A new statistical technique for defining background and baseline values of trace metals in sediments of Sundalbari area, Tripura Asset

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ABSTRACT

Knowledge of the natural geochemical variability is essential for the proper resolution of petroleum macro and micro-seepage and addressing various environmental issues. The geochemical survey generally generates the huge data set and to comprehend or identify the anomalous zones, definition of background values, in contrast to baseline values, is very important, but statistical techniques like mean, mode, median and standard deviation is not always suitable for huge data set where number of variables are more so an attempt is made to resolve that huge data set problem with different statistical technique that is aspect analysis. This methodology is applied where the set of variables are independent whereas existing statistical methodology (mean, mode, median and standard deviation) is applied where the variables are sub-set (interdependent) of each others.

The aim of this study is to demarcate the geochemical background / baseline value and anomalous values of trace metals in sediment samples using aspect analysis. It proved very useful in defining the baseline values by defining various contributors and their relationship with the other contributors.

INTRODUCTION

In recent years, geochemical mapping has assumed an increasing relevance in petroleum exploration. At the beginning, the aim of geochemical mapping programmes was to obtain regional baseline information for mineral exploration. However, resulting databases were multi-purpose basic tools with application in different areas, such as in environmental studies, agriculture, geomedicine, etc but now national geochemical surveys have become a priority for many countries for petroleum exploration.

In past geochemical data were used for defining the base values by statistical techniques such as mean, mode, median and standard deviation using various statistical plots like Box-plot etc but when huge data set is available with various variables correlation matrix is the only way out. This methodology is applied where the set of variables are independent whereas existing statistical methodology (mean, mode, median and standard deviation) is applied where the variables are interdependent (sub-set) of each others.

The aim of this study is to demarcate the geochemical background / baseline value and anomalous values of variables (trace metals) in sediment samples which define various contributors and their relationship with the other contributors using aspect analysis. It proved to be very useful in demarcating the baseline values by defining various contributors and their relationship with the other contributors. It is used in defining trace element anomalies in addition to adsorbed gas anomalies and microbial anomalies for hydrocarbon prospecting.

Sample details and Methodology adopted

250 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. These acid digested samples were 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).

RESULTS AND DISCUSSIONS

These ten elements when studied in 250 samples the huge data set of 2500 as generated. 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.

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 standard deviation values of studied trace elements in the sediments were Zn: 39.08 ppm, Mn: 141.36 ppm, V: 22.95 ppm, Ni: 11.05 ppm, Cu: 58.34 ppm, Cr: 47.04 ppm, Co: 13.34 ppm, Sr: 12.79 ppm, Sc: 2.67 ppm and Ba: 66.53 ppm and when these trace element were plotted for the outlier no or very few outlier were found. When these concentrations were contoured then it was observed that different anomalous zones were present for different trace elements which are depicted in figure: 1, 2 and 3. All trace elemental anomalous concentrations were so wide-spreaded that demarcation of anomalous area was not possible as shown in figure 4.

The mean is a description of location. It can be thought of as a sort of "centre-of-mass" of a data set. The standard deviation is a description of the data's

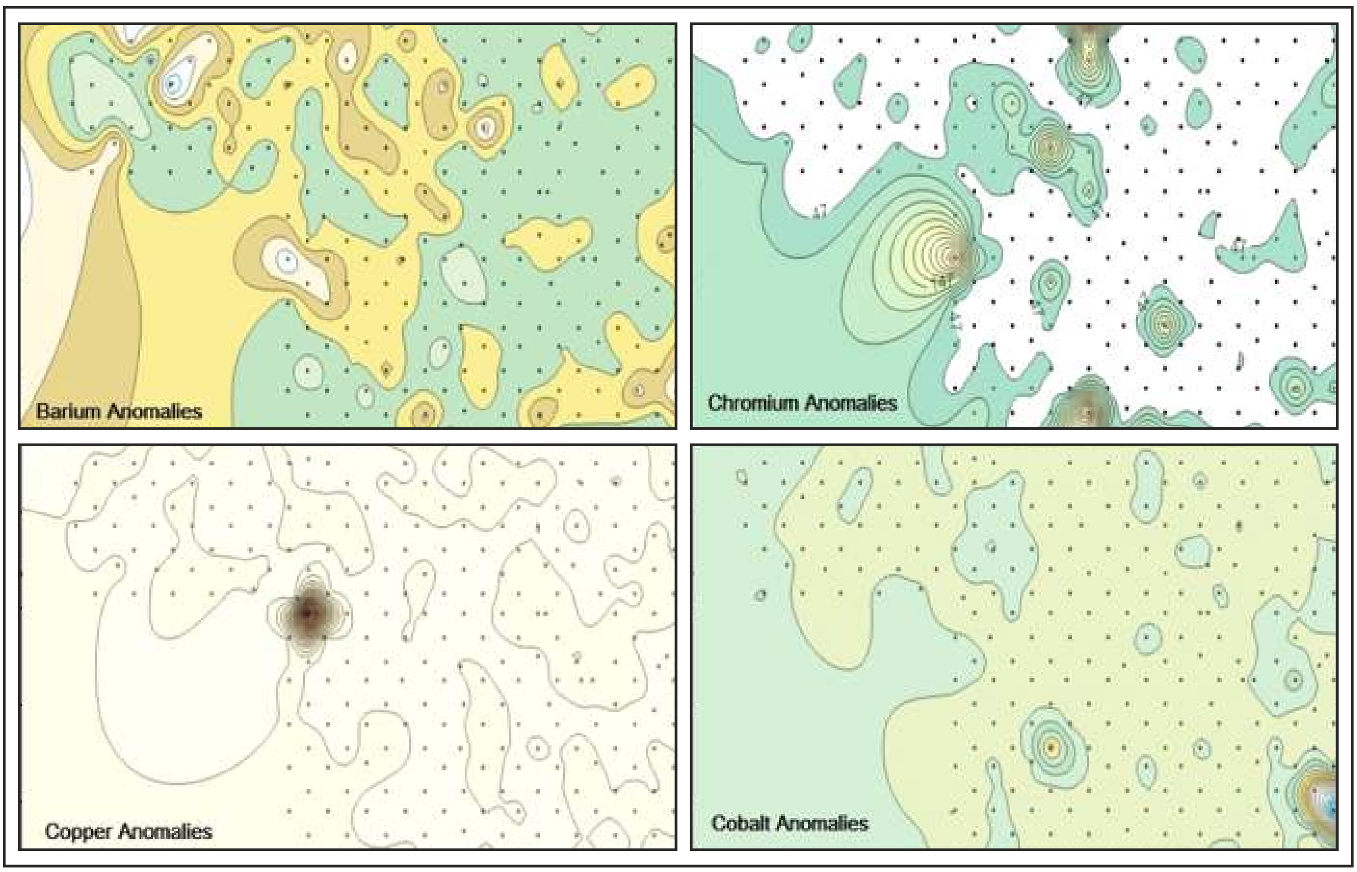

Fig.1: Trace-metal concentration showing anomalous area

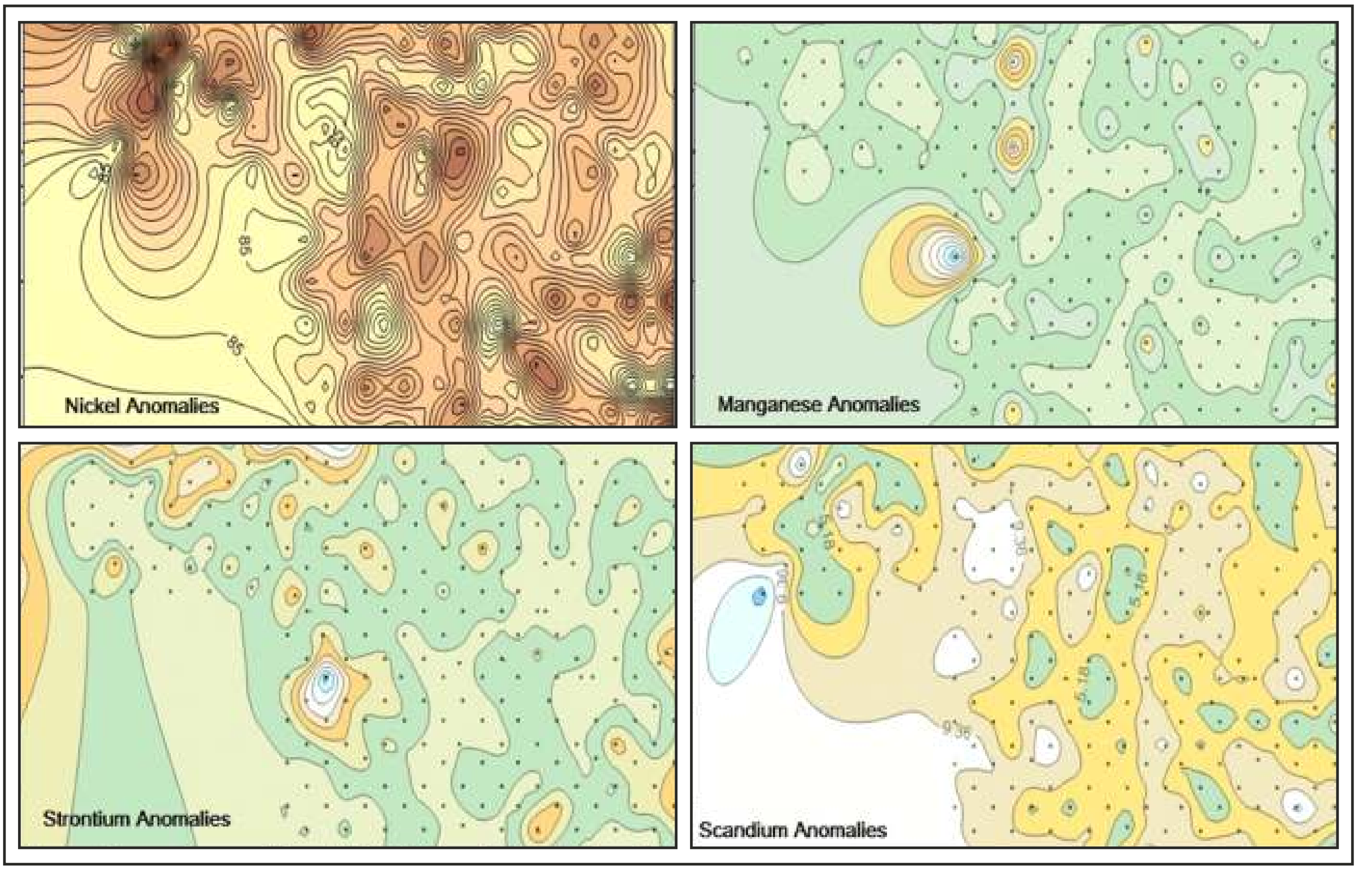

Fig. 2: Trace-metal concentration showing anomalous area

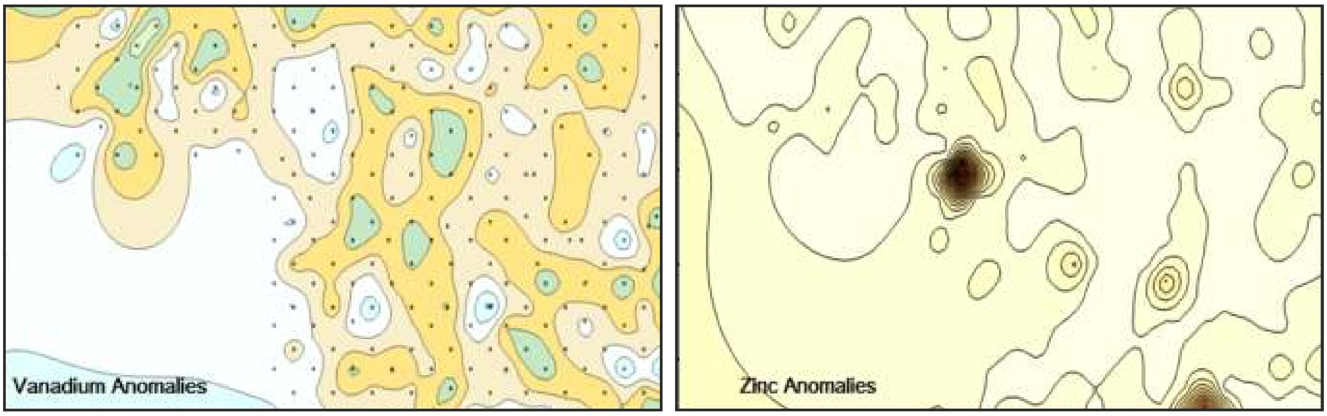

Fig. 3: Trace-metal concentration showing anomalous area

spread, how widely it is distributed about the mean. A smaller standard deviation indicates that more of the data is clustered about the mean. A larger one indicates the data are more spreaded out. In case of Zn, Cu, Cr and Co data were spreaded out but in case of others viz; Mn,V,Ni,Sr,Sc, and Ba the data were clustered about the mean so to discriminate between the background value and the anomalous value was difficult.

Various criterion were employed to measure the sampling adequacy for each variable in the area viz; KMO test and Bartlett's test. The thumb rule for interpreting the results is:

- Values between 0.7- 1 indicate the variable is adequate
- Values less than 0.6 indicate the variable is not adequate.

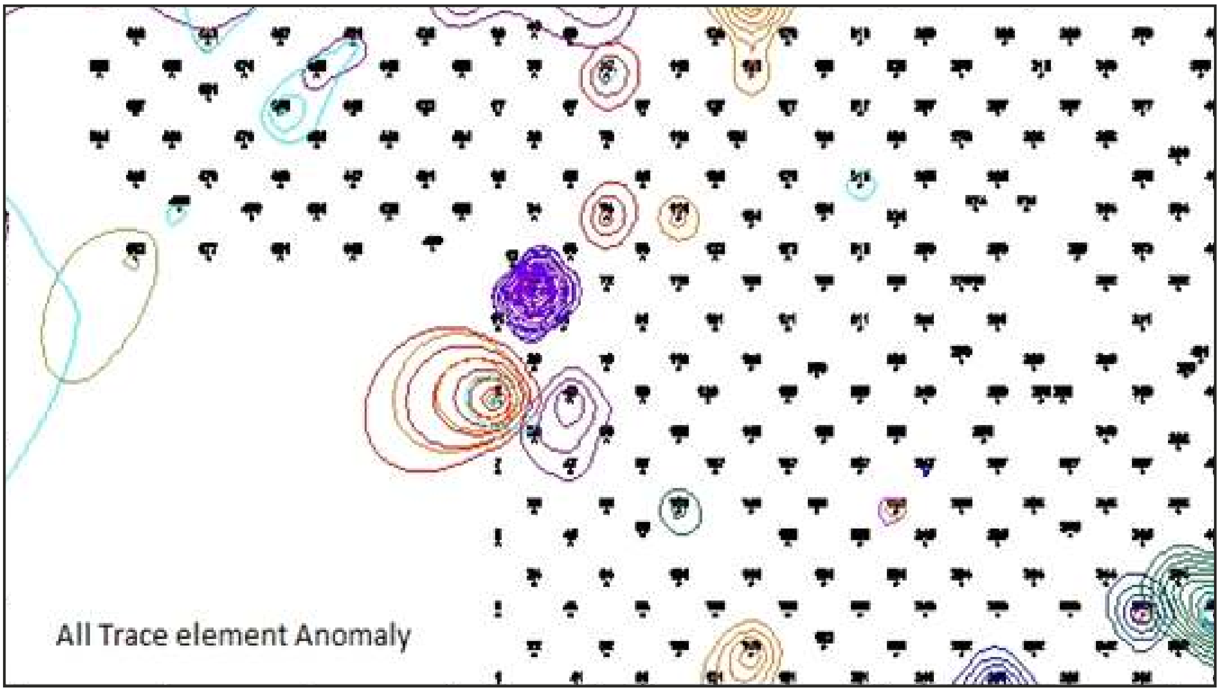

Fig. 4: All Trace-metal concentration showing different anomalous area

On the basis of 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 (Table-1) 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]

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

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

Aspect analysis is carried out to decide the coherent factors using correlation matrix with respect to every variable (table-2). Elemental associations obtained by means of aspect analysis were useful in defining various anomaly contributor and non-anomaly contributors. Aspect analysis allowed us to establish four contributors (C1 to C4) that justify 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.[Table-2].

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-mettalic compound with the metals. A large number of elements are often directly associated with the organic content of the rocks or soils (Henry et al.,

Table 2: Correlation matrix of various contributors

Variables	Zn	Mn	V	Ni	Cu	Cr	Co	Sr	Sc	Ba
Zn	1	0.120	0.264	0.205	0.782	0.153	0.099	0.086	0.266	0.100
Mn	0.120	1	0.379	0.382	0.025	0.246	0.272	0.126	0.351	0.265
V	0.264	0.379	1	0.820	0.113	0.434	0.372	-0.017	0.908	0.189
Ni	0.205	0.382	0.820	1	0.124	0.345	0.281	0.006	0.795	0.176
Cu	0.782	0.025	0.113	0.124	1	0.039	0.037	-0.049	0.130	-0.033
Cr	0.153	0.246	0.434	0.345	0.039	1	0.077	0.054	0.416	0.241
Co	0.099	0.272	0.372	0.281	0.037	0.077	1	0.134	0.292	0.204
Sr	0.086	0.126	-0.017	0.006	-0.049	0.054	0.134	1	0.001	0.754
Sc	0.266	0.351	0.908	0.795	0.130	0.416	0.292	0.001	1	0.233
Ba	0.100	0.265	0.189	0.176	-0.033	0.241	0.204	0.754	0.233	1

1991). The incorporation of metals onto the sediments is largely controlled via the interaction of clay with soluble organic matter present in the soil. The clay minerals are known to constitute more than 50% volume of the sedimentary rocks (Duchscherer, 1984). 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 do not form organometallic complexes and have no correlation. These metals demonstrate an antipathic relationship between the metals and organic carbon which include trace metals like Barium, Strontium, Boron, Sodium, Potassium and Fluorine.

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.

CONCLUSION

Aspect analysis allowed us to establish four contributors, C1 to C4 that justify 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 association of various elements is well explained with the geochemistry of various alkali, alkaline and transition elements.

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.

This study can be useful in geochemical mapping which further allows us to establish relationships between the geochemical signatures of the elements and geological formations.

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