Trace Element Anomaly: An Emerging Exploration tool for finding locales of Hydrocarbon Micro-seepage using new statistical technique for defining background/ baseline values

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Summary

The long-term seepage of hydrocarbons, either as macro-seepage or micro-seepage, can set up near-surface oxidation reduction zones that favor the development of a diverse array of chemical and mineralogical changes. The bacterial oxidation of light hydrocarbons can directly or indirectly brings about significant changes in the values of pH and Eh of the surrounding environment, thereby also changing the stability fields of the different mineral species present in that environment. The paper define the role of hydrocarbon micro-seepage in surface alterations of trace metal concentrations. In this study trace metal alterations were mapped that appear to be associated with hydrocarbon micro-seepage in the oil/ gas fields. Trace metals, such as scandium, vanadium, chromium, cobalt, nickel copper zinc barium and strontium in soil samples were analyzed using inductively coupled plasma-OES. The present study used new statistical technique that is aspect analysis for defining the baseline values by defining various contributors and their relationship with the other contributor which aids in establishing relationships between the geochemical signatures of the elements and geological formations. It was observed that the concentrations of trace elements were tremendously increased when they were compared with the normal concentrations in the soils. The increase in concentrations of trace metals near oil/ gas producing areas, suggests a soil chemical change to a reducing environment presumably due to the influence of hydrocarbon micro-seepage, which could be applied with other geoscientific data to identify areas of future hydrocarbon exploration in frontier area.

Introduction

Oil and gas accumulations and mature source rocks are known to leak hydrocarbons, which may rise to the surface through imperfect seal material or along faults, joints or fractures. This leakage may be macro-seepage visible oil and gas outflow that has reached the surface and can be found at faults, fractures and outcrops (Schumacher, 1996). In the case of micro-seepage, hydrocarbon leakage is not visible, but its surface manifestations are detectable (Khan and Jacobson, 2008). Micro-seepage cannot be observed directly; instead, its effects are detected in the form of anomalous hydrocarbon concentration in soils, microbiological anomalies, mineralogical changes, bleaching of red beds, radiation anomalies, electrochemical changes, biogeochemical changes and geo-botanical anomalies (Schumacher, 1996).The surface geochemical methods are based on the premise that the hydrocarbon gases (CH_4, C_2H_6, C_3H_8, C_4H_{10} and C_5H_{12}) 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 depicts the hydrocarbon potential of an area. These gaseous hydrocarbons may be detected either directly through adsorbed gas or free gas and indirectly using microbial indicators and trace element behavioral geochemistry through the geochemical changes they induce with an anomaly at the surface. The long-term seepage whether macro or micro-seepage can set up a near-surface oxidation reduction zones that favors the development of a diverse range of chemical and mineralogical changes. The bacterial oxidation of light hydrocarbons can further bring significant changes in the pH and Eh of the surrounding

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environment, thereby also changing the stability fields of the different mineral species present in that environment (Rasheed et al;2015). Mineral stability in any environment is dependent on, and is a function of pH and Eh. Hydrocarbons, migrating into the near-surface soils destabilize many compounds and increase the solubility of the trace and minor elements. In the reducing environment, solubility of trace elements increases and transportation occurs, due to hydrodynamic flow in the soil, the soluble elements move towards the reducing area. 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. Trace metals associate forming organo-metallic compounds which have been found as 'haloes' or concentrated over or around the underlying hydrocarbon reservoirs. Oxidation-reduction potential plays an important role on the mobility of elements. Anomalous amounts of vanadium, chromium, nickel, cobalt, manganese mercury, copper, molybdenum, uranium, zinc, lead and zirconium are positive indicators of petroleum deposits (Duchscherer; 1984).

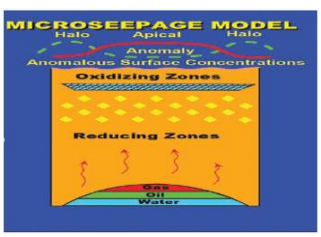

Figure-1 Diagrammatic view showing the vertical migration of elements and compounds, mineralogical haloes (modified after Schumacher, 1996)

Effect on physico-chemical properties around hydrocarbon accumulation

Most of the soil samples are alkaline in nature. It is observed that, the pH ranges 6 to 8 above the oil and gas accumulations, and it is below 6 around the periphery. The acidic nature of soil prevents adsorption of hydrocarbons (Horvitz, 1985). The highly acidic nature around the periphery involves in the mobilization of certain major (viz; Ca, K, Al, Fe etc) and trace (Zn, Mn, V, Ni, Cu, Cr etc) elements to the oxidizing areas and precipitation as oxides and hydroxides. The concentration of certain elements above oil field areas and depletion in the soils around the periphery is the main cause of acidity of soils. The soil acidity is the main reason for creating an oxidation- reduction potential. Similarly electrical conductivity is a supporting parameter to locate gas and gas associated reservoirs. There is significant increase in electrical conductivity above area of gas accumulation (Heemstra et al, 1979).

The present study intends to define the role of trace elements as indicators in locating the hydrocarbon micro-seepage in the study area of Sundalbari 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 using aspect analysis which proved to be very useful in defining the baseline values by defining various contributors and their relationship with the other contributors.

Methodology

502 samples were collected for laboratory analysis of trace metal anomaly, approximately 50 g of sub-soil sample was retrieved from the depth of 1-1.5 m of each dry hole. Samples were collected under sterilized and aseptic conditions and transferred in pre-sterilized whirl pack bags and stored at low temperature till analysis.

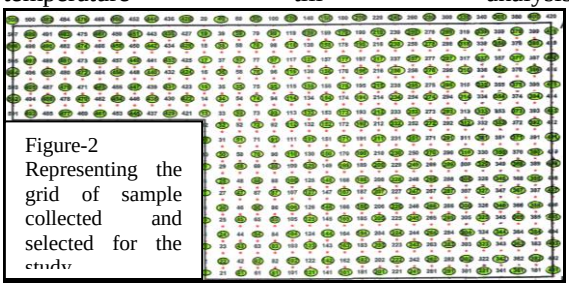

Figure-2 Representing the grid of sample collected and selected for the study

280 Nos. of samples on alternate grid pattern were selected and dried in oven at temperature 60^0C, dried sample were crushed in agate mortar and pestle manually. 0.15gm of powdered sediment sample was taken in Teflon vessel and 3ml of suprapure Nitric acid, 3ml of suprapure per-chloric acid and 4ml of suprapure hydrofluoric acid was added to the sample. This Teflon beaker is subjected to 180^0C for digestion. These acid digested samples were diluted to 50ml in 1% suprapure Nitric acid and then subjected to ICP-OES for analysis of ten elements viz; Zinc (Zn), Manganese (Mn), Vanadium (V), Nickel (Ni), Copper (Cu), Chromium (Cr), Cobalt (Co), Strontium (Sr), Scandium (Sc), and Barium (Ba).

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Result and discussion

Trace metal concentrations

The trace metals Zinc (Zn), Manganese (Mn), Vanadium (V), Nickel (Ni), Copper (Cu), Chromium (Cr), Cobalt (Co), Strontium (Sr), Scandium (Sc), and Barium (Ba) were considered for the study and the concentrations of each of the trace elements varied in the following manner: Zn: 4-511 ppm, Mn: 21.67-1395.85 ppm, V: 6.33 -118.84 ppm, Ni: 1.56-90.24 ppm, Cu: 1.32-935.91 ppm, Co: 0.67-177.76 ppm, Cr: 4.30-450.96 ppm, Sr: 9.66-90.10 ppm, Sc: 1-14.61 ppm and Ba: 86.80-433.13 ppm. It has been observed that the concentration of trace elements is tremendously increased when compared with average concentrations in sediment samples. The average concentration of studied trace elements in sediment samples were Zn: 32.83 ppm, Mn: 180.25 ppm, V: 58.61 ppm, Ni: 21.03 ppm, Cu: 14.14 ppm, Cr: 45.75 ppm, Co: 8.90 ppm, Sr: 23.29 ppm, Sc: 6.7 ppm and Ba: 178.92 ppm. The pH observed in the studied area was acidic having average value of 5.2 which promotes migration of trace elements. Similarly electrical conductivity is a supporting parameter to locate gas and gas associated reservoirs but no such recognizable increase was observed in electrical conductivity of studied area figure-3

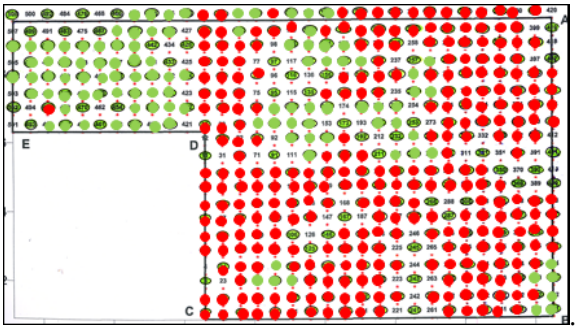

Figure 3: pH variation in studied samples. Green coloured encircled samples having alkaline pH and red coloured samples representing acidic pH.

Negative and Positive Trace Anomaly

A large number of elements are often directly associated with the organic content of the rocks or soils (Henry et al., 1991). The incorporation of metals onto the sediments is largely controlled via the interaction of clay with soluble organic matter present in the soil. In ion exchange process involving the clay minerals, the cations and the anions are interchangeable between the minerals surface and the solution in contact with mineral in a reversible manner. The presence of organic films around the clay particles and that adsorbed in their lattice structures greatly affect the ion exchange capacity either positively or negatively due to seeping hydrocarbons (Duchscherer, 1984). It also plays an important role in the fixation of trace metal assemblage in the near-surface soils overlying the petroleum accumulations. This occurs because the hydrocarbons are present in a reduced environment with respect to the associated clays that are barren of oil and gas and are in an oxidized environment. In reducing environment, in presence of organic matter, the clay exhibits a high cation exchange capacity and adsorbs and desorbs readily (Levinson, 1980). The presence of low molecular weight hydrocarbon in contact with the clay minerals either inhibits or encourages the incorporation of the trace metals and the availability or the deficiency of these metal serve as indirect indicators for seeping hydrocarbons. Metals that form organometallic complexes with the clay particles are known to have positive correlation (Miodrag, 1975). The metal with no affinity for the clay particles have no correlation and do not form organometallic complexes. These metals demonstrate an antipathic relationship between the metals and organic carbon which include trace metals like Barium, Strontium, Boron, Sodium, Potassium and Fluorine. Various test were employed to measure the sampling adequacy for each variable in the area viz; KMO test and Bartlett's test. The criterion for interpreting the results is:

- Adequacy values between 0.7- 1 indicates the variable is adequate
- Adequacy values less than 0.6 indicates the variable is not adequate.

On the above criterion we found Mn (0.866), V (0.728), Ni (0.867), Cr (0.841), Co (0.770) and Sc (0.743) have positive correlation amongst the variables so that coherent factors can be identified. It implies that there should be some degree of collinearity among the variables whereas Zn (0.555), Cu (0.493), Sr (0.472) and Ba (0.545) demonstrate an aversion relationship between the metals and organic carbon [Table-1]

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Variables (Trace elements)	Sample adequacy
Zn	0.555
Mn	0.866
V	0.728
Ni	0.867
Cu	0.493
Cr	0.841
Co	0.770
Sr	0.472
Sc	0.743
Ba	0.545

Table 1: Values of sample adequacy in various variables (trace elements)

Statistical Processing and Mapping

Univariate and multivariate statistical analyses were performed in order to show the single element geochemical distribution and the distribution of elemental association component resulting from aspect analysis. Elemental associations obtained by means of aspect analysis were useful in defining various anomaly contributors and non-anomaly contributors. Aspect analysis allowed us to establish four contributors (C1 to C4) that justifies 63.29 % of data variability. The association of the four contributors in a model is: C1: Mn-V-Ni-Cr-Sc (positive correlation); C2: Sr- Ba (Negative correlation); C3: Zn- Cu (Negative correlation); C4: Co (Positive correlation). In this model contributor one i.e C1 can be further sub divided on the basis of its correlation coefficients as V-Ni has correlation coefficient 0.820, Sc- V has correlation coefficient of 0.908 and Sc- Ni has correlation coefficient as 0.795, which infer Sc-V > V-Ni > Sc-Ni as the order for strong to good positive correlation.The reason why few elements were showing the positive correlation and acting as a positive contributor and why the other showing as negative correlation is their capability of forming organo-metalic compound with the trace metals. The cut off value for the anomalous elemental concentration was decided on the basis of percentiles. 92 percentile to maxima was considered as anomalous point. So this study helps in demarcating the anomalous geochemical signatures which can be further correlated with the various geological formations.

1.Trace Element Zinc (Zn), Copper (Cu), Strontium (Sr) and Barium (Ba)

The trace element Zn concentration is tremendously increased when compared with normal concentration in soils (i.e. 6.6 ppm to 73.4ppm, Average: 40 ppm) of nearby area viz; Tarapadapataliya Ghat and Bandhuar Satrapha soil (EIA/ EMP study for 50 exploratory wells in 9 PML Blocks of Tripura, June 2017). The cut off value selected for the anomalous zinc (Zn) zones is 56 ppm and above. [Figure-4] The samples showing the anomalous behavior in their decreasing trends are 32, 281, 247, 276, 148, 361, 401, 47, 57, 72, 9, 499, 390, 481, 483, 179, 15 and 160.

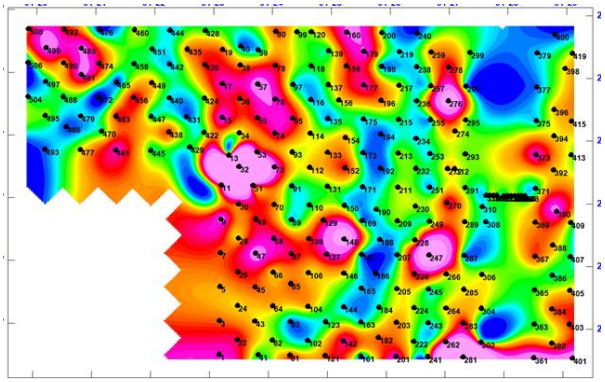

Figure 4: Variation in Zinc (Zn) concentration in the studied area.

The trace element Cu concentration is tremendously increased when compared with normal concentrations in soils (i.e. 3.6 ppm to 34.6 ppm, Average: 19.1 ppm) of nearby area viz; Tarapadapataliya Ghat and Bandhuar Satrapha soil (EIA/ EMP study for 50 exploratory wells in 9 PML Blocks of Tripura, June 2017). The cut off value selected for the anomalous copper (Cu) zones is 20 ppm and above. [Figure-5] Samples showing the anomalous behavior in their decreasing trends are 32, 361, 401, 160, 9, 238, 460, 1, 22, 207, 76 and 219.

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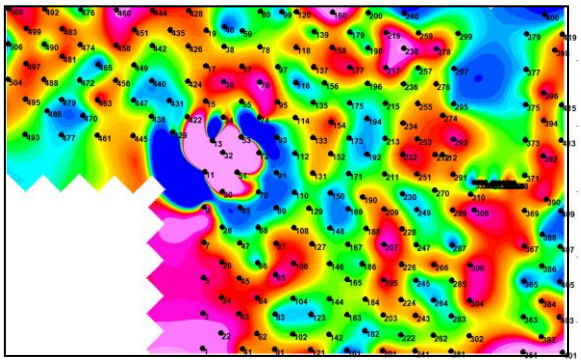

Figure 5: Variation in Copper (Cu) concentration in the studied area.

Strontium concentration ranged between 9.66 and 90.10 ppm with mean value 23.29 ppm. The highest value of Sr concentration is reported in sample no. 49. The cut off value selected for the anomalous strontium (Sr) zone is 44 ppm and above. [Figure-6] The list of samples showing the anomalous behavior in their decreasing trends is 49, 80, 426, 490, 28, 449, 456, 47, 474, 499, 506, 17, 262, 483, 409, 59, 463, 401, 13, 481 and 40.

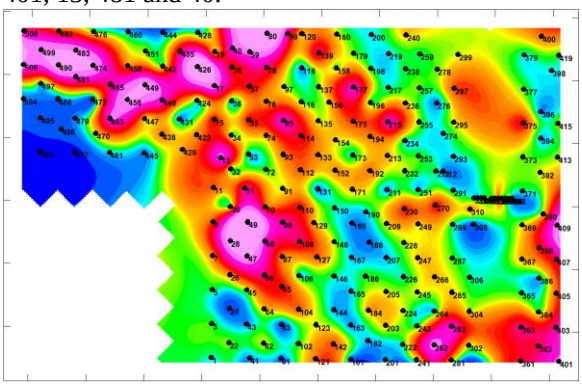

Figure 6: Variation in Strontium (Sr) concentration in the studied area.

Barium concentration ranged between 86.80 and 433.13 ppm with mean value 178.92 ppm. The highest value of Ba concentration is reported in sample no. 463. The cut off value selected for the anomalous barium (Ba) zone is 286 ppm and above. [Figure-7] The samples showing the anomalous behavior in their decreasing trends are 463, 9, 215, 481, 483, 401, 474, 456, 499, 78, 449,142, 28, 361, 426, 177, 508, 492 and 262.

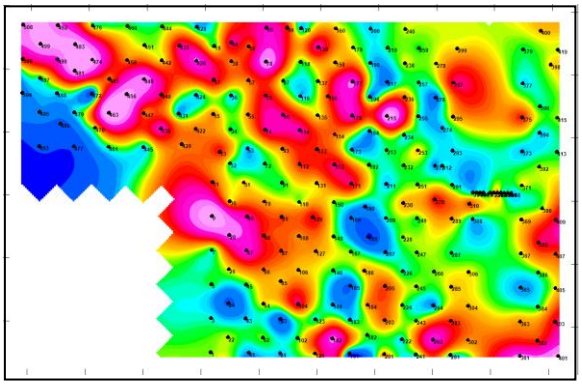

Figure 7: Variation in Barium (Ba) concentration in the studied area.

This increased concentration of trace metals, suggests the chemical change that the soil has under gone in a reducing environment, presumably due to the influence of hydrocarbon micro-seepage (Tedesco, 1995). Pertaining to the contributor model developed using aspect analysis, contributor 2 and 3 follows negative correlation group inferring that Zn-Cu and Ba–Sr have strong correlations which is well corroborating with our numerical data. The sample bearing anomalies defined with Zn-Cu correlation are 9, 32, 361 and 401. The sample bearing anomalies demarcated with Ba-Sr correlation are 28, 262, 401, 426, 449, 456, 463, 474, 481, 483 and 499.

2.Trace Element Manganese (Mn), Vanadium (V), Nickel (Ni), Chromium (Cr) and Scandium (Sc)

Manganese concentration ranged between 21.67 and 1395.85 ppm with mean value 180.25 ppm. The mean value is less than the average value of nearby area which is in the range of 288-817 ppm. The highest value of Mn concentration is reported in sample no. 9. The cut off value selected for the anomalous manganese (Mn) zone is 375 ppm and above. [Figure-8] The samples showing the anomalous behavior in their decreasing trends are 9, 78, 74, 62, 205, 219, 401, 274, 426, 413, 175 and 17.

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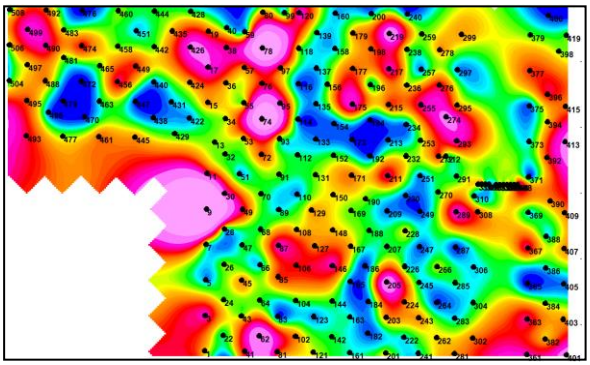

Figure 8: Variation in Manganese (Mn) concentration in the studied area.

Vanadium concentration stretched between 6.33 and 118.84 ppm with average concentration of 58.61 ppm. The highest value of V concentration is reported in sample no. 401. The cut off value selected for the anomalous vanadium (V) zone is 85 ppm and above. [Figure-9] The samples showing the anomalous behavior in their decreasing trends are 401, 226, 361, 367, 481, 106, 438, 74, 492, 217, 30, 1, 26, 483, 76, 463, 428, 177, 154, 36, 9, 205, 85 and 201.

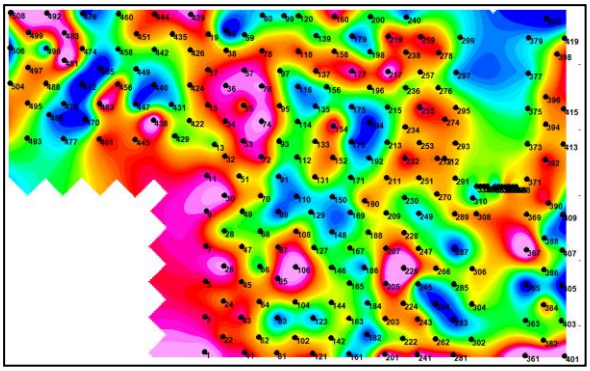

Figure 9: Variation in Vanadium (V) concentration in the studied area.

Nickel concentration varied between 1.56 and 90.24 ppm with mean value of 21.03 ppm. The mean value is less than the average value of nearby area which is in the range of 14.7-80.7 ppm. The uppermost value of Ni is reported in sample no.361. The threshold value selected for the anomalous Nickel sample is 35 ppm and above. [Figure-10] The samples showing the anomalous behavior in their decreasing trends are 361, 481, 492,367, 483, 1, 348, 394, 106, 26, 9, 30, 350, 76, 36, 321, 342, 34, 74, 72, 428, 43, 217, 85, 360, 392, 57 and 118

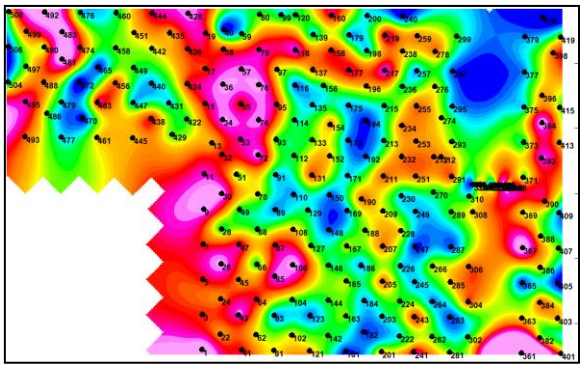

Figure 10: Variation in Nickel (Ni) concentration in the studied area.

Chromium concentration was having minima of 4.30 and maxima of 450.96 ppm, so, the average value comes to 45.75 ppm. The mean value is less than the average value of nearby area which is in the range of 9.03-122 ppm. The highest value of Cr concentration is reported in sample no. 160. The cut off value selected for the anomalous chromium (Cr) zone is 109 ppm and above. [Figure-11] The samples showing the anomalous behavior in their decreasing trends are 160, 142, 9, 114, 158, 121, 226, 201, 361, 76 and 108.

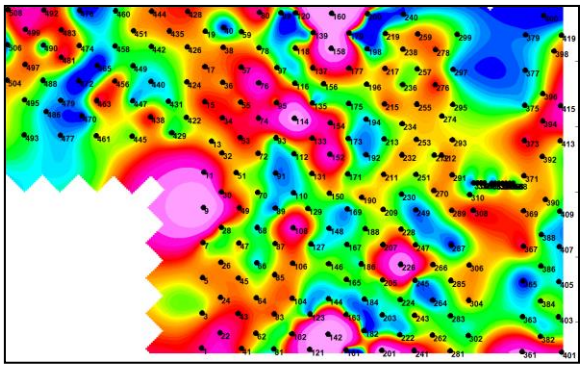

Figure 11: Variation in Chromium (Cr) concentration in the studied area.

Scandium has numerical low of 1 ppm and high of 14.61 ppm with average of 6.7 ppm. The highest value of Sc concentration is reported in sample no.

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492. The cut off value selected for the anomalous scandium (Sc) zone is 10 ppm and above. [Figure-12] The samples showing the anomalous behavior in their decreasing trends are 492, 481, 361, 154, 463, 367, 76, 106, 278, 74, 26, 438, 72, 219, 201, 1, 30, 34, 55 and 3.

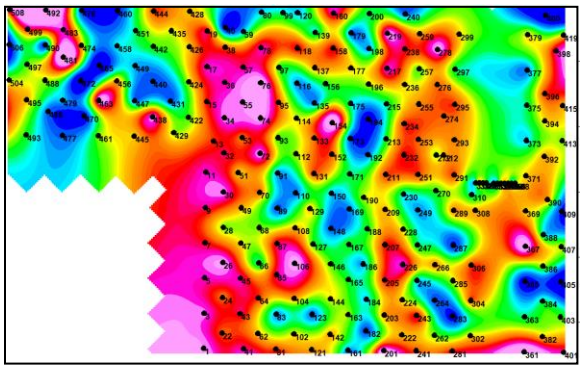

Figure 12: Variation in Scandium (Sc) concentration in the studied area.

Mn-V-Ni-Cr-Sc expressed very strong positive correlation with each other and Sc- V has highest correlation coefficient among the above correlation. Thus, the anomaly based on the above stated model having positive anomaly appears in 1, 26, 30, 74, 76, 106, 154, 201, 361, 367, 438, 463, 481 and 492.

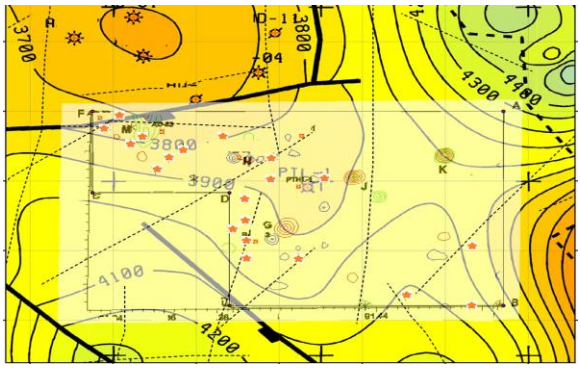

Figure 13: Trace elemental anomalies with Geological settings in the studied area.

When the trace anomaly data was overlayed on geological settings of the area, the acidic pH and the anomalies defined using aspect analysis were well corroborated with the major faults in the area. This confirms the validation of the study.

Conclusion

The average concentration of studied trace elements were Zn: 32.83 ppm, Mn: 180.25 ppm, V: 58.61 ppm, Ni: 21.03 ppm, Cu: 14.14 ppm, Cr: 45.75 ppm, Co: 8.90 ppm, Sr: 23.29 ppm, Sc: 6.7 ppm and Ba: 178.92 ppm.

Aspect analysis allowed us to establish four contributors, C1 to C4 that justifies 63.29 % of data variability. The association of the four contributor model is: C1: Mn-V-Ni-Cr-Sc (positive correlation); C2: Sr- Ba (Negative correlation); C3: Zn- Cu (Negative correlation); C4: Co (Positive correlation).

In this model, contributor one i.e C1 can be further sub divided on the basis of its correlation coefficients as V-Ni has correlation coefficient as 0.820, Sc- V has correlation coefficient of 0.908 and Sc- Ni has correlation coefficient as 0.795, which infer Sc-V > V-Ni > Sc-Ni as the order for strong to good positive correlation.

Pertaining to the contributor model developed using aspect analysis, contributor 2 and 3 follow negative correlation inferring that Zn-Cu and Ba–Sr have strong correlations which is well corroborating with our numerical data. The sample bearing anomalies defined with Zn-Cu correlation are 9, 32, 361 and 401. The sample bearing anomalies demarcated with Ba-Sr correlation are 28, 262, 401, 426, 449, 456, 463, 474, 481, 483 and 499.

Mn-V-Ni-Cr-Sc expressed very strong positive correlation with each other and Sc- V has highest correlation coefficient among the above correlation. Thus, the anomaly based on the above stated model having positive anomaly appears in 1, 26, 30, 74, 76, 106, 154, 201, 361, 367, 438, 463, 481 and 492.

The overall anomalies based on negative and positive correlation of trace metal anomalies are 1, 9, 26, 28, 30, 32, 74, 76, 106, 154, 201, 262, 361, 367, 401, 426, 438, 449, 456, 463, 474, 481, 483, 492 and 499.
The increase in the concentrations of trace metals, suggests a soil chemical change to a reducing environment, presumably due to the influence of hydrocarbon micro-seepage. Enrichment of trace elements seen around the hydrocarbon anomaly helps

to verify the correlation between micro-seepage and trace element concentrations. This methodology may be further integrated with other geo-scientific studies for identification of hydrocarbon potential of the area. The enrichment of trace elements around the hydrocarbon anomalies suggests that trace elements can be a pathfinder for hydrocarbon micro-seepage.

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