Toxic gas emissions from the Kayseri peat deposit, central Anatolia, Turkey

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Toxic gases evolving from the soil in urbanized peatland regions constitute a serious hazard since buildings may be subject to the direct ingress of volatiles into the structures. Peat formed in swamp and rarely exposed to subaerial conditions has been associated with the development of the folded foreland of the Quaternary Kayseri pull-apart basin. The peat deposit is extensively urbanized but so far no studies have evaluated the extent of the ground gas hazard. In this paper, the geology, petrography and chemical variation of the Kayseri peat deposit have been studied in order to predict the public health risk from the land gases' behaviour, especially in soil gases. The main volatile species detected are methane (CH_4), hydrogen sulphide (H_2S) and carbon dioxide (CO_2), all of which are highly toxic. The primary means of gas entry is directly from the ground through the floors, walls, and especially subsurface telephone cable pipes. Indoor vents emit 1000–70,000 ppm CH_4, 330–49,000 ppm CO_2 and 3.8–6.5 ppm H_2S in soil and subsurface pipes; concentrations high enough to present an acute respiratory hazard to persons close to the vents.

1. Introduction

During the Neogene to Quaternary period, several lacustrine basins and peatlands developed in Turkey. The Neogene basins and Quaternary peatlands were filled with clayey, carbonaceous and sandy sediments, and also with explosive products of contemporaneous K-rich calc-alkaline volcanism with various degrees of crustal contamination (Yılmaz 1989; Güleç 1991; İnci 1991; Gündogdu *et al.* 1996). These basins are generally characterized by volcanic-sedimentary successions. Places including the study area are characterized by important fossil fuel and industrial mineral resources such as lignite, oil shale, peat, clays, borates and zeolites (Şener *et al.* 1995; Gündogdu *et al.* 1996; Şener and Gündoğdu 1996; Şener 2007).

The study area is located in the Kayseri pull-apart basin during the Quaternary, central Anatolia (figure 1). Kayseri peatland is a large (45 km^2), low gradient, and pull-apart Kayseri Basin in central Anatolia.

A large part of the studied Quaternary basin is covered by Quaternary peatland and/or peat deposit. Peat is an accumulation of partially decayed vegetation matter. Peat forms in wetlands or peatlands, variously called bogs, moors, muskegs, mires, tropical swamp forests and fens. During and after deposition in peatlands, plant remains undergo a sequence of physical, biochemical and chemical changes (diagenesis and catagenesis), which results in a series of coals of increasing rank. The series begin with practically unaltered plant material and peat (Stach *et al.* 1982).

Keywords. Peat; soil gases; indoor gases; Kayseri; Turkey; methane; mineral matter; public health.

The coalification process in the burial diagenesis of plant materials is the main origin of biogenic methane gas. In this process, the first volatile products liberated in both coal and kerogen at temperatures below 100°C are mainly H_2O and CO_2 with small amounts of CH_4 (Tissot and Welte 1984). Methane gas is odourless and highly explosive when mixed with air at a volume between 5% and 15% (50.000–150.000 ppm), which are the lower and upper explosive limits of methane, respectively. The accumulation of methane gas in structures (e.g., basements, crawl spaces, utility ducts) can result in explosions and fires. Methane gas migrating underground (soil gas) can damage
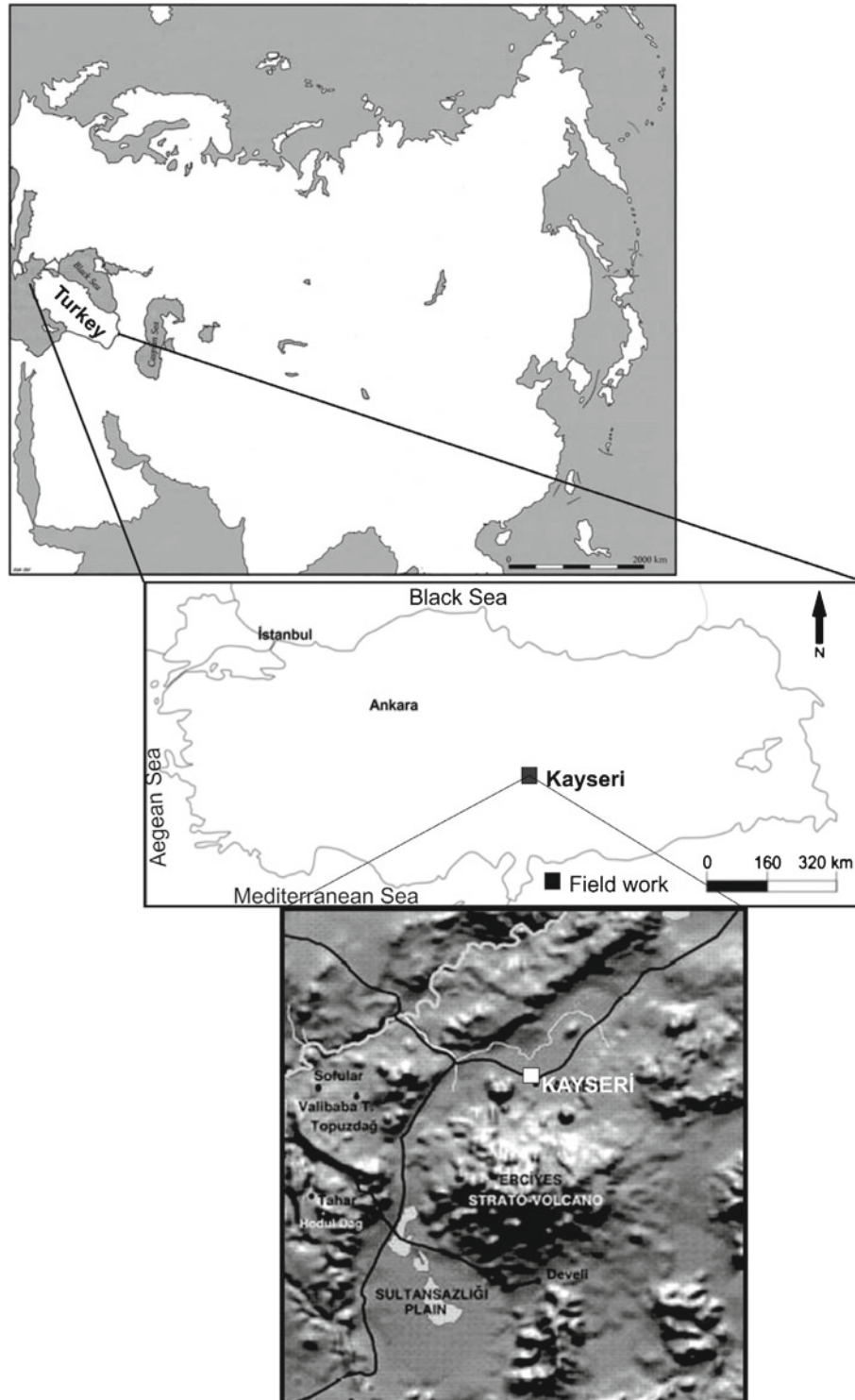

Figure 1. Location map of the study area.

or kill vegetation in surrounding areas since it displaces oxygen and effectively suffocates plant roots (Şener and Uluşahin 2006). CO_2, water vapour and organic volatiles are produced from organic materials when they are buried and decomposed, all of them can accumulate in the soil. Gasoline, diesel oil and fuel oil are very important origins of petroleum gases in soil. These hydrocarbons can be formed as soil by means of infiltration, spilling or being transported. Benzene, toluene, etilbenzene and Xenon are well known petroleum gases and very dangerous for human health because of their combustible and explosive features (table 1). Although carbon dioxide is generated by the biodegradation of all types of organic materials and must be used with caution in soil gas investigations, the presence of a concentrated petroleum source such as gasoline, diesel, kerosene, etc., causes a concentrated build-up of carbon dioxide in the subsurface. The average concentration of carbon dioxide in ambient air is only 0.03%. The biodegradation of typical soil organic matter generally yields carbon dioxide concentrations between 0.2 and 3–5%. Higher concentrations of carbon dioxide measured in various soil vapour samples, collected in the vicinity of subsurface petroleum contamination yield values as high as 5 to 30%, an indication that biodegradation is significantly enhanced within the area of the contaminant plume. Ambient air methane ranges from 1.5 to 2 ppm by volume. The methane concentrations generally range from 0.5 to 1 ppm in areas where there is no pollution or deep gas migration, suggesting that normal soil act as a sink for atmospheric methane. Since the biogenic methane is generated under anaerobic conditions, it is usually generated deeper in subsurface sediments than carbon dioxide and appears to correlate

mainly with the location of free (liquid) product. As with the carbon dioxide, the longer the pollution is present in the subsurface environment, the higher the methane soil gas levels (Knapp *et al.* 1998).

The peat-bearing formation is situated approximately 5 km south of Kayseri. This formation is understood to have been deposited on the Erciyes basalts under stable lacustrine conditions. The area has been studied with respect to geological, stratigraphical and volcanological characteristics (Tchihatcheff 1853; Blumenthal 1938; Yalçınlar 1959; Ketin 1963; Pasquare 1968; Türkecan *et al.* 2003; Dirik 2001; Gönenç *et al.* 2006).

In the present study, we have carried out detailed geological, petrographical and geochemical studies on a large number of samples from all the peat seams and soil gases. The main objective of this study is to focus on the geology, petrography and chemical variation of Kayseri peat deposit in central Anatolia and other rocks formed on the Erciyes volcanics under stable lacustrine conditions. In addition, it has been aimed to predict the risks of their peatland gases' behaviour to public health especially in soil gases. Air in the pores of soil is named as soil gases. Although the origin of these gases is the atmosphere, composition of soil gases is different from atmospheric air. Soil organisms use oxygen and produce carbon dioxide, therefore O_2 content of soil decreases as CO_2 content increases (Lindsay 1979; Knapp *et al.* 1998). Decomposed organic matter has also the same effect on soil gases (Klusman 2002). Well known soil gases are radon, vapour of petroleum hydrocarbons, gases produced from aerobic or aneorobic decomposition of organic compounds, and water vapour. Radon is a radioactive gas and it is rare to find in the soil. Especially in Turkey, the origin of radon in the soil is volcanic in the geothermal regions of the western part of Anatolia. When conducting soil gas surveys and subsequently mapping the subsurface pollution, it is very important to note and measure biogenic gases. Bacteria that attack hydrocarbons generate carbon dioxide under aerobic conditions and methane under anaerobic conditions. Not only the bacterial activities occur, but also percentage levels of carbon dioxide and methane are often generated. These biogenic gases are often the largest magnitude components in the entire soil gas mixture. In general, the longer the pollution is present in the subsurface environment, the higher these biogenic gas levels (both carbon dioxide and methane) can be field screened (measured) with reasonable accuracy in the field using infrared detectors. Soil gases in home pose both safety and health risks. These gases are often highly volatile and when mixed with air, can become flammable or explosive. The chemical compositions of soil gases are the risks that can threaten human health. The health risk potential of

Table 1. *Composition of the soil atmosphere (Bremner and Blackmer 1982).*

Component	Percent
Nitrogen (N_2)	78.09
Oxygen (O_2)	20.94
Argon (Ar)	0.93
Carbon dioxide (CO_2)	0.0332
Neon (Ne)	0.0018
Helium (He)	0.00052
Methane (CH_4)	0.00015
Krypton (Kr)	0.0001
Hydrogen (H)	0.00005
Nitrous oxide (N_2O)	0.000033
Carbon monoxide (CO)	0.00001
Xenon (Xe)	0.000008
Ozone (O_3)	0.000002
Ammonia (NH_3)	0.000001
Nitrogen dioxide (NO_2)	0.0000001

soil gases is determined by chemical composition, concentration and duration of exposure.

2. Geological setting

2.1 *Basement units*

Basement units are represented by Paleozoic aged Kırşehir massive metamorphics. They generally occurred in green schist facies under low–medium grade pressure and high temperature conditions.

They consist of schist, marble and quartzite rocks (Göncüoğlu 1986).

2.2 *Tertiary units*

These units overlie Kırşehir massive metamorphic rocks unconformably and start with a red brown coloured tuff flow including basalt and andesite gravels and blocks. This massive unit (Kırşehir massive metamorphic rocks) contains extensive andesite and basalt lavas and underlied by andesite
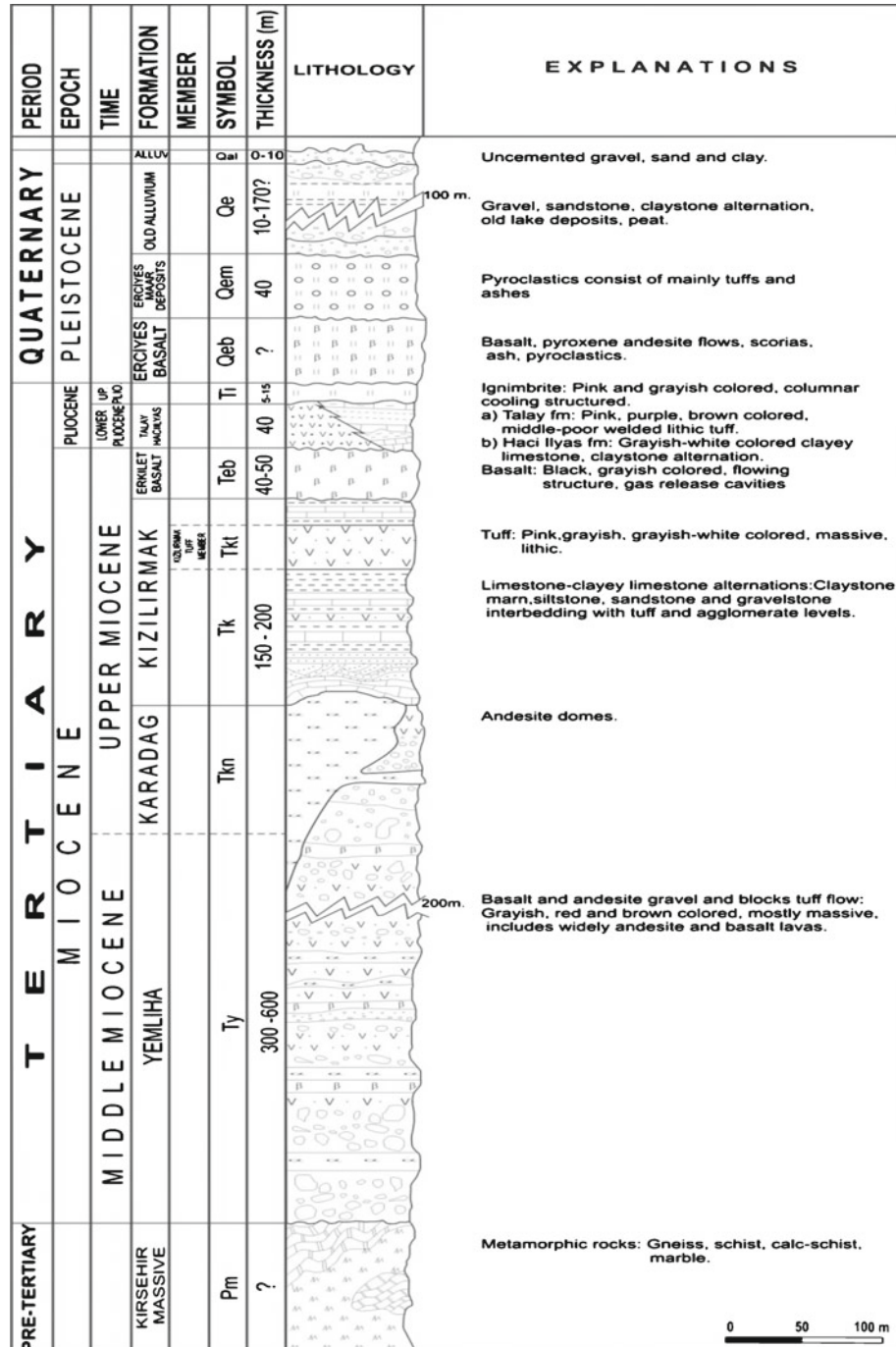

Figure 2. General stratigraphic column section.

Figure 3. Geological map of the study area (modified from Gönenç *et al.* 2006).

Figure 4. Kayseri peat deposit.

doms. A sedimentary sequence consisting of limestone, clayey limestone intercalations overlines the dom sequence consisting of andesite and dacite. This unit also contains claystone, marl, siltstone, sandstone and gravelstone levels, tuff and agglomerate and is named as a Kızılırmak formation in the study area. At the upper levels of the same formation, there is Kızılırmak tuff member described as a different member by Türkecan *et al.* (2003). Miocene series continuing with the carbonate deposition is ended by black, grey coloured Erkilet basalt having flow structure and gas release (figures 2 and 3).

Pliocene begins with pink, purple and brown coloured, medium–low welded lithic tuffs that have horizontal and vertical transitions with sedimentary rocks deposited as greyish white coloured clayey limestone and claystone intercalations and ends with pinkish grey coloured, columnar cooling structured ignimbrites. In the Quaternary, when the Erciyes volcanism was dominant, Pleistocene began with Erciyes basalt that consisted of basalt, pyroxene-andesite flows, cinder cones, ashes and pyroclastics. The sequence continued with Erciyes maar deposits consisting of pyroclastics including tuffs and ashes. At the upper levels, the old alluvium was transitional with the gravelstone, sandstone, claystone intercalated swamp deposits having peat and lignite deposits in some places.

Table 2. *General features of Kayseri peat samples.*

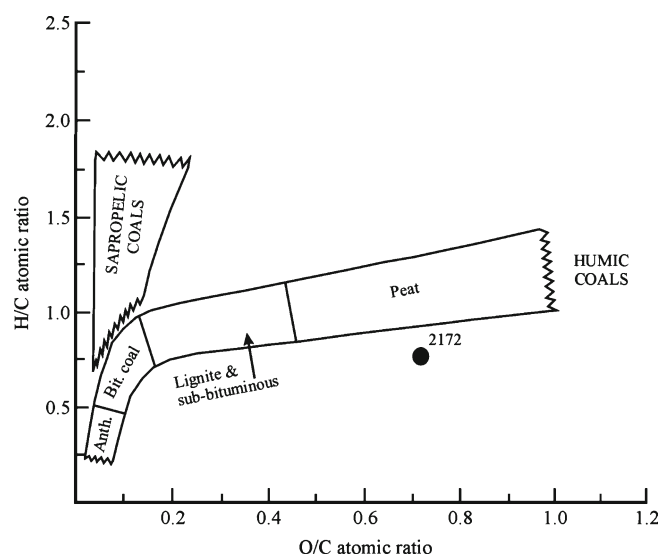| Properties	Value
Calorific value (kcal/kg)	1453–2785
Ash content (%)	25–45
Volatile matter (%)	46–58
C (daf %)	49.1–75.34
H (daf %)	3.14–7.92
N (daf %)	1.43–3.84
S (daf %)	0–1.08
O (daf %)	13.9–46.33
H/C	0.77–1.6
O/C	0.5–0.71
Minerals	Aragonite, Calcite, Labradorite (major), Kaolinite, Mixed clay layers, Carnallite, Dolomite, Quartz (minor) Amorphous Silica, Apatite, Chlorite (traces)
Thickness (m)	16–35
Reserve (ton)	104,926,000

Figure 5. Kayseri peat samples on the van Krevelen diagram (Şengüler *et al.* 2007).

Table 3. *Trace element concentrations of peat samples (mg/kg) determined using ICP-MS (ND: not detected) (Şengüler et al. 2007).*

Element	mg/kg	Element	mg/kg
As	100	Nd	1.5
B	51	Ni	15
Ba	133	Pb	1
Cd	0.1	Pd	0.6
Ce	3.5	Pr	0.4
Co	1.5	Rb	7
Cr	8.5	Sb	1
Cu	10	Sc	39
Dy	0.3	Sm	0.4
Er	0.2	Sn	0.4
Eu	0.1	Sr	135
Ga	8	Ta	ND
Gd	0.4	Tb	ND
Ge	0.4	Th	0.6
Hf	0.2	Ti	221
Hg	0.4	Tl	0.2
Ho	0.1	U	14
Ir	0.1	V	209
La	2	W	4
Li	6	Y	2
Lu	ND	Yb	0.2
Mn	30	Zn	115
Mo	41	Zr	8
Nb	1		

Ambar village, Karasazlık location on the west side of the Kayseri, has a character of a pull-apart basin full of Plio-Quaternary aged lake sediments. In the basin, there are 16–25 m thick peat deposits in the 200 m thick sedimentary unit. In the decomposition conditions during peat deposition, the early diagenetic methane (wet methane) gas occurred first.

3. Methods

Soil gas measurements have been made in total of 128 locations around Karasaz–Ambar village–Oymaağaç village. In 55 locations methane, in three locations H_2S, in six locations H_2 and in all locations CO_2 have been measured.

The determination of soil gases' composition has been done with an LMSxi gas analyser. The LMSxi G3 is a handheld portable instrument that allows the user to quickly and easily determine a number of environmental parameters often found on contaminated land and landfill sites, contaminated land monitoring, site investigation, compliance and regulatory monitoring, research work and composting applications. The unit can monitor methane, CO_2 and O_2 as standard with additional versions offering H_2S and CO, H_2S, SO_2, NH_3, H_2. Some of our inventory units also have the built in borehole gas pressure and flow reading as standard.

4. Results and discussion

The peat of Kayseri peatland has highly volatile matter, low calorific value and low ash content (figure 4, table 2). According to H/C and O/C atomic ratios, all samples are under the peat region in the Van Krevelen diagram (figure 5).

Trace element values of Kayseri are given in table 3. According to the background values of

Table 4. *Background values of trace elements in the Earth's crust, shale, limestone, soil; Finnish, Lithuania and Kayseri peats.*

Trace elements	Earth's crust	Shale (Levinson 1980)	Limestone	Soil	Finnish Peat (Bouska 1981)	Lithuan Peat	Kayseri Peat (Şengüler et al. 2007)
As	1.8	15	2.5	1.5			100
B	10	100	10	2–100			51
Ba	425	700	100	100–3000			133
Mo	1.5	3	1	2	0.5–5	0.63–0.76	41
Pd	0.004	–	–	–			0.6
Sb	0.2	1	–	5			1
Sc	16	15	5	–			39
Sr	375	300	500	50–1000			135
Tl	0.45	0.3	–	0.1			0.2
U	2.7	4	2	13			14
V	135	130	15	20–500	3–200	13–37.5	209
W	1.5	2	0.5	–	10–100		4
Zn	70	100	25	10–300		20–30	115

trace elements in the Earth's crust, shale, limestone, soil, Finnish, Lithuania and Kayseri peats, As, B, Mo, Pd, Sb, Sc, Tl, U, V, W and Zn values of investigated samples are higher than the others (table 4). In a reducing environment, such elements accumulate most frequently which hydrolyse better a lower valency (are less mobile) and are sorbed on highly dispersive substances at the opposite change. Among these elements, there are copper, molybdenum, uranium, vanadium and cobalt; in a reducing environment they can be reduced to metals and concentrated as such (Bouska 1981).

According to Bouska (1981), the rocks richer in bitumen components are usually richer in vanadium, molybdenum, C/org, and the elements B, Mn, Cu, Zn, Mo are considered to be important for higher plants.

The mineral composition of peat samples are aragonite, calcite, labradorite (major), carnallite, kaolinite, mixed clay layers, dolomite, quartz (minor), amorphous silica, apatite and chlorite
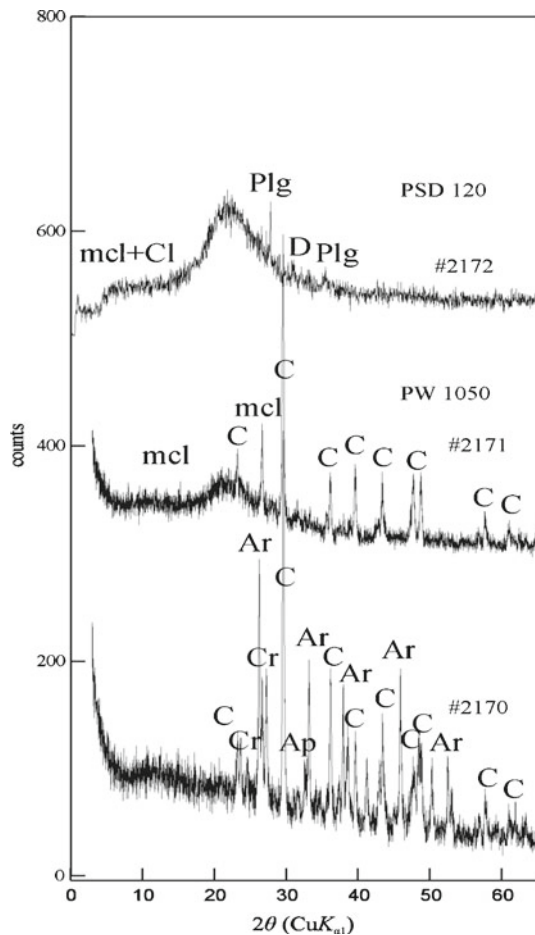

Figure 6. X-ray diffraction patterns of studied samples, obtained using a Philips PW1050 diffractometer and a PSD-120 Nonius Enrauf Position Sensitive Detector (Ap: apatite, Ar: aragonite, C: calcite, Cr: carnallite, cl: chlorite, D: dolomite, mcl: mixed clay-layers, Plg: plagioclase).

Table 5. *Hydrogeochemical features of groundwater of Kayseri peatland.*

Well no.	pH	$ECX10^6$ (25°C)	Cations (me/lt)				Anions (me/lt)					Sodium (%)	S.A.R	Category of water	Hardness Fs°	Ammonium	Organic matters	Consideration
			Na^+	K^+	$Ca^{++}+Mg^{++}$	Total	CO_3^-	HCO_3^-	Cl^-	SO_4^-	Total							
3179	7.2	680	2.8	≤0.25	2.45–1.75	7	0	4.04	1.4	1.56	7	40	1.98	C2S1	21	–	1.2	S
6117/A	7.6	1200	2.8	0.18	8.9	11.88	0	8.04	3.2	0.64	11.85	23.55	1.32	C3S1	44.5	+	4	
6117/B	7	1200	3.3	0.23	7.8	11.93	0	4.4	0.5	2.99	11.93	32.7	1.97	C3S1	39	+	1.9	
6117/C	7.1	630	2.05	0.2	4.35	6.6	0	0.4	4.4	1.8	6.6	31	1.38	C2S1	21.7	–	2.5	
6118	6.6	1200	3.9	0.25	8	12.14	0	7.14	0.4	4.6	2.14	32	1.95	C3S1	40	–	0.7	
6257	8.2	1500	6.2	0.16	8.5	14.86	0.44	6.48	5	2.94	14.86	41.7	3	C3S1	42.5	+	0.9	
7779/B	7.5	650	1.99	0.2	2.4	7.19	0	4.42	1.4	1.37	7.19	27.67	1.25	C2S1	25	–	5.2	
7780	6.6	2000	134.3	3.6	52.60–4.30	194.8	0	44.16	1.29	21.7	194.85	68.9	25.2	C5S4	284.5	–	2.6	
7782/A	6.8	3720	123.8	4.2	14.90–28.00	170.9	0	40.54	110	20.36	170.9	72.44	26.72	C5S4	214.5	+	2.5	
7782/B	6.8	4000	19	2	9.90–10.00	40.9	0	24.04	14.4	2.46	40.9	46.45	6.02	C4S2	99.5	–	1.6	
7783/A	6.2	900	4.1	0.44	2.90–2.50	9.94	0	6.76	1.16	2.02	9.94	41.24	2.49	C3S1	27	–	0.9	S
7783/B	6.7	710	2.15	0.26	3.00–2.50	7.91	0	5.46	1	1.45	7.91	27.18	1.29	C2S1	27.5	–	0.8	S
7784	7.1	880	2.8	0.2	3.00–3.50	9.7	0	6.34	2.84	0.52	2.7	28.86	1.52	C3S1	33.5	+	7.6	×

Figure 7. CH$_4$ distribution map of Kayseri peatland.

So far, 113 hydrogeologic wells were drilled for usage in the study area. Among these, the number of wells for research, operating, drilling water and observation purpose are 51, 50, 10 and 2, respectively. The characteristic features of underground water are determined by the well water sample and given in table 5. From this table, according to the USA Salinity Laboratory, the categories of water are C2S1, C3S1 and C5S4 in the peat deposite area. Peat accumulation in the Neogene aged lake environment is negatively affected by the groundwater quality.

Methane determined by in-situ measurements is early diagenetic methane and originated organically. Carbon dioxide is volcanically originated gas coming from deeper parts. While methane, carbon dioxide, hydrogen and oxygen gases are measured in the 1 m soil zone, H$_2$S gas can also be measured in the deep wells opened for different purposes in past years. Although the methane gas lacks in the soil gases in the literature, methane gas was determined in our measurements in the soil gases usually in all locations of our study area. Consequently, methane gas should be evaluated in both soil and toxic gases due to their suffocating and health-risk features, respectively. In the basin, the main faults that affect the basin formation are active faults that also affect Plio-Quaternary deposits and they formed water and gas exit holes in the field. Described as bottomless, methane gas cannot be measured in the area that peat outcrops, but in the covered areas methane gas formation directly proportional to the peat thickness still continues.

The peat of Kayseri peatland has high volatile matter, low calorific value and low ash content (table 2). Based on this information, point coordinate CH$_4$, CO$_2$, H$_2$ and O$_2$ values are given in table 3 (Şener and Uluşahin 2006), and CH$_4$,

(traces). Carbonate minerals of aragonite and calcite are major minerals in peat samples and were deposited much more commonly during the second stage of the coalification process. Labradorite, quartz and amorphous silica originated from volcanic rocks derived from Erciyes maar deposits. Evaporation is a very important process of Kayseri peatland because of carnellite (figure 6).

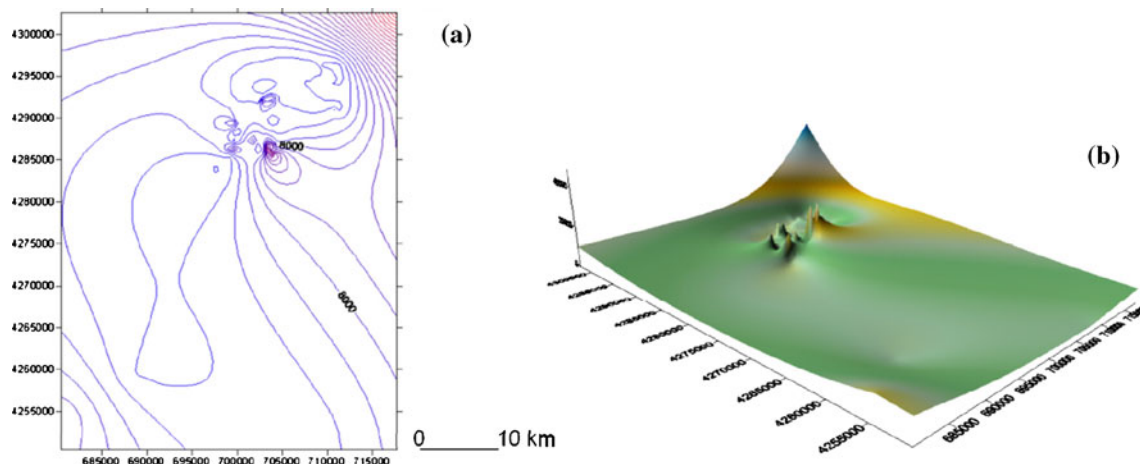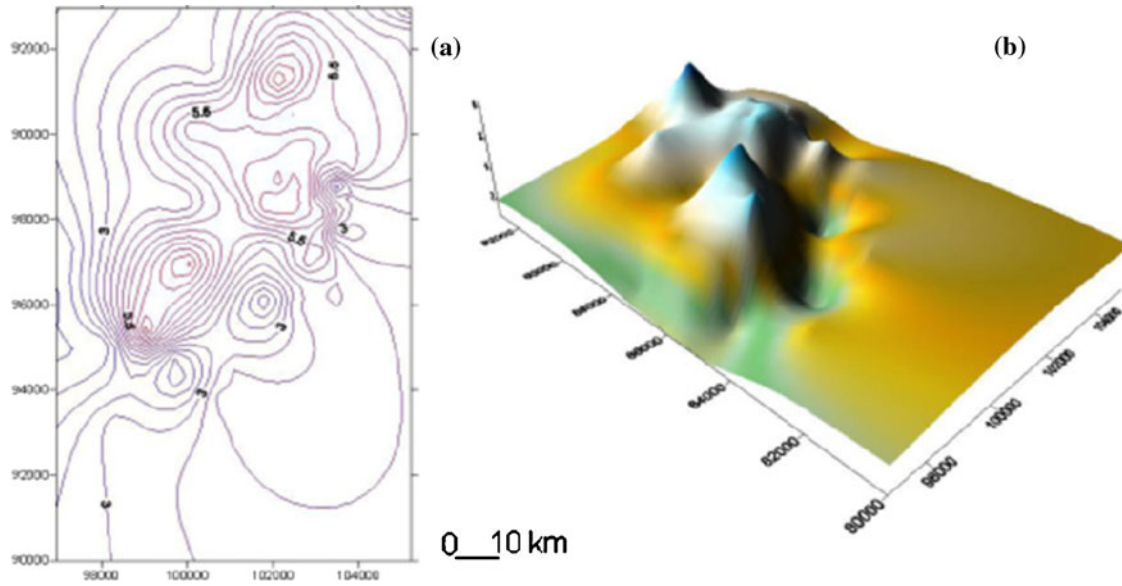Figure 8. CO$_2$ distribution map of Kayseri peatland.

Figure 9. Isothickness map of peat zone of Kayseri peatland.
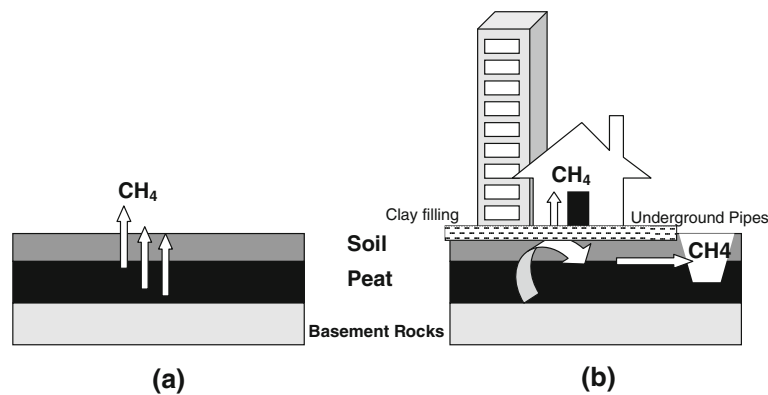

Figure 10. Without danger and dangerous conditions of soil gases on Kayseri peatland.

CO_2 anomaly maps and peat isothickness map are prepared (figures 7–9) from these results.

Based on these figures, we can say that the CH_4 map overlies the isothickness map. Methane gas depends on peatification and early diagenetic biogenic methane. Naturally, biogenic methane gas in the soil is not dangerous for public health (figure 10a). If the peatland is used as residential area, there are big risks for health and safety for the potential settlers (figure 10b).

5. Conclusion

After the construction of the organized industrial estates and free zone of Kayseri, soil gases turn into indoor gases because methane may migrate on-site and off-site areas surrounding the peatland, and there is a potential danger to the development

and activities associated with development as the methane may enter buildings through the sewage or the substructure corridors or other means. Trenching during construction activities associated with development also has the potential to expose workers to methane. The methane gas is explosive when the concentration in the air reaches a certain level. Peatland gas may also be a health hazard due to other by-product gases. As a result of the above concerns, the following Interim Guidelines for Development (Interim Guidelines) within the city designated peatland buffer zones (Buffer Zones) which are to be followed by all developments within the city's jurisdiction. These guidelines apply to all active or inactive designated peatland buffer zones of the city. Development projects will include inputs from a professional engineer, with expertise in peatland and peatland gas issues, to determine if peatland gas (including

but not limited to methane) exists on the property in question and whether there is a potential for the migration of peatland gas to impact on the property or other properties in the future. If peatland gas is present at the property in question or there is a potential for the property to be impacted in the future, the plans must include risk abatement measures, which are suitable to address any existing and/or future risk related to peatland gas.

While such isolated cases as the peatland in Kayseri may be amenable to direct engineering solutions, for capturing the gasses and putting the methane to use as a fuel, we may not have such an easy solution ready for widespread methane outgassing from the warming of larger bodies of peat.

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