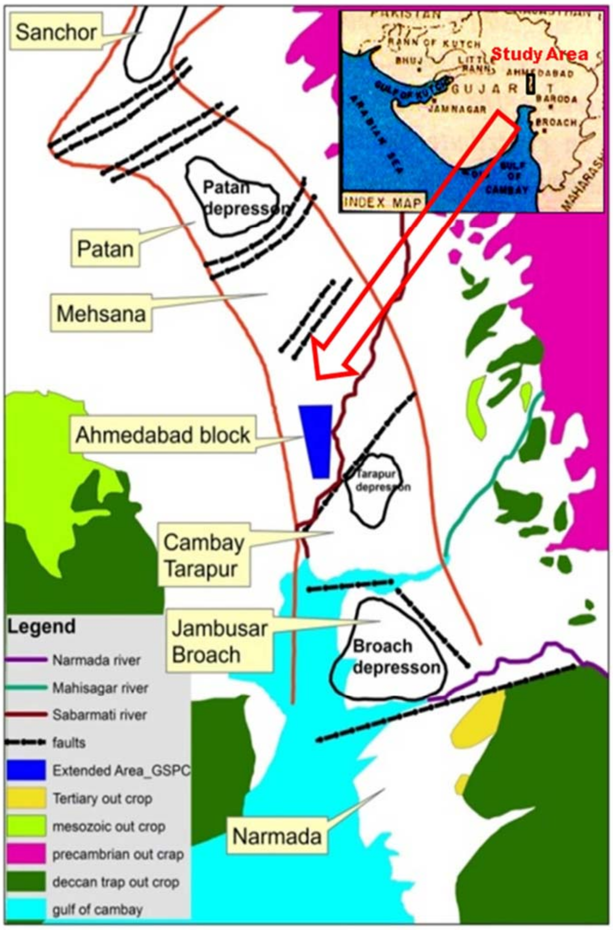


Fig.2. Geological location map of the study area Basin.

from Africa and Madagascar the rift grabens began to form on the western margin, The boundary faults and grabens are initiated through reactivation of Precambrian faulting. On the north-western margin of the Indian shield, three craton-margin-embayed basins came into existence; Kutch, Cambay and Narmada aligned with major Precambrian tectonic trends Aravalli, Dharwar and Satpura.

The study area forms an integral part of the Cambay basin (Fig.2). Entire Cambay basin experienced different stages of extensional tectonic episodes, essentially confined to Cenozoic, and related stratigraphic evolution. Hydrocarbon exploration in the basin dates back to 1958 and persistent geoscientific search led to the discovery of existing 79 oil and gas fields. The main features of the study area the Kadi in the north and Nawagam in the south traversed by the Sabarmati river. The sedimentary sequence starts with the trap conglomerates succeeded by claystone, trap-wacke, sideritic marls constituting the lower Cambay shale. The sequence is sub-areally exposed from time to time creating localised development of reservoir facies with hydrocarbon accumulations in Nawagam (Kundu and Wani, 1992).

MATERIALS AND METHODS

Soil Sampling

A total of 36 samples are collected from a depth of 2 m using a hollow metal pipe by manual hammering. About 500g of core soil samples collected are wrapped in aluminum foil and sealed in poly-metal packs. For microbial analysis about 100 g soil samples are collected in pre-sterilized whirl-pack bags under aseptic conditions from a depth of about 1m (Wagner et al. 2002) and stored at 2-4°C for laboratory analysis. The samples are sealed in the plastic bags with their sample number and its location using Global Positioning System (GPS). Disturbed areas, excavated areas, soils contaminated with hydrocarbons, chemicals or animal infected areas, swamps and areas under watershed are avoided for sampling. While collecting the samples, rocks, coarse materials, plant residues, and animal debris have also been excluded (Rasheed et al. 2008).

Isolation of Hydrocarbon Oxidizing Bacteria

Isolation and enumeration of hydrocarbon oxidizing bacteria is carried out by standard plate count (SPC) method. 1 gm of soil sample is suspended in 9 ml of pre-sterilized water for the preparation of decimal dilutions (10^{-1} to 10^{-5}). A 0.1 ml aliquot of each dilution is placed on to mineral salts medium (MSM) (Ronald and Lawrence, 1996). These plates are placed in a glass desiccator, filled with hydrocarbon gas with 99.99% purity and zero air (purified atmospheric gas devoid of hydrocarbons) in a ratio of 1:1. For isolation of propane oxidizing bacteria, the desiccator is filled with propane gas and zero air. These desiccators are kept in bacteriological incubators at 35 ± 2°C for 10 days. After incubation, the developed bacterial colonies of propane oxidizing bacteria (POB) are counted using colony counter and reported in colony forming units (cfu g^{-1} of soil sample) (Rasheed et al. 2008).

Analysis of Trace Elements using Atomic Absorption Spectroscopy (AAS)

The analysis of trace metals in the soil samples is carried out using AAS (Perkin-Elmer AAnalyst-400) at the Petroleum Research Lab, GERMI, Gandhinagar. 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 standards can be used to determine unknown sample concentrations by measuring the amount of light they absorb. Photo multiplier tube detector has been used to determine the concentration of trace metals. 100 gm of soil sample is taken in 250 ml of distilled water and soaked overnight. The soaked soil sample is mixed by using constant speed mixture with 500 RPM. The mixed soil sample sieved with 63 micro sieve using electrolab sieve shaker for 20 minutes. The 63 micron sieved sample is kept for drying in petri dishes. Dried soil sample was powdered in an agate mortar and filled into a plastic vial. 0.3 gm powdered soil sample is taken in a Teflon vessel and 6 ml of conc. Nitric acid (HNO_3) and 1 ml of Hydrofluoric acid (HF) mixture is added. This mixture is digested for approximately 45 minutes at 40 bar pressure and temperature of 175°C in microwave digestor (of M/s. Perkin Elmer TITAN-MPS). The digested samples are filtered using Whatman No.1 filter paper and subsequently analyzed using atomic absorption spectroscopy (Rasheed et al., 2015).

RESULTS AND DISCUSSION

Microbiological Studies

The soil samples collected are analyzed for the presence of hydrocarbon oxidizing bacteria using standard plate count (SPC) method. The bacteria, which are able to utilize methane gas as a sole carbon source, are merely developed as bacterial colonies on the mineral salts

Table 1. Statistical analyses of the propane oxidizing bacteria in study area

Parameters	POB (cfu/g)
Minimum	1×10^3
Maximum	1.59×10^6
Mean	4.52×10^5
Standard Deviation	4.11×10^5

medium (MSM) plates. The microbial prospecting study is based on the determination of bacterial cell concentration of hydrocarbon oxidizers in the soils. In this study hydrocarbon oxidizing bacterial counts ranged between 1.0×10^3 and 1.59×10^6 cfu/g with mean of 4.52×10^5 cfu/gm of soil sample respectively (Table 1). The results of hydrocarbon oxidizing bacterial population and trace element concentrations are plotted on the surveyed map using Arc GIS 10.2 and Golden Surfer 11 Software. The anomalous zones, hydrocarbon oxidizing bacteria are observed in the study area (Fig. 3). Hydrocarbon micro-seepage is dependent upon the pressurized reservoirs driving the light hydrocarbon microseepage upward. The pattern of reduced microbial counts adjacent to producing wells has been commonly observed phenomenon for older producing fields. Over some well-drained gas reservoirs, the microbial values have been found to be anomalously low. The phenomenon of apparent microseepage over the shutdown producing fields is thought to be due to a change in the drive mechanism controlling microseepage. When a well is brought into production, the drive mechanism changes from vertical, buoyancy driven force to horizontal gas streaming to the pressure sinks created around producing wells. This change in drive mechanism and microbial population densities can be used to define the reservoir drainage direction, radius, and heterogeneities around existing wells in producing fields (Tucker and Hitzman, 1994). The possibility of discovering oil or gas reservoirs using microbiological method is emphasized by the fact that the hydrocarbon-oxidizing bacteria ranges between 10^3 and 10^6 cfu/gm in soil/sediment. They receive hydrocarbon micro-seepages depending on the ecological conditions (Rasheed et al. 2008; Wagner et al. 2002). In the present study area, the hydrocarbon oxidizing bacteria ranged between 10^4 and 10^5 cfu/gm of soil sample, which is significant and thereby substantiates the seepage of lighter hydrocarbon accumulations from oil and gas reservoirs (Nimmi Singh et al. 2003; Rasheed et al. 2008; Wagner et al. 2002). Geo-microbial prospecting studies suggest that hydrocarbon micro-seepage of sub-surface origin is present. The evidence of upward migration of hydrocarbons from the deep subsurface source to base demands further application of microbial prospecting study.

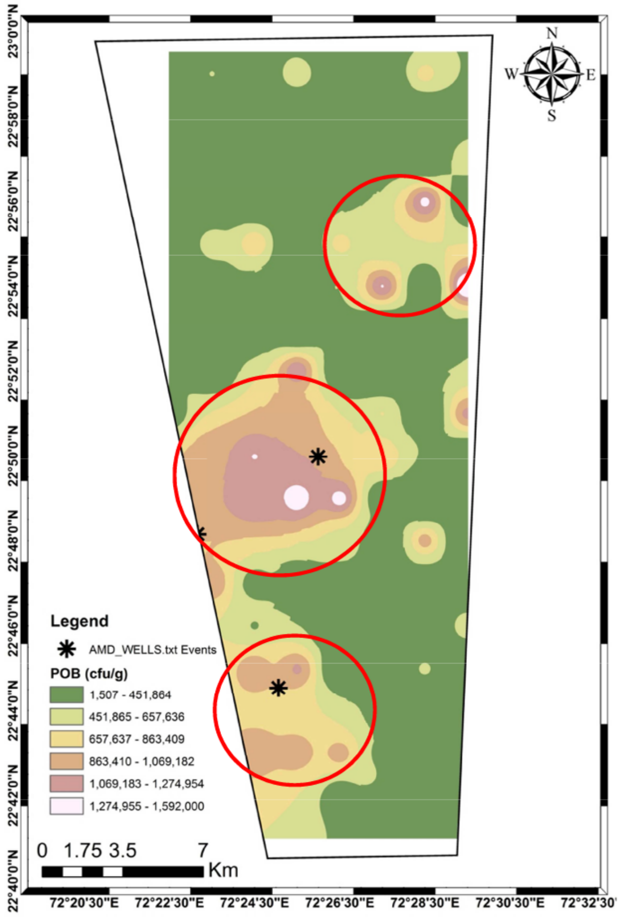


Fig.3. Microbial anomaly map of the study area.

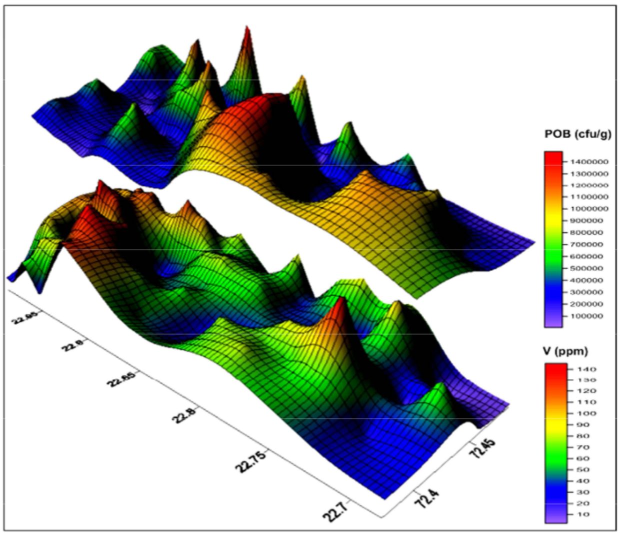
Trace Element Geochemistry

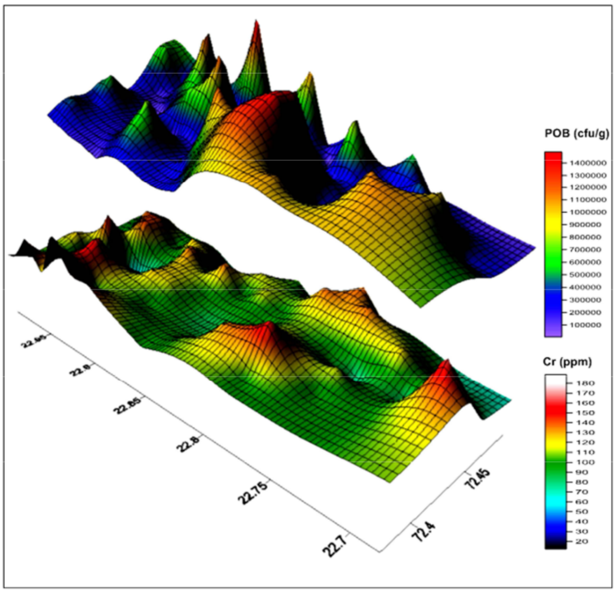
The trace metals vanadium (V), chromium (Cr), copper (Cu), zinc (Zn) and selenium (Se) are considered for the study and the concentrations of each of the trace elements (Table 2) varied in the following manner. The concentrations of each of the trace elements V (0 to149 ppm), Cr (2 to 192 ppm), Cu (4 to 171 ppm), Se (98 to 440 ppm), Zn (56 to 1215 ppm) are obtained. The concentrations of trace elements in normal soils are as follows for V (90 ppm), Cr (70 ppm), Cu (30 ppm), Zn (90 ppm) (Bowen, 1979). It is observed that the concentrations of trace elements have

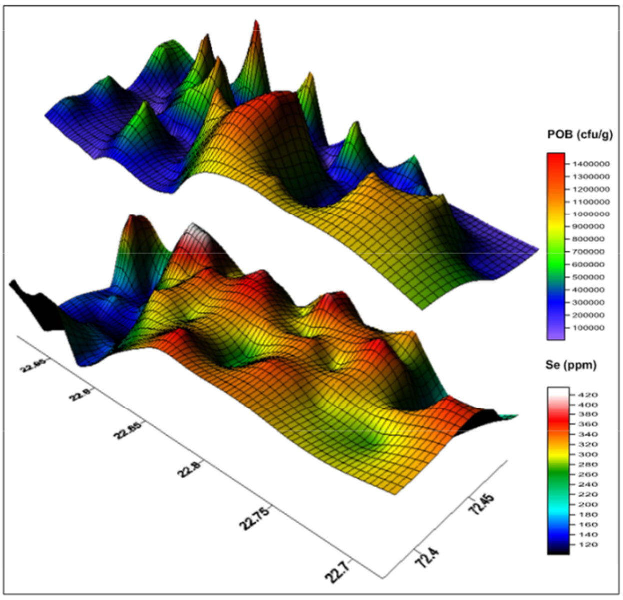
Table 2. Descriptive statistics of trace metals (ppm) in soil samples of the study area

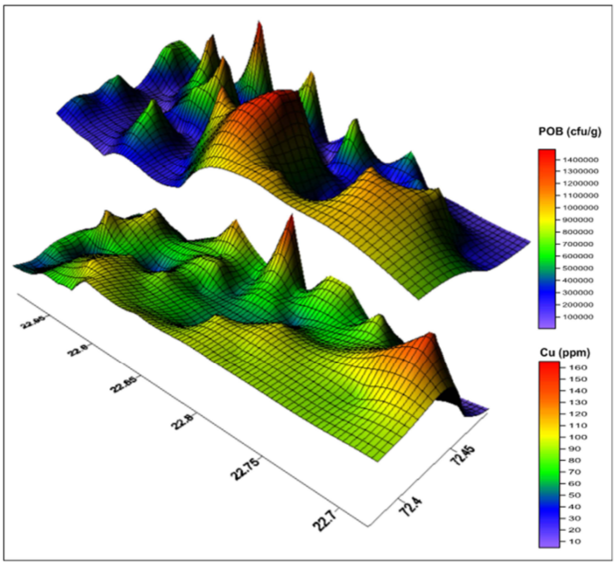
Elements	Min.	Max.	Mean	Std. Dev.	Median	Normal soil values[a]
Cr	2*	192	109	27	106	70
Cu	4	171	21	17	19	30
Se	98	440	276	88	305	-
Zn	56	1215	146	133	119	90
V	0	149	66	35	64	90

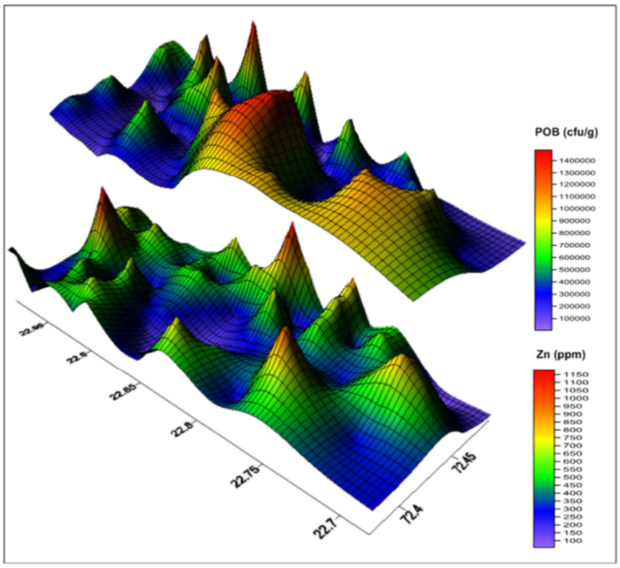
*(ppm); [a]Values from Bowen (1979).











Figs.4-8. Composite map of **(4)** Vanadium, **(5)** Chromium, **(6)** Selenium, **(7)** Copper, **(8)** Zinc and hydrocarbon oxidizing bacteria in the study area.

tremendously increased when compared with normal concentrations in soils (Rasheed et al., 2013). Increased amounts of soluble Ni, V, Cu, Cr, Zn, Ba and Co have been observed in the reducing environment caused by the seepage of hydrocarbons. In the reducing environment solubility of metals increases and transport occurs. Due to hydrodynamic flow the solubile elements move around, in the soil, although they do not leave the reducing area (Tedesco, 1995). The trace metal content of oil will also be accompanied by migration, get added to trace metals of soil and might experience the same chemical changes as that of soil trace metals in the hydrocarbon seepage areas. Vanadium and nickel are the only heavy metal elements that occur in crude oils in appreciable quantities as soluble organic complexes (Al Shahristani, 1972). Other Trace elements such as Mn, Cr,Cu, Zn, Sb, Se, Br, I anomalies related to hydrocarbon reservoirs have been reported by Clark et al. (2003). A boundary is formed between the reducing and oxidizing zone by the deposition of carbonate, oxide and sulphide minerals. Several metals including Ni, V, Cu, Cr, Zn and Co are mobilized in soils and accumulated around the hydrocarbon anomaly when impeded hydrocarbon accumulation leads to reducing condition (Nissenbaum and Swaine, 1976). Recent geochemical studies carried out by Larriestra et al. (2010) in Neuquen basin of Argentina have revealed that trace metal vanadium is transported to the surface by uplifting pushed by microbubbles of hydrocarbon gases and in fact vanadium content is closely related to bacterial anomalies that feed on the seeping hydrocarbons. The concentrations of V, Zn and Ba are seen concentrated along the faults and lineaments which might have provided the migrational pathway for their transportation (Rasheed et al., 2013).

Integrated Trace Elements and Microbial Indicators

Trace element concentrations have been used as indirect indicator for hydrocarbon microseepage (Madhavi et al, 2011; Rasheed et al., 2013). This study compares the trace elements with microbial anomalies and explains how the trace elements concentrations vary near the hydrocarbon oxidizing bacterial anomalies. The compositional correlation is fundamental in understanding the link between trace element concentrations and hydrocarbon oxidizing bacterial anomalies. Integrated maps of trace elements over bacterial anomalies showed good correlation (Figs. 4, 5, 6, 7 and 8). The bacterial anomalies and the trace metal anomalies are well corelatable with each other, and showed same pattern. Most of the trace metal anomalies (Cr, V, Co and Zn) are observed in northeast, central and southwest parts of the study area. The enrichment of trace elements seen along with the hydrocarbon oxidizing bacterial anomaly helps to verify the correlation between hydrocarbon microseepage and trace elements concentration. The enrichment of trace elements along with microbial indicators in one or more prospective zones are seen as apical anomalies and can be suggested that trace elements and hydrocarbon oxidizers may be a pathfinder for hydrocarbon anomalies. The concentration distribution maps of these trace elements in the study area can be seen with their respective composite anomaly maps with microbial anomaly (Figs. 4, 5, 6, 7 and 8). The study shows that most of the trace elements follow an apical pattern of hydrocarbon seepage indicating the presence of a reduced body in the sub-surface. In the present study area, the concentration/distribution maps of vanadium, chromium, copper, and zinc showed a positive correlation with the migrating hydrocarbons.

CONCLUSIONS

Integrated geo-microbial signatures along with trace metals anomalies showed good correlation over oil and gas proven area of Cambay basin. It has revealed a good correlation between both these anomalies and observed as apical in relation. Integrated studies between trace elements and hydrocarbon oxidizing bacterial anomalies showed positive correlation in the study area. The composite anomaly maps of microbial and trace elements correlate well with the underlying hydrocarbon reservoirs in the study area. The trace element studies in correlation with microbial studies confirmed the seepage of lighter hydrocarbon accumulation from the subsurface and further application of these types of studies will be helpful in finding hydrocarbon microseepage in petroliferous regions and in frontier basins.

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