EVALUATION OF COAL AND WATER SAMPLES FROM MANİSA-SOMA-DENİŞ REGION CONCERNING BALKAN ENDEMIC NEPHROPATHY AND DETERMINATION OF BALKAN ENDEMIC NEPHROPATHY RISK

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ABSTRACT

EVALUATION OF COAL AND WATER SAMPLES FROM MANİSA-SOMA-DENİŞ REGION CONCERNING BALKAN ENDEMIC NEPHROPATHY AND DETERMINATION OF BALKAN ENDEMIC NEPHROPATHY RISK

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The water and coal samples from the Manisa-Soma-Deniş region were studied on the basis of their basic characteristics, inorganic and organic parameters. Coal samples were determined as low-quality lignite. They have high concentrations of arsenic, uranium and lead. The organics in the coal samples are of aliphatic hydrocarbons and their derivatives (alkanes and alcohols), methyls, phthalates, naphtalenes and benzenes. They are inactive and low in concentrations. Water samples have basic characteristics within the range of drinking waters. They also have high arsenic and uranium concentrations indicating a possible leaching. Their organic compounds are similar to those in the coal samples. However, these organic compounds are not as toxic as those found in endemic samples and their concentration is also very low. Therefore, they are considered not to be a potential for Balkan Endemic Nephropathy (BEN)-disease. On the basis of the findings of this study, the area can be concluded as non-endemic region.

Keywords: Lignites, Balkan Endemic Nephropathy, Organic compounds, Manisa-Soma-Deniş

ÖZ

MANİSA-SOMA-DENİŞ BÖLGESİNDEKİ KÖMÜR VE SULARIN BALKAN ENDEMİK NEFROPATİYLE İLİŞKİLENDİRİLMESİ VE BU BÖLGEDEKİ BALKAN ENDEMİK NEFROPATİ RİSKİNİN BELİRLENMESİ

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Manisa-Soma-Deniş bölgesinden alınan kömür ve su örnekleri genel karakterleri, inorganik ve organik özellikleri açısından incelendi. Kömür örnekleri düşük kaliteli linyit olarak belirlendi. Yüksek oranda arsenik, uranyum ve kurşun elementi saptandı. Organik bileşenler genel olarak alifatik hidrokarbonlar ve bunların türevleri (alkanlar ve alkoller), metiller, fatalatlar, naftalinler, ve benzenlerdir. Bunlar az miktarda ve inaktif olarak gözlemlenmiştir. Su örnekleri ise genel olarak içme suyu standartlarına uymaktadır. Yüksek arsenik ve uranyum içermeleri kömür ve su arasında muhtemel bir etkileşim göstermektedir. Organik bileşenleri de kömür örneklerindekilerle çok benzerdir. Fakat, bu organik bileşenler toksik olmamakla birlikte çok az miktarlarda tesbit edilmiştir. Dolayısıyla, bunların Balkan Endemik Nefropati (BEN)'ye neden olacağı düşünülmemektedir. Elde edilen bulgular ışığında, çalışma bölgesi endemik olmayan bölge olarak kabul edilmiştir.

Anahtar Kelimeler: Linyit, Balkan Endemik Nefropati, Organik Bileşenler, Manisa-Soma-Deniş

to my mother,

as her first son

to my supervisor,

as her first Medical Geology student

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CHAPTER 1

INTRODUCTION

1.1 Purpose and Scope

Coal deposits are consumed as an important source of energy and the demand for coal worldwide is rapidly increasing because of increasing costs due to decreasing reserves of other energy sources such as oil (Finkelman, 2000; Orem and Tatu, 2001). The coal use worldwide has increased by 1.5 billion tones (36%) for the last 30 years (Energy Information Administration, EIA, 1999). However, as a conflicting issue with its importance and wide use, studies indicate that several environmental diseases would be directly or indirectly linked to the coal deposits (Finkelman, 2000, Orem and Tatu, 2001). One of the diseases, thought to be linked to coal deposits (Feder et al., 1991) is Balkan Endemic Nephropathy (BEN) (Orem and Tatu, 2001). The study of BEN is important to understand both the environmental affects of coal deposits, and the relation between geology and medicine, and their integration into a new discipline named as "Medical Geology" (Orem and Tatu, 2001).

BEN has first been diagnosed in Bulgaria (Tanchev et al., 1956, revised in 1991) as a slowly-progressive and fatal kidney disease resulting kidney shut-down (Feder et al., 2002; Orem and Tatu, 2001; Orem et al., 1999; Orem et al., 2004; Voice et al., 2003). Further studies shown that the villages affected by BEN (referred to as endemic villages) are not limited to Bulgaria but also occur in the other countries on the margins of Balkan Peninsula: former Yugoslavia, Bosnia, Croatia, Serbia and Romania (Figure 1-1; Orem et al., 1999; Radovanovic, 1991; Ceovic et al., 1992; Hall, 1992; Dimitrov, 2001; Orem et al., 2002). The total number of people affected by BEN is unknown, but only in former Yugoslavia; 15.000-25.000 individuals are estimated to have been affected (Orem et al., 1999; Danilovic, 1979; Orem and Tatu, 2001; Orem et al., 2002).

Figure 1-1. The countries in Balkan Peninsula with BEN (grey-colored areas) and the endemic villages dominated at the tributaries of Danube River (pink-colored areas) (Orem and Tatu, 2001).

The studies in early 1990's indicated a close correspondence between the location of BEN-affected areas and the occurrence of weathered and low-rank coal deposits (Orem et al., 1999; Feder et al., 1991; Orem and Tatu, 2001). Further research indicated that toxic organic compounds were abundant in both the coal deposits and the waters taken from shallow-wells in the endemic areas. On the basis of the research of Feder et al. (1991) and Finkelman et al. (1991), "Pliocene Lignite Hypothesis" has been developed (Orem and Tatu, 2001). According to this hypothesis, when coal is leached by groundwater, a high amount of toxic organic compounds is released into water and transported into shallow-wells in the endemic villages. Even when these toxic organic compounds are as low as in ppm levels, the continuous use of well-water over many years causes progressive kidney damage resulting BEN (Orem et al., 1999; Feder et al., 1991; Finkelman et al., 1991; Orem and Tatu, 2001).

The geographic distribution of the disease, however, has not changed significantly since 1950's and remained restricted (Tatu et al., 2001; Orem et al., 2002; Feder et al., 2002). The reason why BEN remained restricted to the Balkan Peninsula can be explained by geochemical composition of coal deposits, and the local hydrogeological environments. The low-rank Pliocene lignites are also common in other countries of Balkan Peninsula, such as Hungary and Slovenia, and also in Greece, Albania and Turkey, where no BEN cases is diagnosed so far (Feder et al.,2002). The lignites from Greece and Turkey show great similarities with those from endemic areas, but there is no BEN cases reported due to the lack of any epidemiological studies on BEN (Orem et al., 1999). Therefore, such studies in these areas are strongly advised and encouraged.

The purpose of this study is to determine the basic characteristics, inorganic and organic parameters of the coal and water samples from the Manisa-Soma-Deniş region and to evaluate these results concerning BEN. Basic characteristics of coal and water samples will be studied to understand the general view of the samples and to obtain if any linear trend between basic characteristics and the organic parameters exist. If any linear trend occurs, this will help us to establish a link between these parameters. Inorganic parameters will be used to understand if any toxic elements are observed through the coal and water samples and also there is any link between inorganic and organic parameters. Organic parameters will be used to understand the general characteristics of the coal and water samples, the type and concentrations of organic compounds. These organic compounds found in the samples will be correlated with those found in endemic and non-endemic locations in Balkan Peninsula to understand which one they resemble the most. The results will be finally compared to the medical findings of Prof. Dr. Rezzan Topaloğlu, Medical Faculty at Hacettepe University (personal communication with Prof. Dr. Rezzan Topaloğlu).

1.2 Geographic Setting

The study area is located in Manisa-Soma-Deniş (Figure 1-2) and comprises the area involved in the J19-D2 quadrangle of 1:25000 scale topographic map of Turkey within the coordinates of 39°11′24′′ N - 39°12′36′′ N latitudes and of 27°41′00′′ E - 27°45′00′′ E longitudes. The nearest town to the study area is Manisa-Soma. Manisa-Soma is at the northern side of Western Anatolia.

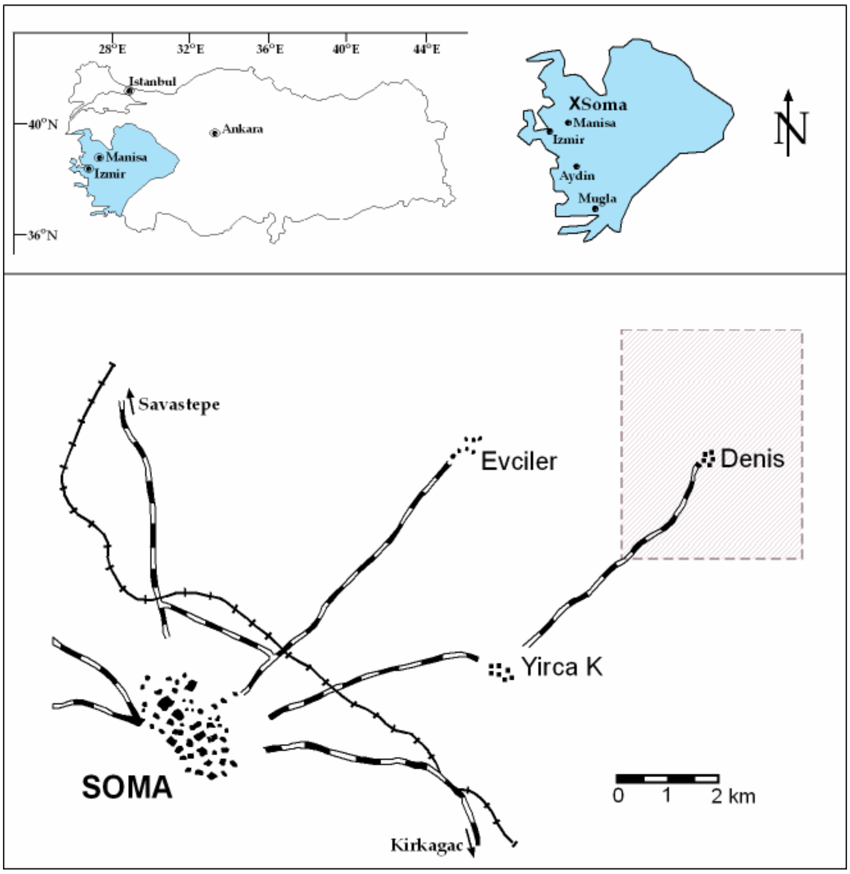

Figure 1-2. Location map showing the study area (Manisa-Soma-Deniş).

The accessibility to Soma region is supplied with Akhisar-Bergama highway and the Ankara-İzmir railway. A stabilized road between Soma and Deniş can be used to access the study area.

The altitude of town is 160 m above the sea level in average. The important topographically elevated areas to be mentioned are Yanar Hill (607 m), Akkaya Hill (596 m), Tepecik Hill (534 m), Türkmen Hill (533 m) (Figure 1-3).

The major river in the region is Bakırçay. The E-W flowing river has many small tributaries on both its northern and southern sides. These tributaries carry important supply of water into Bakırçay. The tributaries of Bakırçay in the study area are Bahçe River, Bozkaya River, Tabak River, Söğütlü River, Taşlı River and Soğucak River (Figure 1-3).

The climate represents the typical condition of central Aegean region. Summer is sunny, hot and dry, and winter is warm and rainy. Spring and fall are the major rainy seasons. Annual rainfall is about 662 mm. Rainfall is especially high on December and April, whereas extremely low on May and November. In winter, snow can only be observed on hillsides. The temperature ranges between +25°C and +35°C during the summer whereas it falls to -3°C to +10°C in winter. The plants, on the other hand, represent the basic characteristics of Mediterranean climate. Pine trees cover the hillsides, whereas through valleys, farming areas, gardens and flattenings are observed. People live on farming, mining and animal growth.

1.3 Methods of Study

The study mainly contains two stages as field and laboratory studies.

1.3.1 Field Study

Because the leaching of organic compounds from coal deposits into water is much more abundant in rainy seasons, the field study has been carried out during the wet season (March, 2005). During the field study, six Pliocene and four Miocene lignite samples from mines and outcrops and four water samples from various sources (springs and water tanks) were sampled, and their in-situ properties for water samples (pH, temperature, TDS, conductivity) were determined.

Fresh lignite samples were collected from mines or outcrops avoiding the effects of alteration. They were put into plastic bags and double-sealed. The collection sites are listed in table 1-2 and figure 1-3. Coal samples were sampled considering their distance to the sampled springs and their contacts with water.

Four water sites were sampled. The collection sites are listed in table 1-1 and shown in figure 1-3. All water samples were collected and stored in pre-cleaned bottles for both organic and inorganic properties. Waters were sampled considering if they are consumed for drinking purpose.

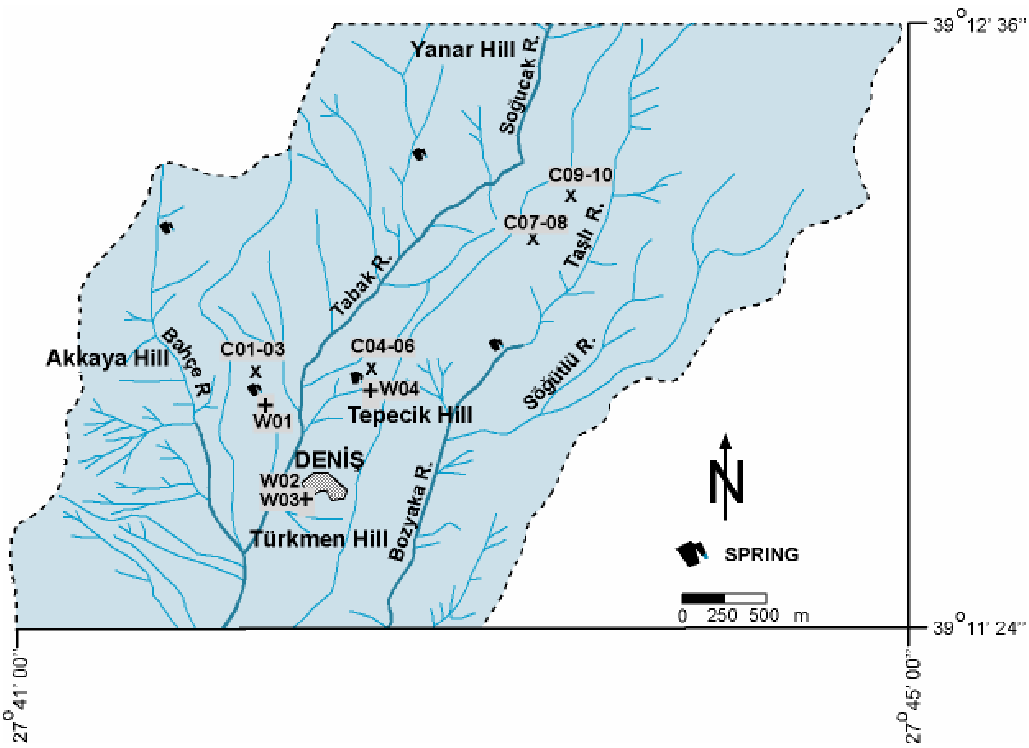

Figure 1-3. Drainage system, distribution of springs, and sampling sites for water and coal samples from the Manisa-Soma-Deniş region (x for coal samples and + for water samples).

Table 1-1. Sampling sites for water samples, collected during the field study

ID	Name	Latitude Longitude	Elevation (m)	Collection date	Use of water
W01	Deniş	27° 42′ 08″ 39° 11′ 51″	420	03/12/2005	Spring used as public water
W02	Deniş	27° 42′ 15″ 39° 11′ 41″	392	03/12/2005	Water tank at a private household
W03	Deniş	27° 42′ 18″ 39° 11′ 43″	393	03/12/2005	Water tank at a private household
W04	Deniş	27° 42′ 35″ 39° 11′ 53″	432	03/12/2005	Spring used as public water

Table 1-2. Sampling sites for coal samples, collected during the field study.

ID	Name	Latitude Longitude	Elevation (m)	Collection Date
C01	Deniş	27° 42′ 05′′ 39° 11′ 54′′	424	03/12/2005
C02	Deniş	27° 42′ 06′′ 39° 11′ 56′′	427	03/12/2005
C03	Deniş	27° 42′ 08′′ 39° 11′ 53′′	428	03/12/2005
C04	Deniş	27° 42′ 34′′ 39° 11′ 59′′	433	03/12/2005
C05	Deniş	27° 42′ 36′′ 39° 12′ 01′′	431	03/12/2005
C06	Deniş	27° 42′ 39′′ 39° 12′ 02′′	435	03/12/2005
C07	Deniş	27° 43′ 19′′ 39° 12′ 12′′	454	03/12/2005
C08	Deniş	27° 43′ 23′′ 39° 12′ 14′′	456	03/12/2005
C09	Deniş	27° 43′ 29′′ 39° 12′ 16′′	459	03/12/2005
C10	Deniş	27° 43′ 31′′ 39° 12′ 15′′	457	03/12/2005

1.3.2 Laboratory Studies

The general characteristics of the coal samples, including ultimate and proximate properties were determined. All coal samples were ground to 60-mesh for chemical analysis. Inorganic properties of coal samples were analyzed by a commercial laboratory (ACME Labs, Canada), using inductively-coupled plasma-mass spectrometry (ICP-MS). The results of ICP-MS analysis will be mentioned in the relevant section of "Results".

For water samples, inorganic properties (metals) were analyzed by a commercial laboratory (ACME Labs, Canada) by using inductively coupled plasma-mass spectrometry (ICP-MS). The results of ICP-MS for water samples will be mentioned in the relevant section of "Results".

Methanol extracts were prepared to determine the organic properties of coal. Organic properties of coal samples, methanol extracts and water samples were determined by Gas Chromatography/Mass Spectrometry (GC/MS) in the Clinical Laboratory No.1, Timisoara, Romania. The results of GC/MS analysis will be mentioned in the relevant section of "Results".

1.4 Previous Studies

The only study in Turkey related to BEN is Yerlikaya et al. (1998). At this study, coal samples were studied in İstanbul but no BEN-indicating compounds were measured at those samples. Due to lack of any previous studies in Turkey directly corresponding to the purpose of study, the previous studies about Soma-Deniş area will be limited to those about lignite deposits. Additionally, previous studies in Balkan Peninsula about Balkan Endemic Nephropathy and relation to low-quality Pliocene lignite deposits will be mentioned.

1.4.1 Previous Studies about Lignite Deposits in Denis

The first observations in the area are the unpublished field notes of Philipson (1910) and Chaput (1936). These notes included basic geological studies of the area.

Gencer (1932) and Gratacap (1943) studied the coal deposits in Soma region, and they focused in the geological, economical, and industrial evolution of coal deposits in this region. They mentioned that the coal deposits could be used economically when considered on the basis of their economical and industrial value. These studies were effective on the improvement of mining operations in that region. The mining company has increased the working capacity and the area of mining regarding these studies.

Kleinsorge (1939, 1940, and 1941) studied geology of the Soma region and surrounding areas. He divided the region into two main facies in these studies as (1) the north region facies and (2) the south region facies. According to this classification, the north region facies were formed of lacustrine sedimentary deposits, pyroclastic rocks and the lower coal seam of Soma region. The south region facies, on the other hand, were composed of tuff and volcanogenic material.

Kleinsorge (1941) mentioned a folding process during Neogene that also affected the coal deposits.

Arni (1942) indicated the three coal layers as one single coal layer with a thickness more than 100 m.

Brinkmann et al. (1970) separated the coal seam into three distinct seams but they also determined the age of all of three seams as Miocene.

Nebert (1978) studied both Miocene and Pliocene deposits of the area, and named the formations as Soma Formation for Miocene deposits and Deniş Formation for Pliocene deposits and determined their basic characteristics. He also separated three coal seams from each other, and as different than Brinkmann et al. (1970) claimed that the first two coal seams were formed in the Miocene whereas the latest one during the early Pliocene. The deposits of Soma Formation was determined to be Early to Middle Miocene by the studies of Kleinsorge (1941) from the plant fossils, collected from the area.

Gemici et al. (1991) studied macro and micro flora of the Soma region. He determined the taxonomy of the flora and distinguished 72 different flora species in this region. They used this flora to find out the age of the three coal seams. According to this flora, the age of lower and middle seam was Miocene and the age of the latest (upper) seam was Pliocene.

1.4.2 Previous Studies on BEN

BEN has been first diagnosed by nosological studies of Tanchev el al (1956) in Bulgaria. Orem et al. (1999) described the disease as a slowly-progressive and fatal kidney disease resulting kidney shut-down.

The first official observation of BEN was made by Danilovic et al. (1957). This study included the regions comprising former Yugoslavia. This observation was followed by similar descriptions from Bulgaria and Romania by studies of Radovanovic et al., 2000; Ceovic et al., 1992; and Craciun and Rosculescu, 1970.

The distribution of BEN is geographically confined and restricted to the rural regions of Balkan Peninsula at the tributaries of Danube River, covering the regions of central and southeastern Serbia, southwestern Romania, northwestern Bulgaria, southeastern Croatia, and parts of Bosnia and Kosovo.

Plestina (1992) and Theisen (1995) noticed that the villages afflicted by BEN in the past continue to be afflicted, whereas non-endemic villages (sometimes even located a few km remained free of disease.

Studies of Tanchev et al. (1956, 1965) in Bulgaria, Danilovic et al. (1957) in Yugoslavia, Fortza and Negoescu (1961) clarified and clearly delineated the endemic regions.

However, despite these significant findings, the etiology of BEN remained unclarified. Many factors for BEN have been proposed including bacteria and viruses, heavy metals, radioactive compounds, trace element imbalances in the soil, chromosomal aberrations, mycotoxins (ochratoxin A), plant toxins (aristolochic acid), and industrial pollution. Radovanovic et al. (2000) suggested live biological agents (bacteria and viruses) as the possible causative factor of BEN, however, his studies and conclusions excluded such probability. On the other hand, Orem et al. (2002) studied the nitrate content of waters in endemic and non-endemic villages, and he noticed that the nitrate concentrations in the endemic villages are rather higher than those in non-endemic villages. Therefore, he concluded that nitrate should definitely be considered as a possible co-factor for BEN.

Besides, several studies involved establishment of links between BEN and other diseases. Ceovic et al. (1992) first concluded that BEN is strongly associated with UUT (upper urinary tract) cancer. He stated that the factor of BEN is not only nephrotoxic but also carcinogenic. The study determined that the UUT cancer ratios in the endemic villages were extremely high with respect to those of non-endemic villages, and the BEN patients have UUT with much higher ratios. Another study by Susa (1976) indicated such links also exist between BEN and familial kidney atrophy.

Recent studies of Feder et al. (1991), Tatu et al. (1998), and Orem et al. (1999) including field and laboratory investigations, indicated an environmental etiology for the disease, with a prime role played by geological background of the endemic settlements. These studies also suggested the involvement of toxic organic compounds present in the drinking water of endemic areas.

Further studies of Feder et al. (1991), Goldberg et al. (1994), and Finkelman et al. (1991) established a hypothesis based on the leaching of these toxic organic compounds by groundwater from low rank Pliocene lignite deposits topographically linked to endemic villages, and the transportation of water into shallow wells or springs in these endemic villages - the so-called Pliocene Lignite Hypothesis.

Orem et al. (1999) studied coal samples, collected from endemic areas in Yugoslavia, and they carried ^{13}C-NMR (^{13}C- Nuclear Magnetic Resonance) analysis for solid samples. As a result of ^{13}C-NMR analysis, they observed major peaks at the potentially toxic organic compounds, suggesting a link between an environmental factor and BEN. They stated that the high concentrations of such aromatic compounds are related with the low-rank of lignites whose organic functionality is very high. They carried out water extraction analysis and they also noticed that the potentially toxic organic compounds were released into water in high concentrations.

Tatu et al. (2000) studied natural bioavailability of coals by conducting laboratory water extraction analysis of different coals. At the end of these demonstrations, Tatu et al. (2000) concluded that the difference of GC/MS plots for different coal samples could be due to distinctive paleogeographic coal-forming conditions during the last period of the Tertiary in the corresponding endemic and non-endemic areas.

Feder et al. (2002) conducted a field trip to endemic and non-endemic areas of Romania, and they collected Pliocene lignite samples from mines and/or outcrops and water samples from a variety of sites. They obtained high concentrations of organic compounds in the lignite and water samples of endemic regions. They concluded the study in such a way to explain why the disease is geographically restricted. According to their conclusion: (1) The chemistry of the lignites is a significant factor for development of BEN, (2) The occurrence of BEN can be influenced by several factors including (a) proximity to formations containing toxic organic compounds, differences in concentrations of toxic compounds in sediments, (b) differences in flux of groundwater through the sediments, and (c) difference in dilution of toxic compounds due to rainfall and permeability of the soils, especially in the vicinity of water wells.

Orem et al. (2002) collected and analyzed water and coal samples from endemic and non-endemic areas, and they stated that the inorganic properties have no relevance with the BEN distribution, but the organic properties of water and coal samples can be a major factor determining the distribution of endemic and non-endemic areas. Organic analysis of coal samples indicated that aliphatic and aromatic compounds were high in concentrations, and nitrate concentrations were also much higher in endemic villages with respect to non-endemic villages. Orem et al. (2002) lastly pointed out several points, that (1) the medical geography of BEN is not clearly determined yet, (2) discovering the factor of BEN would be a better understanding for other kinds of kidney diseases, (3) the emergence of UUT in endemic regions has been attributed to the agent of BEN itself, and (4) discovering the factor of BEN will definitely lead to the improvement of treatment methods, and prevent generation of new BEN patients.

Tatu and Orem (2003) studied the inorganic properties of water samples and organic properties of both water and coal samples collected from endemic and non-endemic areas of Romania. No significant findings related with inorganic properties could be observed at the end of this study. However, the results for organic properties of water and coal samples collected indicated that different types of aliphatic and aromatic were observed in much higher abundances for the samples collected from endemic sites when compared to those collected from non-endemic sites. Tatu and Orem (2003) concluded that the results are consistent with the Pliocene lignite hypothesis of BEN etiology.

Orem et al. (2004) studied and analyzed water samples to identify the organic compounds in water supplies in endemic and non-endemic regions of Romania and to determine their environmental significance. Water samples were collected from various endemic and non-endemic locations in different seasons (wet and dry seasons) and analyzed with respect to their organic compound contents by GC/MS. The study showed that the dissolved organic content shows seasonal variations, being higher in rainy seasons such as spring when compared with those in dry seasons such as summer. The study also concluded that the organic compounds in endemic areas were much higher and more abundant than those in non-endemic areas. The aliphatic hydrocarbons (linear and cyclic) and their functional derivatives were abundant in the water samples taken from endemic areas and they are ubiquitous in ground water. Another conclusion by the study of Orem (2004) is that the very low concentration of these toxic organic compounds can be a reason for the long incubation period (usually 20-30 years) needed for the kidney failure to develop.

Tatu et al. (2000) and Orem et al. (2002) also mentioned that most of the organic compounds are unidentified or only tentatively identified and BEN-causing factor could be among these compounds.

Dimitrov (2001) was concerned with the incidence of the disease and he concluded that the incidence of BEN is decreasing throughout the years based on his research of medical reports on BEN patients. This may be due to variety of reasons such as prevention of well-water usage, or distillation of water, or even the immigration of people in endemic villages to non-endemic villages. However, studies about BEN are still important to understand the exact etiology of disease, and try to find out more scientific solutions to the problem.

CHAPTER 2

GEOLOGY OF MANISA-SOMA-DENIS

2.1 Stratigraphy

The units from older to younger in the study area can be summarized as the Kırkağaç Formation of Mesozoic age, the Soma Formation of Miocene age and the Deniş Formation of Pliocene age. These units are overlain by colluvium and alluvium of Quaternary age (Figures 2-1 and 2-2; Akyürek and Soysal, 1981; Nebert, 1978; İnci et al., 2003). Two main coal seams are observed in the study area, one Miocene lignite seam inside the Soma Formation and one Pliocene lignite seam inside the Deniş formation (Nebert, 1978).

The first description and naming of Kırkağaç formation (Tm) is contained in the geological studies of Akyürek and Soysal (1978). The main rock type observed through Kırkağaç formation is recrystallized limestone (Nebert, 1978). Dolomite particles through the limestone blocks can be observed. Limestone blocks are generally thick, but not well-layered, and have a grey-reddish color (Akyürek and Soysal, 1978). The fossil content of limestone is high. According to paleontological data acquired from the Kırkağaç Formation, the age was determined as Mesozoic (Akyürek and Soysal, 1978).

Tertiary units include two main formations: the Soma Formation, considered to be Miocene, and the Deniş Formation, considered to be Pliocene. These two formations have been first described and distinguished by Nebert (1976).

The only unit belonging to the Soma formation, observed in the study area is the middle lignite seam (KM3). The lignite seam KM3 overlies limestone blocks. It has been considered to be of economical value. It was first described by Nebert (1976) as the middle lignite seam. Its calorific value and quality is not as high as the lower lignite seam, and its color is dark-brown to black and the hardness is also lower than that of lower lignite seam (Nebert, 1978).

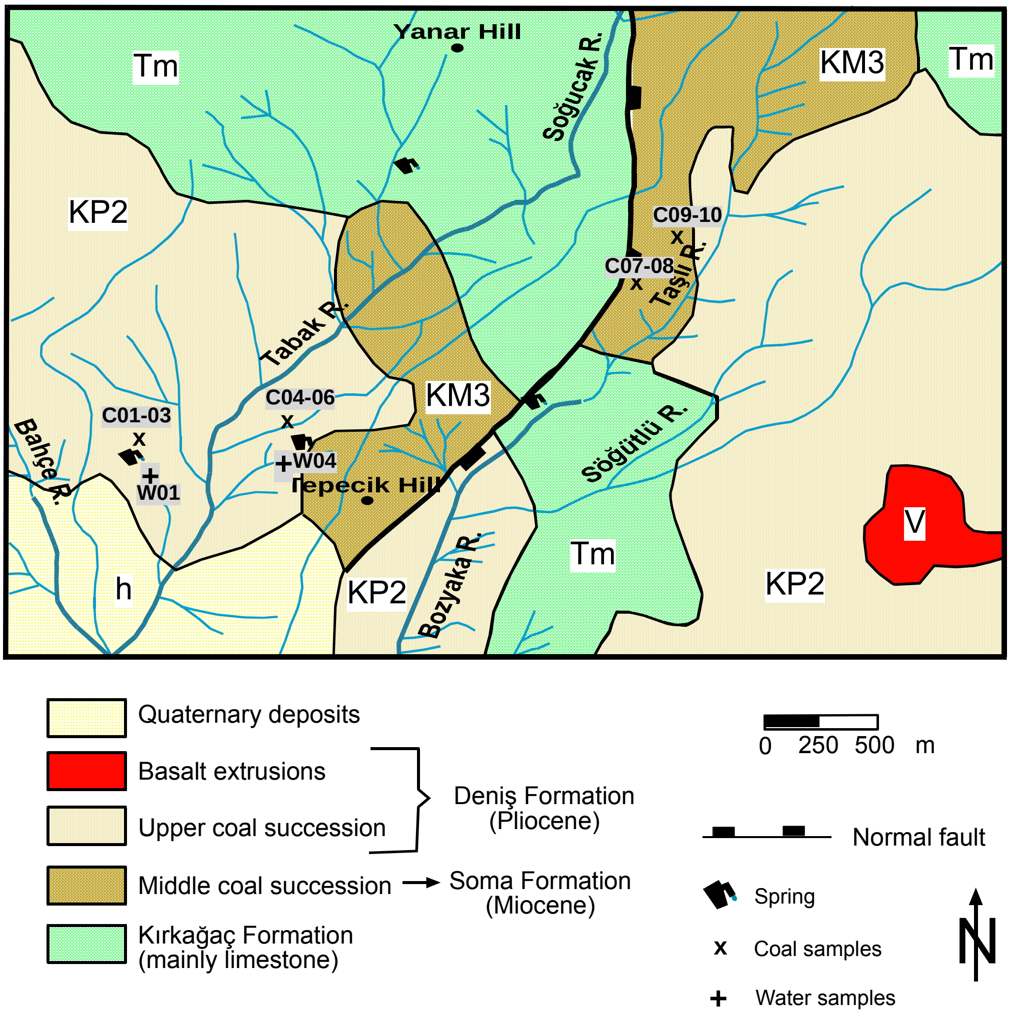

Figure 2-1. Geological map of study area showing Deniş and Soma Formations and coal seams with drainage system, distribution of springs, and sampling sites for water and coal samples from the Manisa-Soma-Deniş region (x for coal samples and + for water samples) (modified from İnci, 1995).

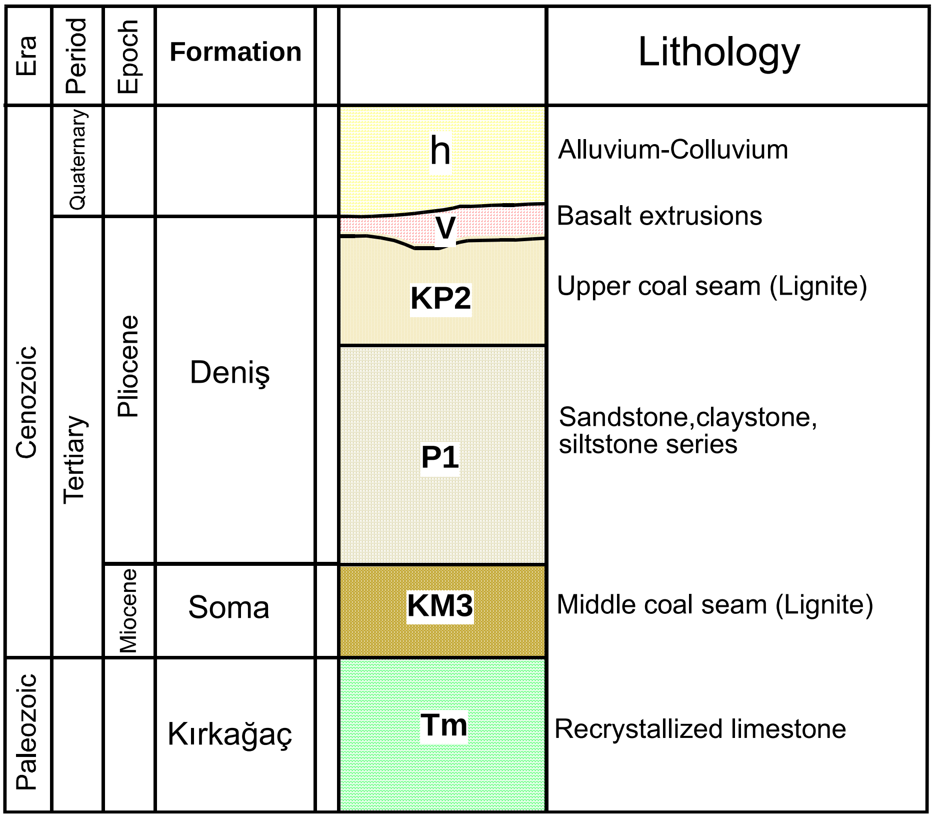

Figure 2-2. Generalized geological columnar section of the study area (Manisa-Soma-Deniş) (modified from Nebert, 1978).

Pliocene units (Deniş Formation) in the study area are represented by P1 (sandstone, claystone and siltstone series), the upper lignite seam (KP2) and basalt extrusions (V). Pliocene rocks are first named by Nebert (1978) as the Deniş Formation as they are mainly exposed around Deniş Village. Thereafter, the scientists preferred the same term for the Pliocene aged rocks in literature. P1 has no outcrop in the study area, but observed in the core samples from drilling studies (e.g. Nebert, 1978). The sandstone in this member is distinguished with its yellow color, coarse-to-medium grain size with cross bedding developed within its structure. Siltstones and claystones are gray to green colored (Nebert, 1978). Through the upper parts of the member, the thickness of coal lenses increases and it is overlain by a Pliocene lignite seam (Gemici et al., 1991). The coal seam KP2 has relatively high clay content. The fossil content of the coal is rich. Coal appears to be black to brown colors. General thickness of coal seam is low (Nebert, 1978). Volcanism also can be observed in the study area. Existence of tuff and agglomerate is strong evidence of the volcanic events. The products of these volcanic events appear as the basaltic rocks observed widely in the area in the form of volcanic flows. These basaltic rocks (B) are hard, green colored, with calcite inclusions (Brinkmann et al., 1970).

Quaternary rocks (h) in the area are alluvium and colluvium. Alluvium is very rarely observed; occurring in small amounts in river beds and is not mappable (İnci, 1981). Colluvium is generally formed of limestone fragments with sizes varying between 1-1.5 cm (Nebert, 1978).

2.2 Structural Geology

Well-developed layering and folding does not exist in the study area. The layering is either horizontal or nearly-horizontal. Two main faults are observed in the Manisa-Soma-Deniş area. One of them is a normal fault observed in Bahçe-Açıkmeydan, and the other fault is in the west of Soğucak. However, the exact effect of faulting over the coalification in the study area is unknown or not clearly mentioned in the previous studies (Nebert, 1978).

2.3 Paleogeography

An ancient sea existed in Mesozoic, which became shallower through the end of Mesozoic and land was formed. A lake environment was dominant later in the study area during Pliocene. This shallow environment can be a reason for the formation of low-quality Pliocene lignites (Nebert, 1978).

2.4 Hydrogeology

The study area involves many small tributes of rivers with very small flow rates. Two samples were taken from the wells with low flow rates varying between 0.013 and 0.3 lt per second (during rainy and wet seasons). These rivers and groundwater are in contact with lignite deposits in several regions of study area. The aquifer type is unconfined and composed of rocks varying in grain size and lithology (conglomerate to mudstone with marl and limestone). The permeability of these rocks is high

(Nebert, 1978). According to the drilling studies, it is obvious that the groundwater is in contact with lignite deposits. The wells related to the lignite and water samples (Figure 2-3) carried out during the study and their general information including the water level and lignite depths are given in table 2-1.

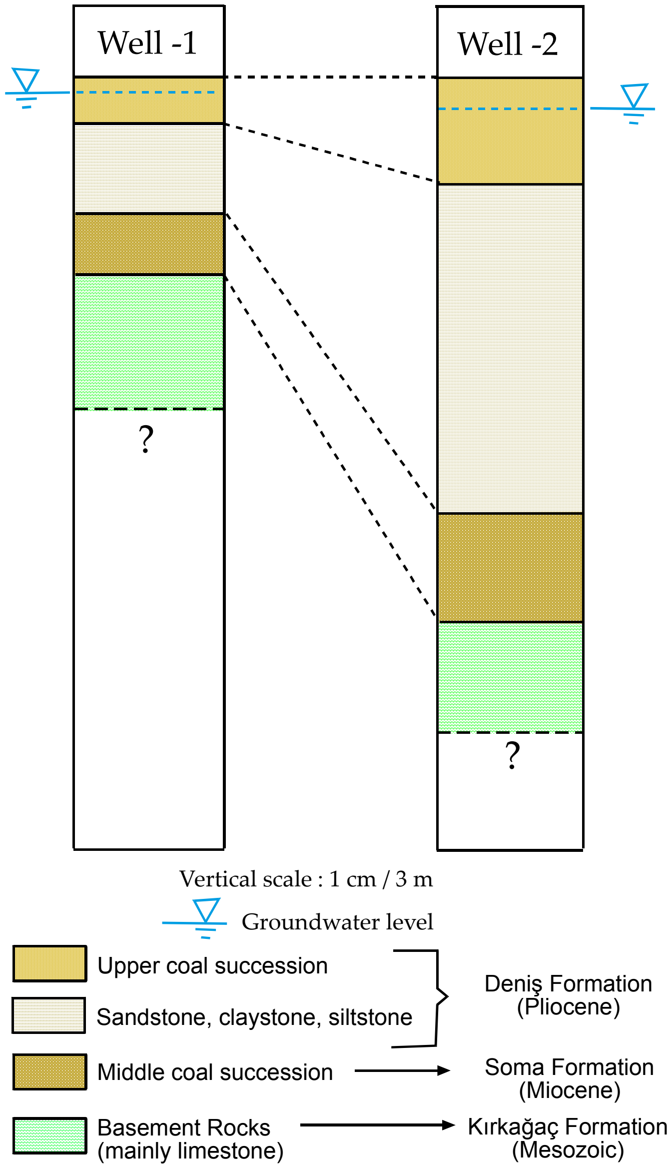

Figure 2-3. The columnar sections showing the contact between coal and water in the wells drilled in the sampling locations from the study area.

Table 2-1. The information about water level and lignite base depth of wells and the samples associated (Nebert, 1978).

Well ID	Lignite samples	Water samples	Water level	Lignite base depth
01	C01-03	W01	2,18 m	31 m
02	C04-06	W02	5,30 m	128 m

CHAPTER 3

BASIC PARAMETERS OF THE SAMPLES

3.1 Introduction

Basic physical and chemical parameters of water (during the field study) and coal (in laboratory) samples were determined using standard analyses. The methodology of these analyses and the results will be given in this chapter.

3.2 Coal Samples

Basic physical and chemical parameters for coal samples are the ultimate (carbon, hydrogen, oxygen, nitrogen, and sulphur) and proximate (moisture, ash, volatile matter) parameters. These parameters are used to determine the technological properties, rank and quality of coal.

3.2.1 Ultimate Parameters

The coal samples were grinded and powdered to 60-mesh, and sent for analyses. Ultimate parameters (C,H,O,N and S) of four coal samples (C01, C02, C04 and C05) were determined by elemental analyses, in the Central Laboratory of METU and in the laboratories of USGS, Reston, VA, USA. The results of elemental analyses are given in Table 3-1.

Table 3-1. Ultimate values (C,H,O,N,S) and ratios of H/C and O/C of the coal samples the from Manisa-Soma-Deniş region.

ID	C01	C02	C04	C05
C	27,68	39,81	35,97	42,34
H	25,14	31,26	29,47	37,21
O	9,76	13,18	11,15	14,12
N	0,66	0,75	0,54	0,35
S	1,49	1,45	1,23	1,66
H/C	0,91	0,79	0,82	0,88
O/C	0,35	0,33	0,31	0,33

H/C and O/C ratios (Table 3-1) are used for the determination of coal rank. When these parameters are used in the coal-rank determination diagram (Beckmann, 1976), all samples fall into the range of lignite (Figure 3-1).

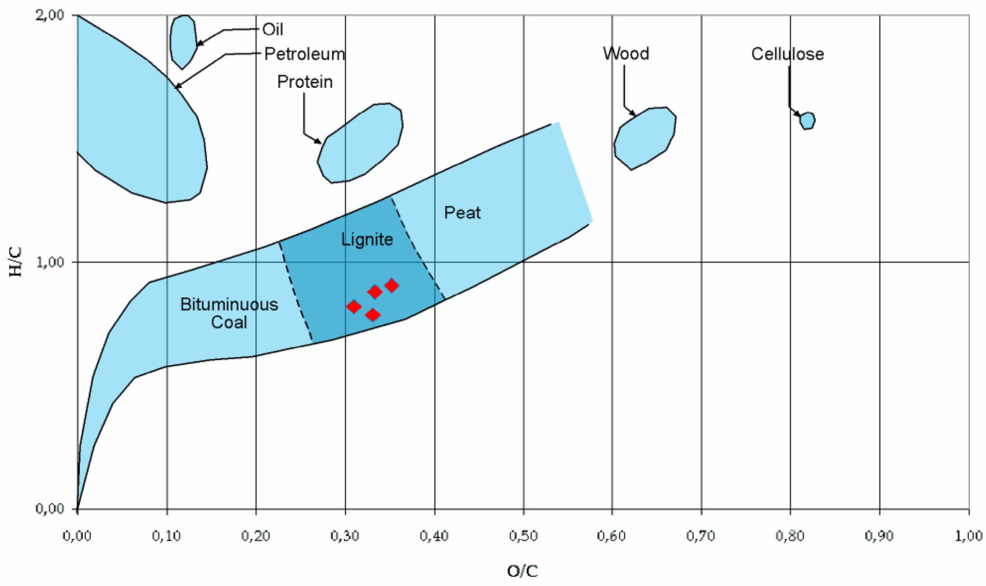

Figure 3-1. Plot of the coal samples from the Manisa-Soma-Deniş region, on the coal-rank determination diagram of Beckmann (1976).

3.2.2 Proximate Parameters

The coal samples were grinded and powdered to 60-mesh, and sent for analyses. Proximate parameters (ash, moisture and volatile matter) of the four coal samples (C01, C02, C04 and C05) were determined at the laboratories of USGS, Reston, VA, USA using standard methods. The results are given in Table 3-2.

Table 3-2. Proximate parameters (ash, moisture, volatile matter) of the coal samples from the Manisa-Soma-Deniş region.

ID	C01	C02	C04	C05
Ash	23,0	22,3	24,7	25,5
Moisture	32,9	31,6	30,5	34,5
Volatile matter	58,5	59,3	57,3	58,5

Proximate parameters for coal (ash, moisture and volatile matter) are used to determine technological properties of coal and the rank / quality of coal.

Moisture for lignites is considered to range between 30-75% according to American Society for Testing and Materials (ASTM, 1980) standards for coal (increasing with increasing moisture value). The coal samples from the Manisa-Soma-Deniş region have moisture values between 30,5% and 34,5% with an average of 32,4%. These values fall into lignite range with low-quality when moisture is considered.

Volatile matter for lignites is considered to range between 52-64% according to ASTM (1980) standards for coal (decreasing with increasing volatile matter value). The coal samples from the Manisa-Soma-Deniş region have volatile matter values between 57,3% and 59,3% wih an average of 58,4% (Table 3-2). These values also indicate that the coal samples from the Manisa-Soma-Deniş region are lignite samples with low-quality. Volatile matter values are well-matched with moisture ranges having the same conclusion.

Ultimate parameters indicated that the coal samples are lignites with high-quality indication low-degree of coalification when compared to the standard classification of coals by rank (ASTM, 1980).

3.3 Water Samples

Basic parameters of water samples determined in this study are pH, conductivity, TDS, and temperature. These parameters were measured during the field study using a pH/T°/TDS/conductivity meter. For pH-measurement, a standard liquid (with pH of 7.0) was used for calibration before sampling. The results for basic parameters of the water samples are given in Table 3-3.

Table 3-3. The results of basic parameters for the water samples taken from Manisa-Soma-Deniş region (pH:unitless, conductivity: microsiemens, TDS-total dissolved solid-:mg/L and temperature:degree celcius).

ID	W01	W02	W03	W04	AVERAGE
pH	6,9	7,3	7,5	6,8	7,1
Conductivity	720	230	195	382	382
TDS	162	324	112	782	345
Temperature	17	12	11	16	14

The range of pH (Table 3-3) for the water samples from Manisa-Soma-Deniş region is narrow. However, conductivity and TDS have a wide range. The TDS value permitted for the drinking waters by EPA (1980) is 500 mg/l. The only water sample with TDS value higher than permitted is W04. The water samples have low-temperature values. Permitted pH values for drinking waters are 6.5-8.5 and all samples fall into the allowed range of EPA (1980).

The basic parameters of the water samples will used for the comparison of the water samples from endemic and non-endemic regions of Balkan Peninsula to understand if any linear trend occurs between those samples and if the samples are representative for those of either endemic or non-endemic regions in Discussion.

CHAPTER 4

INORGANIC PARAMETERS

4.1 Introduction

Any element on the periodic table may cause an environmental or human health problem in the case of any high concentrations or deficiency (Finkelman and Gross, 1999). For a study involving the health effects of coal deposits, 22 environmentally sensitive elements (Table 4-1) are discussed (Finkelman, 1991) During this study, the concentrations of these environmentally sensitive elements were determined for both coal and water samples from the Manisa-Soma-Deniş region.

Table 4-1. The environmental sensitive elements those are found in coal deposits and may cause health and environmental problems and their modes of occurences in coal deposits (Finkelman and Gross, 1999).

Element	Symbol	Modes of occurrence of elements in coal
Aluminum	Al	Multiple associations
Arsenic	As	Pyrite
Antimony	Sb	Organic association, pyrite and accessory sulfides
Beryllium	Be	Organic association
Boron	B	Organic association
Cadmium	Cd	Sphalerite
Chromium	Cr	Organic association, illites, chromites
Copper	Cu	Chalcopyrite, pyrite

Table 4-1 continued

Element	Symbol	Modes of occurrence of elements in coal
Germanium	Ge	Multiple associations
Lead	Pb	Galena
Mercury	Hg	Pyrite
Manganese	Mn	Carbonates: siderite, and ankerite
Molybdenum	Mo	Accessory sulfides, organic association
Nickel	Ni	Multiple associations
Selenium	Se	Organic association, pyrite, accessory selenides
Silver	Ag	Sulfides
Thallium	Tl	Pyrite
Thorium	Th	Monazite, xenotime, zircon, clay
Tin	Sn	Oxides and sulfides
Vanadium	V	Clays and organic association
Uranium	U	Organic association, zircon, silicates
Zinc	Zn	Sphalerite

4.2 Coal Samples

4.2.1 Methodology

Inorganic parameters of four coal samples (C01, C02, C04 and C05) were determined. All coal samples were grinded to the size 60 mesh and then analyzed by a commercial laboratory (ACME Labs, Canada), using inductively coupled plasma-mass spectrometry (ICP-MS).

4.2.2 Results

The inorganic parameters of coal samples, determined by ICP-MS are listed in Appendix A. When these parameters are compared to the standards of EPA (1980) for drinking water, it is normal to observe much more higher values than permitted levels. Therefore, it is of no importance to normalize the inorganic parameters for the coal samples from the Manisa-Soma-Deniş region with respect to the standards of EPA (1980). At this part, these elements will be discussed taking consideration in their potential health impacts individually.

When inorganic parameters of the coal samples from the Manisa-Soma-Deniş region are studied, several elements should seriously considered to have health problems as they are observed in much more amounts according to the coal standards of ASTM (1980).

Arsenic concentration of the coal samples from the Manisa-Soma-Deniş region is high. Indeed, the arsenic content of Turkish low-quality lignites is very high and can be considered as a general problem (Tuncalı et al.., 2002). Arsenic in coal can be found in the structure of pyrite/arsenopyrite (Finkelman and Gross, 1999). The pathway of exposure for arsenic into human body is inhalation or physical contact and it is responsible for the lung diseases. However, it has no direct link for any kidney diseases so far (Agency for Toxic Substances and Disease Registry, ATSDR, 2005). The major disease, linked to arsenic exposure is "black lung disease". Black lung disease is the major health problem, which the coal miners are exposed and suffer, and the major cause of the disease is inhalation of arsenic in the structure of pyrite during the combustion of coal (Plumlee and Ziegler, 2004). Therefore, even though arsenic may not be linked to BEN disease, it should be considered as a serious problem considering its effects (ATSDR, 2005). Arsenic content in water samples will also be evaluated to understand if any leaching through the water samples. However, the relation of As to BEN is unclear. There is no finding suggesting that the high exposure to As in endemic villages is a contributing factor for BEN-disease (Orem et al., 2004).

Other element with high concentration in coal samples is lead (Pb) and like arsenic content, lead concentration is also very high in all elements. Lead can be found in coal deposits in the structure of galena (Finkelman and Gross, 1999). Exposure to lead can be by breathing during the coal combustion and by drinking of contaminated water. Lead can affect nervous system, kindeys and respiratory system. However, there is no proof that lead causes any cancer (ATSDR, 2005). However, it should be considered seriously as it has adverse effect on kidneys and may be linked to BEN-disease.

The other element with high concentrations in the coal samples is uranium (U). Uranium is already present in soils or rocks throughout environment. High concentration of uranium can cause damage in kidneys (ATSDR, 1999). Uranium can be found in coal deposits in the structure of organic assocciations, zircon and silicates within coal (Finkelman and Gross, 1999).

These three elements have high concentrations in the coal samples and it seems to be possible to cause health problems in any case of exposure to these elements. However, it is also important to evaluate the concentrations of these elements in water samples as BEN is resulted by drinking water sources in contact with coal deposits.

4.3 Water Samples

4.3.1 Methodology

Inorganic parameters of four water samples were determined. All water samples were collected and stored in pre-cleaned bottles. For determination of inorganic properties of water samples, plastic bottles were used. The bottles were soaked overnight in 10% nitric acid and rinsed with milli-Q water. Before collection of water samples, water was passed through 0.4 μm pore size polycarbonate filters. Inorganic parameters of water samples were then analyzed by a commercial laboratory (ACME Labs, Canada), using inductively coupled plasma-mass spectrometry (ICP-MS).

4.3.2 Results

The inorganic parameters of the water samples, determined by ICP-MS are listed in Appendix B. The environmentally sensitive elements for the water samples from the Manisa-Soma-Deniş region were also normalized using EPA (1980) standards (Table 4-2).

Table 4-2. The permitted levels of EPA (1980) for the environmentally sensitive elements in drinking waters.

Element	Symbol	Limit
Aluminum	Al	0,2 ppm
Arsenic	As	5 ppb
Beryllium	Be	4 ppb
Cadmium	Cd	5 ppb
Chromium	Cr	0,1 ppm
Copper	Cu	1 ppm
Mercury	Hg	2 ppb
Manganese	Mn	50 ppm
Nickel	Ni	1 ppm
Selenium	Se	50 ppb
Antimony	Sb	0,2 ppm
Silver	Ag	0,1 ppm
Thallium	Tl	2 ppb
Zinc	Zn	20 ppb
Uranium	U	5 ppm

The normalized values of environmentally sensitive elements are given in Figures 4-1 to 4-4. The elements with values higher than 1.0 can be considered to cause potential health problem as they are over the permitted values. During the normalization, the elements below the detection limits may be excluded as they are considered negligible in amounts.

When the inorganic parameters of water samples from the Manisa-Soma-Deniş region are studied, it can be easily mentioned that nearly all elements are in the safe range, determined by EPA (1980). However, a variety of elements have higher values than permitted levels of concentration and may cause health problems in the case of exposure.

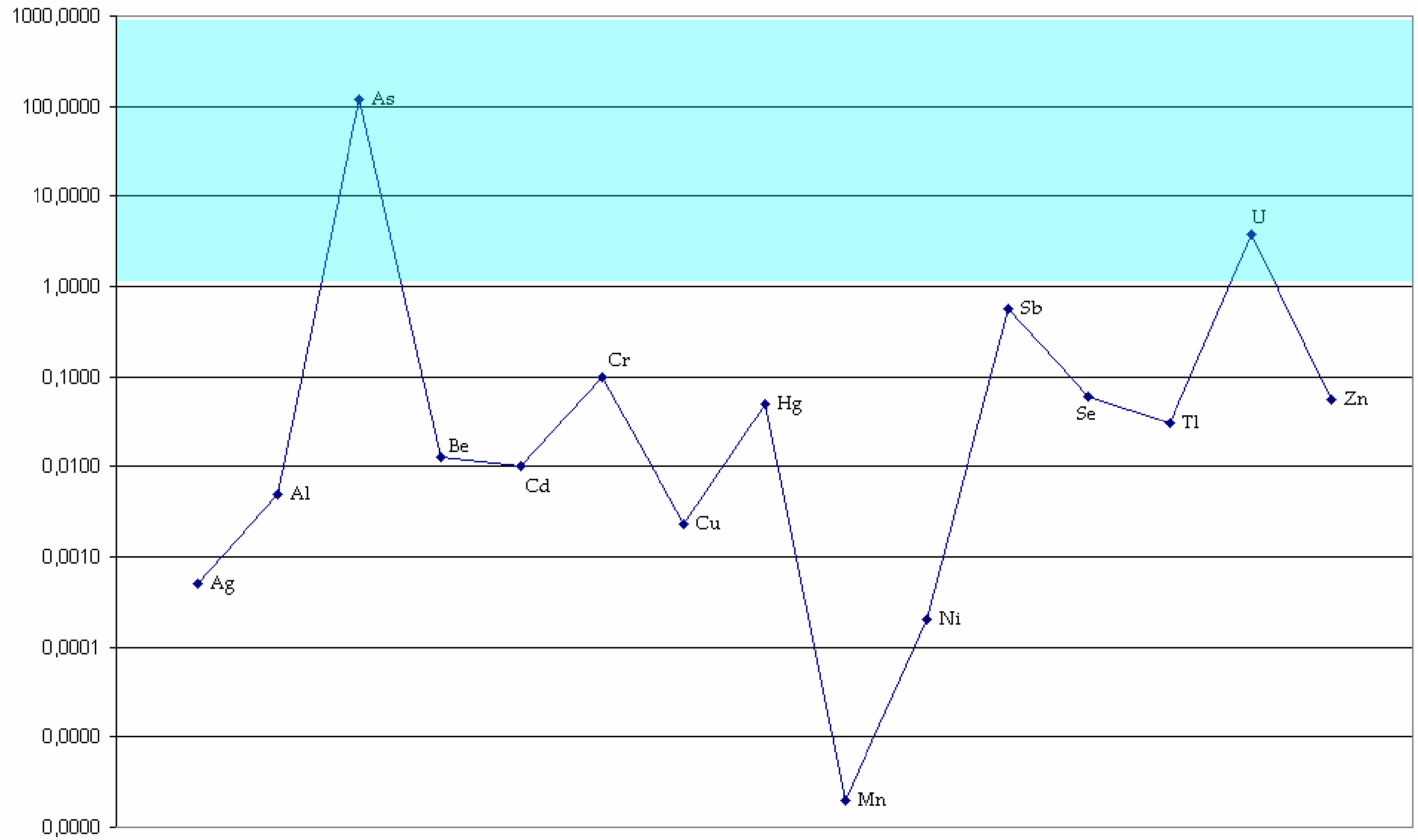

Figure 4-1. The environmentally sensitive elements of sample W01 after normalization by the standards of EPA(1980).

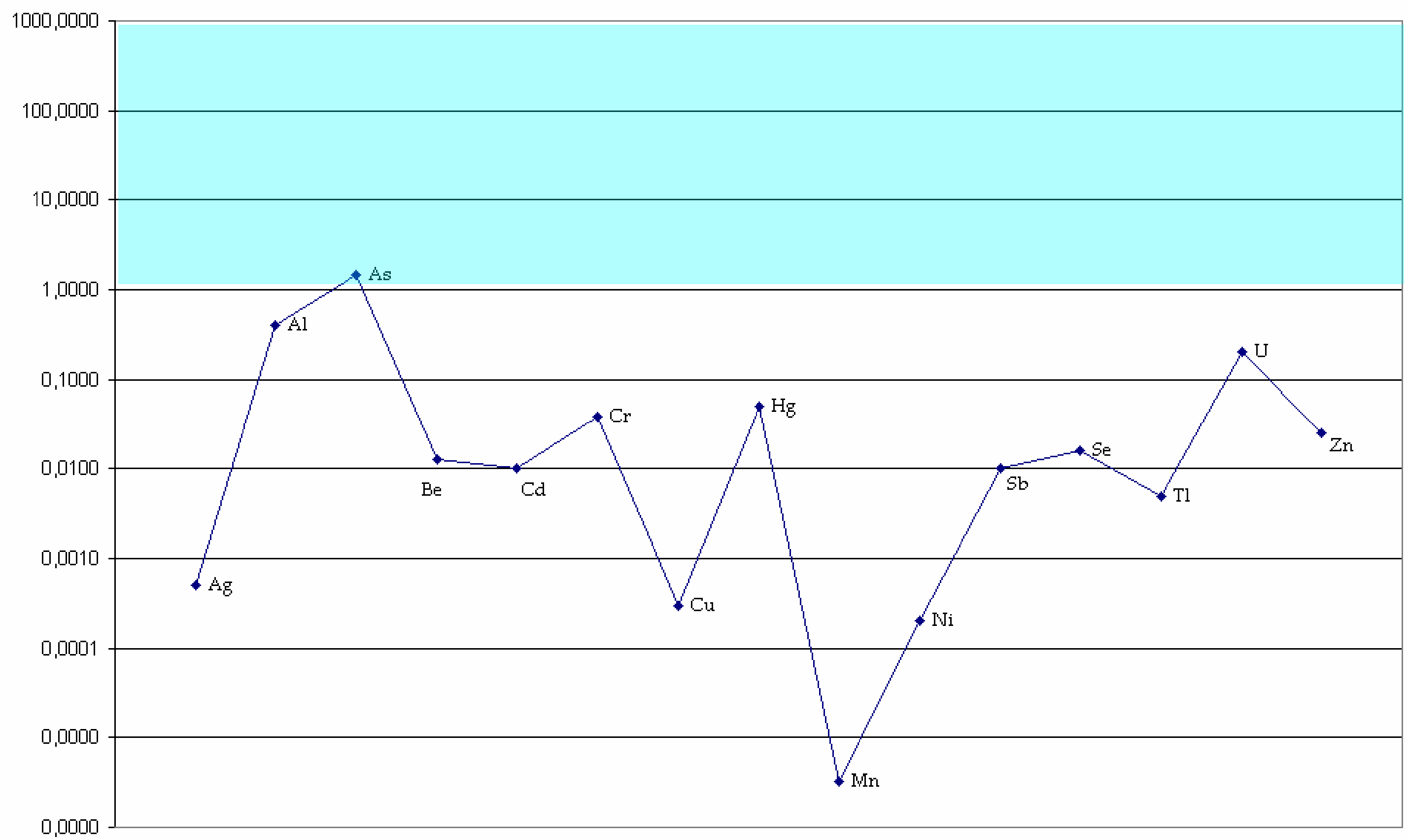

Figure 4-2. The environmentally sensitive elements of sample W02 after normalization by the standards of EPA (1980).

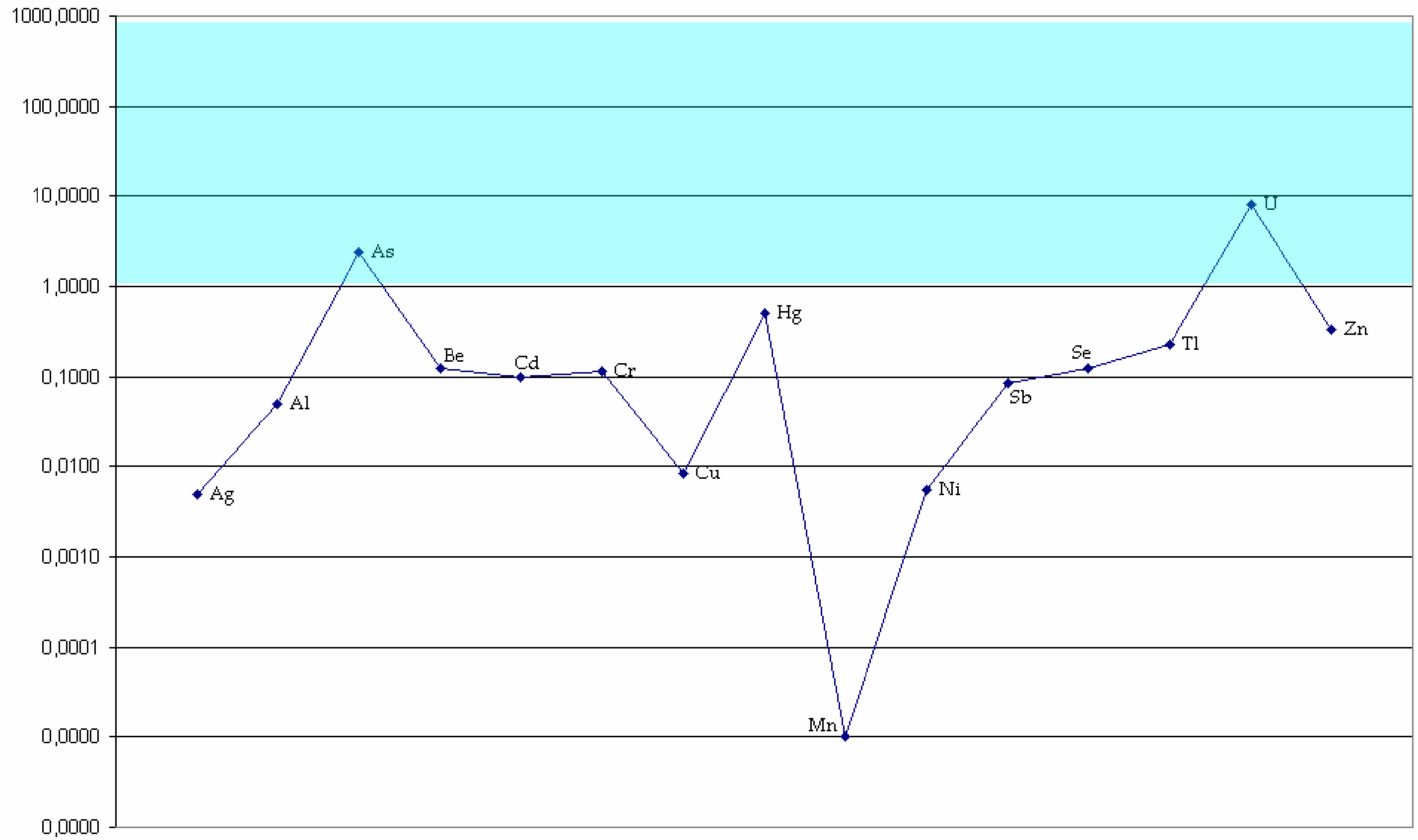

Figure 4-3. The environmentally sensitive elements of sample W04 after normalization by the standards of EPA (1980).

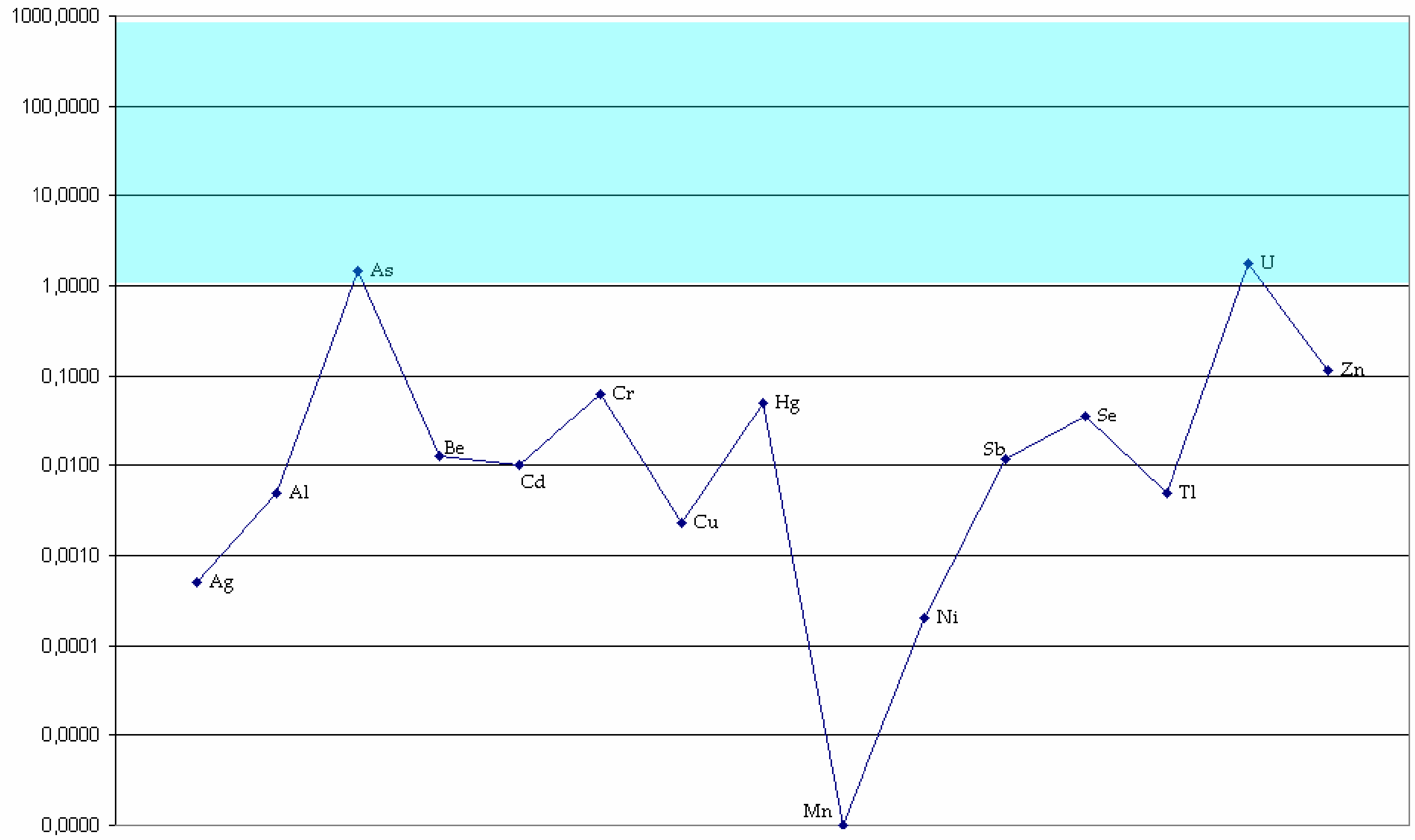

Figure 4-4. The environmentally sensitive elements of sample W05 after normalization by the standards of EPA (1980).

The only element, with higher concentrations than permitted levels of EPA (1980) for all water samples is arsenic (Figures 4-1 to 4-4). For the samples WO1, WO4 and WO5, uranium concentrations are higher than the permitted values (Figures 4-1, 4-3 and 4-4); hence, they are considered to cause serious health problems. When the element concentrations of the water and coal samples are compared with each other, it may be stated that only lead (Pb) is not leached into water from the coal deposits. However, arsenic (As) and uranium (U) concetrations are similar between the water and coal samples. This may indicate that these elements were enriched in water as a result of leaching. Their concentrations in the water samples are not as much as those in the coal samples. However, they are still considered to cause health problems as they are higher than the standards of EPA (1980).

CHAPTER 5

ORGANIC PARAMETERS

5.1 Introduction

"Pliocene Lignite Hypothesis" is based on leaching of organic compounds from low-quality coal deposits into water sources and use of water sources for a variety of purpose such as drinking, washing etc (Feder et al., 1991; Finkelman et al., 1991). Therefore, determination of organic parameters of both coal and water samples is important to understand if the coal deposits have toxic organic compounds and if the water leached these organic compounds.

5.2 Coal Samples

5.2.1 Methodology

All coal samples were grinded to 60-mesh and then analyzed by gas chromatography/mass spectrometry (GC/MS) in the Clinical Laboratory No.1, Timisoara, Romania.

5.2.2 Results

The organic parameters of the coal samples from the Manisa-Soma-Deniş region were determined by Gas Chromotography/Mass Spectrometry. The results will be given in table 5-1 (chromotograms are given in Appendix C).

Table 5-1. List of organic compounds determined in the coal samples from Manisa-Soma-Deniş region and the samples containing these organic compounds.

Organic Compound	C01	C02	C03	C04	C05	C06	C07	C08	C09	C10
Phenol, 2,4-bis (1,1-dimethylethyl)	✓	✓	✓	✓	✓	✓	✓	✓	✓	✓
2,2,4-trimethyl							✓	✓	✓	✓
Benzathiazole 2-methyl			✓							
Benzene 1,3-dimethyl							✓		✓	✓
Decanol		✓		✓	✓		✓			
Di-n-butyl phthalate				✓	✓		✓	✓	✓	✓
Dodecane									✓	
Eicosane	✓									
Heptadecane	✓									✓
Hexane 2,2,5-trimethyl							✓	✓		
Naphtalene 2,6-dimethyl										✓
Naphtalene 1,3-dimethyl								✓		
Naphtalene 1,5-dimethyl									✓	
Naphtalene 2-methyl									✓	
Octadecane								✓		✓
Octane	✓									
Pentadecane								✓		
Pentane 2,4-dimethyl	✓									
Propanoic acid				✓						
Tridecanol								✓	✓	✓
Undecane	✓	✓			✓			✓	✓	✓

Major organic compounds found in the coal samples, taken from Manisa-Soma-Deniş region are phenol, 2,4-bis(1,1-dimethylethyl), octane, undecane, eicosane, heptadecane, pentane,2,4-dimethyl, decanol, benzathiazole,2-methyl, propanoic acid, di-n-butyl-phthalate, hexane,2,2,5-trimethyl, octadecane, 2,2,4-trimethyl, benzene,1,1-dimethyl, benzene,1,3-dimethyl, tridecanol, naphtalene,1,3-dimethyl. This organic compounds will be discussed in this chapter separately.

Phenol, 2,4,bis(1,1-dimethylethyl) is a kind of phenol group and it is dominantly observed through the coal samples. It is considered to be less harmful relative to other kinds of phenols and inactive. Therefore, it is not expected to observe this organic compound in the water samples as it is inactive.

Eicosane is a typical example of aliphatic hydrocarbons. Indeed, aliphatic hydrocarbons are extremely hazardous organic compounds, found in the samples from endemic regions. However, eicosane is not as toxic as other aliphatic hydrocarbons and its concentration in the sample is really low to prevent any leaching of compound to water samples. Therefore, it will be probably very low in water sample. Eicosane is only observed in sample C01.

Like aliphatic hydrocarbons, their functional derivatives (alkanes and alcohols) are also considered to occur within the samples from endemic regions in high concentrations. Octane is a kind of alkane group, and it is only observed at the first sample (C01). Another alkane-group organic compounds are undecane, heptadecane, octadecane, dodecane and pentadecane. All of these alkanes are nearly inactive and of low-toxicity. Their concentrations are also very low when compared to those of endemic samples. The distribution of alkanes through the coal samples are as octane in C01, undecane in C01, C02, C05, C07, C08 and C10, heptadecane in the coal samples C01 and C10, pentadecane in only C8 and dodecane in only C9, and finally octadecane in the coal samples C06, C08 and C10. Major examples of alcohols, observed through the samples taken from Manisa-Soma-Deniş region, are decanol and tridecanol. These compounds are also very low and nearly inactive kind of this group, therefore, they resemble non-endemic samples like the organic compounds mentioned so far. Decanol is observed in the samples C02, C04, C05, C06 and C07 whereas tridecanol is observed in coal samples C08 and C10.

Methyl groups are also known to be toxic in coal deposits and they are evaluated carefully. The methyl group compounds observed through the samples are pentane,2,4-dimethyl, benzathiazole,2-methyl, hexane,2,2,5-trimethyl, and 2,4,4-trimethyl. These compounds are rarely observed in the coal samples and with very low concentrations. Therefore, they are not expected to cause health problems. Pentane,2,4-dimethyl is observed only in sample C01 and benzathiazole, 2-methyl in sample C03. Hexane,2,2,5-trimethyl and 2,4,4-trimethyl can be more frequently observed in the coal samples (both is observed in the samples C6, C7, C8 whereas C10 has only 2,4,4-trimethyl).

Phthalate esters and their derivatives are also considered as toxic organic compounds. The only member of this group is di-n-butyl phthalate. The distribution of this compound is indeed much more than expected. It is observed nearly all coal samples (C04, C05, C07, C08, C09 and C10). However, at each sample, its concentration separately is very low.

Propanoic acid is among toxic organic compounds but only observed in sample C04. Its concentration is very low so it can be accepted as negligible.

Naphthalenes also have only one member through the coal samples (Naphtalene,1,3-dimethyl). This compound is only observed in the coal samples of Miocene age like the methyl group compounds. This can be considered as an interesting result to be considered.

All these compounds are considered among the toxic organic compounds to be evaluated in a BEN-study. However, the members of the groups in the coal samples are both inactive types and in very low concentrations. Therefore, the organic parameters of coal samples from Manisa-Soma-Deniş region resemble the typical non-endemic characteristics when they are compared with those from both endemic and non-endemic samples in Romania (data from Feder et al., 2002).

5.3 Water Samples

5.3.1 Methodology

All water samples were collected and stored in precleaned bottles. For the samples to be analyzed by GC/MS, amber glass bottles rinsed three times with analytical grade dichloromethane, were used. Before collection, water was passed through 1 μm pore size glass fiber filters. Immediately after collection, the water samples were stabilized with 60 ml of analytical grade dicholoromethane. The organic compounds were subsequetly extracted with an additional 180 ml of analytical grade dichloromethane at the laboratories of USGS, Reston, VA, USA. The extracts from the water samples were analyzed by gas chromotography/mass spectrometry (GC/MS) in the Clinical Laboratory No.1, Timisoara, Romania.

5.3.2 Results

The organic parameters of the water samples taken from Manisa-Soma-Deniş region determined by Gas Chromotography/Mass Spectrometry (GC/MS). The organic compounds determined in the water samples did not show any differences. Therefore, for the water samples, the sample numbers will not be mentioned separately. The results of GC/MS are given in table 5-2 (chromotograms are given in Appendix D).

When these organic compounds are examined, general compositions of organic compounds, observed in water samples are alcohol and alkane derivatives of hydrocarbons. However, they are not as toxic as the organics observed through the endemic samples. They also have low concentrations resembling typical non-endemic type samples. Therefore, they are not expected to cause a health problem to be linked to BEN-disease. The variation of their concentration through rainy and wet seasons should be monitored carefully to understand the seasonal changes.

Table 5-2. List of organic compounds for the water sample W04 taken from Manisa-Soma-Deniş region determined by GC/MS.

No	Organic compound
1	Eicosanol
2	Tetradecanol
3	Decanol
4	Dodecane
5	Eicosane
6	Octadecane
7	Pentadecane
8	Propanoic acid
9	Tetradecane
10	Tridecanol
11	Undecane

The organic compounds, observed in water samples from Manisa-Soma-Deniş region can be listed as alcohol derivatives (eicosanol, tetradecanol, decanol and tridecanol), alkane derivatives (tetradecane, dodecane, octadecane, pentadecane, and undecane), eicosane and propanoic acid.

Alcohol derivatives (tridecanol and decanol) are similar to those found in coal samples. They are also in very low concentrations in water samples, and not considered to cause any health problem.

Alkane derivatives (tetradecane, dodecane, octadecane, pentadecane and undecane) are also similar to those found in coal samples. They were most probably leached into water samples from coal deposits. However, as they are not active as the toxic organic compounds in the coal samples from endemic regions, the concentrations of leached organic compounds are very low.

CHAPTER 6

DISCUSSION OF RESULTS

6.1 Discussion of Basic Parameters of the Samples

Ultimate (C, H, O, N and S) and proximate parameters (moisture, ash, and volatile matter) of the coal samples (Tables 3-1 and 3-2) indicated that they are low-quality lignites. The toxic organic compounds can be found in low-quality lignite deposits as they can be observed in the initial stages of coalification. These toxic organic compounds are replaced with their non-toxic and inactive derivatives as the quality of coal increases (Orem et al., 2004). Therefore, the coal samples from the study area are similar to those from endemic regions in Balkan Peninsula. It should be noted that such similarities are important for us to establish any link between the mode of occurence of organic compounds in the coal samples and the other parameters. However, when the coal samples from the study area are compared to those from endemic and non-endemic regions in Romania (Figure 6-1) (data is obtained from Orem et al., 2004), they do not show any linear trend through the samples. Therefore, no relation betweeen the basic parameters of the coal samples and the toxic organic compounds causing BEN can be established. Therefore, they can be considered to be irrelevant to the purpose of a BEN-study.

For water samples, basic characteristics are pH, TDS, conductivity, and temperature (Table 3-3). These parameters indicated that the water samples from the study area can be considered to be in the standard range of drinking waters. However, no relationship can be established between the water samples from the study area and those from endemic and non-endemic regions in Romania (Figure 6-2) (the data is obtained from Orem et al., 2004). There is no trend between the data therefore, these can be considered to be irrelevant for the purpose of this study.

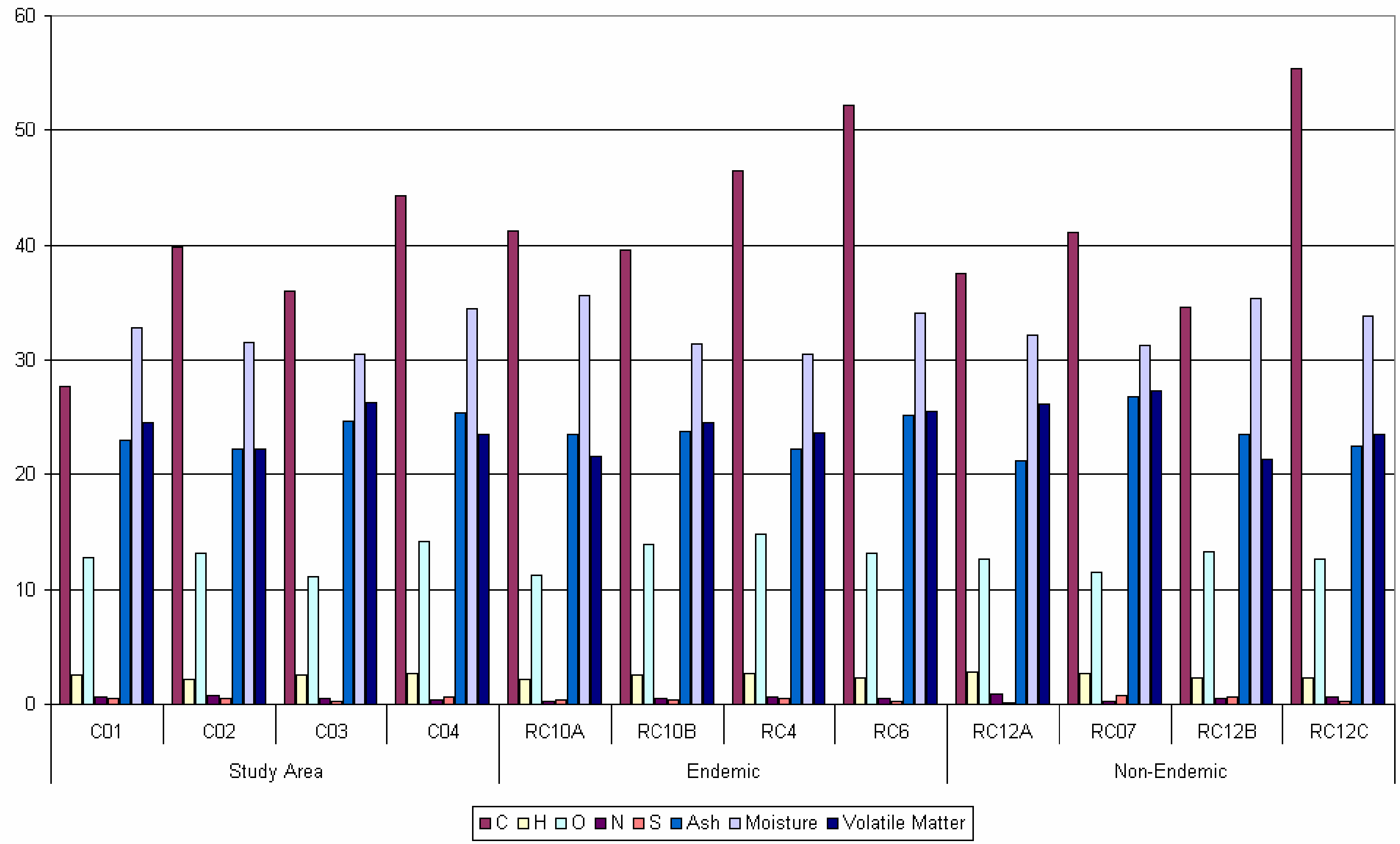

Figure 6-1. Comparison of the basic characteristics of the coal samples from the study area and those from the endemic and non-endemic regions in Romania (the data is obtained from Orem et al., 2004)

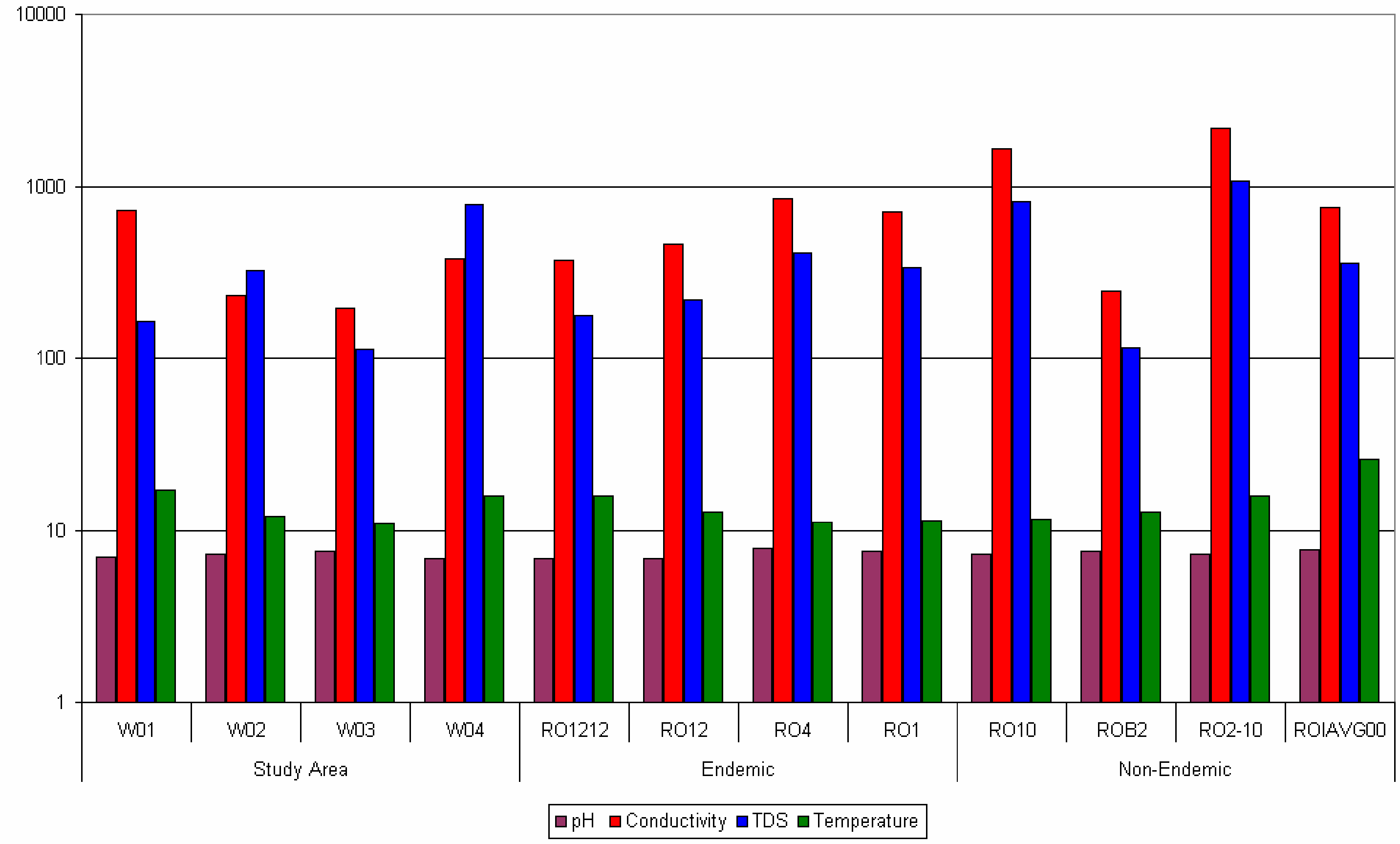

Figure 6-2. Comparison of the basic characteristics of the watersamples from the study area and those from the endemic and non-endemic regions in Romania (the data is obtained from Orem et al., 2004)

6.2 Discussion of Inorganic Parameters

The inorganic parameters for the coal and water samples from the study area indicated that the samples were enriched in arsenic and uranium. In the coal samples, lead concentration was also high. This may indicate that lead could not be leached into water.

The results of inorganic parameters for coal (Figure 6-3) and water (Figure 6-4) samples were compared to those of samples taken from endemic and non-endemic regions in Romania (data is obtained by Orem et al., 2004). However, the comparison did not give any linear relationship between the organic compounds and elements found in the samples. They have random distribution.

The elements found in the coal samples from the study area are generally higher than those of other locations in Romania. However, generally the elements represent nearly linear trend through all the samples. That means they have no major differences between the samples from endemic and non-endemic regions in Romania. This prevents us to make any link between the inorganic parameters of the coal samples and the organic compounds causing BEN. Therefore, they can be accepted as irrelevant for the purpose of a BEN-study. However, especially arsenic, uranium and lead concentrations are high and should be considered seriously in a study involving the health effects of coal deposits.

The elements found in the water samples from the study area were normalized with respect to the standards of EPA (1980). They are compared to the normalized element values of the water samples from endemic and non-endemic regions in Romania (the data was obtained from Orem et al., 2004). The comparison of normalized inorganic parameters for the water samples also did not give any linear relationship between the occurrence of toxic organic compounds in coal deposits and the concentration of any elements. The elements in the coal samples from the study area have higher values than other samples.

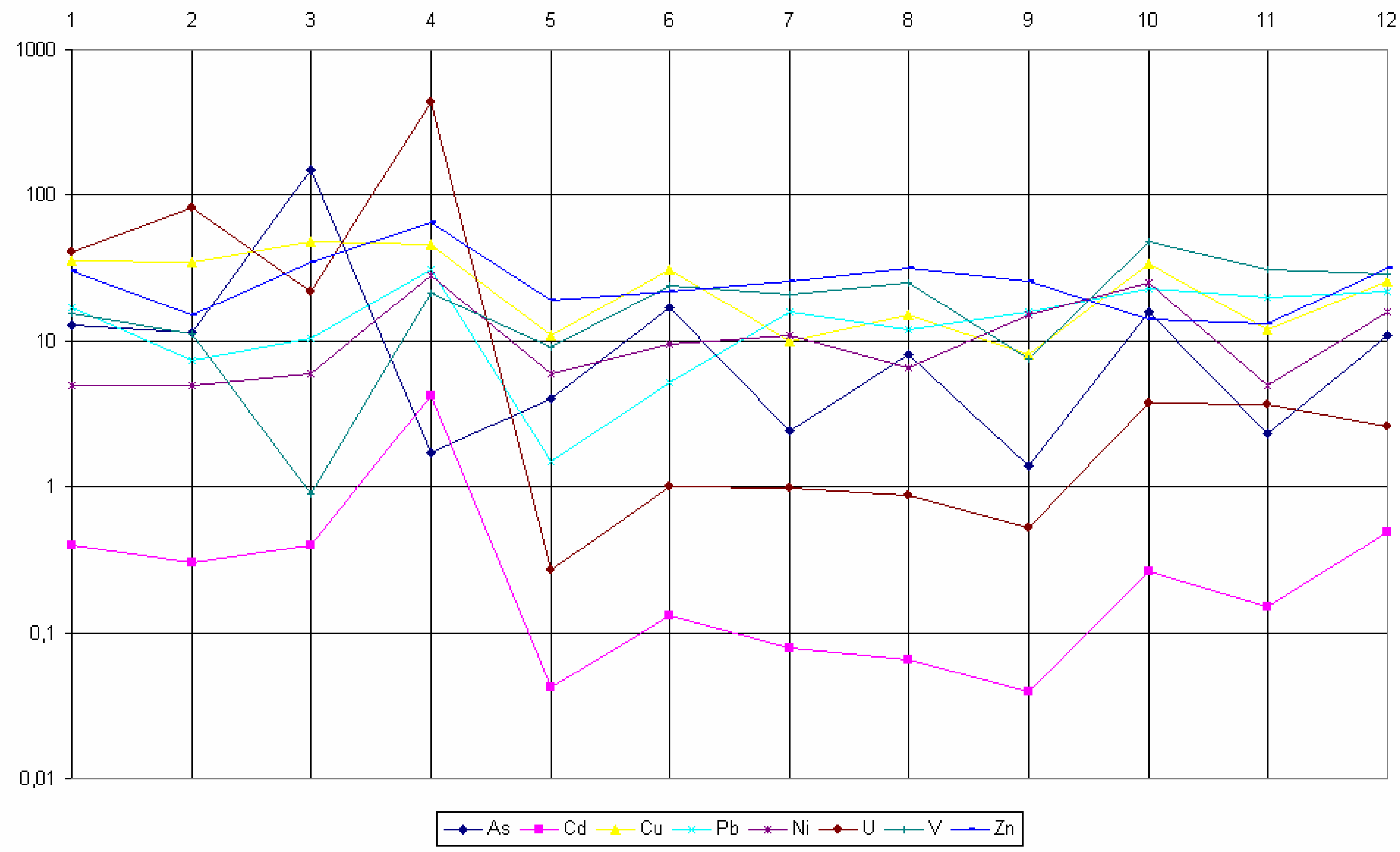

Figure 6-3. Comparison of inorganic parameters of the coal samples from the study area and from endemic and non-endemic regions in Romania (the data is obtained from Orem et al., 2004) (1-4: samples from study area, 5-8: samples from endemic regions in Romania, 9-12: samples from non-endemic regions in Romania)

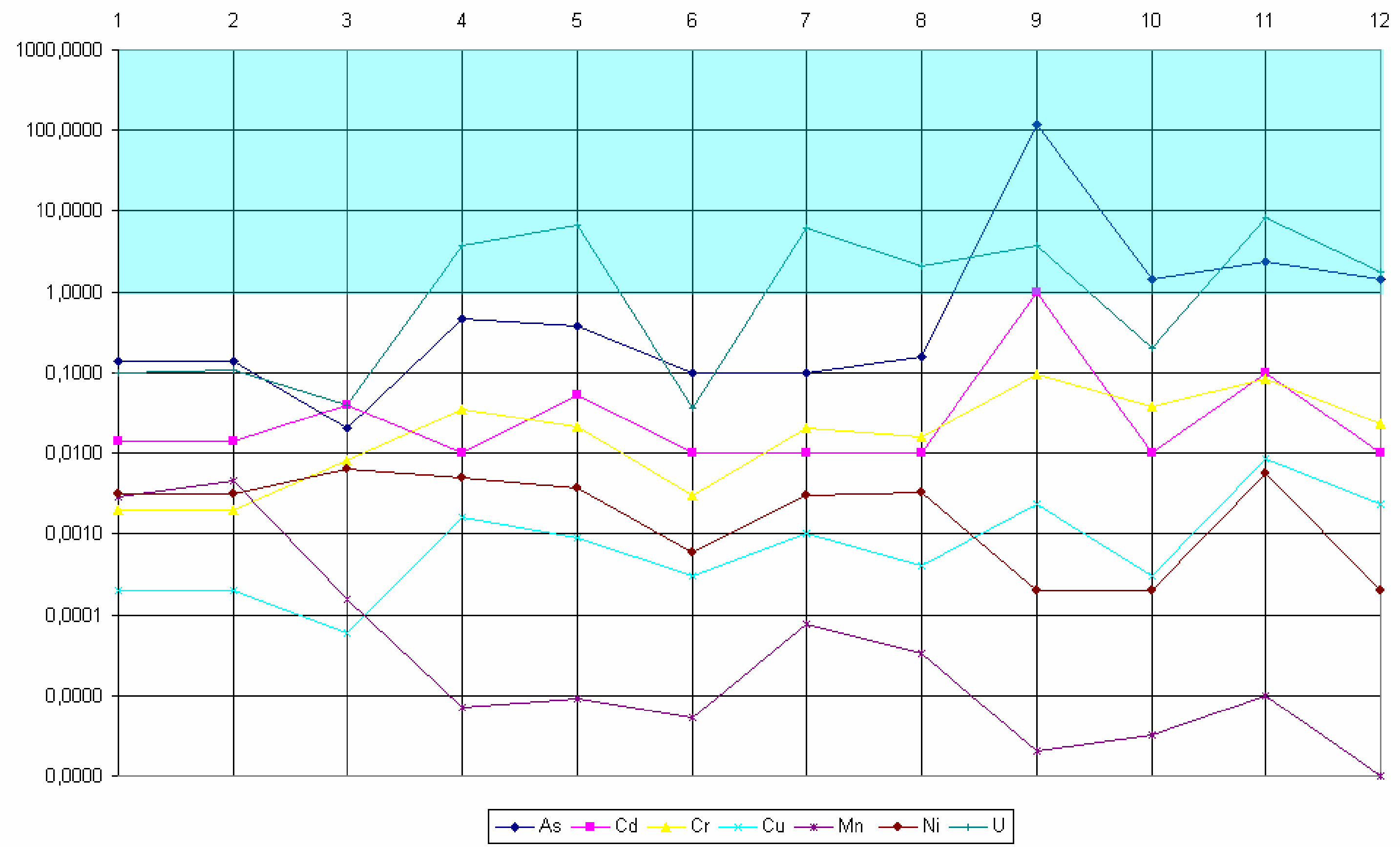

Figure 6-4. Comparison of inorganic parameters of the water samples from the study area and from endemic and non-endemic regions in Romania (the data is obtained from Orem et al., 2004) (1-4: samples from endemic regions in Romania, 5-8: samples from non-endemic regions in Romania, 9-12: samples from study area)

On the other hand, the element concentrations of the water samples from non-endemic regions have higher values than those from endemic regions in Romania. For instance, the concentration of uranium is higher than the permitted levels of EPA (1980) in non-endemic regions. However, it is in the safe range when the samples from endemic regions in Romania are involved.

Another element; arsenic (As), is high in both coal and water samples. The high concentration of arsenic in water samples may be derived from the coal deposits. Coal deposits from where the coal and water samples were taken are in contact with water; therefore, the leaching of arsenic from coal into water is extremely possible. It can be considered as a serious problem to cause health problem. However, when arsenic concentrations of water samples from both endemic and non-endemic regions were compared, all water samples have lower concentrations than the permitted levels of EPA (1980). Therefore, yet arsenic concentration in the samples of Manisa-Soma-Deniş region is high, no relationship between arsenic and BEN-disease can be established.

The results of inorganic parameters of both water and coal samples suggest that there are a variety of elements with high concentrations for both water and coal samples, however, since they have no distinct pattern in endemic and non-endemic regions in Romania, they will not be considered as a possible contributing factor to BEN-disease.

6.3 Discussion of Organic parameters

When organic parameters of coal samples from Manisa-Soma-Deniş region are evaluated, the toxic organic compounds found in the coal samples from endemic regions can not be observed within samples. The coal samples have similar organic compounds. The coal samples have hydrocarbon, methyl, alkane and alcohol groups, which are generally considered to be potential toxic organic compounds. However, these organic compounds are not as toxic as the compounds found in endemic samples. They are nearly inactive so they can be leached into water in very small concentrations. They are also in very low concentrations. Therefore, the coal samples resemble those of non-endemic regions. It should be noted that the coal samples of Soma Formation (Miocene) have relatively more abundant organic compounds with high concentrations. The variation of their concentration through rainy and wet seasons should be monitored carefully to understand the seasonal changes.

Most of the toxic organic compounds, observed in coal samples such as phthalates, phenols, and hydrocarbons can not be observed in water samples. This can lead us to conclude that the organic compounds in the coal deposits, found in large amounts were not highly active to be leached by water and they could not be observed through the water samples.

CHAPTER 7

CONCLUSION

- Basic characteristics of the coal samples from the Manisa-Soma-Deniş region (ultimate and proximate properties) indicated that the coal samples are low-quality lignites. Basic characteristics of the water samples from study area indicated that they are compatible the standards of drinking waters.

- Inorganic parameters also did not reveal any significant relationship when correlated with the samples taken from endemic and non-endemic areas of Romania. However, the concentrations of elements arsenic, uranium and lead for coal samples, and arsenic and uranium for water samples are higher than permitted levels, and are expected to cause health problems. These findings also support a potential leaching.

- The samples have low-concentrations of organic compounds, which generally belong to aliphatic hydrocarbons and their derivatives (alkanes and alcohols), methyls, phthalates, naphthalenes and benzenes. However, these compounds are not as toxic as those found in endemic samples and their concentration is also very low. Therefore, they are considered not to be a potential for BEN-disease.

- The samples resemble typical pattern of non-endemic regions. On the basis of the obtained evidences from this study, the area can be concluded as non-endemic region.

CHAPTER 8

FUTURE WORK AND RECOMMENDATIONS

- This study is the first BEN-study in the Manisa-Soma-Deniş region. Such studies are required. For instance; in other regions of Turkey, having low-quality lignite deposits, the organic compounds of these deposits should be studied. In this study, several locations were observed with low-quality lignite deposits. These are Adana-Tufanbeyli, Adıyaman-Gölbaşı, Ağrı-Eleşkirt, Bursa-Keleş-Harmanalan, Erzurum-Horasan-Aliçeyrek, Erzurum-İspir-Karahan, K.Maraş-Afşin-Elbistan, Konya-Seydişehir-Bayavşar, Sivas-Kangal-Kalburçayırı.

- The parameters not included in this study should also be determined for both Manisa-Soma-Deniş region and other locations in Turkey to understand whether any supporting factors exist or not. The required parameters to be studied are organic petrography and mineralogy for coal samples, inorganic parameters for water samples (e.g. nitrate, nitrite, and ammonium concentrations). These parameters can be involved in a study to evaluate for the existence of any possible link to BEN-disease.

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APPENDIX A. INORGANIC PARAMETERS OF THE COAL SAMPLES FROM THE MANISA-SOMA-DENIS REGION

ELEMENT	UNIT	C01	C02	C04	C05
SiO2	%	1,18	1,61	0,04	9,83
Al2O3	%	0,61	0,96	0,04	5,78
Fe2O3	%	0,14	0,39	0,79	0,77
MgO	%	0,07	0,08	0,02	0,46
CaO	%	2,38	2,05	0,78	1,81
Na2O	%	0,01	0,01	0,01	0,06
K2O	%	0,04	0,05	0,04	0,28
TiO2	%	0,02	0,03	0,01	0,21
P2O5	%	0,03	0,01	0,01	0,04
MnO	%	0,01	0,01	0,01	0,01
Cr2O3	%	0,001	0,002	0,001	0,006
Ag	ppm	<0,1	<0,1	<0,1	<0,1
As	ppm	12,7	11,4	150,9	1,7
Au	ppb	<0,5	1	0,6	6
Ba	ppm	101,7	712,5	27,3	116,1
Be	ppm	<1	<1	<1	2
Bi	ppm	0,1	0,1	<0,1	0,2
Cd	ppm	0,4	0,3	0,4	4,2
Ce	ppm	3,3	2,7	1,4	26,1
Co	ppm	<0,5	0,9	0,9	6,3
Cs	ppm	1,2	2,6	<0,1	4,5
Cu	ppm	35,8	34,4	47,9	45,5

ELEMENT	UNIT	C01	C02	C04	C05
Dy	ppm	0,26	0,26	0,16	2,48
Er	ppm	0,23	0,13	0,14	1,99
Eu	ppm	0,08	0,14	<0,05	0,59
Ga	ppm	0,8	1,2	<0,5	7,1
Gd	ppm	0,51	0,31	0,25	2,56
Hf	ppm	<0,5	<0,5	<0,5	3,3
Hg	ppm	0,04	0,06	0,46	0,19
Ho	ppm	0,09	<0,05	<0,05	0,56
La	ppm	2,6	1,7	0,7	14,8
Lu	ppm	0,03	0,03	0,02	0,29
Mo	ppm	0,9	0,6	0,3	1,3
Nb	ppm	0,9	0,8	2,7	6,2
Nd	ppm	1,5	0,9	0,6	12,1
Ni	ppm	5	5	6	28
Pb	ppm	16,9	7,4	10,5	31,1
Pr	ppm	0,42	0,33	0,13	3,12
Rb	ppm	1,6	4,1	<0,5	18,3
Sb	ppm	0,2	0,2	0,1	0,3
Sc	ppm	1	1	1	6
Se	ppm	0,5	0,6	6,7	1,3
Sm	ppm	0,4	0,2	0,1	2,6
Sn	ppm	1	<1	<1	<1
Sr	ppm	24,6	37,4	9,4	43,2
Ta	ppm	<0,1	0,1	<0,1	0,4
Tb	ppm	0,05	0,03	0,01	0,45
Th	ppm	0,6	0,7	0,2	7,1
Tl	ppm	<0,1	0,1	2,2	0,1
Tm	ppm	<0,05	<0,05	<0,05	0,25

ELEMENT	UNIT	C01	C02	C04	C05
U	ppm	15,3	11,1	0,9	21,6
V	ppm	41	81	22	434
W	ppm	0,4	0,4	1,6	1,9
Y	ppm	3,1	1,9	1,3	20,8
Yb	ppm	0,25	0,16	0,08	1,7
Zn	ppm	30	15	35	65
Zr	ppm	5,2	6,9	6,8	123,6

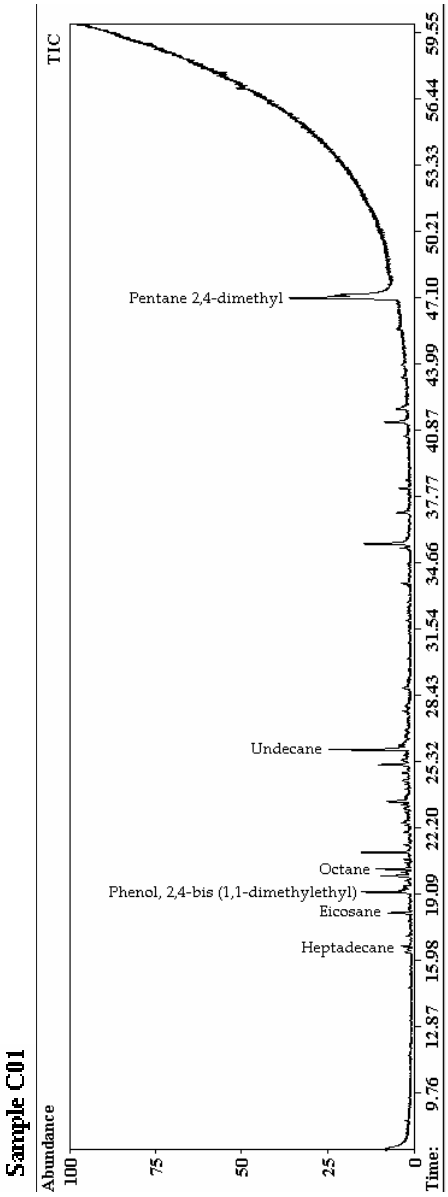
APPENDIX B. INORGANIC PARAMETERS OF THE WATER SAMPLES FROM THE MANISA-SOMA-DENIS REGION

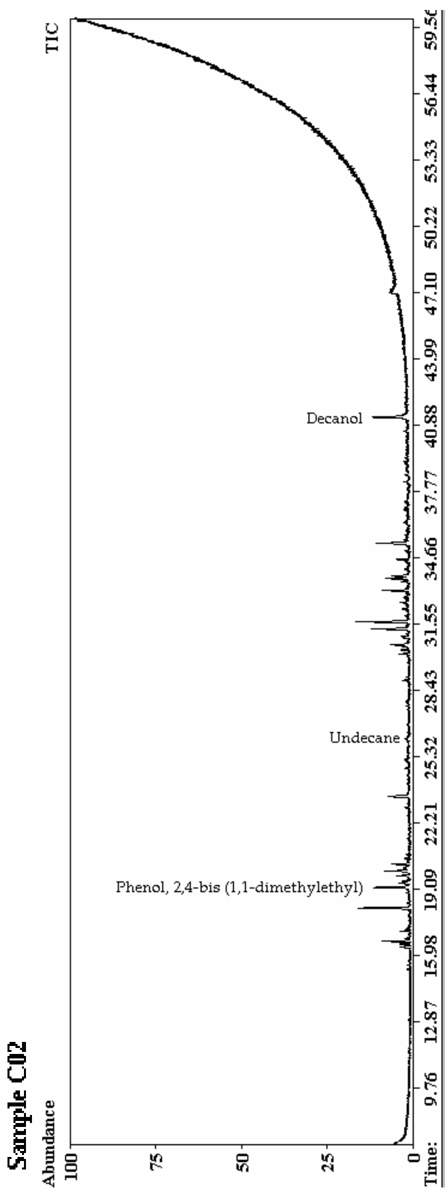
ELEMENT	UNIT	WO-1	WO-2	WO-3	WO-4
Ag	ppb	<0,05	<0,05	<0,5	<0,05
Al	ppb	<1	81	<10	<1
As	ppb	604,9	7,3	11,9	7,2
Au	ppb	0,14	0,09	<0,5	0,07
B	ppb	305	69	1205	267
Ba	ppb	33,8	66,75	13,13	91,07
Be	ppb	<0,05	<0,05	<0,5	<0,05
Bi	ppb	<0,05	<0,05	<0,5	<0,05
Br	ppb	94	31	116	70
Ca	ppb	165289	39278	616916	188499
Cd	ppb	<0,05	<0,05	<0,5	<0,05
Ce	ppb	<0,01	0,03	<0,1	<0,01
Cl	ppm	43	6	21	14
Co	ppb	0,03	0,02	<0,2	0,03
Cr	ppb	9,7	3,8	11,5	6,3
Cs	ppb	3,22	0,7	8,09	1,59
Cu	ppb	2,3	0,3	8,4	2,3
Dy	ppb	<0,01	<0,01	<0,1	<0,01
Er	ppb	<0,01	<0,01	<0,1	<0,01
Eu	ppb	<0,01	<0,01	<0,1	<0,01
Fe	ppb	<10	35	<100	<10
Ga	ppb	<0,05	<0,05	<0,5	<0,05

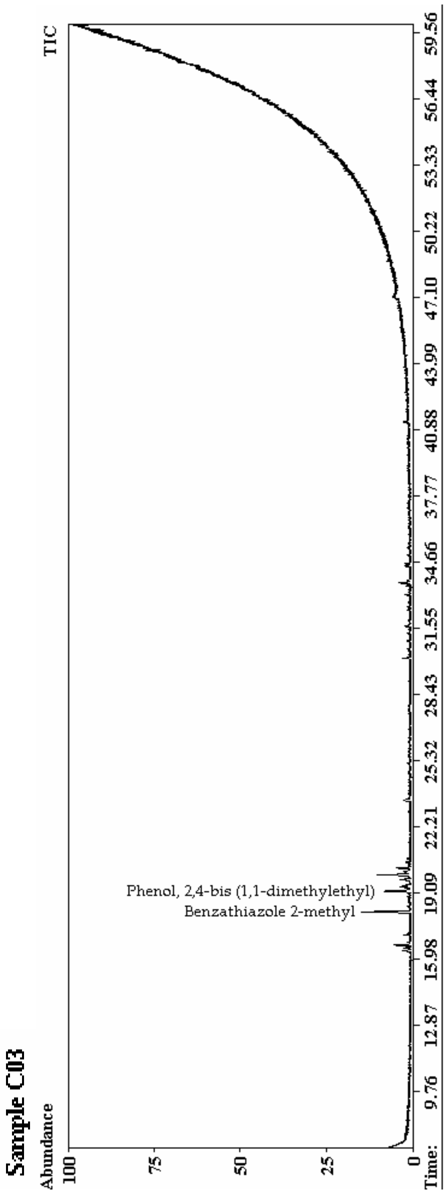
ELEMENT	UNIT	WO-1	WO-2	WO-3	WO-4
Gd	ppb	<0,01	<0,01	<0,1	<0,01
Ge	ppb	0,1	0,12	<0,5	0,29
Hf	ppb	<0,02	<0,02	<0,2	<0,02
Hg	ppb	0,1	0,1	<1	<0,1
Ho	ppb	<0,01	<0,01	<0,1	<0,01
In	ppb	<0,01	<0,01	<0,1	<0,01
Ir	ppb	<0,05	<0,05	<0,5	<0,05
La	ppb	<0,01	0,04	<0,1	<0,01
Li	ppb	59,1	8,2	231,6	50,6
Lu	ppb	<0,01	<0,01	<0,1	<0,01
Mg	ppb	65428	7478	141619	35858
Mn	ppb	0,1	0,16	<0,5	<0,05
Mo	ppb	19,9	0,6	1,6	0,9
Na	ppb	21846	5226	28654	11313
Nb	ppb	0,05	0,01	<0,1	0,03
Nd	ppb	<0,01	0,01	<0,1	<0,01
Ni	ppb	0,2	<0,2	5,5	0,2
Os	ppb	<0,05	<0,05	<0,5	<0,05
P	ppb	<20	<20	<200	<20
Pb	ppb	<0,1	0,1	<1	<0,1
Pd	ppb	<0,2	<0,2	<2	<0,2
Pr	ppb	<0,01	<0,01	<0,1	<0,01
Pt	ppb	<0,01	<0,01	<0,1	<0,01
Rb	ppb	24,97	1,55	29,01	5,02
Re	ppb	0,14	<0,01	0,9	0,26
Rh	ppb	<0,01	<0,01	<0,1	<0,01
Ru	ppb	<0,05	<0,05	<0,5	<0,05
S	ppm	121	15	688	143
Sb	ppb	3,46	0,06	<0,5	0,07

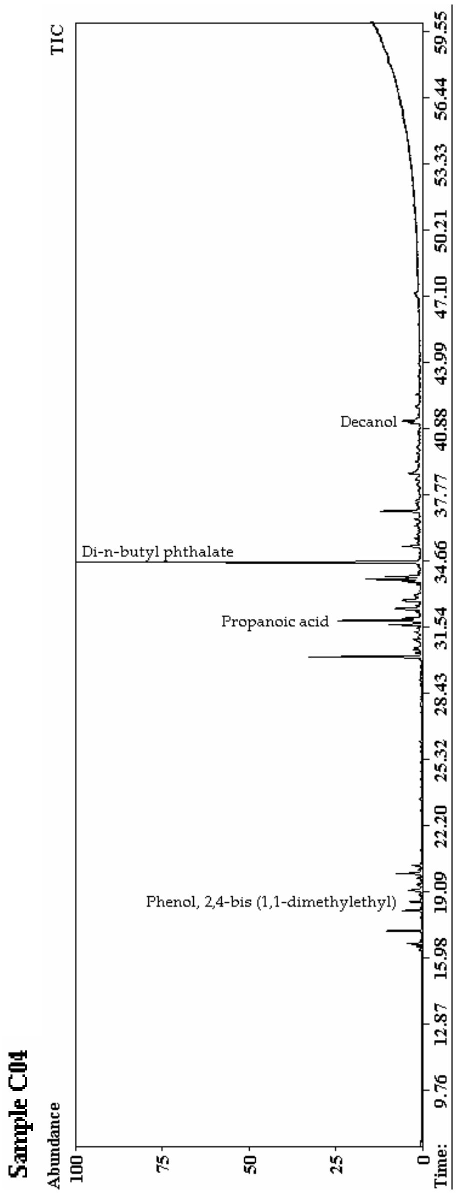
ELEMENT	UNIT	WO-1	WO-2	WO-3	WO-4
Sc	ppb	<1	<1	<10	<1
Se	ppb	3	0,8	6,2	1,8
Si	ppb	29558	5337	11544	11457
Sm	ppb	<0,02	<0,02	<0,2	<0,02
Sn	ppb	<0,05	<0,05	<0,5	<0,05
Sr	ppb	1132,45	135,83	2355,56	458,32
Tb	ppb	<0,01	<0,01	<0,1	<0,01
Te	ppb	<0,05	<0,05	<0,5	<0,05
Th	ppb	<0,05	<0,05	<0,5	<0,05
Ti	ppb	12	<10	<100	<10
Tl	ppb	0,06	<0,01	0,45	0,01
Tm	ppb	<0,01	<0,01	<0,1	<0,01
U	ppb	18,64	1,01	40,69	8,97
V	ppb	2,2	1,1	<2	0,6
W	ppb	0,06	<0,02	<0,2	0,02
Y	ppb	<0,01	<0,01	<0,1	<0,01
Yb	ppb	<0,01	<0,01	<0,1	<0,01
Zn	ppb	1,1	<0,5	6,6	2,3
Zr	ppb	<0,02	0,07	<0,2	<0,02

APPENDIX C. ORGANIC PARAMETERS OF THE COAL SAMPLES FROM THE MANISA-SOMA-DENİS REGION

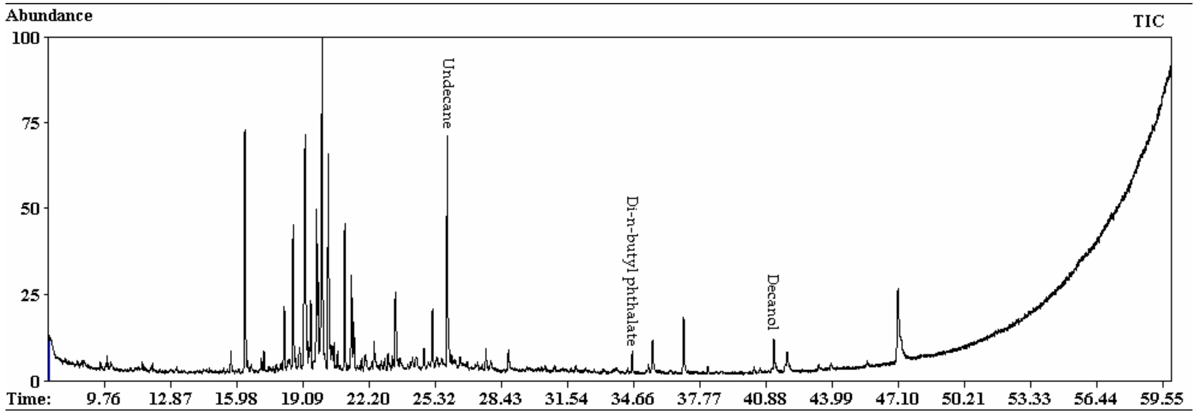




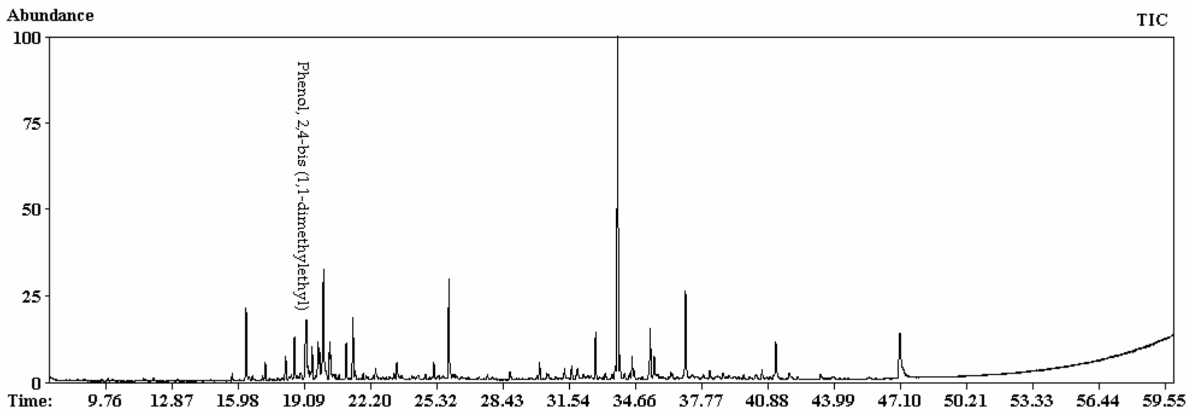

Sample C03
Abundance
TIC
Time:
Phenol, 2,4-bis (1,1-dimethylethyl)
Benzathiazole 2-methyl

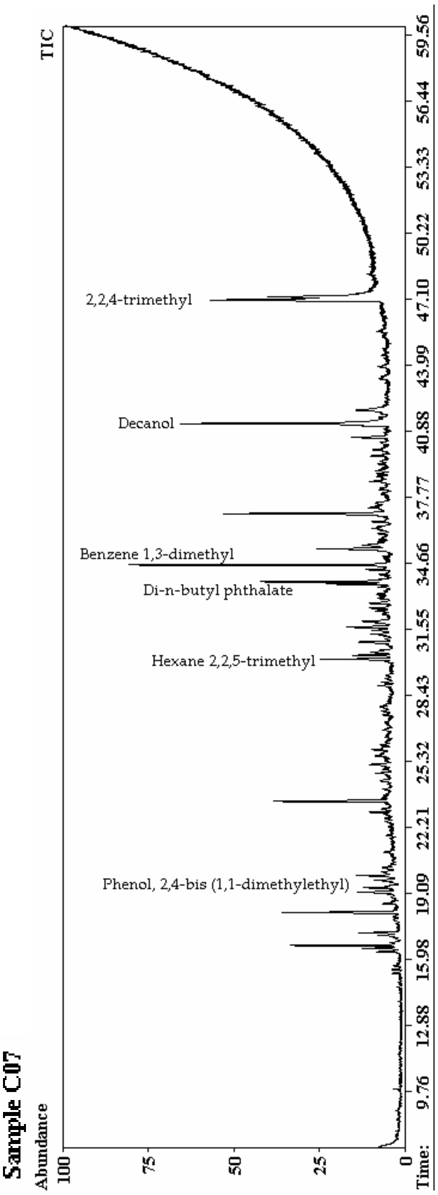

Sample C04
Abundance
TIC
Time:
Di-n-butyl phthalate
Propanoic acid
Decanol
Phenol, 2,4-bis (1,1-dimethylethyl)

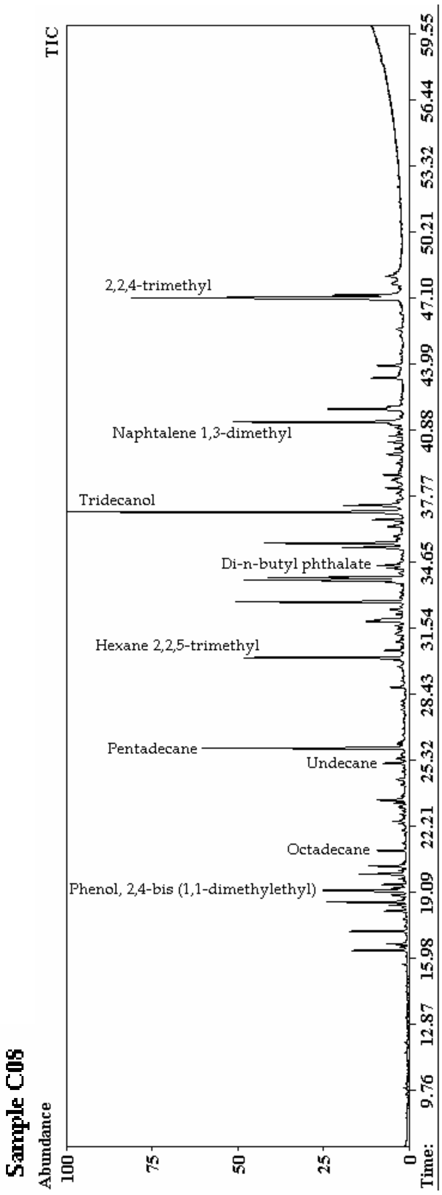
Sample C05



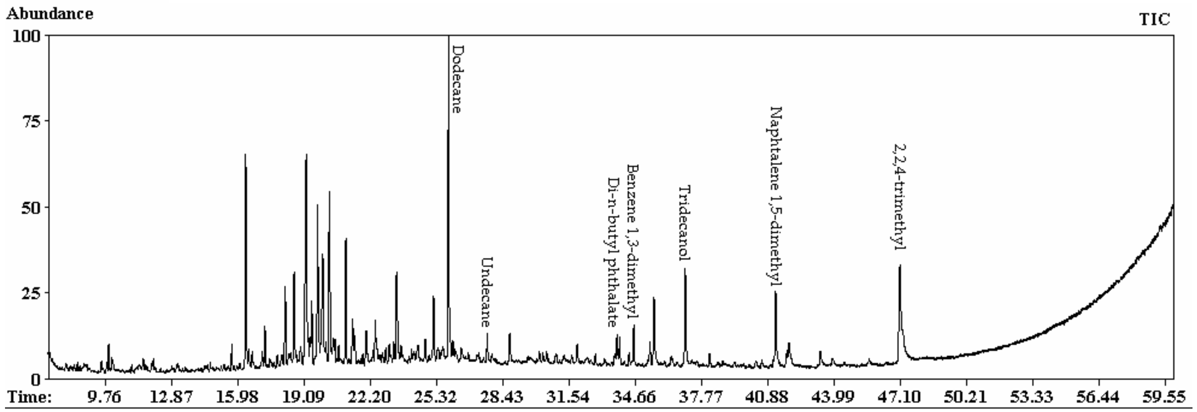
Sample C06



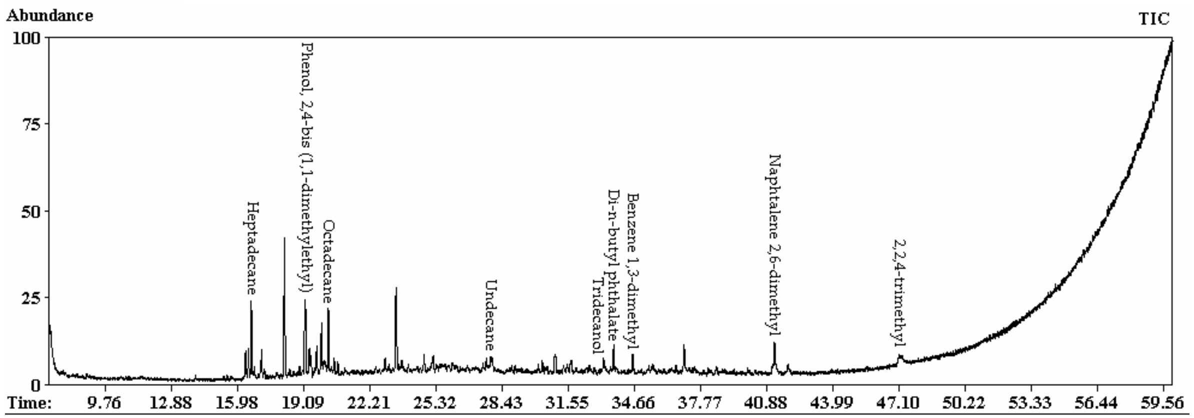

Sample C07
Abundance
TIC
100
75
50
25
0
Time:
9.76
12.88
15.98
19.09
22.21
25.32
28.43
31.55
34.66
37.77
40.88
43.99
47.10
50.22
53.33
56.44
59.56
Phenol, 2,4-bis (1,1-dimethylethyl)
Hexane 2,2,5-trimethyl
Di-n-butyl phthalate
Benzene 1,3-dimethyl
Decanol
2,2,4-trimethyl


Sample C08
Abundance
TIC
100
75
50
25
0
Time:
9.76
12.87
15.98
19.09
22.21
25.32
28.43
31.54
34.65
37.77
40.88
43.99
47.10
50.21
53.32
56.44
59.55
Phenol, 2,4-bis (1,1-dimethylethyl)
Octadecane
Undecane
Pentadecane
Hexane 2,2,5-trimethyl
Di-n-butyl phthalate
Tridecanol
Naphtalene 1,3-dimethyl
2,2,4-trimethyl

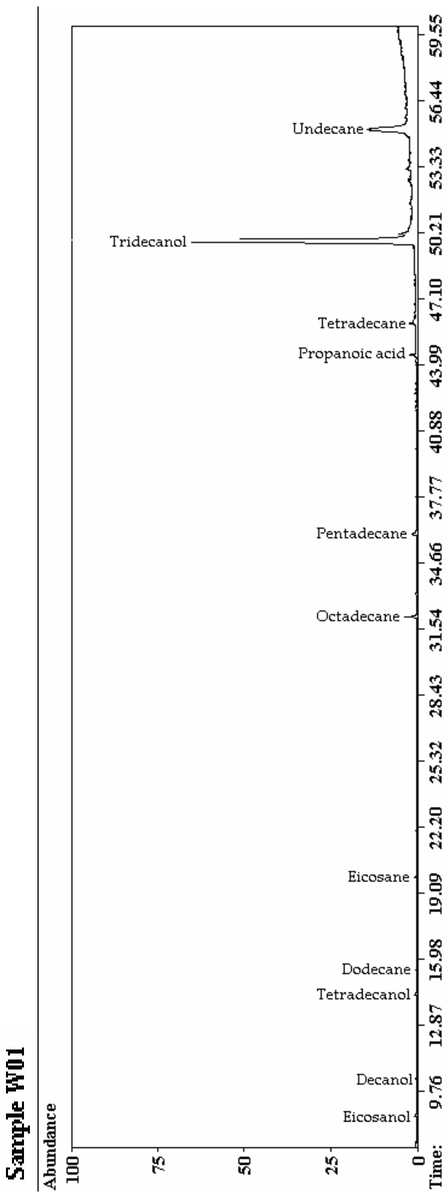
Sample C09

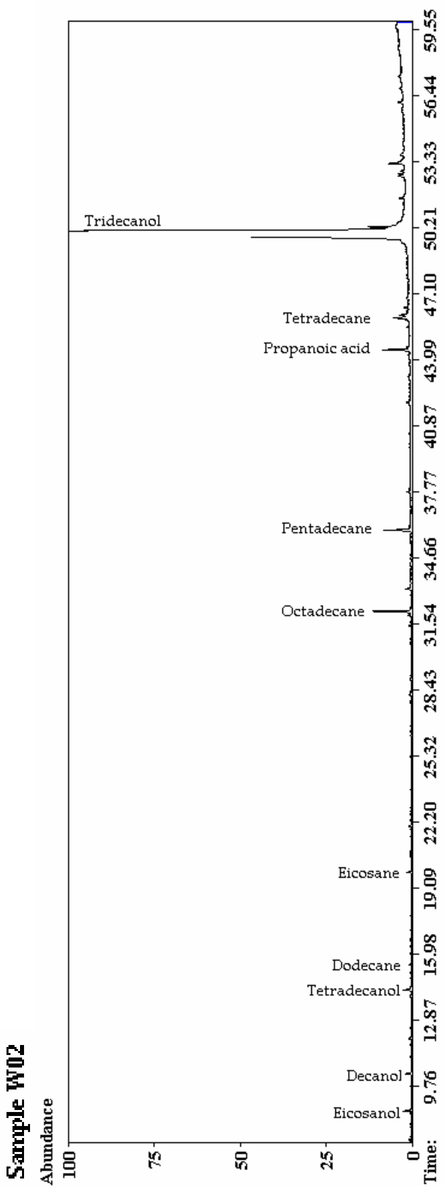


Sample C10

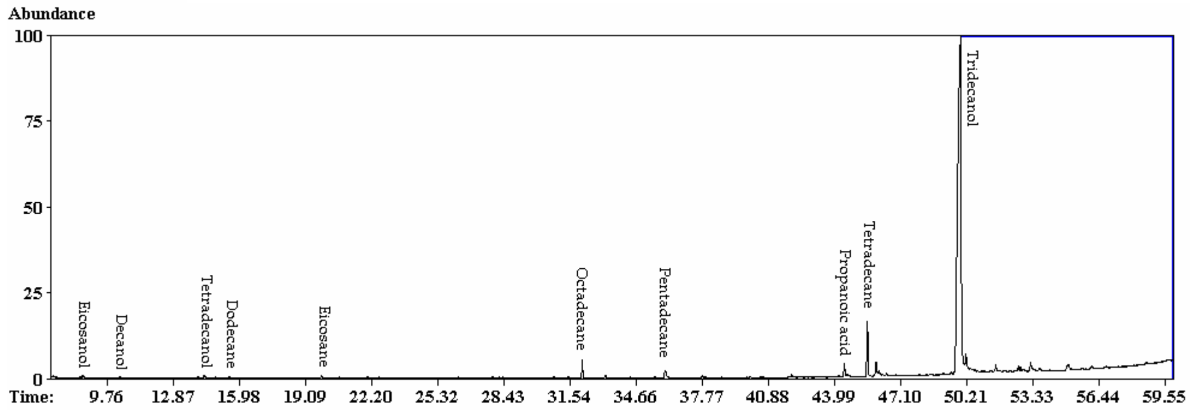


APPENDIX D. ORGANIC PARAMETERS OF THE WATER SAMPLES FROM THE MANISA-SOMA-DENİŞ REGION





Sample W03



Sample W04