HYDROCARBONS IN SOIL GAS AS PATHFINDERS IN GEOTHERMAL RESOURCE SURVEYS IN INDONESIA

R. PUDJIANTO[1], M. SUROTO[1], M. HIGASHIHARA[2], M. FUKUDA[2], AKHADIANA[3] AND JAN ONG[3]

[1] Geothermal Div., Pertamina, Jakarta, Indonesia
[2] Mindeco, Tokyo, Japan
[3] PT Geoservices, Jakarta, Indonesia

SUMMARY - A surface geochemical technique utilizing normal paraffin (C_{7+}) and aromatic (C_8) hydrocarbons in soil gas has been successfully used as pathfinders in surveys for geothermal resources in Indonesia. The Dieng field was used to test the technique. The result shows the paraffin anomalies to be near and over productive wells. Because productive wells usually lie over upflow zones it reinforces our hypothesis that paraffins define the upflow of geothermal systems. The aromatic hydrocarbon alkylbenzene C_8 was found near and around productive wells in the southeast quadrant of the Dieng field (Sikidang-Merdada area) but they are more spread out and more diffuse than the paraffins. The shape of their anomaly seem to suggest a tendency of spreading into the direction of lower elevations. It is thought that the aromatics, which are much more soluble than their corresponding paraffins, express at the surface as anomalies not only of locations of the upflow but also of the outflow of the geothermal system as well. Therefore the combined paraffin and aromatic anomalies, and topography, may be used as an indicator for the direction of the outflow or the flow of the under ground waters. The scarcity of the aromatics in the northwest quadrant of the Dieng field (Sileri area) is unique. A hypothesis has been proposed which could explain this unique feature.

1. INTRODUCTION

The Dieng geothermal field is approximately a square area of about 15 to 20 square kilometers and it is located in Central Java, Indonesia. The area is a plateau with elevations of about 1,800 to 2,000 m asl. It is a hilly area and surrounded by mountains peaks which are about 500 m higher than the general elevation of the plateau. The Dieng field can be subdivided into at least three areas, the Sileri, the Sikidang-Merdada and the Pakuwaja areas. The Sileri area which is associated with the G. (mountain) Pagerkandang has an age of 460,000 years, the Sikidang-Merdada (G. Pangonan) is 370,000 years and the Pakuwaja has an age of 90,000 years. Twenty seven wells have been drilled. Production are usually from 1,500 to 2,100 mVD (meter Verticle Depth) with the highest capacity being measured between 5 - 10 MWe (DNG - 1, 4, 7 and 12). Figure 1 (taken from Boedihardi et al., 1991), shows a simple geology map with location of wells, hot pools, craters, hot springs, mountain peaks and major lineaments which have been observed from aereal photographs and which have been interpreted as faults. A number of wells can be classified as productive (the cut off is taken as 2.5 MWe). While the

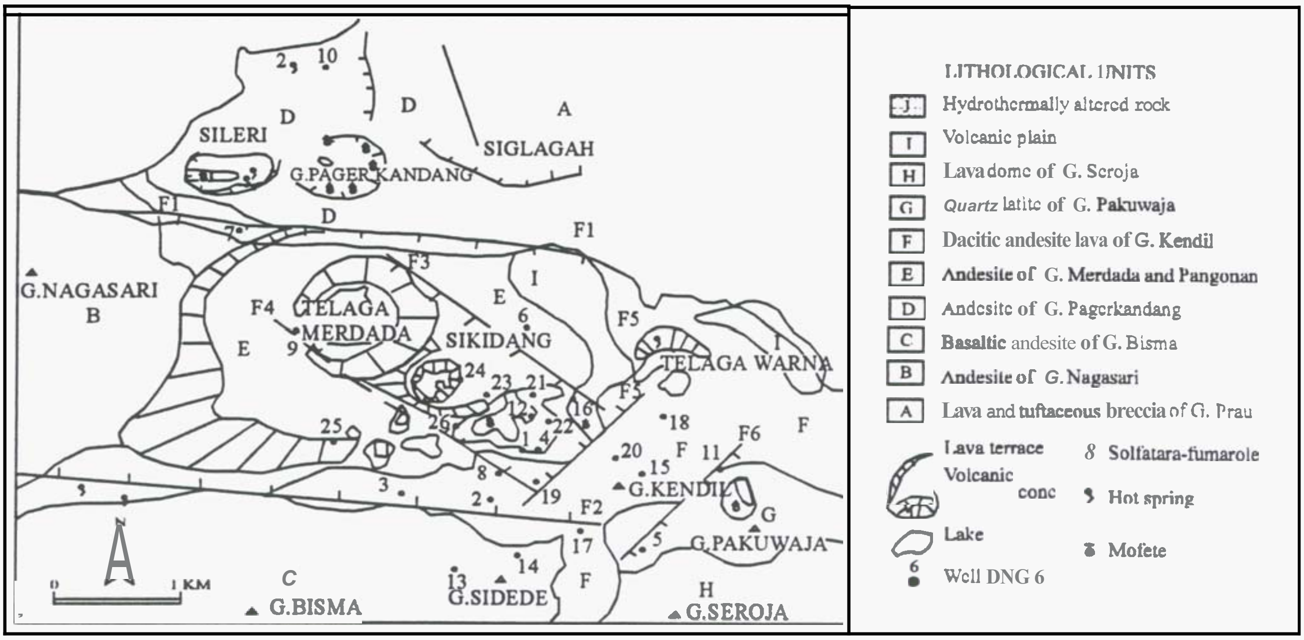

Figure 1 - Geological map and well locations of Dieng geothermal field

temperature gradient is generally high in the Dieng area it was found that non-productive well may co-exist next to a prolific one, e.g. DNG - 20 and 15, raises the possibility of pockets of isolated sources but with the further possibility that those sources connect to a common source deeper down. The Sikidang-Merdadareservoir, for example, is thought to consists of a dome-shaped steam cone overlying a brine reservoir. The permeability at depth which could vary from one location to the next may also be the reason for the varied productivity of the wells in the area.

It has been well established that geothermal fluids and gases contain C_1-C_{12} organic compounds (Nehring and Truesdell, 1978; Nehring et *al.*, 1982; Porshnev and Bondarev, 1986; Capaccioni *et al.*, 1993; Higashihara, 1993b, 1993c). Paraffin (C_7-C_{11}) and aromatic (C_8) hydrocarbons have also been found in soil gas over geothermal areas. Their identities have been established by the technique described in this paper and confirmed by GC-MS analysis (Higashihara and Fukuda, 1992; Higashihara 1993a). The hydrocarbons have been used as pathfinders in geothermal surveys in *Japan* with success (Higashihara and Fukuda, 1992; Higashihara 1993a; Noda et *al.*, 1992). The near-surface technique used in the surveys has been the passive integrative collection of the hydrocarbons from soil gas on activated carbon and analyzing the collected hydrocarbons by direct introduction MS (diMS). This paper reports the application of the technique in Indonesia. The Dieng area will be used to test the technique and to calibrate the results obtained. Two sections of the area are the focus of this report: the Sileri *area,* which is located in the northwest quadrant and the Sikidang-Merdada area, located in the southeast section of the Dieng area.

2. METHODS

The near-surface technique utilizing volatile hydrocarbons in soil gas as pathfinders for geothermal resources has been applied in the Dieng geothermal field. The hydrocarbons were integratively collected from soil gas on activated carbon samplers which have been buried in the ground for 4 weeks at approximately 40 cm below the surface. Each sampler was made by glueing (inorganic glue) pulverized carbon to one end (top end) of a 20 or 24-gauge Curie wire of about 7" long. The samplers were activated and one to three wires were placed (top end down) in glass test tubes of approximately 1-1/4" in diameter and 9" long. The activity of the carbon was maintained by using Nitrogen gas and keeping the tube screw capped tight utilizing a Special seal until use. The tubes were buried bottoms up. After retrieval of the wires from the ground each of the samplers were analyzed by pyrolysis desorbtion of the adsorbed hydrocarbons which were swept straight into the MS cavity. The ionization energy (EI) was set at 21 eV. This low energy setting will reduce the sensitivity by about an order of magnitude compared to the usual 70 eV normally used. However the 21 eV setting will allow larger fragments to be detected in the mass spectra than a 70 eV would. There is also more chance of molecular ions to be detected with lower ionization energies. The larger fragments quite often are indispensible for the understanding, and they allow easier interpretation, of the fragments detected. The spectra obtained was the result of a mixture of compounds adsorbed on the carbon.

Principal Components Analysis (PCA) was used to identify groups of correlating fragment ions (m/z's or amu's). Ions originating from the atmosphere (e.g. CO_2, N_2, *Ar)* and known or strongly suspected contaminants were eliminated from all data processing and only ions above a certain level of relative intensity were analyzed. Below that level the intensity readings are considered as background noise (or largely due to background noise). We have taken 5% as the level for the survey. Furthermore if in any one sampler within the survey area shows ions having a percentage which is above the set level (i.e. 5%) those ions (amu's) will be included in the analysis for all the sample points even for those that are below the set level.

There are 37 ions that satisfy the above criteria. Eight factors with eigenvalues more than 1 were extracted. The resulting Varimax (i.e. loadings for Varimax-rotated PCA solution) is shown in Table 1. Ions generated from the same compound show numerically high factor loading of the same sign on the same factor column because they are highly and positively correlated. Usually a numerical loading of .5 or greater of the ions in a Factor column can be taken as correlated. The higher the number (of the same sign) the better the correlation is.

The correlating ions (see Tabel 1) of the still unknown compound were matched against spectra of known and published compounds obtained from mass spectral libraries.

3. RESULTS

Three hydrocarbon compound classes have been successfully identified from 3 factors (i.e. Factors 1, 2 and 3).

(1) Paraffins, C_{7+} ("P"). Fragmentation patterns of straight chain hydrocarbons are characterized by clusters of peaks which are 14 amu (CH_2) apart. The largest peak in each cluster is the C_nH_{2n+1} fragment and it is accompanied by the C_nH_{2n} and C_nH_{2n-1} fragments. Factor 1 in Table 1 shows sets of clusters of 85, 84, 83, and 71, 70, 69, and 57, 56, 55 having positive factor loadings between .6293 and .9250. They are highly correlated to one another. The fragments correspond to the C_nH_{2n+1}, C_nH_{2n}, and C_nH_{2n-1} of the alkane hydrocarbon fragmentation pattern with n = 6 or higher; and each set is 14 amu apart from the next. A high positive factor loading of mass fragment of 112 might correspond to the C_nH_{2n} fragment with n = 8. Taken together it is safe to conclude that paraffin hydrocarbons are being detected in the mixture of samples adsorbed on the carbon from the Dieng soil gas.

(2) Alkylbenzene aromatics, C_8 ("X"). The compound can be recognized from the m/z91, m/z106 and m/z105 fragments. The ions are known to be characteristic fragment ions of alkylbenzenes: the tropylium ion (m/z91), the molecular ion (M, m/z106) and the often prominent M-1 fragment (m/z105). They show factor loadings of -0.6349, -.6891 and -.7388, respectively, on Factor 2. Furthermore a factor loading of -.5469 for m/z65 can be taken as the resultant of further fragmentation of the tropylium ion after the typical and facile elimination of its acetylene fragment. Taken altogether it can be concluded that C_8 aromatics has been detected in the soil gas in the Dieng area.

Table 1 - Factor Loadings

m/z	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5	Factor 6	Factor 7	Factor 8	Communality
29	-.2663	{ .8332}	-.2223	-.1848	-.0595	-.0406	-.0313	.0454	.8570
41	-.1288	(.8871}	-.1600	.2225	.1966	-.0571	-.0137	-.0371	.9220
42	-.0561	{ .7385}	-.2949	.4305	.2710	-.0936	-.0304	.0303	.9045
43	.2226	.1258	.0599	.4920	.2515	-.2047	.1805	.2155	,4951
54	.0293	.0374	.0345	-.0098	{ .8356}	.0069	.0383	.0788	.7094
55	(.6293)	.3318	-.0771	.1069	(.5182)	-.0254	-.0913	.0120	.8011
56	(.6921)	.4124	-.2671	.3698	.1203	-.0981	-.0270	.0028	.8820
57	{ .8458 }	.1204	-.1374	.1724	-.1593	-.0666	-.0212	-.0241	.8094
58	.0159	{ .8578}	-.2404	.0303	-.0641	-.0582	-.0340	.0191	.8037
64	-.0311	.0425	.0108	-.0150	.0684	.0042	-.0136	{ .9405}	.8925
65	-.4442	(-.5469)	-.1654	.2554	-.0195	.4472	-.1079	.0259	.8016
67	.1529	.2482	(.6254)	-.1530	(.6042)	-.0303	.0046	-.0751	.8711
69	{ .9217]	.0299	.0688	.0897	.1536	-.0099	-.0628	-.0758	.8966
70	{ .9250}	-.0133	-.1410	-.0268	.1708	.0008	.0200	.0601	.9096
71	{ .9210}	-.0484	-.0990	.0067	-.1930	-.0042	,0240	-.0006	.8985
78	-.3429	(.5211)	-.2490	.0119	.0424	.2862	.1812	.0236	.5683
79	(-.5701)	-.3510	.4497	-.0435	.0756	.4934	-.0877	-.0039	.9092
80	-.1566	-.1326	{ .8936}	-.0190	.0850	.0771	-.0353	-.0592	.8589
81	.2672	.2433	.1610	-.4971	.1928	-.1383	-.1484	.1165	.4955
83	{ .9116}	-.1167	-.1044	-.1648	.1504	.0198	-.0386	.0037	.9071
84	{ .9111}	-.0562	-.1586	.1278	.1421	.0086	-.0489	-.0091	.8974
85	{ .8908}	-.1338	-.0670	-.0047	-.1970	.0170	.0336	.0401	.8578
86	.1563	.1250	-.1055	(.8388}	-.0478	-.0605	-.1042	-.0450	.7735
91	(-.6150)	(-.6349)	-.3237	.0038	-.0980	-.1949	-.0828	-.0923	.9490
92	-.2655	.1168	.2765	.4386	-.0324	(-.5878)	-.0683	-.0064	.7042
93	-.1668	-.0279	(.8287}	.0159	.0420	-.0941	-.0525	.0972	.7385
94	-.0747	-.0291	(.6712)	-.0536	-.0042	-.1838	.0676	.2105	.5425
105	-.2679	{-.7388}	-.1202	-.0748	-.1529	(.5076)	-.0577	-.0563	.9252
106	(-.5526)	(-.6891)	-.3713	-.0763	-.0927	.0015	-.0724	.0821	.9445
107	-.2902	-.3002	.4969	-.0858	.0234	-.2778	-.0442	-.1688	.5367
112	{ .7801}	-.2431	-.1068	-.1967	.1212	.0260	.0049	-.0146	.7333
119	.3467	-.2031	(.6685)	-.1484	-.2031	.1343	.1176	-.0782	.7097
120	.4714	-.4391	.1170	-.1467	-.2732	.3638	.0824	-.0707	.6690
121	-.1447	-.0796	{ .9255}	-.0097	.0093	.0208	-.0342	-.0517	.8883
130	.0083	.0118	-.0420	.0671	.0409	.0095	(.9415}	.0145	.8948
132	-.2023	(.6118)	.0651	-.1881	-.0646	-.0041	(.5493)	-.0872	.7683
136	-.1539	-.0631	{ .9388}	-.0075	.0272	.0009	-.0142	-.0436	.9120

{ } : Factor Loading ≥ 0.7 or Factor Loading ≤ -0.7 ; ( ) : 0.7 > Factor Loading ≥ 0.5 or -0.7 < Factor Loading ≤ -0.5

3) Monoterpenes ($C_{10}H_{16}$). Monoterpenes can be identified from the characteristic fragment ions m/z93, m/z121 and the molecular ion (m/z136). The fragment ions show factor loadings of 0.8287 and higher on Factor 3. The m/z80 fragment with a loading of .8936 often appears as a typical fragment in many monoterpenes. Monoterpenes are detected in the Dieng soil gas as well.

4. DISCUSSIONS

Of the three hydrocarbon compound classes indentified the spatial distribution of the monoterpenes does not seem to correspond to the geothermal structure of the Dieng field. It is also known that monoterpenes is a class of compounds which originates from plant material. Therefore, only "P" and "X" will be discussed below.

Past experiences show that the integrative collection of the hydrocarbons on activated carbon reaches an equilibrium level within 3 to 4 weeks. It is reasonable to assume that the equilibrium level gives a relative measure of the true strength of the flux (of each of the individual compounds present in the soil gas) at that location (R.W.Klusman, personal commun., 1995). In general 3 weeks collection in the ground have been found to be adequate for the equilibrium to be reached. Generally longer collection time have been found to give no additional adsorption of hydrocarbons. Four weeks in the ground is thus considered adequate even for areas with poor hydrocarbon fluxes. In order to distinguish anomalously high flux samples from background samples a log-probability (cumulative frequency) plot for each hydrocarbon compound class was constructed. In the case of "P" where no molecular ions were observed, the sum of the ion intensities of the characteristic fragment ions (i.e. m/z57+m/z71+m/z85) was plotted (see Fig. 2). For Figure 2 breaks were recognized at 450,000, 210,000 and 27,000 ion counts. Samples with higher than 27,000 ion counts were considered anomalous. In the case of the alkylbenzene anomaly the ion intensities of the molecular ion (m/z106) were plotted (see Fig. 3) and breaks were recognized at 140,000, 30,000 and 10,000 ion counts. Samples with higher than 30,000 ion counts were considered anomalous.

Figures 4 and 5 show spatial distribution of the paraffins ("P") and that of the aromatics ("X"), respectively. Each map also shows anomalous zones which have been obtained from the distribution of the anomalous samples. Comparing spatial distribution of these zones with that of the geothermal productivity and the topography of the Dieng geothermal field, the following can be concluded:

(1) Zones with extremely high emission of the paraffins (see Fig. 4) were found around productive wells with capacity

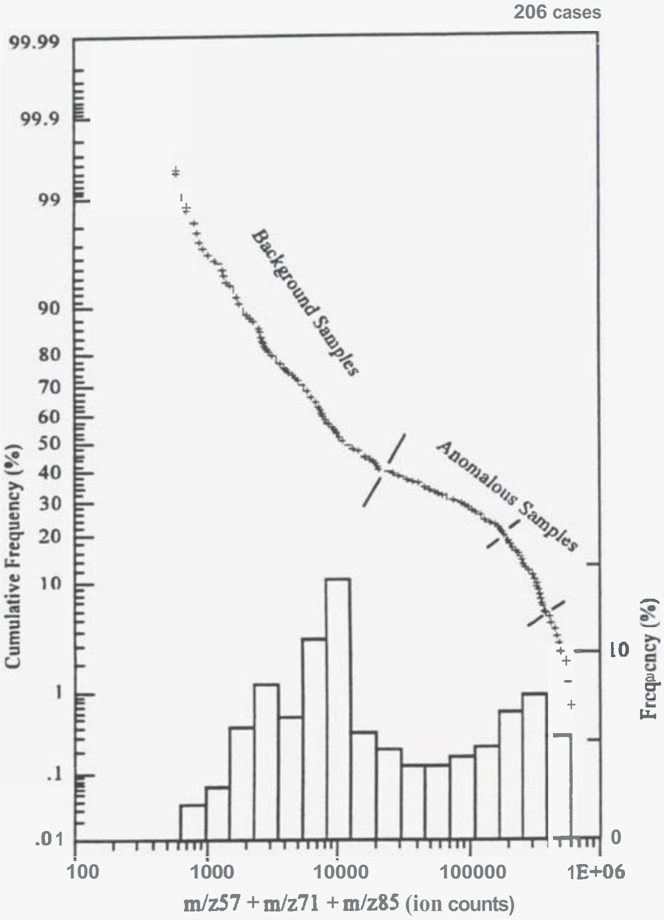

Figure 2 - Probability plot of m/z57 + m/z71 + m/z85

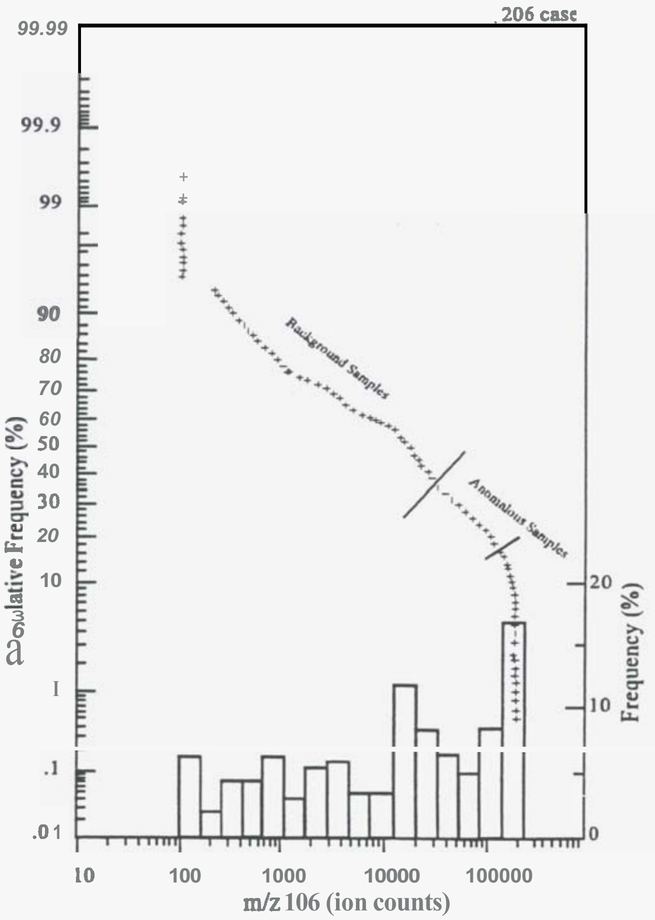

Figure 3 - Probability plot of m/z106

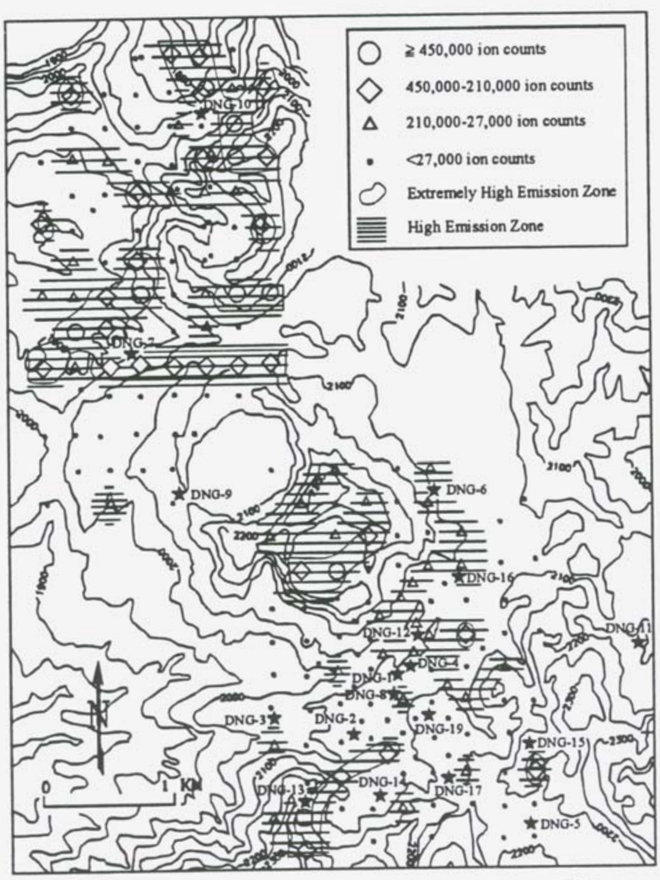

Figure 4 - Distribution of m/z57+m/z71+m/z85

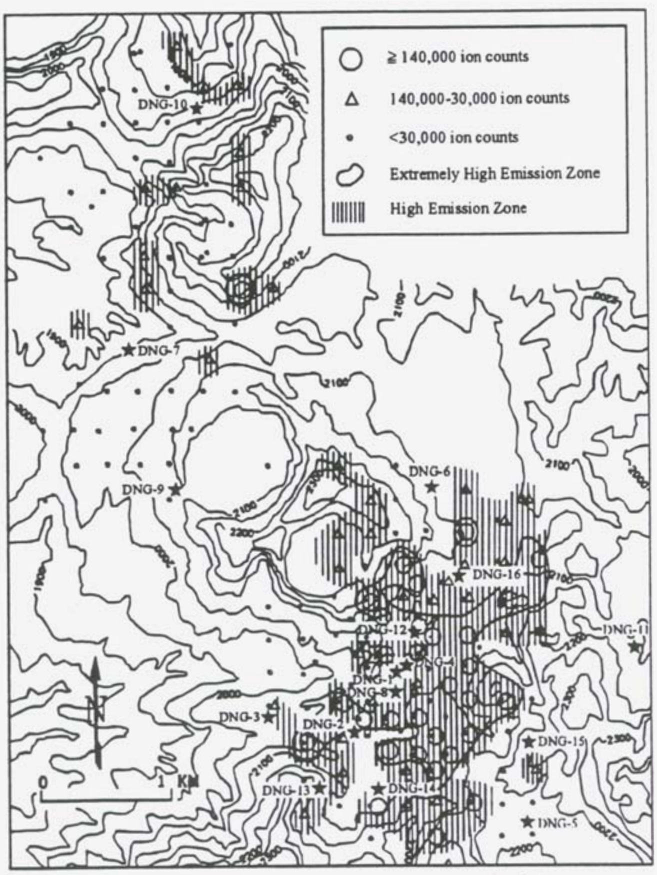

Figure 5 - Distribution of m/z106

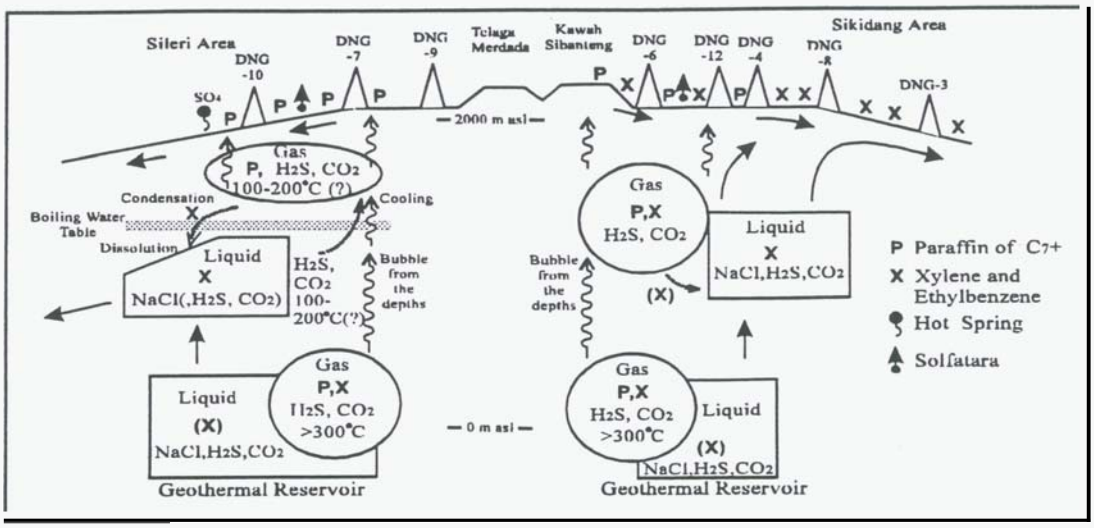

Figure 6 - Model for migration of hydrocarbons and magmatic **gases**

of 2.5 **MWe** or higher (DNG - 1, 2, 4, 6, 7, 10, 12, 13, 16, 20, 21, 22, 23 and 24). On the other hand, zones around wells with less than 2 MWe capacity (DNG - 3, 5, 8, 9, 11, 14, 15, 17, 18, 19, 25, 26 and 27) were populated with background samples. Well DNG - 7, which is one of the high capacity wells in the area and which is located near the F1 fault system in the Sileri area has been associated with the high east-west paraffin anomaly along and in the vicinity of the fault.

(2) Widespread zones with anomalously high emissions of the aromatics were found in the Sikidang-Merdada area (see Fig. 5). When compared to "P" the anomalous zones of "X" extend toward lower elevations (to the east and southeast). It can be taken as showing the hydromorphic distribution pattern of the C_8 aromatics. The aromatics have higher aqueous solubility and lower vapor pressures than their corresponding paraffins. They are more readily dissolved in the cooler discharge waters (and shallower ground water) and be carried' with the flow towards lower elevations (see Fig. 5).

(3) In the Sileri area (Fig. 5) narrow "X"-anomalies were found within the widespread "P-anomalous zones. The near-surface expression of Sileri area (mostly "P") and that of the Sikidang-Merdada area ("X" and "P") are different. This difference may be explained by the underground boiling mechanism (see Fig. 6) as proposed below. The mechanism could also explain the existence of many solfataras and SO_4 -type hot springs in the Sileri area:

i. Large scale boiling take place at relatively shallow depth, possibly around temperatures of 100°C - 200°C. Large amounts of comparatively cool gas is generated. Volatile components (e.g. H_2S, CO_2) are fractionated from the more soluble and higher boiling compounds (e.g. HCl).

ii. Hot bubbles containing "P" and "X" ascend from the deep geothermal reservoirs up to the boiling zone.

iii. The bubbles are diluted with "cool" gas. The aromatics (C_8) have comparatively lower vapor pressure and they are much more soluble than the paraffins (C_7-C_8). The aromatics are therefore partitioned from the paraffins by preferential condensation and dissolution into the ground water. The aromatics are therefore more apt to spread with the outflowing waters than the paraffins. Generally its spread tends to follow the under ground water flow which generally, in the absence of strong convection currents, tend to spread to lower elevations.

The exact mechanism of the generation of the hydrocarbons in this geothermal field has not been determined. Sedimentary rocks are known to outcrop in the periphery of the Dieng field. They may be the source of the hydrocarbons. Catagenesis of the organics in the sedimentary rock and the transport of the organic molecules by the recharging waters which could be driven by the geothermal convection system (see Fig. 7) could be the source of the paraffins and aromatics. Further thermal cracking of the larger compounds carried by the waters to produce the C_{7+} paraffins and C_8 aromatics in the geothermal kitchens (reservoirs) may also contribute to the source. Under reservoir conditions, many of the hydrocarbons would be in the supercritical and gaseous state (200°C - 350°C). Large amounts of microbubbles could be generated. The microbubbles flow upward with the upflowing geothermal fluids and ascended further through cracks and microfractures of the covering rocks. Eventually they are expressed as hydrocarbon anomalies in the soil gas of the upflow zones.

5. CONCLUSIONS

The Dieng geothermal field consists of volcanic rocks. Its soil gas was shown to contain C_{7+} paraffins and C_8 aromatics. These classes of hydrocarbons are known to be proven pathfinders for geothermal resource (Higashihara and Fukuda, 1992; Higashihara, 1993a). Zones of C_{7+} paraffins anomalies are found around productive wells and apparently they define the production zones of the Dieng field. It appears that paraffin anomalies suggest location of geothermal reservoirs or their upflow zones.

The C_8 aromatics anomalies also appear on and around production zones, especially in the Sikidang and Merdada area, but their distributions are more spread out and they seem to also reflect the hydrogeology of the area (i.e. shallow ground water flow and underground boiling).

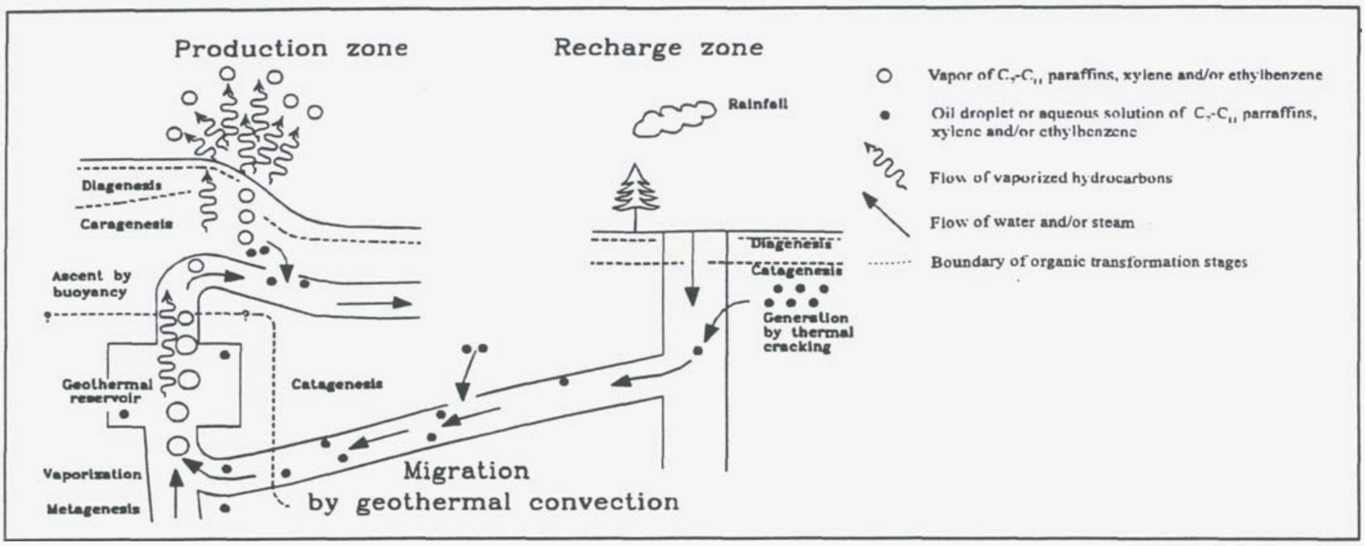

Figure 7- Model of hydrocarbon migration in a geothermal convection system

flow and underground boiling).

(1) A hydromorphic distribution pattern is found in the southeastern part of the Sikidang-Merdada area where the ground water seems to flow to the east and south-southeast.

(2) Only a few zones with anomalously high flux of C, are found in the Sileri area. This is in contrast to the paraffin anomalies which are abundant throughout the area. The proposed mechanism of underground boiling of water at shallow depth (100 - 200^0 C) allows the system to cool down. The resulting condensation and the solubilization of the aromatics in the ground water probably keeps them from reaching the surface.

(3) Differences of spatial distributions that depend on differences of vapor pressures and of aqueous solubilities between those hydrocarbon classes may contribute toward revealing not only the upflow system, i.e. the geothermal resources, but also the hydromorphic pattern.

(4) The Sileri area and the area to its east (the Siglagah area) may have greater potential than thus far recoqnized. Hot water at shallow depth can be expected.

(5) The existence of the east-west F1 fault, the high paraffin anomaly along the general area of the fault and the high capacity DNG - 7 well which is also located near the fault supports the assumption that the technique identifies upflow zones.

6. REFERENCES

Boedihardi, M., Suranto and Sudarman, S. (1991). Evaluation of the Dieng geothermal field: Review of the development strategy. Proc. *20th Annual Convention Indonesian Petr. Assoc.*, Vol. 1, 347-361.

Capaccioni, B., Martini, M., Mangani, F., Giannini, L., Nappi G. and Prati, F. (1993). Light hydrocarbons in gas-emission from volcanic areas and geothermal fields. ***Geochemical Jnl.***, Vol. 27, 7-17.

Higashihara, M. (1993a). Distribution of hydrocarbons in the Okuaizu geothermal area., Fukushima prefecture (in Japanese with English abstract). ***Jnl. Geothenn. Res. Soc. Japan,*** **Vol** ¹⁵ 231-252.

Higashihara, M. (1993b). C_{2+} hydrocarbons in geothermal flu..., a review (in Japanese). ***Jnl. Japan Geothenn. Energy Assoc.,*** Vol. 30, 60-66.

Higashihara, M. (1993c). &hydrocarbons in geothermal fluid, a review (supplement) (in Japanese). ***Jnl. Japan Geothem. Energy Assoc.,*** Vol. 30, 144-145.

Higashihara, M. and Fukuda, M. (1992). Distribution of hydrocarbons in Sumikawa area, Akira prefecture (in Japanese with English abstract). ***Jnl. Japan Geothenn. Energy Assoc..*** Vol. 29, 142-162.

Nehring, N.L. and Truesdell, **A.H.** (1978). Hydrocarbon gases in some volcanic and geothermal systems. ***Jnl. Geothem. Resour. Counc. Trans.,*** **Vol.** 2, 483-486.

Nehring, N.L., Des Marais, DJ. and Truesdell, A.H. (19.. Thermal decomposition of hydrocarbons in the Cerro Prieto, Mexico, geothermal reservoir. ***Jnl. Geothenn. Resour. Counc. Trans.,*** Vol. 6,305-307.

Noda, T., Takahashi, M. and Shigeno, H. (1992). Application of the Fingerprint Geothermal Method in the Geothermal Exploration Survey of the Sumikawa Area (in Japanese). ***Jnf. Japan Geothenn Energy Assoc.,*** Vol. 29, 129-146.

Porsnev, N.V. and Bondarev, V.B. (1986). Analysis of the aromatic fraction in geothermal fluids. ***Jnl. Chromatography,*** Vol. 365, 463-472.