Proceedings World Geothermal Congress 2005
Antalya, Turkey, 24-29 April 2005

Abiogenic Hydrocarbon's Emission in the Modern Rift Zone, Iceland

Alfred Geptner[1], Hrefna Kristmannsdottir[2], Yurii Pikovskii[3] and Bjarni Richter[4]

[1] Geological Institute, Russia [2] University of Akureyri, Iceland [3] Moscow State University, Russia, [4] Icelandic Geosurvey, Reykjavik

[1] remheptnet@mtu-net.ru [2] hk@unak.is 3 yurii.pikovskii@mtu-net.ru [4] br@isor.is

Keywords: hydrothermal alteration, hydrocarbons, Iceland

ABSTRACT

The results presented in this paper are based on the study of polycyclic aromatic hydrocarbons (PAHs) content and distribution in volcanic and sedimentary deposits. The rock and sedimentary samples were collected from different parts of the Miocene-Pliocene lava piles and from geothermal fields in the modern rift zone. Hot and cold groundwater was collected from springs and from well's discharge. In special constructions (traps) containing diatomite as an adsorbent there were collected hydrocarbons from fumarole steam and gas emission in geothermal fields. To identify and measure PAHs the fluorescence spectra of hydrocarbon solutions in n-hexane were compared with those of standard solution SRM 1491 (mixture of 23 PAH) at nitrogen boiling temperature (77K). Data giving an evidence of hydrocarbon emission were obtained for some active geothermal regions of Iceland. Several types of natural polycyclic aromatic hydrocarbon associations have been determined.

1. INTRODUCTION

The study of volcanic and sedimentary deposits and hydrothermal minerals selected from various geological structures revealed that they contain dispersed bituminous materials with polycyclic aromatic hydrocarbons (PAH) (Geptner et al., 1999a, b, 2002). Polycyclic aromatic hydrocarbons are important constituents of carbonaceous substances and may be used as geochemical markers of natural or technogenic processes of carbon accumulations in the Earth's crust. There are two main sources of natural PAHs in geologic environments: (1) transformation of fossilised organic matter (biogenic source) and (2) synthesis from carbon monoxide and hydrogen or conversion of simple organic compounds (methane, ethane, benzene and others) to PAHs in the Earth's crust and mantle (abiogenic source). The Earth's crust is a great reactor for synthesis of PAHs and it is a main source of natural PAHs in the environment. Natural PAHs occur in volcanic products, igneous and sedimentary rocks, hydrothermal deposits, and oil and ore accumulations. The composition of PAHs depends on the geological situation. The PAHs occur widely in the products of volcanic eruptions (lava, tephra). It has been found that in the high temperature formations (lava and, hyaloclastite, tephra) structures of naphthalene and phenanthrene predominate as well as biphenyl and fluorene. In low temperature formations (hydrothermally altered volcanic and sedimentary deposits) an increase in amount of more condensed molecules (pyrene, benzo(a)pyrene, benzo(ghi)perylene, perylene and others) occur.

Recent studies of PAHs show that natural unsubstituted structures (benzo(a)pyrene, benzo(ghi)perylene, coronene and other) are more often detected on large active fault zones as well as in modern rift zones than in other regions. Results of hydrocarbon studies of geothermal fields in Iceland’s modern rift zone suggest that hydrothermal emissions all over the country contain hydrocarbons, including PAH and high-molecular hydrocarbons. Based on the accumulated data, several types of natural PAH associations have been determined. These associations are considered as typical for modern hydrothermal activity in the rift zone of Iceland (Geptner, Pikovskii, 2003).

The interpretation of the data suggests that studies of the PAH geochemistry may be an important instrument to identify patterns of hydrocarbon distribution in zones of volcanic and hydrothermal activity both for academic and practical purposes and can be used to identify the characteristics of hydrothermal activity in the Earth´s crust and for the exploration of oil and gas.

2. SAMPLING AND ANALYSIS

Samples have been collected during the years 1996-2003. The samples are characteristic for different parts of the Miocene-Pliocene lava piles in Iceland and for geothermal fields in the modern rift zone: in north (Öxarfjörður), in the south-west (Reykjanes, Svartsengi and Hveragerði, Nesjavellir). Several groups of samples were collected: unaltered lava and tephra of recent eruption, modern and ancient marine and lagoon deposits, soil samples, hydrothermally altered clayey deposits and water samples. Water samples were collected from hot and cold springs. Hot water samples were taken from well's discharge and one sample was obtained from a boiling mud pool in the Reykjanes geothermal field.

Soil profiles are considered as natural absorbents for trapping of hydrocarbon emission during long periods of tens to hundreds of years. 138 soil profiles were described and sampled in the course of the field studies, 55 of them were located within the Öxarfjörður region, 30 within Krafla-Myvatn region, and the other 53 were from the Reykjanes-Svartsengi and Hveragerði geothermal fields. An experiment to collect hydrocarbon emissions was performed in 2001, 2002 and 2003 by installing traps with diatomite absorbent for 15-30 days in the north and south-western parts of the modern rift zone in the present day geothermal fields of Reykjanes, Nesjavellir, Krisuvik and Öxarfjörður.

All the samples were analysed by method Shpol’sky spectroscopy (Alekseeva, T.A. and Teplitskaya, T.A., 1981, Rovonskii, F.Ya. et al., 1988, Geochemistry of polycyclic…, 1996). To identify and measure PAH the fluorescence spectra of hydrocarbon solutions in n-hexane were compared with those of standard solution SRM 1491 (mixture of 23 PAH) at nitrogen boiling temperature (77K). This method is capable of identifying very small amounts of PAH and to study their quantitative relationship in rocks of different genesis.

3 UNALTERED MODERN VOLCANIC ROCKS

The polycyclic aromatic hydrocarbons were detected in similar quantities (35-62 ppb) in all the investigated samples of lava, hyaloclastite and tephra (Krafla, Askja, Surtsey and Hekla volcanoes). Homologues of biphenyl and fluorene – hydrocarbons, whose synthesis occurs mainly at high temperature (above 500°C) – are the predominant compounds in the PAH composition. The rest of the hydrocarbons are represented by homologues of naphthalene, phenanthrene or benzofluorene. Unsubstituted are represented by pyrene (Geptner et al., 1999a). The character of distribution in unaltered rocks allows us to suggest that these hydrocarbons are syngenetic to volcanic rocks and are synthesised directly during their cooling. Different conditions of crystallization of the volcanic rocks (lava, hyaloclastite, and tephra) are not reflected by the amount of PAH formed during the eruption. A later slight contamination by PAH from the surrounding rocks is possible for tephra due to its high porosity (e.g. Hekla tephra of 1104, Table 1).

Table 1: PAH content in unaltered modern volcanic rocks

Substituted and unsubstituted PAHs	Krafla	Askja		Surtsey		Hekla
	Date of eruption					
	1977	1875	1961	1963		1104
	1	2	3	4	5	6
Total, ppb	**37**	**50**	**52**	**36**	**35**	**408**
Distribution (%) homologues of						
biphenyl and fluorene	62	52	67	50	51	46
naphthalene	35	42	25	31	29	27
phenanthrene	3	4	2	9	-	20
benzofluorene	-	2	6	10	20	4
unsubstituted						
pyrene	-	-	-	-	-	3

Note: 1 – basalt, glass crust on the lava flow, 2 – acid tephra, pumice fragment, 3 – basalt, surface crust on the lava flow, 4 – basalt, glass crust on the lava flow, 5 – basaltic hyaloclastite, 6 – acid tephra; (-) not detected

4. HYDROTHERMALLY ALTERED VOLCANIC ROCKS

Samples of hydrothermally altered basalt and secondary minerals were collected from different locations in the Miocene-Pliocene lava piles in Iceland. The composition and distribution of secondary minerals suggest that some components of secondary minerals (e.g. K in celadonite) found in fissure and dyke swarms were transported with groundwater from the acid subvolcanic intrusions (Geptner and Petrova, 1996). The composition of secondary minerals (smectites, celadonite, zeolites, siliceous minerals) indicates that the rocks investigated in the course of this work were washed by groundwater heated to temperatures less than 150°C (Kristmannsdottir, 1982). Small accumulations (fine drop-like segregation) of the bituminous substance were found in altered rocks in close association with low temperature hydrothermal minerals in Berufjörður and Eyjafjörður locations (Geptner et al.,1999a). Some species of PAH were identified in a sample of asphalitie found in the Miocene lava pile in South-eastern Iceland at the same association of hydrothermal minerals. In the last case it was concluded that the bituminous substance was formed due to a close contact and heating of lignite by a sill intrusion (Jakobsson and Fridleifsson, 1990). The total PAH content in the hydrothermal mineral assemblages is 1-2 orders of magnitude higher than that of unaltered rocks. The different mineral assemblages differ in hydrocarbons composition and content. The highest content (672-2543 ppb) was encountered in a smectite-celadonite mineral assemblage associated with siliceous minerals and zeolites. The basaltic rocks with amygdales filled by secondary minerals are characterised by an approximately similar content of biphenyl-fluorene and naphthalene homologues (47 and 41%, respectively), other hydrocarbons compounds are as follows: phenanthrene 7%, and benzofluorene homologues 3%, and unsubstituted pyrene 2%. Secondary minerals precipitated in gas cavities contain ten times more PAH, which are highly dominated by naphthalene homologues (69%). Biphenyl and fluorene (16%) and phenanthrene (11%) homologues represent another substituted species. Pyrene accounts for 1% of the total amount. The PAH content in nontronite-zeolite mineral assemblages ranges from 233 to 822 ppb. The hydrocarbons composition in such assemblages differs from the one described above. Only half of the samples contain biphenyl and fluorene homologues (19-46%). Some samples contain a considerable amount of chrysene homologues (9-38%). Among the secondary minerals, siderite is characterised by the highest content of PAH (2326 ppb) mainly represented by naphthalene homologues (83%). One can suggest that the sum and composition of hydrocarbons in different secondary mineral assemblages reflect the conditions of mineral formation, paleotemperature of the groundwater, the intensity of circulation, and time of secondary mineral formation.

5. MODERN AND ANCIENT SEDIMENTARY DEPOSITS

The content of PAH in modern and ancient sedimentary deposits was studied in marine, lagoon and lake deposits in areas in the north (Tjörnes, Skjálfandi, Öxarfjörður), west (Snaefellsnes) and southern (Svinafell) parts of Iceland. An association of smectite-zeolite secondary minerals characterises the Pliocene-Pleistocene sedimentary deposits in all the studied regions. Zeolites are represented mainly by chabazite that points to a rather low temperature during the hydrothermal alteration (Kristmannsdottir, 1982). In modern marine fine-grained sandstone and aleurolite in the Skjálfandi bay secondary minerals consist of smectite only. In lagoon sand collected at surface in a geothermal field of Öxarfjörður there were only found amorphous silica and Fe-hydroxides in present-day hydrothermal mineral precipitates. Hydrocarbons in the analysed deposits show a wide range in both content and composition. In the northern part of the rift zone total PAH values from 9 to 2635 ppb were measured in the surface lagoon sediments of the Öxarfjörður geothermal field. At the same geothermal field total PAH values of the Pleistocene marine deposits (well 4, 10 cores analysed from 333 to 437 m depth) range from 39 to 309 ppb. Pliocene and Pleistocene marine deposits sampled out of the rift zone showed a rather low content of PAH (Table 2, 3).

Table 2: PAH in marine Pliocene deposits

Substituted and unsubstituted PAHs	Locality, Tjörnes beds					
	Lab. sample numbers					
	7256	7228	7235	7249	7250 R=0,45*	7260 R=0,23
Total, ppb	**10.2**	**36,7**	**45,1**	**134**	**54,4**	**128,8**
Distribution (%) homologues of						
naphthalene	58,8	57,2	64,3	76,8	40,5	61,3
benzofluorene	19,6	35,4	22,2	16,4	34,9	33,4
unsubstituted						
pyrene	21,6	7,4	-	3,4	7,9	5,3
benzo(ghi)perylene	-	-	13,5	3,4	16,7	-

Note: 7256 – Fine grained sandstone, 7228 – Sandstone and alerolite with carbonificated plant detritus, 7235 – Piece of carbonificated wood, partly replaced by calcite, 7249 –

Board coal, 7250 – Lignite, 7260 – Lignite; (*) index of refraction.

Values of total PAH obtained in the modern Skjálfandi marine sediments scatter from 9 to 200 ppb (Table 4).
Comparison shows that hydrothermally altered marine deposits at the Tjörnes, Breiðavik, and Búlandshöfði (Snaefellsnes) localities, with exception of the ones containing carbonificated plant remnants show only those species of PAH that were fixed in unaltered lava, tephra and hyaloclastite. In hydrothermally altered deposits carbonised plant remains worked as a geochemical barrier for concentration of secondary minerals and PAH species.

Table 3: PAH in marine Pliocene and Pleistocene fine-grained sandstone

Substituted and unsubstituted PAHs	Localities			
	Breiðavik beds		Snaefellsnes, Búlandshöfði	
	Lab. sample numbers			
	7271	72180	72219	72224
Total, ppb	**18.1**	**11.6**	**66.2**	**81.6**
Distribution (%) homologues of				
biphenyl and fluorene	-	-	15,1	-
naphthalene	93,9	94,8	55,9	71,1
phenanthrene	-	-	19,6	20,8
benzofluorene	-	-	6,1	6,1
unsubstituted				
pyrene	6,1	5,2	3,3	2,0

Table 4: PAH in modern marine sediments of Skjálfandi (selected samples).

Substituted and unsubstituted PAHs	Site A	Site B		Site C
	Core 2	Core 3	Core 4	Core 5
Total, ppb	**58**	**9**	**123**	**200**
Distribution (%) homologues of				
naphthalene	21	56	19	-
benzofluorene	33	33	17	-
chrysene	34	-	7	-
pyrene	-	-	15	-
unsubstituted				
pyrene	12	-	15	-
picene	-	-	24	-
benzo(a)pyrene	-	-	1	-
benzo(ghi)perylene	-	6	-	-
perylene	-	5	2	100

A higher content and a more varied composition of PAHs have been fixed on the flank rift zone in Kirkjubaerklaustur and Svinafell sedimentary beds (Table 5).

Naphthalene dominates everywhere in the substituted homologues. Homologues of biphenyl and fluorene, phenanthrene and benzofluorene are common in Kirkjubaejarklaustur and Svinafell sedimentary beds and in the marine Búlandshöfði deposits. Substituted homologues of pyrene and chrysene (the last one only in Svinafell) were revealed in the Kirkjubaejarklaustur and Svinafell sedimentary beds. Unsubstituted PAH is only represented by pyrene.

Composition of PAH in Skjálfandi marine deposits differs considerably from what is discussed above. Substituted homologues are represented by naphthalene (19-56%), benzofluorene (17-33%), chrysene (7-34%), and pyrene (15%). Among the unsubstituted PAH there were found pyrene (12-50), picene (24%), benzo(a)pyrene (1%), benzo(ghi)perylene (6%), and perylene (2-100%).

Table 5: PAH in marine and lake Pliocene-Pleistocene deposits

Substituted and unsubstituted PAHs	1	2	3		4	
	Lab. sample numbers					
	7358/1	7350	7380	7385	7395	7399a
Total, ppb	**120.2**	**646.5**	**668.2**	**330**	**59**	**72.8**
Distribution (%) homologues of						
biphenyl and fluorene	-	21,7	12,7	13,7	-	23,4
naphthalene	84.8	64,0	59,4	59,8	62,7	60,4
phenanthrene	-	6,5	17,4	14,9	25,4	8,2
benzofluorene	7,5	5,1	7,7	6,6	11,9	5,5
chrysene	-	-	-	2,0	-	-
pyrene	-	0,6	0,4	1,5	-	-
unsubstituted						
pyrene	7,7	2,1	2,4	1,5	-	2,5

Note: Kirkjubaejarklaustur sedimentary beds: 1 – Marine deposits with coccolith, Foss locality; 2 – Lake deposits with flora, Núpsstaðúr locality; The Svinafell sedimentary beds: 3 – Lower part of the section with flora remnants, 4 – Upper part of the sedimentary section.

Subsurface marine (Late Pleistocene-Holocene, well 4) (Ólafsson et al., 1993) and modern surface lagoon deposits in the Öxarfjörđur geothermal area have appreciable differences in hydrocarbons composition. At the first locality they are mainly represented by naphthalene (98-99%) and in unsubstituted only pyrene (1-2%) was found. At Skógalón locality in hot sediments at the lagoon bottom and beach there were detected among the substituted naphthalene (2-73%), benzofluorene (45-97%), pyrene (5%), and chrysene (1-14%). Of the unsubstituted PAH pyrene (15%), perylene (2-8%), benzo(a)pyrene (3%), benzo(ghi)perylene (3-22%) and coronene (57%) were detected. In surface sediments in Skógar the following substituted PAH species were revealed: naphthalene (6%), benzofluorene (7%), pyrene (7%), and chrysene (16%), and the list of unsubstituted consists of pyrene (7%), perylene (1%), benzo(ghi)perylene (18%), and coronene (37%).

Summarising the data for sediments of different genesis and intensity of hydrothermal alteration one can state a high diversity in concentration and composition of polycyclic aromatic hydrocarbons. No correlation was detected between the genesis of deposits, hydrothermal mineral assemblages and hydrocarbons composition. One may assume that the variation in hydrocarbons composition reflects differences in activity and succession of the hydrothermal events.

6. SOILS

The PAH composition was analysed in soils from several localities in the north and south-west parts of the modern rift zone. In Öxarfjörđur soil sections were studied and sampled in the Skógalón and Skógar geothermal fields and in some warm places of the Vestursandur (Thórseyri, Kilfarvegur), in deep open fissures (gjá) on the Holocene lava field (Kelduhverfi), and at the west border of the rift zone (Auđbjargarstađabrekkur). The total content of PAH in this region ranges from 1 to 309 ppb with the highest value revealed for soils sampled in Skógar geothermal area (309 ppb) and in fault zone on the north slope of Ástjörn locality (241 ppb). Most of the soil samples in Skógalón geothermal area have a very low PAH total content, from 1 to 8 ppb. Values in 17-33 ppb were fixed here in a few samples only. These data show that the content of soil hydrocarbons does not appear to correlate with present-day surface temperature in geothermal fields. A great variation of hydrocarbons species was discovered in soil sections filling up a big open fault (gjá) and in a fault zone which both are outside of the modern geothermal fields.

The correlation of PAH composition with geological structures in the Crust has been disclosed by sampling in a profile through the Skógalón geothermal field. On the cold flanks of the field naphthalene homologues (63-91%) and pyrene (38-100%) dominate. In warm and hot zones unsubstituted PAH are more common: pyrene (26-100%), benzo(a)pyrene (2%), perylene (50-100%), benzo(ghi)perylene (14-23%), coronene (37%), and value of substituted PAH is observed to decrease (Figure 1).

A clear correlation of hydrocarbons composition with rift faulting is disclosed in Reykjanes by studying soil samples collected along a profile extending from the volcano Skálafell to Kisilhóll fumarole field across several active faults. The appearance and domination of pyrene homologue (65-93%) and benzo(ghi)perylene (7-16%) in the soil profile coincide with the zone of faulting on the surface of the Holocene lava field (Figure 2).

7. GROUNDWATER

Samples of groundwater for the study of hydrocarbons were collected from the discharge of geothermal wells in the northern (Öxarfjörđur, Skógalón and Skógar geothermal fields) and southern (Svartsengi, Reykjanes) parts of the modern rift zone. In Skógalón water samples have been collected frequently during a week. Water samples for the analysis of PAH composition from the west flank of the rift zone were collected in the Aðaldalur region at the Husavikurhöfði, Hafralaekur, and Laugar localities. Water samples were also obtained from hot springs and mud pools in Myvatn and Reykjanes regions, providing additional data on PAH participating in hydrothermal activity.

There has been demonstrated a great difference in PAH composition in groundwater sampled within different tectonic structures. Groundwater in the northern part of the modern rift zone (Skógalón and Skógar localities) has 10-20 times higher total content as compared with those from the Pliocene basalt piles of the flank rift zone (Husavikurhöfði, Hafralaekur, and Laugar localities) (Table 6, 7).

Table 6: PAH in groundwater and surface sediments in Öxarfjörđur

Substituted and unsubstituted PAHs	1	2	3	4	5
Total, ppb	**262**	**235**	**505**	**9**	**98**
Distribution (%) homologues of					
naphthalene	5	6	4	-	6
phenanthrene	16	23	21	-	-
benzofluorene	19	24	22	-	7
chrysene	13	13	12	-	16
pyrene	2	5	3	-	7
unsubstituted					
pyrene	18	17	26	15	7
benzo(k)fluoranthne	1	2	1	-	-
benzo(a)pyrene	1	1	1	3,5	-
benzo(ghi)perylene	5	2	2	22	18
coronene	9	5	4	57,5	38
perylene	6	1	-	2	1
tetraphene	4	2	2	-	-

Water: 1. Skógar well, 102°C; 2. Skógalón well-1, 97°C; 3. Skógalón well-4; 4 5. Skógalón, bottom sediments: 4 - sampling in 2002, 77°C, 5 - sampling in 2003

The PAH composition of bottom sediments in the Skógalón geothermal area differs strongly from values found in discharge from wells. These sediments contain coronene and benzo(ghi)perylene as the main species and are characterised by the absence of phenanthrene homologues.

Table 7: PAH in groundwater in the Pliocene basalt lava piles

Substituted and unsubstituted PAHs	1	2	3	4
	T 52°C	T 74°C	T 64°C	
Total, ppb	**13**	**7**	**26**	**3**
Distribution (%) homologues of				
naphthalene	15	77	77	-
phenanthrene	8	15	4	33
unsubstituted				
pyrene	53	8	19	67

Note: 1. Husavikurhöfði, 2. Hafralaekur, 3, 4 Laugar.

Similar relation in PAH composition between water and sediments was found in spring water from the Myvatn area and precipitates from lake Myvatn. The PAH composition (maximum values are shown) of warm spring water (Helgavogur) is characterised by homologues of naphthalene (40%), phenanthrene (7%) and unsubstituted pyrene (53%). In bottom sediments there are found apart from naphthalene (29%) benzofluorene (30%) and chrysene (16%) homologues. Unsubstituted PAHs are here represented by pyrene (40%), picene (4%) and benzo(ghi)perylene (56%). In clay minerals from a mud pool in the Námafjall solfataric area there was found, apart from naphthalene (39%) unsubstituted benzo(ghi)perylene (19%) and coronene (34%) as the main components.

In the southern part of the rift zone much lower concentrations of PAH have been identified in groundwater (Table 8) than in the northern part. In water samples from a deep well (Svartsengi) and of water obtained from mud pool (Reykjanes) unsubstituted pyrene dominates. In silica precipitate from deep groundwater (Svartsengi) and in clay minerals from a mud pool (Reykjanes) coronene and benzo(ghi)perylene are dominant species. In geyserite precipitated by thermal waters form a deep well in the Eldvorp location naphthalene homologues (57%) and coronene (31%) are dominant species. It is worth to mention that coronene (58-47%) and benzo(ghi)perylene (22-23%) association was also revealed in sediments from warm lake in Nesjavellir where thermal waters from deep wells of the power station are discharged.

Table 8: PAH in Svartsengi geothermal field

Substituted and unsubstituted PAHs	1	2*	3	4	5
	80°C				
Total, ppb	**45**	**407,9**	**49,1**	**58**	**51**
Distribution (%) homologues of					
naphthalene	11	0.8	-	9	-
benzofluorene	18	0.7	-	-	-
pyrene	-	-	-	24	-
unsubstituted					
pyrene	58	0.3	2.7	67	8
benzo(ghi)perylene	13	3.3	5.7	-	53
coronene	-	92,2	91.6	-	39

Note: Svartsengi: 1 - effluent water from wells utilized by the Power Plant, sampling in 2003; 2, 3 - silica precipitates: 2 - sampling in 2001, 3 - sampling in 2002. * - 2.5% of PAH of not determined composition; Reykjanes: 4 - water from a mud pool in Kisilhóll solfataric area, 5 - clay minerals from the mud pool.

Summarising the considered data there is found a significant difference in PAH composition between groundwater samples collected in the north and south-west regions of the modern rift zone. Phenanthrene homologues are typical for deep hot groundwater and warm springs in the modern rift zone and in the Pliocene basalt pile of the north Iceland. These species were not detected in water in south and south-west regions. Phenanthrene (19-30%) was discovered in cores from deep-seated hydrothermally altered hyaloclastite in Reykjanes (wells Rn -6 and Rn-8) (Table 9). Coronene was only discovered in groundwater in the Öxarfjörður geothermal field. At the same time coronene is a constant and more essential part of PAH in sediments and mineral precipitates formed by deep hot water and solfataric mud pools in the north and south parts of the rift zone.

Table 9: PAH in hydrothermally altered hyaloclastite, Reykjanes

Substituted and unsubstituted PAHs	Well and Lab. numbers		
	Rn-8 77327	Rn-6 81316	Rn-6 81317
Total, ppb	**426.4**	**1130**	**4888**
Distribution (%) homologues of			
biphenyl and fluorene	12,2	-	11,5
naphthalene	63,1	45,8	39,5
phenanthrene	19,9	27	30,8
benzofluorene	3,5	16,5	10,4
pyrene	-	3,5	0,9
unsubstituted			
pyrene	1,3	7,2	6,9

8. TRAPS WITH DIATOMITE ABSORBER

In special constructions containing diatomite (called traps) as an adsorbent there were collected hydrocarbons from fumarole steam and gas emission in geothermal fields. In 2001 traps were installed in the Nesjavellir, Krisuvik and Reykjanes fumarole fields. In 2002 and 2003 hydrocarbons were collected by such traps from the gas emissions in the Skógalón and Skógar geothermal fields (Öxarfjörður).

A sample of the standard diatomite contained no bituminous substances nor PAH. Its concentration of aggregate organic carbon there was below 0.07% of the sample weight. After a month-long exposure in 2002 in Skógalón, carbon concentration in the diatomite from the trap grew to 1.5 % by weight. At the end of the experiment small amounts of PAHs were detected in the diatomite of all traps.

The highest total concentration (128,2 and 434,4 ppb) was discovered in two traps, which were installed in the Reykjanes field for 15 days. During the same period of time PAH values of 54 and 72,6 ppb were found in the Nesjavellir and Krisuvik fields. The trap in Skógalón was left exposed for 30 days in 2002 and for 15 days in 2003. The total amount of PAH at this locality was 31 ppb in 2002 and 26 ppb in 2003. The diatomite yielded 134 ppb PAH in Skógar in a trap exposed there for 15 days in 2003.

The PAH composition consists mainly of naphthalene homologues (35-98%) and pyrene (2-27%). A more varied PAH composition was detected in a trap exposed during 30 days above a gas upflow zone in the Skógalón locality. Here substituted PAH consist of homologues of naphthalene (35%) and benzofluorene (26%) and unsubstituted compounds include picene (26%), perylene (7%) and benzo(ghi)perylene(6%).

Those data on PAH composition have produced a convincing evidence for the existence of modern natural gas emissions of hydrocarbons, including PAH, that rise to the surface up from the deep levels of the Earth crust. One may assume that at a certain depth there is a big fluidal source containing high-molecular hydrocarbons. Hydrocarbons are brought up to the surface together with the waters from the boreholes or natural springs, and with gas emission.

9. CONCLUSION

The study of the distribution of polycyclic aromatic hydrocarbons in geothermal fields strongly indicates a close association with the dynamics of the modern hydrothermal environment. Hydrocarbons, coming up to the surface together with the hot fluids and gas from the heated foci in the earth crust are mostly emitted to the atmosphere. A certain part of this hydrocarbon flow as coming closer to the ground surface at lower temperatures seems to accumulate in the altered rocks together with secondary minerals. There are good reasons to assume that it is due to the long-term hydrothermal effect that secondary mineral assemblages may become substantially enriched in hydrocarbons. Such an environment could thus produce and accumulate isolated occurrences of bitumen substances.

The total PAH content and composition differ significantly between various geothermal fields and samples collected at the same locality. Sediments of different mineral composition and intensity of hydrothermal alteration have a high diversity in content and composition of PAH. No correlation was detected between the genesis of deposits, hydrothermal mineral assemblages and PAH composition. One can suggest that the total PAH concentration as well as the composition in different secondary mineral assemblages would be expected to reflect the conditions of mineral formation – paleotemperature of groundwater, masflow circulation intensity, and the succession of the hydrothermal events.

There has been discovered a great difference in PAH composition in groundwater sampled from different tectonic structures. It is very important to note that at the same location (e.g. Helgavogur in Myvatn and Kisilhóll fumarole field in Reykjanes) PAH composition in water and minerals or sediment precipitates differs significantly. It suggests a great fluctuation of PAH compounds in groundwater and a fluctuating accumulation of PAH within secondary minerals or fine grained sediments. A long-term study of hydrocarbon accumulation from steam and hot effluent water is needed to explain the nature of irregular trapping of hydrocarbons in secondary mineral assemblages and hydrothermally altered rocks.

The correlation of PAH composition with geological and geothermal structures has been demonstrated by the study of soils. In Skógalón the PAH composition in soils from cold flanks of the geothermal field differs significantly from those revealed in warm and hot zones of the field (Figure 1). A clear correlation of PAH composition with rift faulting is disclosed in Reykjanes by studying soil samples collected along a profile extending from volcano Skálafell to Kisilhóll fumarole field across some active faults (Figure 2). These data as well as the accumulation of PAH from gas upflow jets by traps demonstrate the main pathways of hydrocarbon transportation from the deep levels of the Earth crust.

ACKNOWLEDGEMENTS

Fieldwork was supported by the NATO science grants provided by Icelandic Research Council in 1996, 1997 and 2001-2003. We are grateful to rector, Dr. Thorsteinn Gunnarsson, and the staff of the University of Akureyri for support in making field work successful. The National Energy Authority (Orkustofnun) of Iceland is thanked for accommodation facilities for a field team provided in Öxarfjörður and Myvatn regions in 2002-2003. We wish to thank T.A. Alekseeva and N.I. Khlynina for assistance with analytical work performed in Research Laboratory of Biosphere Carbonaceous Substances of the Lomonosov Moscow University, Faculty of Geography.

REFERENCES

Alekseeva, T.A., and Teplitskaya, T.A.: Spectrofluorometric Methods of Analysis of Aromatic Hydrocarbons in Natural and Technogenic Media, Leningrad, *Gidrometemoizdat,* (1981) 215p. (in Russian).

Gennadiyev, A.N., and Pikovsky, Yu.I. (eds.): Geochemistry of polycyclic aromatic hydrocarbons in rocks and soils, Moscow: Moscow University publ., (1996) 192p. (in Russian).

Geptner, A.R., Alekseeva, T.A., Pikovskii, Yu.I.: Polycyclic Aromatic Hydrocarbons in the Unaltered and Hydrothermally Altered Volcanics of Iceland, *Doklady Earth Sciences*, **369A**(9), (1999a). 1352-1355. (English copy of the Journal)

Geptner, A.R., Alekseeva, T.A., Pikovskii Yu.I.: Polycyclic Aromatic Hydrocarbons in Volcanic Rocks and Hydrothermal Minerals from Iceland, *Lithology and Mineral Resources*, **34**(6), (1999b) 567-578. (English copy of the Journal)

Geptner, A.P., Alekseeva, T.A., and Pikovskii, Yu. I.: Polycyclic Aromatic Hydrocarbons in Holocene Sediments and Tephra of Iceland, *Lithology and Mineral Resources*,. **37**(2), (2002), 172-191. (English copy of the Journal)

Geptner AR, and Pikovskii YuI (2003) Hydrocarbons in fresh and hydrothermally altered rocks in Iceland, their genesis and distribution patterns. Results of laboratory research in 2001-2002, Reykjavik, RANNIS, (Icelandic Research Council), 24 p

Geptner, A.R., and Petrova, V.V.: Siliceous Minerals in Basalts of Iceland: Composition and Formation Conditions. *Lithology and Mineral Resources*, **31**(1), (1996) 28-37. (English copy of the Journal)

Jakobsson, S.P., and Fridleifsson, G.O.: Asphaltic Petroleum in Amygdules in Skyndidalur. Lon. SE Iceland, *Natturufraedingurinn,* **59**(4), (1990) 169-188.

Kristmannsdottir, H.: Alteration in the IRDP Drill Hole Compared With Other Drill Holes in Iceland, *Journal of Geophysical Research,* **87**(B8), (1982) 6525-6531.

Ólafsson, M., Fridleifsson, G.O., Eiríksson, J., Sigvaldason H., and Ármannsson, H.: On the Origin of Organic Gas in Öxarfjörður, NE-Iceland, Orkustofnun, OS-93015/JHD-05, Reykjavik, (1993).

Rovonskii, F.Ya., Teplitskaya, T.A and Alekseeva, T.A.: The Background Monitoring of Polycyclic Aromatic Hydrocarbons. Leningrad, *Gidrometeoizdat,* (1988) 224p. (in Russian).

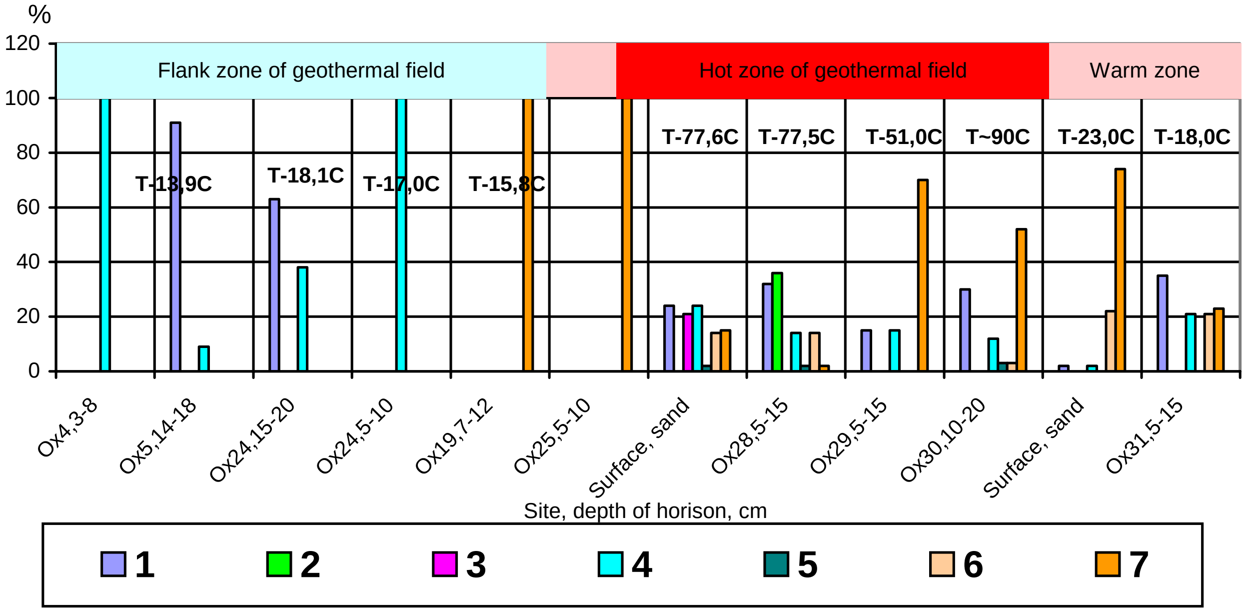

Figure 1: PAH in soil profile through Öxarfjörður geothermal field, Skógalón

Substituted PAH, homologues of: 1 - naphthalene, 2 - chrysene, 3 - benzofluorene; unsubstituted, 4- pyrene, 5 - benzo(a)pyrene, 6 - benzo(ghi)perylene, 7 - perylene

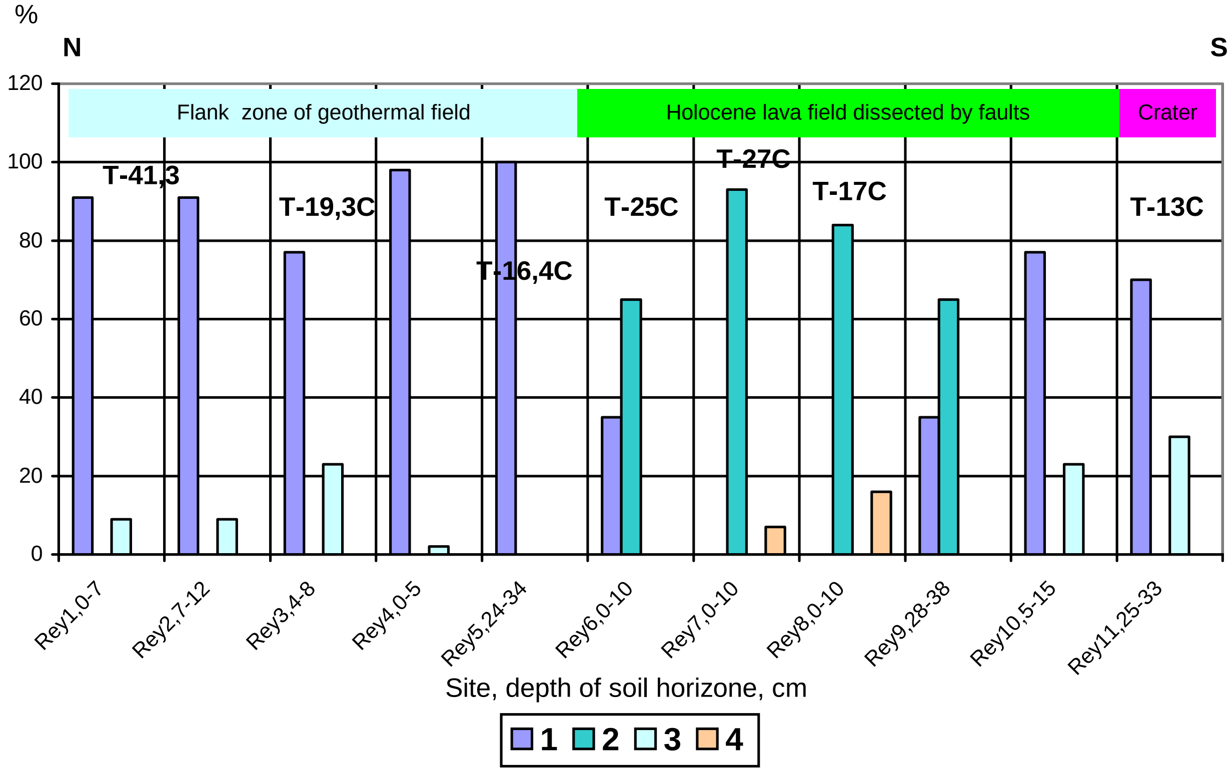

Figure 2: PAH in soil samples collected in a line from crater of volcano Skálafell to solfatara field Kisilhóll, Reykjanes

Substituted PAH, homologues of: 1 - naphthalene, 2 - pyrene, unsubstituted, 3 - pyrene, 4 - benzo(ghi)perylene