

HYDROCARBON ANOMALY IN SOIL GAS AS NEAR-SURFACE EXPRESSIONS OF UPFLOWS AND OUTFLOWS IN GEOTHERMAL SYSTEMS

H.L.Ong¹, M. Higashihara², R.W. Klusman³, K.J. Voorhees³, R. Pudjianto⁴ and J. Ong¹

¹PT Geoservices, Jl Taman Matraman Timur 11, Jakarta 10320, Indonesia

²Mindeco (Japan), ³Colorado School of Mines (USA), ⁴Pertamina (Indonesia)

ABSTRACT

A variety of hydrocarbons, C₁ - C₁₂, have been found in volcanic gases (fumarolic) and in geothermal waters and gases. The hydrocarbons are thought to have come from products of pyrolysis of kerogen in sedimentary rocks or they could be fed into the geothermal system by the recharging waters which may contain dissolved hydrocarbons or hydrocarbons extracted by the waters from the rocks. In the hot geothermal zone, 300^o+ C, many of these hydrocarbons are in their critical state. It is thought that they move upwards due to buoyancy and flux up with the upflowing geothermal fluids in the upflow zones together with the magmatic gases. Permeability which could be provided by faults, fissures, mini and micro fractures are thought to provide pathways for the upward flux. A sensitive technique (Petrex) utilizing passive integrative adsorption of the hydrocarbons in soil gas on activated charcoal followed by desorption and analysis of the hydrocarbons by direct introduction mass spectrometry allows mapping of the anomalous areas.

Surveys for geothermal resources conducted in Japan and in Indonesia show that the hydrocarbon anomaly occur over known fields and over areas strongly suspected of geothermal potential. The hydrocarbons found and identified were n-paraffins (C₇-C₉) and aromatics (C₇-C₈). Detection of permeable, i.e. active or open faults, parts of older faults which have been reactivated, e.g. by younger intersecting faults, and the area surrounding these faulted and permeable region is possible. The mechanism leading to the appearance of the hydrocarbon in the soil gas over upflow zones of the geothermal reservoir is proposed. The paraffins seems to be better pathfinders for the location of upflows than the aromatics. However the aromatics may, under certain circumstances, give better indications of the direction of the outflow of the geothermal system. It is thought that an upflow zone can be defined when conditions exist where the recharging waters containing the hydrocarbons feed into the geothermal kitchen. The existence of open and active faults, fissures, mini and micro fractures allow sufficient permeability for the gases to flux up and express themselves at the surface as hydrocarbon anomaly in the soil gas. When any of the requirements is absent, i.e. in the absence of the recharging waters,

hydrocarbons, temperature, or permeability, no anomaly can be expected. It assumes a dynamic convective system, i.e. recharging waters, upflow and outflow. The anomalies however can define to a certain extent, regions of geothermal upflow, buoyant transport of gases, and frequently down-gradient of cooling waters.

INTRODUCTION

A new near-surface geochemical technique utilizing volatile hydrocarbon in soil gas ("Petrex Hydrocarbon Fingerprint") as pathfinders for geothermal resource surveys have been applied in Indonesia (Pudjianto, R. *et al.* 1995) and in Japan (Higashihara, M. *et al.* 1993a, b, c). A brief review of the occurrences of hydrocarbons in volcanic areas and geothermal systems is summarized below and some of the more common hydrocarbons are tabulated in Tables 1(1) and 1(2).

Hydrocarbons in volcanic and geothermal systems have been reported by various authors. Stoibers *et al.* (1971) reported numerous kinds of organic compounds: pairs of alkanes/alkenes, aromatics, ketones, aldehydes, alcohols, methylacrolein and a variety of halogenated (fluorinated and chlorinated) compounds. The compounds are thought to be derived from the heating of sedimentary rocks by magma, while the halogenated organics were thought to be product of the reaction between the organics and that of HF, HCl or inorganic halides at high temperatures. Gunter (1978) reported normal alkanes (C₁-C₄), isobutane, ethene and propene from 22 gas samples from Yellowstone National Park. The author concluded that the data supports the organic sedimentary origin rather than from abiogenic derived sources.

Nehring and Truesdell (1978) of the United States Geological Survey (USGS), Menlo Park, California analyzed gases of several volcanic and geothermal systems. The volcanic gases are characterized by the low content of the hydrocarbons. Methane and alkanes (C₂ - C₄) and their corresponding alkenes and 2-butene were identified. Where sedimentary (and metamorphosed sedimentary) input is strongly suspected much higher concentrations and a wider variety of the hydrocarbons were found. Alkenes are absent but a variety of branched alkanes are present in large amounts. Benzene is usually found in larger concentrations than the C₄ alkanes. The methane was

Table 1. Summary of concentration of hydrocarbons in geothermal fluids (1).
(Higashihara, 1993a)

Area	U. S. A. Yellowstone National Park						U. S. A. Sweetwater Mineral Springs	U. S. A. Grand Teton National Park		U. S. A. The Geysers	U. S. A. Steamboat Springs	U. S. A. Lassen Volcanic Nation. Park	U. S. A. Morgan Springs	U. S. A. Mount Hood Volcano	U. S. A. St. Augustine Volcano	U. S. A. Kilauea Volcano	Guatemala Santiaguito Volcano	
	Hot spring 81°C Gas	Hot spring Gas	Hot spring/fumarole? Gas	Hot spring/fumarole? Gas	Hot spring Gas	Hot spring Gas	Hot spring Gas	Hot spring Gas	Hot spring? Gas	Well Gas	Hot spring/fumarole Gas	Hot spring/fumarole Gas	Hot spring Gas	Fumarole Gas	Fumarole Gas	Fumarole Gas	Fumarole Gas	
Sampling point	(unit) ppm, v/v mole ratio						ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v
Paraffins																		
Methane	772,300	1	⊙ ¹⁾	⊙	40,000	110,000	140,000	600	957,000	105,000	⊙	⊙	⊙	○	⊙	○	>14	
Ethane	28	0.01000	○	⊙	690	630	2,700	4	187	1,970	△	△	△	△	△	△	⊙	
Propane	3.2	0.00816	△	⊙	180	210	1,400	2.7	1.7	1,100	△	△	△	△	△	△	⊙	
i-Butane	0.5	0.00076	△	△	21	32	360	0.6	0.4	10	△	△	△	△	△	△	△	
n-Butane	1.6	0.00174	○	△	36	53	690	0.9	0.6	560	○	○	△	△	△	△	△	
i-Pentane			△	△						10	△	△	△	△	△	△	△	
n-Pentane				△						30	△	△	△	△	△	△	△	
i-Hexane				△						10							△	
n-Hexane			△	○						10	△						} △	
i-Heptane										10							} △	
n-Heptane																	} ⊙	
i-Octane																	} △	
n-Octane																	} △	
n-Nonane																		
n-Decane																		
n-Undecane																		
Cycloparaffins																		
Cyclopentane										6								
Cyclohexane																	△	
Methylcyclohexane																	○	
Aromatics																		
Benzene										285	△	△	△				△	
Toluene																	△	
Ethylbenzene																		
Xylene																		
C ₃ (or C ₄ ?)-benzene																		
Naphthalene																		
Methylnaphthalene																		
Biphenyl (M. W. = 154. 21)																		
Unsaturated hydrocarbons																		
Acetylene	0.8		△															
Ethylene	0.3	0.00003	△	△	2	19	20	0.4	3.1	3	△	△	△		△		△	
Propene			△								△	△					○	
Butene			△	△							△	△	△	△		△	○	
Pentene																	○	
Hexene																	△	
Heptene																	△	
Octene																	△	
Total R gas	16 ²⁾						9	5	5	99	99	15						
Total gas (excluding H ₂ O)	16 ²⁾						9	5	5	99	99	15						
Reference	Gunter & Musgrave (1971)	Gunter (1978)	Nehring & Truesdell (1978)	do	Kvenvolden et al. (1989)	do	do	do	do	Nehring (1981)	Nehring & Truesdell (1978)	do	do	do	do	do	Stoiber et al. (1971)	

Concentration = hydrocarbon/total R gas. 1) : ⊙Peak height in chromatogram/full scale response ≥ 50%. ○25-50%, △ < 25%; 2) : Gunter & Musgrave (1966)

Table 1. Summary of concentration of hydrocarbons in geothermal fluids (2).
(Higashihara, 1993a)

Area	Mexico Cerro Prieto						Italy Vulcano Volcano	Italy Larderello	Japan Nasu Volcano		Japan Matsukawa		Russia South Kamchatka Lower Koshelevskii		Russia South Kamchatka East Pauzhetskii	
	Well	Well 340°C	Well 290°C	Fumarole 100°C	Well 276°C	Well 330°C	Fumarole 100°C	Well	Fumarole 90-150°C	Fumarole 90-150°C	Well 240°C ³⁾	Well 220°C ³⁾	Well Ambient 600m	Well ≥300°C 1,000m	Fumarole 98°C	Fumarole 98°C
State of sample	Gas	2,000m Gas	2,000m Gas	Gas	1,300m Gas	2,000m Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas	Gas in condensate
(unit)		ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v	ppm, v/v				ppm, v/v	ppm, v/v	ppm, w/w ⁴⁾	ppm, w/w ⁴⁾	ppm, w/w ⁴⁾	ppm, w/w ⁵⁾
Paraffins																
Methane	⊙	25,000	50,000	2,000	34,000	42,000	87,000	⊙		1	1	188,000	238,000	121,860	46,800	10,000
Ethane	⊙	3,500	15,000	45	1,000	310	tr.	⊙	0.00160	0.00160	1,380	1,740	6,426	2,600	38	
Propane	⊙	250	4,000	15	170	36	tr.	⊙	0.00013	0.00011	76	117	2,458	778	13	
i-Butane	⊙	6	550	10				△			6	2	341	92	2.5	
n-Butane	⊙	10	1,000	.75	} 100	} 5	} tr.	○	} 0.00017	} 0.00006			552	161	3.5	
i-Pentane	△	2	252	4				△			3	13	106	35	1	
n-Pentane	△	2	300	7				△					130	42	1	
i-Hexane	△							△					<1	<1		
n-Hexane	△	1	1,000	30				△					25	15	<1	
i-Heptane				?												
n-Heptane		2?	300?	50?												
i-Octane													20	13		
n-Octane													16	9		
n-Nonane													9	6		
n-Decane													7	2		
n-Undecane													8	1		
Cycloparaffins																
Cyclopentane	△	≤1	≤200	≤4										<1	<1	
Cyclohexane														<1	<1	
Methylcyclohexane			?	?										<1	<1	
Aromatics																
Benzene	⊙	2,000	6,000	900	100	97		⊙					1,560	2,028	54	15
Toluene		8	1,000	250									629	650	6	2.5
Ethylbenzene													26	39		
Xylene													264	392	} 1.5	} 1
C ₃ (orC ₄ ?)-benzene													84	45	<1	1
Naphthalene													201	61	1	4
Methylnaphthalene													<2	<2		<2
Biphenyl													<1	<1		<1
Unsaturated hydrocarbons																
Acetylene																
Ethylene		0.05	2	9			tr.		0.00190	0.00038	4					
Propene				3			tr.									
Butene				22			tr.									
Pentene	△	≤1	≤200	≤5												
Hexene																
Heptene				?	?											
Octene																
Total R gas (%)							66				3	3				
Total gas (excluding H ₂ O)																
Reference	Nehring & Truesdell (1978)	Nehring et al. (1982)	do	do	Des Marais et al. (1988)	do	Chaigneau & Conrad (1970)	Nehring & Truesdell (1978)	Asada & Kiyosu (1991)	do	Kiyosu et al. (1992)	do	Porshnev & Bondarev (1986)	do	do	do

3) : Kiyosu(1983) ; 4) : concentration=hydrocarbon/total gas ; 5) : concentration=hydrocarbon/total dissolved gas

observed to reach as high as 10-30% of the total gas found. Nehring and Fausto (1979) reported that the hydrocarbons found in the steam of both the hot-water dominated systems, in the Cerro Prieto (Mexico) and the Larderello (Italy), and the vapor dominated system of The Geysers (California, USA) closely resemble one another, and that the hydrocarbons could be derived from sedimentary rocks. The presence of C₄-C₆ branched alkanes, the absence of alkenes and the variety of the hydrocarbons found are thought to be characteristic of sedimentary derived sources. Repeating earlier tests Nehring et al. (1982) found C₁-C₇ alkanes, benzenes and toluene in the Cerro Prieto geothermal steam. The USGS group also reported the presence of C₂-C₅ alkenes in the fumarole gas in the same area (Des Marais *et al.*, 1982).

Porshnev and Bondarev (1986) identified 34 organic volatile compounds from samples taken from different geothermal fluids from the South Kamchatka area (formerly in the USSR). The samples were taken from two wells and a fumarole. They found methane, normal alkanes (C₂-C₁₁), branched saturated alkanes (isobutane, iso-pentane, 2,2-dimethylpentane and hexane isomers), cyclic alkanes (cyclohexane and methylcyclohexane), monoaromatics (benzene, toluene, ethylbenzene, o,m,p-xylenes, propylbenzene and possibly also C₄-benzenes), fused aromatics (naphthalenes, 1- and 2-methylnaphthalene) and biphenyl. No alkenes were reported and the concentration of the aromatics by far outweighs the C₆ alkanes. Methane gas predominates and it constitutes over 90% of the total hydrocarbon gas found. Des Marais and Truesdell (1987) also reported methane and higher hydrocarbons in geothermal areas in the western North America.

Giggenbach (1990) found between 20 to 51 ppm (v/v) of ethylbenzene and xylenes which is higher in concentration than the toluene (3-12 ppm), methane (200,000-271,000 ppm) and smaller amounts (lower than 1 ppm) of C₂-C₄ alkanes and benzene from gas discharges in the Lake Nyos area, Cameroon. More recently Cappaccioni et al. (1993) reported a variety of hydrocarbons in volcanic gases.

There is abundant evidence of hydrocarbons in geothermal and volcanic systems. The origins of the hydrocarbons are not completely clear and the reaction mechanisms that led to the generation of some of them are not understood. Sedimentary kerogens are suspected for most of the hydrocarbons found but it is not clear whether the conditions (hydrous or anhydrous, rock types and the higher temperatures) to which they are subjected would give the same

mechanistic breakdown and products as those occurring in sedimentary basins where coal, bitumens, oil and natural gas are produced. Although aromatics are abundant in oil, alkenes are absent. The unsaturated compounds could be thought of as pyrolysis products of their saturated parent molecule and/or from the kerogen. It is quite common to find about equal amount of alkane/alkene pairs from laboratory anhydrous pyrolysis gas chromatography (pgc) of kerogen (Huizinga *et al.* 1987; Dembicki, 1990). Hydrous pyrolysis (or pyrolysis in the presence of hydrogen donors, such as tetrahydronaphthalene or cyclohexadiene) of kerogen would only give alkanes. A review of the results of anhydrous and hydrous pgc has been summarized by Tannenbaum *et al.* (1986). The possibility of microbial oxidation of the alkanes to the corresponding 1-alkenes can not entirely be discounted but it is unlikely they could be major contributor to the presence of the alkenes. Microbes have been associated with the generation of methane, ethane, ethene and propene in marshes, refuse and garbage dumps (Rice and Claypool, 1981). But they are not known to produce higher alkenes in detectable amounts. Metabolic products of thermogenic microbes have not been studied in detail in volcanic and geothermal systems. Therefore, if indeed higher members of the alkene series are fairly common in these systems (thus far reports of their existence have only been spotty and no real effort has been made to search for them) they might have been due to high temperatures and anhydrous conditions. The conditions can be mimicked and indeed the 1-alkenes, along with their corresponding alkanes, can be generated in the laboratory by anhydrous pyrolysis of kerogen.

Alkynes (e.g. acetylene) have been reported to be present in some geothermal and volcanic systems. Earlier workers (Craig, H. 1953; Ellis, A.J. 1957; Gunter, B.D. and Musgrave B.C. 1971; Krauskopf, K.B. 1959; Stoiber, R.E. *et al.* 1971; Welhan, J.A. 1988) have proposed abiogenic generation of methane from hydrogen and sources of carbon under anhydrous as well as hydrous conditions. The methane could further react to form higher molecular weight hydrocarbons, though not as complex in their structure as hydrocarbon derived from sedimentary origins (Gordon, A.S. 1948). It is clear that these abiogenic processes would be taking place in different environment and temperature regimes than processes occurring in sedimentary rocks where alkynes can also be produced by anhydrous thermal cracking of the kerogen.

While the origins and mechanisms in the generation and formation of the hydrocarbons in geothermal and

volcanic systems need to be studied further their widespread occurrences have been recognized.

A near-surface geochemical method based on the integrative adsorptive collection of hydrocarbon in soil gas on activated charcoal was introduced about a decade ago. The hydrocarbons collected were analyzed by Mass Spectrometry (MS). The MS spectral results followed by statistical processing are able to identify the types of hydrocarbons that are useful as pathfinders for geothermal surveys. Higashihara (1993a,b,c) suggested that hydrocarbons carried by recharge waters into geothermal hot zones (roughly 250 - 350^o C) are pyrolyzed into smaller molecules and vaporized. Some of the molecules, C₆-C₁₁ paraffins, xylene/ethylbenzene and toluene aromatics, have been detected in the soil gas and used as pathfinders for geothermal resource exploration. At geothermal temperatures most of the molecules are in or near their critical state. The mechanism and transport of the molecules to the surface is not clear. It is thought that the vapors form micro bubbles in the predominantly hydrous environment. A constant flux of the hydrocarbon bubbles, driven by buoyancy and with the geothermal upflow system move up towards the surface through permeable rocks and micro fractures.

The method, known initially as the "K-V" technique, was originally developed for hydrocarbon exploration by Colorado School of Mines' professors, Klusman and Voorhees (1983). The technique, now known as Petrex (Petroleum Exploration) Fingerprint Technology, was first applied to fault/fracture detection and geothermal exploration by Sakai (1986, 1987). It was also reported at The Pacific Rim Congress 87 (Villeneuve, J.H. *et al.* 1987). Since 1987 it has been regularly applied in Japan by Mindeco (the Mitsui group). The technique seems to be increasingly accepted (Shigeno, H. 1991) because of its predictive value. Higashihara (1993 a,b,c) proposes that the saturated hydrocarbons anomaly detected by the Petrex Fingerprint method is an expression of the deep geothermal upflow whose "focus" is generally vertically below. The method seems not to suffer from as many interferences as other surface geochemical methods have. While the method can be used as a stand alone survey, its value is the supportive evidence it lends to other geophysical and geological knowledge of the area.

METHODOLOGY

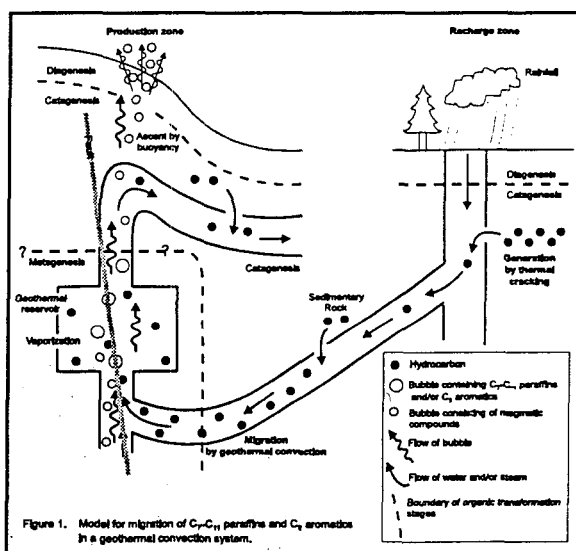
The method and techniques have been described elsewhere (Pudjianto, R. *et al.* 1995). Basically the method involves the integrative adsorption (collection) of hydrocarbons in the soil gas on activated charcoal

which has been glued to a wire. The wire is inserted in a glass test tube (6" x 1" OD) and buried about 40 cm in the ground with the open end of the tube downwards. The buried collector is retrieved after about 4 weeks. Through diffusion the hydrocarbons are being integratively collected (adsorbed). The assumption is that the collected hydrocarbons reflects the strength of the hydrocarbons fluxing from depth. It is also assumed that the collection (adsorption) is not interfered by irreversible deactivation of the active sites of the charcoal during the collection or substitution processes of the adsorbed molecules. Substitution may be unlikely because of the low concentration of the hydrocarbons in soil gas in volcanic areas.

RESULTS, REVIEW AND DISCUSSION

The Dieng Geothermal Survey.

The Petrex Fingerprint survey was tested in the Dieng Geothermal Field, Indonesia. Hydrocarbon anomalies were found to occur around well locations with 3 MWe capacity and higher. The anomalies were determined according to the technique described elsewhere (Pudjianto, R. *et al.* 1995). A model for hydrothermal convection and buoyant transport of oversaturated gases has been proposed and is shown in Figure 1.



The Okuaizu and Sumikawa Geothermal Surveys.

The Okuaizu geothermal field in Japan has been studied in some detail (Seki, Y. 1991; Nitta, T. *et al.* 1988). Thirty nine wells have been drilled through 1991. Well data, including the sub-surface temperature profile of the area have been most valuable in modelling the Okuaizu geothermal field (Figures 2 and 5). Table 2 shows the presence of the monoterpenes in factor 1, the alkanes in factor 2. The aromatics (C₈) are

identified in factor 6. An excellent agreement in identifying the productive zones using the Petrex Fingerprint technique can be seen from Figures 3a and 4a. Figures 3 and 4 show breaks of the probability plots and where ranges of concentration anomalies of the hydrocarbons were determined. It is thought that the location of the upflow is located below the surface (hydrocarbon) anomaly. The Okuaizu geothermal field is controlled by the Chinoikezawa, Sarukurazwa and Oizawa parallel fault systems striking NW. The temperature profile, which is largely governed by hydrodynamics, shows skewing to the NE towards the Oizawa fault (hot water is thought to be leaking from the reservoir and flowing with the shallow ground water towards the Oizawa fault). The interplay of deep hot temperature and hydrodynamics, which could be governed by the nature of the permeability (faults and fractures), the location of the upflow zone and the shallow groundwater could influence the "epicenter" of the hydrocarbon anomaly at the surface. However the sub-surface location (focus) of the upflow seems to be dominant factor in the location of the surface (epicenter) anomaly (Higashihara, M. 1993a,b,c). Recent Petrex surveys with closer sample spacing were successfully identified in greater detail of the geothermal resources of the area (Higashihara, M. 1993 a,b,c).

The Sumikawa Geothermal Area The Petrex Fingerprint technique has also been applied to the Sumikawa area (Higashihara, M. and Fukuda, M. 1992; Noda, T., *et al.* 1992) and it produces results confirming the existing well data. Figures 6 and 7 show probability plots and inflection breaks at which anomaly ranges

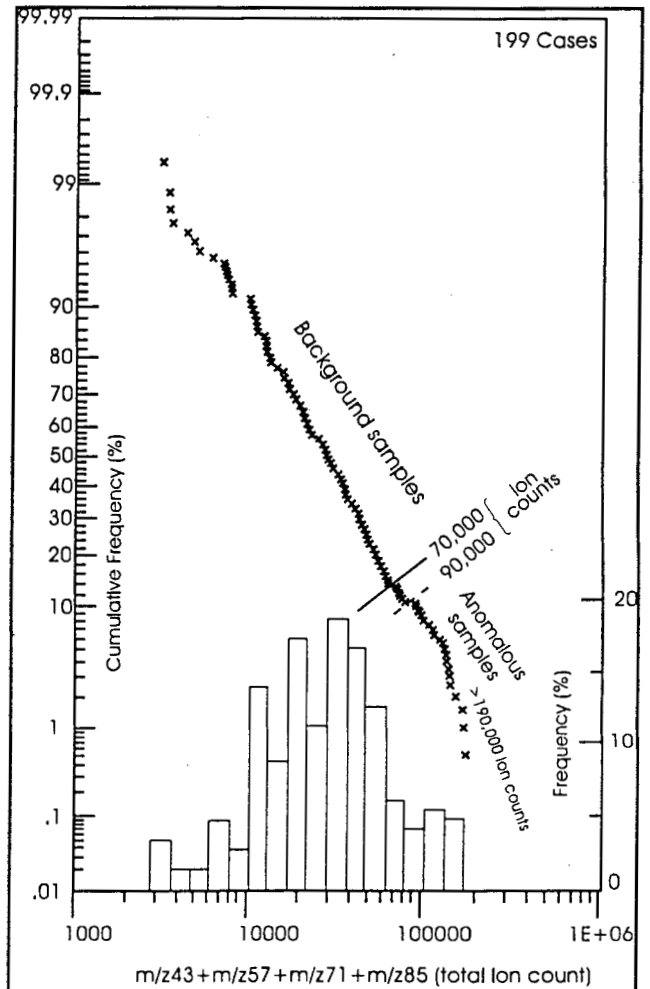


Figure 3. Probability plot of $m/z_{43}+m/z_{57}+m/z_{71}+m/z_{85}$ (C, paraffins) flux in the Okuaizu geothermal area.

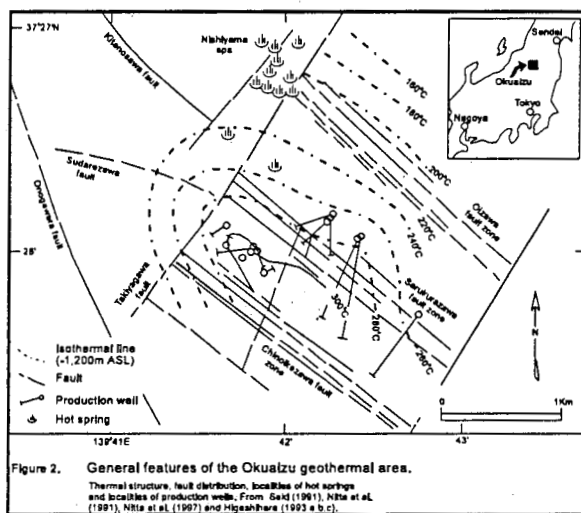


Figure 2. General features of the Okuaizu geothermal area. Thermal structure, fault distribution, localities of hot springs and localities of production wells. From Seki (1961), Nitta *et al.* (1981), Nitta *et al.* (1987) and Higashihara (1993 a,b,c).

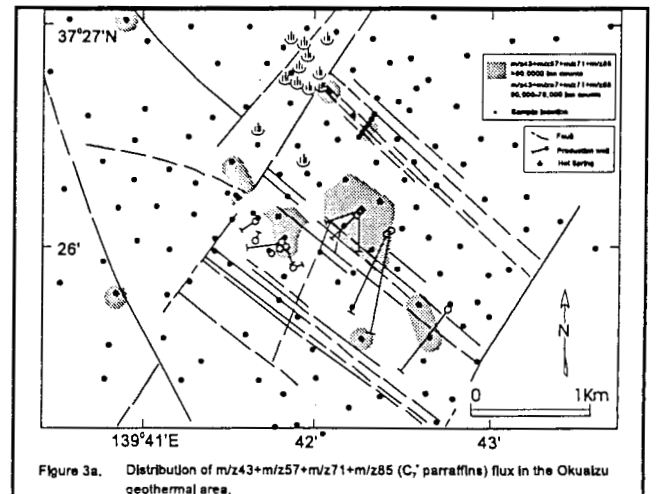
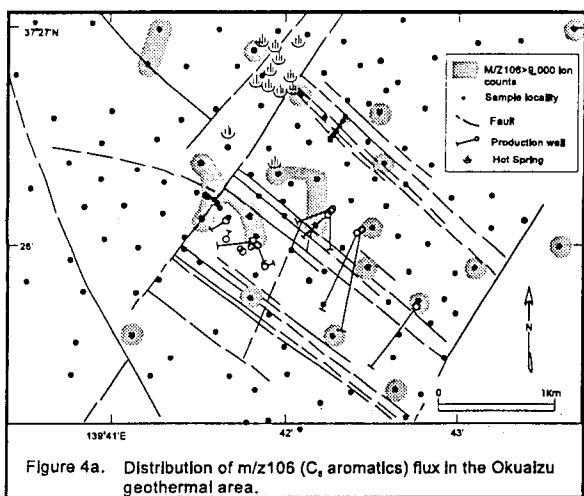
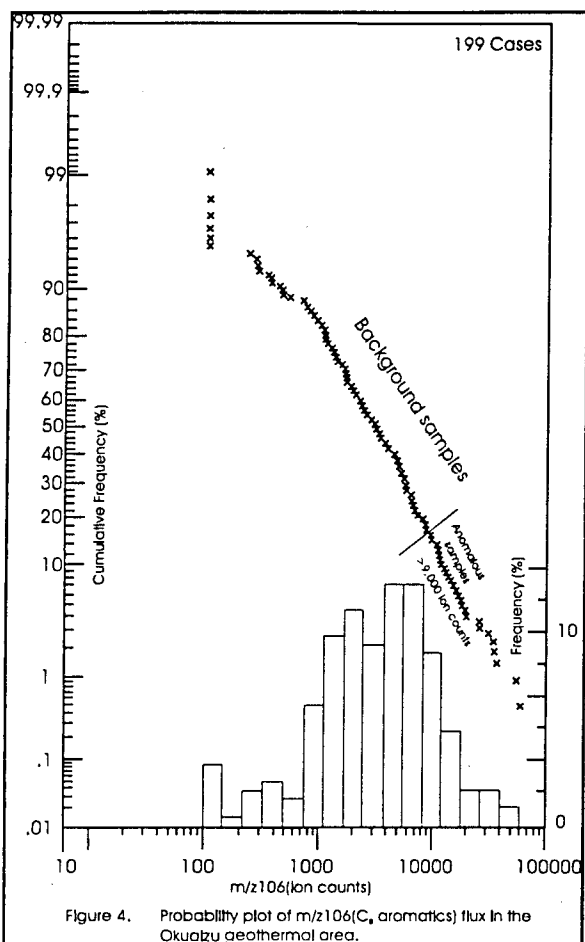
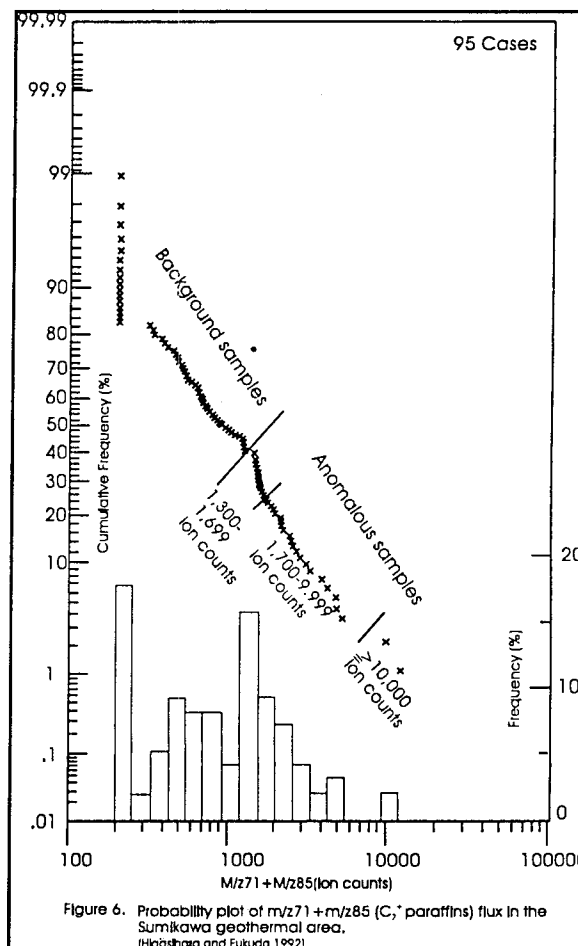
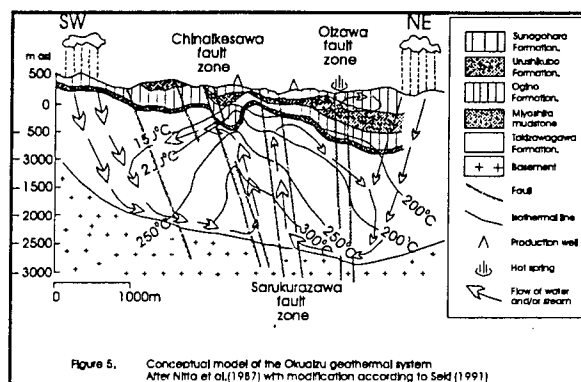


Figure 3a. Distribution of $m/z_{43}+m/z_{57}+m/z_{71}+m/z_{85}$ (C, paraffins) flux in the Okuaizu geothermal area.



were determined. Figures 6-a and 7-a show the locations of anomalies. Noda, Takahashi and Shigeno (1992) using a different statistical approach confirmed the result obtained by Higashihara and Fukuda (1992). A conceptual model of the geothermal resource has been proposed (Kubota, 1985; Sakai and Matsunaga, 1988;



Sakai, Kubota and Hatakeyama, 1986). Table 3 shows results of the Principle Components Analysis (PCA). It shows C_8 aromatics and the monoterpenes in factor 1. The presence of the alkanes are indicated infactor 2.

Faults and Fractures

Many geothermal fields are controlled by faults and fractures and the Fingerprint technique has been reported and useful in identifying them (Higashihara, M. Horita, A., Fukuda, M. and Nakashima, K. 1988;

Table 2.
Factor loadings and communality for fragment ions detected in soil gas in the Okuaizu geothermal area

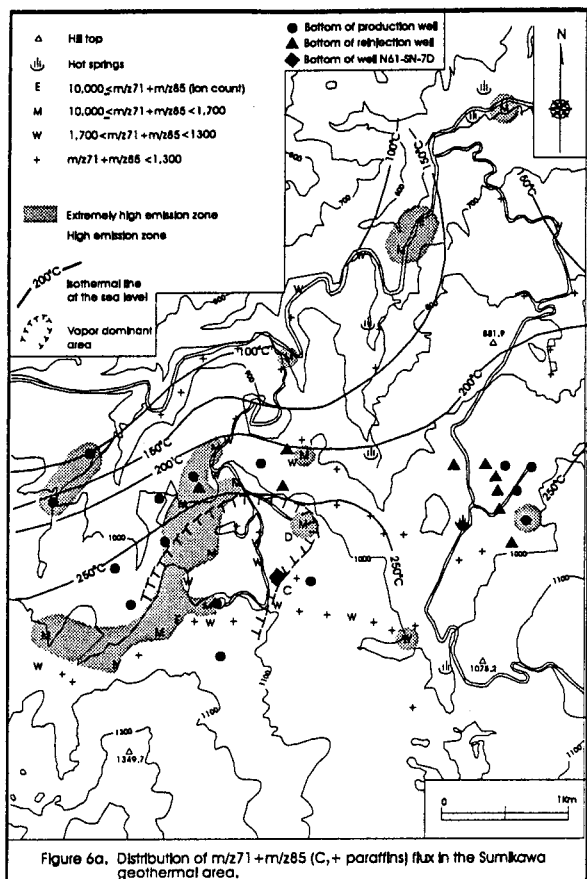
m/z	factor 1	factor 2	factor 3	factor 4	factor 5	factor 6	factor 7	factor 8	factor 9	factor 10	factor 11	factor 12	factor 13	communality
31	-0.2311	.10184	.02250	-.07832	.00232	.09529	-.03045	-.00372	-.03818	-.02432	[.74894]	.09909	-.16569	.62780
43	-.20368	[.82745]	.12607	-.00936	-.10977	.07055	-.06018	.04512	.03123	-.01255	.00631	.07481	.10615	.78287
55	-.18995	.19797	.07983	[.72424]	-.06352	-.11930	-.03856	.38629	.09066	-.13679	-.13062	-.02258	.00780	.81970
56	-.29692	[.73787]	.01117	.21811	-.06796	.05683	-.08651	-.01188	-.13407	.04146	.06510	-.09877	.03831	.73094
57	-.34556	[.76069]	-.10931	-.00622	-.14316	-.04968	-.06222	-.08286	.03031	.03735	.02909	.04000	.07533	.75418
68	[.69690]	-.15626	.18487	-.03681	-.12088	.12317	-.18831	.002237	-.07140	-.06195	.02052	-.11317	.01813	.63336
69	.05102	.13069	.11864	[.82873]	.06645	.08848	-.08607	.03839	-.03772	.16996	-.04863	-.09192	-.02917	.78366
70	-.29038	[.74888]	-.01886	.15505	-.14738	.04807	-.07950	.01078	-.03337	.02576	-.03285	-.03791	-.06468	.70848
71	-.30366	[.63545]	.16379	.13965	-.15671	.07830	-.06424	.26621	.03352	.03232	.19756	.01918	.00428	.68959
80	[.89405]	-.20457	.10728	-.03083	.02485	.03653	.01060	-.12332	-.02004	.11010	-.02285	.05351	-.00176	.88682
83	-.31224	.01380	.032154	[.69852]	-.08084	.16236	-.04684	.16732	-.01811	.02723	.13231	-.03164	-.06256	.77558
85	-.29059	[.55995]	.39777	.22707	-.10074	.11771	-.04251	.03814	.07742	.10145	.25277	-.07281	-.06586	.72486
91	-.22805	.17258	.26846	-.13367	-.17565	[.76750]	-.14241	-.03510	.00730	.02756	-.11258	.04979	-.08340	.83607
92	-.12220	.33841	.15051	-.17171	-.18813	-.44577	-.15806	-.11449	.15791	.08979	-.23642	-.15776	-.11999	.58196
93	[.63931]	-.10926	.11777	-.20630	.04730	.04386	.01355	.16315	-.05331	-.36396	.01330	-.20776	.00499	.68672
94	.07170	[.68601]	.290053	.06907	-.03719	.42623	.09607	-.25094	-.00664	.06032	.05241	.06096	.04464	.83232
95	.13587	-.46973	.35028	-.07715	.07631	.29134	.34274	.03867	-.03845	-.09210	.07612	-.11848	.02127	.60766
97	-.15993	.00839	[.87135]	-.14114	-.11389	.10732	-.05971	-.13074	-.03652	-.07232	-.05705	.05811	.04754	.86542
98	-.13957	-.02583	-.00523	.14585	-.03927	.05407	-.13617	[.72915]	-.00773	.18206	-.12398	.00606	-.15946	.67016
99	-.11134	.02680	[.91129]	-.12568	-.11067	.08910	-.02610	-.06353	-.03385	-.04853	-.04308	.03492	.01592	.89110
100	-.06976	.22700	.02439	.17611	-.10070	.01187	.05869	[.72925]	-.00916	-.05803	.14550	.06169	.15867	.68714
101	-.08511	-.14289	[.75640]	-.07723	-.06780	.08201	.01982	.16937	.00178	.01544	.12628	-.09937	-.05616	.67539
106	-.18377	-.19066	.08720	-.11625	-.01867	[.73893]	.02956	-.05903	-.09758	-.07488	.06237	.17207	-.03843	.69207
110	-.00153	-.03697	-.01214	-.07463	.02605	-.09653	-.04734	.04802	-.00383	.03936	.06099	[.80030]	.06110	.67113
115	[.71164]	-.15736	-.19706	-.04217	.24126	.04312	.16486	-.01005	.00203	-.09945	.02433	.04430	-.02650	.67231
120	.06248	-.16178	.291488	-.00700	[.82133]	.08609	-.03332	-.05194	.03425	.00239	.07839	-.02583	-.02749	.80964
121	[.76233]	-.24371	.05184	-.08933	.13000	.07064	.24428	.01936	.37877	.00207	-.02805	-.02143	-.01555	.87810
122	-.05952	-.07067	-.06290	-.40950	.15822	.13570	-.14308	.07875	-.14355	[.57855]	-.03065	-.26246	-.01865	.67580
133	.07180	-.21457	.04594	-.02417	[.89353]	.07870	.08994	-.05950	-.02211	.00397	-.04031	.03779	.01008	.87378
134	[.64741]	-.12823	-.02593	.03471	.34368	.02559	.24454	-.16438	-.01145	.17117	-.05638	.09574	-.02942	.68569
135	-.24320	[.63069]	.33346	.10768	.06110	.40820	.05870	-.23474	.039099	.06530	.11034	.05703	.01968	.82965
136	[.87111]	-.29837	.17508	-.11244	.00099	.11528	-.07141	-.06365	-.03059	-.05534	.00258	-.04126	.01353	.91974
137	[.64099]	-.24174	.07746	.08741	-.17565	.09688	-.07465	-.20892	-.04730	.23547	.02290	.14352	-.00544	.65125
143	-.08361	.05476	.10161	-.18081	-.06214	.38640	-.00679	-.000023	-.09691	-.11039	-.48064	.31936	-.44134	.75557
155	-.03990	-.09369	-.12317	-.15786	.03256	.03413	-.12054	-.06774	-.06565	-.65120]	-.00950	-.10663	-.01288	.51199
169	-.04094	.06872	.00919	.08055	-.02682	.14032	-.01684	-.00787	-.03074	-.01103	-.16399	.09656	[.81535]	.79581
175	.00601	-.18157	.05166	-.06844	-.03326	.06948	[.86859]	-.03643	-.01234	.05578	-.01723	-.03947	-.01103	.80731
204	.10976	-.18533	-.01011	-.06436	[.56140]	.06176	[.67962]	-.08540	-.02407	.02777	-.04000	-.00628	-.00849	.84187
238	-.01735	-.00614	.05089	-.06229	.00710	.02944	-.03682	-.01803	[.95551]	.01321	-.02010	-.00355	-.01350	.92317

[...] denotes factor loadings with absolute values greater than .5.

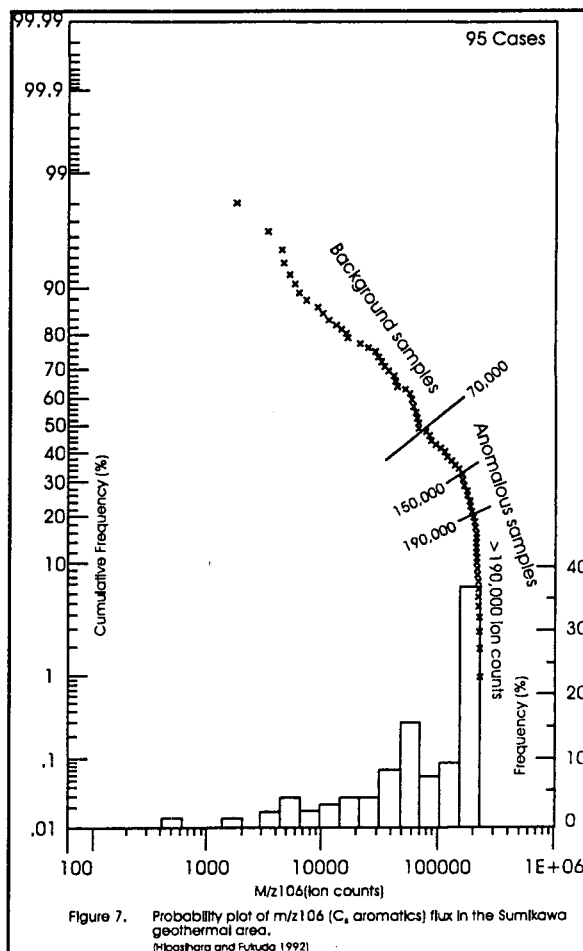
Table 3.
Factor loadings and communality for fragments ions detected in soil gas in the Sumukawa geothermal area

m/z	factor 1	factor 2	factor 3	factor 4	factor 5	factor 6	factor 7	factor 8	communality
41	-.04750	-.01748	[.94510]	.01924	-.02704	.02438	-.05384	-.07563	.90609
42	-.07558	.17464	[.96602]	-.04433	-.03867	.00922	-.03745	-.11227	.98697
43	.14159	[.64194]	.02447	-.00009	-.00353	-.23005	.18710	-.17555	.55149
54	.08832	.15662	-.01371	[.93991]	.01457	.12836	.00867	-.08072	.93923
55	-.06995	[.96661]	.04681	.15461	.01906	.09393	.01160	-.03595	.97594
56	-.12843	.36137	[.90452]	-.01562	-.03711	.08354	.06645	-.10500	.98927
57	-.10093	.20153	[.73328]	-.00701	-.04403	.36514	.41863	-.02859	.89988
58	.02250	-.08648	[.93296]	.04319	.01071	.02229	-.01160	-.02975	.88189
67	.49131	.25248	-.12157	[.77860]	.06110	-.14403	-.09865	-.04786	.96263
68	[.61337]	.35902	-.07177	[.60935]	-.00781	.14696	-.02695	-.03113	.90493
69	.21734	[.90130]	-.04872	.17037	-.01289	-.04728	-.10547	-.02045	.90493
70	-.10498	[.97152]	.05873	.01557	-.01043	.10069	.11264	-.04873	.98387
71	-.11185	.45927	.12436	.06604	-.01344	.31271	[.75274]	.06334	.91186
77	[.80802]	-.05689	-.13256	.13642	-.00397	-.00484	-.20613	.02491	.73547
78	-.17978	-.16011	[.89685]	-.09063	-.05450	.04105	-.00439	.05649	.87838
79	[.89759]	-.04133	-.11285	.14902	-.01155	-.09939	-.04454	.04190	.85607
80	[.92381]	-.04391	-.14251	.14371	-.06153	-.03505	-.11070	-.02649	.91429
81	.49224	.12320	-.04728	[.79265]	.04169	.11184	-.04842	-.00907	.90468
82	.20500	[.86831]	-.05247	.33211	.04405	-.02231	-.11196	-.02789	.92478
83	-.10203	[.97780]	.01401	.01777	-.00064	-.07203	-.03783	-.00218	.97364
84	-.13235	[.95284]	.07591	.02539	-.00153	.10150	.19585	.00340	.98050
85	-.15351	.22954	.11689	.07988	-.08612	.45465	[.72834]	.11140	.85331
91	[.87580]	-.21157	-.23635	-.10740	-.15785	-.05081	-.07214	.01190	.91203
92	[.72051]	-.08475	.08183	-.19085	-.01443	.13826	.12874	-.11090	.61764
93	[.92876]	-.02670	-.12818	.08669	-.03833	.01574	-.04214	-.11324	.90356
94	[.90359]	-.05163	.24187	.09677	-.03923	-.09954	-.12184	-.04885	.91568
95	.15131	-.01512	-.04812	-.00419	[.96817]	-.01483	-.01262	-.10487	.97418
96	.02023	.07827	-.05692	.27281	[.81896]	-.05968	.11716	.13538	.79051
104	[.76817]	-.14422	-.22234	-.10472	-.02813	-.09141	-.04682	.23079	.73590
105	-.41652	-.15645	-.21515	.00339	-.08039	-.08874	-.09350	[.74774]	.82647
106	[.09289]	-.11590	-.13817	-.12980	-.11364	-.00702	-.02711	-.25757	.94463
107	.08837	-.01775	-.09631	-.14682	.00999	.04282	-.11858	[.68717]	.52715
108	[.74994]	-.03067	-.23625	.31645	-.02245	-.15709	-.03129	-.08320	.75239
110	.10080	.05115	-.00326	[.94432]	.00793	.05851	.03955	-.07774	.91562
112	-.14128	[.96332]	.05960	-.01925	-.01925	.08216	.10561	-.01797	.97014
119	[.80659]	-.09347	-.08549	.02866	-.08110	-.03950	.27065	-.02405	.74942
120	-.04998	-.08331	-.09439	-.01803	.01451	-.12090	.14732	[.72746]	.84441
121	[.94097]	-.00928	-.12876	.10683	-.01706	.06150	-.05059	-.05454	.92310
122	[.74407]	.00478	-.07959	.01329	.26508	-.05895	-.09018	-.10118	.65228
124	-.05966	-.02338	-.01706	-.06301	[.97775]	.01513	-.03867	-.09056	.97428
125	-.08524	-.03525	-.02623	-.07572	[.97354]	.01025	-.03593	.05574	.96721
130	.04160	-.04207	.08730	-.10717	.07435	-.16759	[.79001]	-.11793	.69425
132	.03537	-.08051	[.87148]	-.11306	-.00966	.05465	.27486	-.20209	.89946
134	[.78002]	-.11442	-.09710	.00123	-.07244	-.11805	.31131	.02828	.74785
136	[.96340]	-.03146	-.14294	.09589	-.04831	-.04073	-.07228	-.06809	.97261
137	[.79049]	-.00692	-.15831	.09953	-.01423	.01125	-.18501	-.07154	.69957
164	-.03098	-.00303	.11747	.08445	-.02007	[.93438]	.02052	-.07234	.90102
166	-.07139	-.00665	.12875	.09640	-.00596	[.93998]	.10206	-.08873	.93290

[...] denotes factor loadings with absolute values greater than .5.



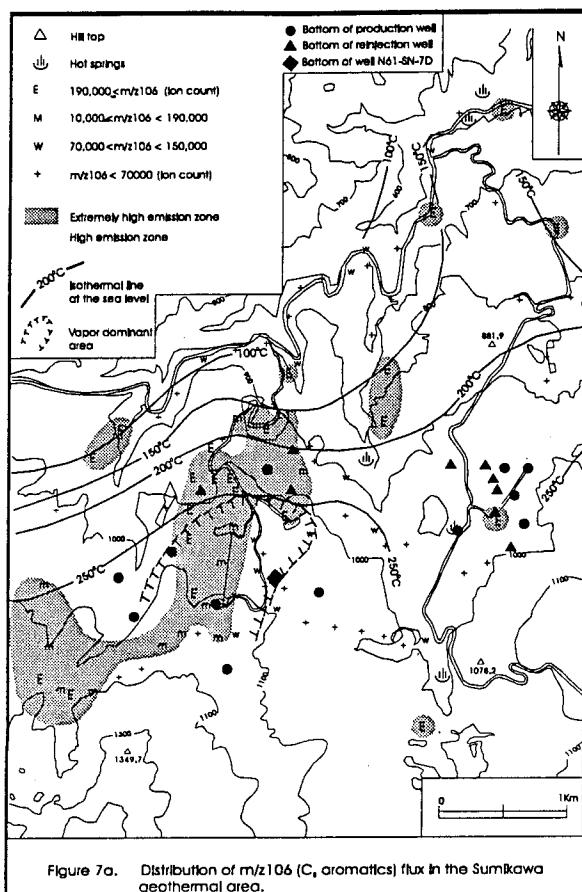
Shibata, K., *et al.* 1990). In the Onikobe Okunoin geothermal area the technique has been used and results reported by Suzuki, T., Abe, M. and Higashihara, M. (1989). Three large hydrothermally altered zones (Katayama, Okunoin and Arayu) were found in and near the area. Two faults were identified from previous shallow seismic reflection (Mini-Sosie) survey. The result of the Fingerprint survey showed clustering into 3 groups according to the strength of the hydrocarbon flux: high hydrocarbon emission, background and low emission clusters. The high emission clusters are anomalies characteristic of faults because of the characteristically high molecular weight compounds found. The low emission anomalies are anomalously low compared to background. The low emission clusters are thought to reflect faults and fractures that have been hydrothermally altered and sealed. It was observed that the low emission clusters are usually sandwiched between the high ones. It was therefore thought that the sealed faults area are flanked by permeable and highly hydrocarbon emitting faults. It is interesting to note that the technique seems not only able to suggest open and active faulted areas but also sealed faults, fractures and highly impermeable areas. The surface width of the hydrocarbon fingerprint



surface expression of faults is generally about 10-20 m. Close sample gridding is necessary in order to successfully detect (open or sealed) faults.

SUMMARY AND CONCLUSIONS

Hydrocarbon anomalies were detected in the soil gas over known geothermal areas. Repeated Petrex Fingerprint surveys have been done in Japan and the result were stable (Higashihara, private comm). The anomalies seem to be over producing geothermal wells and fields both in Japan and in Indonesia. Because geothermal production is usually located over the upflow portion of a convective geothermal system, it is proposed that the hydrocarbon anomalies at the surface are expressing the deep upflow. The hydrocarbons identified were aromatics, paraffins and monoterpenes. The paraffins show tighter anomalous zones than the more dispersed aromatics. It was observed that in some cases the dispersions tend to have direction and they tend to shift to lower elevation when compared to the paraffin anomaly. Assuming the sub-surface hydrology to be influenced by the present-day topography the



explanation of the shift could be the solubility of the aromatics. The solubility of aromatics are a few orders of magnitude greater than their corresponding (normal) paraffins. The cooling and outflowing waters and the shallower sub-surface waters could carry and disperse relatively more of the aromatics than the paraffins. Paraffins are also more volatile than their corresponding aromatic compounds. Paraffins tend to be buoyed up at a faster rate than the aromatics. Therefore the more diffuse aromatic anomaly resulted and the aromatic anomaly may indicate the outflow of the system or the groundwater flow.

Monoterpenes have been found not to be a consistent pathfinder for geothermal upflow systems. Only in the Sumikawa area have their anomalies been associated with the geothermal field. Monoterpenes in soil gas, however, increased in a significant way in areas of re-injection (Higashihara, private comm). The re-injected water may be acquiring and being charged with monoterpenes at the surface and re-injection causes them to find their way in the soil gas. Or, it may be that an increase in pressure after re-injection causes the increase. The question of the increase will be a future topic of a tracer study. Selected hydrocarbons may be

suitable for use as tracers and they may be useful in the study of the origins of the hydrocarbons and the mechanism of the geothermal closed cycle or discharge outflow systems.

It is suspected that the source of the hydrocarbons may be from surface waters carried downward into the convective geothermal system. Additional sedimentary-derived hydrocarbons may be added in the zones of increasing temperature. Thus a dynamic system of recharging inflow of water containing the hydrocarbons, upflow and outflow can be envisioned.

Des Marais *et al.* (1988) suggests kinetic reasons for the excess hydrocarbons in fluids of the Cerro Prieto geothermal reservoir. The excess has been calculated to be several orders of magnitude larger than at thermodynamic equilibrium. It is reasonable to assume that the reason could be the (kinetic) addition of the hydrocarbons into the Cerro Prieto pool of fluids (assumed to be between 227-427^o C) by the recharging or mixing of the incoming waters which have extracted hydrocarbons from the surrounding sedimentary rocks. Thus a dynamic system (not a system at equilibrium) is thought to explain the excess hydrocarbons.

The hydrocarbons over geothermal areas could be thought of as being brought about because of a system of inflow, upflow and outflow where above the hot upflow zones the hydrocarbons are being carried up by the ascending geothermal and magmatic fluids. Because of buoyancy they can express themselves as hydrocarbon anomalies in the soil gas if there is enough permeability in the overlying rocks. The technique has been proven to be able to detect permeable and active open fracture systems from those that are sealed.

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