Chapter

Fossil Fuel Fires: A Forgotten Factor of Air Quality

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Abstract

Spontaneous fossil fuel fires, especially coal fires, are known worldwide. They occur in numerous sites, both completely natural (coal seam outcrops) and anthropogenic (burning mining waste heaps, or BMWHs). Coal and waste/barren rock fires produce gaseous emanations, acting within exhalative processes. This factor is rarely being considered as influencing quality of the atmospheric air. The paper shortly discusses most important available methods for field gas analysis, with an emphasis on a portable FTIR spectrometer. It summarizes results of gas analyses from Polish BMWHs, using a multi-tool approach. It also lists a number of additional analyses from 53 vents of these environmentally important objects, with the main purpose of enlarging the knowledge of the span of concentrations of the particular compounds. This is especially true for formaldehyde, pyridine, CO, 1,1,1-trichloroethene, 1,1-dichloroethene, cumene, SO_2, and, to a lesser extent, NO_2, CCl_4, ethane, propane, ethene, and thiophene. The latter, and DMS, are confirmed as gaseous S source more frequent and rich than SO_2.

Keywords: natural spontaneous coal fires, combustion gas emissions, in situ FTIR gas analysis

1. Introduction – fossil fuel fires

Spontaneous fires of fossil fuels – mainly coals but also bituminous shales and oil shales – are known worldwide. They both concern natural environments and their anthropogenic analogues – burning mining waste heaps (BCWH). The CWHs are, more or less, permanent elements of the environment of coal basins. Although sometimes under reclamation, their recultivation procedures may also negatively influence the surroundings. The phenomena taking place in the BCWH are described, e.g., in Nasdala & Pekov [1], Cebulak et al. [2], Sokol et al., [3], Stracher [4], and papers of Ł.K. The later largely characterize complex products of gaseous emissions related to both coal and barren rock – mutually known as mining waste – burning. This chapter characterizes the composition of these emissions, by juxtaposing published concentrations and their related mean values with new data obtained for new BCWH-type object. As such, the chapter extends knowledge about the geochemical charge of the BCWH gaseous emissions and, as such, their potential atmospheric input.

2. Environmental gas emission measurement methods

Numerous methods of gas analysis in the environment exist. One of the most simple one, based on colorimetric chemical reactions, uses indicatory tubes (IT).

This method is based on colorimetric interaction of measured gaseous species with a chemical filler. In particular, Dräger tubes allow to detect and measure amounts of gases like O_2, CO_2, CO, NO_2, SO_2, NH_3, PH_3 (phosphine), acetic acid, acetone, propane, benzene, toluene, styrene, *o*-xylene, butadiene, total mercaptans (thiols), methanol, *i*-propanol, trichloroethene (TCE), vinyl chloride, methyl *tert*-butyl eter (MTBE), and others. However, the IT method brings large errors due to cross-sensitivity and numerous coincident reactions of the emanation-contained gaseous species, and humidity. Positive determinations for the BCWHs gases were thus single, and the following substances were observed (with semi-quantitative due to the above factors): H_2S (up to 1140 ppm), HCN (single determination (s.d.), 16 ppm), acetaldehyde (possibly up to 1150 ppm), diethyl ether (up to 1100 ppm), trimethylamine (and/or other amines; ca. 57 ppm), ethyl formate (s.d., <23 ppm), and I_2 (s.d., 1.7 ppm). Gas Chromatography (GC) is a method of choice for the analysis of environmental organics. A sample is put into specialized columns, where retention time of a particular molecule, related to its mass and charge (*m*/*z* parameter), is measured. However, it is relatively rarely used for gas analysis due to a need of a more sophisticated sample loader. This is overcame by a method of Colman et al. [5], where a sample sucked into a steel can and sent to laboratory (here: overseas) is reheated (to the temperature measured *in situ*), divided into aliquots with various pre-treatments including (1) passing heated aliquots over a glass for low-volatile compounds exerting and (2) water-immersion-driven revolatization, and (3) chromatographic separation. Analyses of such portioned sample using 3 detection methods: Mass Spectrometry (MS), Flame Ionization (FI), and Electron Capture (EC), both shown in Kruszewski et al. [6] and this chapter, proven to be problematic, as explained below.

The GC method is, however, useful in the environmental gas analyses if coupled with tools like Nitrogen-Phosphorus-Detector and cryo-focusing. A good example is a work of Wickenheiser et al. [7], who analyzed gases emitted from Italian wetland bogs. The compounds included PH_3, ethane, ethene, and NO_x. GC coupled with Inductively Coupled Plasma – Mass Spectroscopy (ICP-MS) allowed them to address heavy organo(semi/non)metallic gases like trimethylarsine (TMA), $(CH_3)_3As$, and trimethylstibine (TMS), $(CH_3)_3Sb$, and also metallic Hg, emitted from algal mats. The same method allowed to Feldmann et al. to detect (via cryo-trapping) trimethylbismuthine, $(CH_3)_3Bi$, as a common gas in municipal solid waste and sewage gas. Traces of tetramethyltin and TMS were also detected this way (*vide* [8]). Another method mentioned by the latter author is hydride generation. The use of tedlar bags, a gas trapping solution (with HNO_3 and H_2O_2), charcoal sorbent tubes, preconcentrators, and analysis with GC–MS and GC-PID (GC with photo-ionization detection) is also widely exploited, e.g., to measure TMA and propanethiol [9]. A method to be exploited by the author (Ł.K.) is a GC in conjunction with Atomic Emission Spectroscopy (AES). This two-step method involved very-low-detection-limit analysis, both qualitative and quantitative, of mainly (semi)metals in a gas sample, followed by analysis of their immediate surroundings for proposing types of organic and inorganic (semi)metal forms (R. Stasiuk, *pers. comm.*).

3. Mining waste heaps and products of their fires

A large number of coal mining waste heaps bear numerous spontaneous fire foci. In these burning coal-mining waste heaps (BCWHs), the fire incidents are due to criss-crossing influence of coal petrography (i.e., maceral composition), sulfide mineral content (especially pyrite), coal rank, and microbial activity. The fires

induce three types of mineral-forming phenomena: a high-temperature solid–solid and gas–solid transformation of the waste, known as pyrometamorphism (up to ~1200°C in the coal case; [3]); medium-temperature exhalative processes; and low-temperature supergene weathering processes ([6, 10–12], and references therein). Of the Air Quality interest is, of course, the second group of processes, involving both gas emission and gas-waste interface reactions. The latter include direct gas desublimation (condensation) and pneumatolysis-like gaseous extraction of various waste-contained metals followed by hydrothermal mineralization. The first process mainly produces minerals like native sulfur (S_8), salammoniac (NH_4Cl), and a number of less frequent species like kremersite, $(NH_4,K)_2[FeCl_5(H_2O)]$ and other chlorides. The second one is responsible for vast, thick sulfate crusts mainly comprising godovikovite-sabieite solid solution, $(NH_4)(Al,Fe)(SO_4)_2$, millosevichite-mikasaite solid solution, $(Al,Fe)_2(SO_4)_3$, steklite, $KAl(SO_4)_2$, tschermigite, $(NH_4)Al(SO_4)_2{\cdot}12H_2O$ (natural ammonium aluminum alum), alunite-supergroup minerals, and many others. Pyrometamorphic processes and their product in Polish BCWH – within both the Upper and Lower Silesian Coal Basins (USCB and LSCB, respectively) was extensively studied, e.g., by Kruszewski [13, 14] and Kruszewski et al. [15, 16], with process imitation experiments described, e.g. by Kruszewski [10]. Mineralogy of the exhalative processes and gas phase composition of the local fumaroles was largely addressed by Kruszewski [6, 12, 17–19]. Fabiańska et al. [20] and Lewińska-Preis et al. [21] addressed some environmental aspects of the gas emissions in question. Supergene mineralogy was described in Kruszewski [11]. Presentation of the BCWH as models of various natural environments, including extraterrestrial ones, was shown by Kruszewski et al. [22, 23]. Biological aspects of the BCWH environment were brought up by Kruszewski & Matlakowska [24].

The fumaroles bear numerous minerals rich in trace and toxic elements, like zinc, copper, nickel, arsenic, thallium, lead, bismuth, selenium, bromine, iodine, indium, silver, and others. The mineral segregations are, obviously, related to the gas phase composition. Analyzing the latter was somewhat pioneering, as we could not find any literature sources showing the use of a portable FTIR (Fourier-Transformed InfraRed) spectroscopy for *in situ* analyzing of gaseous emissions, at least in the BCWH or the coal-fire environment in general. The IR method is a type of spectroscopy where vibrations of chemical bonds in molecules are being addressed, and depicted by their interaction with IR laser (a similar method is Raman spectroscopy). Various types of vibrations (i.e., stretching, bending, rocking, and other types) are responsible for various peaks in the spectra observed. Most compounds show response to the IR light (i.e., IR laser), by a pattern more or less characteristic for the particular molecule. Some exceptions include H_2S (hydrogen sulfide), which – in the variation of the IR method described here – gives only weak signals, thus making the aforementioned IT method somewhat more useful. The main components were shown (in [6]) to be H_2O and CO_2, with minor but variable add of CH_4 and CO. However, the composition was shown to be much more complex. The portable FTIR GASMET DX-4000 (OMC ENVAG) system was thoroughly characterized in Kruszewski et al. [6, 12]. It system a tool of choice for analysis of complex, hot, chemically aggressive and char- and ash-rich emanations, including combustion/exhaust gases. It comprises a probe with stainless-steel tip, connected with special wires with gas conditioning system (with a pressure control, pump, and system of 2 μm filters for catching any solid and liquid contaminants) and then the FTIR spectrometer. The interferometer has a ZnSe beam splitter; the sample cell has its path length of 5.0 m, volume is 0.4 L; Viton gaskets, MgF_2 protective coating, and BaF_2 window are present, too. The whole sampling system is internally coated by protective layers of rhodium and, gold and nickel.

FTIR results obtained for total 52 fumaroles in four BCWHs located in Pszów, Rybnik-Rymer, Radlin, and Rydułtowy (USCB), respectively, showed up to [in ppm, unless noticed; whole-range maximums underlined]: H_2O 57.5, 19.3, 12.5, 36.2 vol.%; CO_2 67.2, 7.63, 6.82, 30.6 vol.%; CO 2690, 694, 21, 347; NO 434, 38, 123, 151; N_2O not observed (n.o.), 0.42, 1.2, 8.7; NO_2 16430, 116, 24, 191; NH_3 1715, 646, 14, 98; SO_2 582, 74, 64, 226; HCl 58, 23, 2.4, 8.9; CCl_4 22, 1.5, 6.0, 14; HF 4.0, 2.2, n. o., 5.1; SiF_4 1890, 228, 504, 1980; AsH_3 8.2, 0.49, 0.18, 0.64; CH_4 82970, 1050, 838, 888; ethane 511, 306, 42, 316; propane 1446, 100, 16, 284; hexane 921, 123, n.o., 262; ethene 92, 28, 21, 21; dichloromethane (DCM) 5472, 1730, 241, 1980; 1,1-dichloroethane (1,1-DCE) 2110, 580, 175, and 742; 1,2-DCE 573, 28, 7.4, n.o.; 1,1,1-trichloroethane (1,1,1-TCE) 7.7, n.o., 40, 23; 1,2-dichloropropane (1,2-DCP) 4900, 12, n.o., 44; 1,1-dichloroethene (1,1-DCEe) 51, 3.3, 34, 140; vinyl chloride 1700, 809, n.o., 1980; chlorobenzene 416, 71, 92, 100; cumene (*i*-propylbenzene) 194, 84, 35, 75; phenol 43, 348, 37, and 103; *o*-cresol (2-methylphenol) 1620, 99, n.o., 99; furan 27, 29, 130, 12; tetrahydrofuran (THF) 598, 372, n.o., 2830; thiophene 781, 578, 773, 550; acetic acid 7000, 12, 12, 650; dimethyl sulfide (DMS) 6650, 2230, n.o., 6780; dimethyl disulfide (DMDS) 518, 36, n.o., 97; formaldehyde 5.7, n.o., n.o., and 3.1. Pyridine was observed only in Radlin, in very constant amounts, 10–11 ppm. Although certified (as in the case of other compounds in the calibration library), the maximum contents of germanium tetrachloride, $GeCl_4$, i.e., 3130, 209, 333, and 2098 should be treated with care due to possible coincidence as yet unresolvable by the Calcmet software. Geometric means of the concentration values (Pszów, Rybnik-Rymer, Radlin, Rydułtowy, whole series) are: H_2O 31, 12, 3.0, 21, and 19 (n_{total} = 46); CO_2 31, 4.0, 0.22, 11, and 7.0 (n_{total} = 50) [vol.%]; CO 84, 186, 9.6, 81, and 81 (n_{total} = 41); NO 87, 15, 14, 66, and 42 (n_{total} = 24); NO_2 334, 38, 14, 42, and 41 (n_{total} = 26); N_2O -, 0.10, 0.66, 4.3, and 0.83 (n_{total} = 17); NH_3 287, 22, 3.4, 59, and 88 (n_{total} = 18); SO_2 110, 18, 17, 48, and 56 (n_{total} = 31); HCl 7.4, 4.2, 0.56, 3.0, and 3.8 (n_{total} = 46); CCl_4 3.2, 0.18, 0.91, 2.5, and 1.6 (n_{total} = 51); HF 4.0, 2.2, −, 3.3, and 3.4 (n_{total} = 9); SiF_4 16, 114, 94, 182, and 65 (n_{total} = 29); AsH_3 1.1, 0.19, 0.17, 1.0, and 0.58 (n_{total} = 26); CH_4 1945, 500, 23, 537, and 457 (n_{total} = 47); ethane 46, 114, 15, 75, and 59 (n_{total} = 37); propane 148, 70, 16, 27, and 46 (n_{total} = 27); hexane 160, 25, −, 15, and 38 (n_{total} = 26); ethene 7.9, 7.3, 11, 8.3, and 8.2 (n_{total} = 28); DCM 230, 119, 160, 295, and 214 (n_{total} = 45); 1,1-DCE 235, 190, 98, 99, and 139 (n_{total} = 32); 1,2-DCE 153, 28, 7.4, −, and 91 (n_{total} = 9); 1,1,1-TCE 5.4, −, 40, 9.5, and 7.7 (n_{total} = 19); 1,2-DCP 1038, 5.7, −, 20, and 166 (n_{total} = 9); 1,1-DCEe 19, 2.6, 31, 25, and 20 (n_{total} = 35); vinyl chloride 329, 38, −, 394, and 289 (n_{total} = 32); chlorobenzene 24, 36, 92, 32, and 32 (n_{total} = 12); cumene 28, 30, 35, 15, and 22 (n_{total} = 38); phenol 14, 36, 3.8, 32, and 19 (n_{total} = 32); *o*-cresol 115, 21, −, 99, and 73 (n_{total} = 15); furan 11, 9.8, 72, 12, and 31 (n_{total} = 18); THF 126, 372, −, 643, and 195 (n_{total} = 10); thiophene 251, 200, 90, 156, and 186 (n_{total} = 40); formaldehyde 3.5, −, −, 0.54, and 0.82 (n_{total} = 8); acetic acid 189, 6.6, 8.1, 83, and 54 (n_{total} = 22); DMS 517, 433, −, 921, and 533 (n_{total} = 16); DMDS 68, 11, −, 31, and 41 (n_{total} = 35); and pyridine -, −, 11, −, and 11 (total 8 records).

GC results were also published in the paper, with confirmed occurrence of carbonyl sulfide, COS, carbon disulfide, CS_2, freons (CCl_3F, CCl_2F_2, $CHClF_2$), *i*-butane, *n*-butane, *i*-pentane, *n*-pentane, *n*-hexane, *n*-heptane, *n*-octane, *n*-nonane, *n*-decane, propene, 1-butene, *i*-butene, *trans*- and *cis*-2-butene, *trans*- and *cis*-2-pentene, ethyne, 1,3-butadiene, isoprene (2-methyl-1,3,-butadiene), 2,3-dimethylbutane; 2- and 3-methylpentanes; benzene, toluene, *m*/*p*- and *o*-xylenes, styrene, ethylbenzene, *n*- and *i*-propylbenzene; 2-, 3,- and 4- (or *m*-, *p*- and o-) ethyltoluene; 1,2,3-, 1,2,4-, and 1,3,5-trimethylbenzenes; and α- and β-pinene. As shown in the paper, the GC results may be quite unreliable due to their non-*in situ* character and possible intra-gas and gas-steel interactions, and are thus not resumed

here. In turn, we have later used a second and third mode of the FTIR spectra reading. The first one is an external library search, where the spectra are read and calculated using libraries containing other compound sets, thus reporting semi-quantitative results with fit factor (r^2, in %), as described in Kruszewski et al. [12]. Any misfits are due to recording the standards in different conditions than in the DX-4000 calibration library case. Applying this method allowed to detect additional compounds for the previously listed 4 BCWH sites [in ppm, with results for fit ≥90%, 75–90%, 50–75%, and < 50%, and whole-data maximums underlined]: acetylene, C_2H_2 (up to 0.81; up to 27; up to 38; up to 288), *n*-butane (–; –; 7.1; 1.5), *i*-butane (–; –; 9.7; 0.25), propene (–; –; up to 101; up to 30), *n*-pentane (–; –; 4.0; 1.9), *i*-pentane (–; –; 11; 0.91), heptane (–; –; up to 2.1; –), octane (–; –; up to 2.3; –), nonane (–; –; up to 2.1; –), decane (–; –; up to 2.0; –), undecane (–; –; up to 2.0; –), 1,3-butadiene (3.2; –; up to 144; up to 169), cyclohexane (–; –; up to 2.7; –), α-pinene (–; –; up to 4.0; up to 1.1), limonene ($C_{10}H_{16}$; –; –; up to 4.9; 2.7), 3-carene ($C_{10}H_{16}$; 512; up to 2.2), benzene (8.8; up to 5.1; up to 52; up to 5700), toluene (–; –; up to 74; up to 18), styrene (–; 88; 0.76; up to 154), *m*-xylene (–; –; 19; up to 51), *p*-xylene (–; –; 16; up to 23), ethylbenzene (–; –; –; up to 8.4), 1,3,5-TMB (–; –; up to 729; up to 32), 1,2,4-TMB (–; –; up to 1610; up to 27), 1,2,3-TMB (–; –; up to 1360; up to 23), tetrachloroethene (–; up to 4.3; up to 28; up to 27), methanol (11; 5.4; up to 18; up to 75), ethanol (16; 5.4; up to 38; up to 126), *i*-propanol (isopropanol; –; –; –; up to 16), *i*-butanol (isobutanol; –; –; –; 5.4), *n*-propanol (–; –; 982; –), methanethiol (methylmercaptan), CH_3SH (–; –; –; up to 55), ethanethiol (ethylmercaptan), C_2H_5SH (–; –; 2500; up to 14), HCN (up to 8.4; up to 16; up to 88; up to 65), acrylonitrile (prop-2-enenitrile, CH_2 = CHCN; –; 6.0; up to 63; up to 82), isocyanic acid (–; –; –; up to 717), formic acid, HCOOH (3.0; 8.7; up to 29; up to 48), trimethylamine, $(C_2H_5)_3N$ (–; –; –; up to 1.5), acetaldehyde (up to 45; up to 97; up to 1810; up to 6270), propionaldehyde (propanal), $(C_2H_5)CHO$ (–; –; –; up to 24), 2-ethylhexylaldehyde ($C_4H_9CH(C_2H_5)CHO$; –; –; up to 342; –), acrolein (propenal, CH_2 = CHCHO; –; 1.6; up to 57; up to 25), acetone (propan-2-one) (–; –; –; up to 98), methyl ethyl ketone (MEK, or butan-2-one), $CH_3C(O)C_2H_5$ (–; –; –; up to 28), methyl isobutyl ketone (MIBK, or 4-methylpentan-2-on), $(CH_3)_2C_2H_3C(O)CH_3$ (–; –; –; up to 2.6), diethylether (ethoxyethane, $(C_2H_5)_2O$; –; –; 1.7; up to 24), MTBE (–; –; –; up to 9.4), 2-ethoxyethanol, $(C_2H_5)O(CH_2)O(C_2H_5)$ (–; –; up to 47; up to 32), 2-ethoxyethyl acetate (–; –; –; up to 19), butyl acetate (–; –; –; up to 15), 2-(2-butoxyethoxy) ethyl acetate (–; –; –; up to 13), methyl metacrylate (methyl 2-methylprop-2-enoate; –; –; –; up to 10), PH_3 (phosphine; –; up to 43; up to 144; up to 152), COS (up to 0.88; up to 6.1; up to 0.40; –), and last but not least SF_6 (–; –; up to 1.6; up to 1.5). The last compound is environmentally very important, as it is said – by the Intergovernmental Panel on Climate Change – to be the most potent greenhouse gas [25]. The measured BCWH emanation concentrations are also much higher (over 170000 times) than the highest ones measured at Mauna Loa fumaroles [26]. Calculated geometric means (whole series; with values for fit ≥50% in the parentheses): 13 (2.3) for acetylene (*n* = 14 (31)), 25 (51) for propene (*n* = 9 (3)), 17 (29) for 1,3-butadiene (*n* = 15 (5)), 0.76 for α-pinene (*n* = 6), 3.5 for limonene (*n* = 3), 6.2 for 3-carene (*n* = 4), 55 (9.7) for benzene (*n* = 34 (14)), 7.4 (21) for toluene (*n* = 11 (3)), 9.6 for styrene (*n* = 9), 9.9 (10) for *m*-xylene (*n* = 11 (8)), 13 for *p*-xylene (*n* = 7), 13 (13) for 1,3,5-TMB (*n* = 11 (8)), 11 for 1,2,4-TMB (*n* = 10), 4.5 for 1,2,3-TMB (*n* = 6), 15 (5.5) for methanol (*n* = 24 (4)), 32 (8.6) for ethanol (*n* = 26 (7)), 6.9 for *i*-propanol (*n* = 7), 23 for ethanethiol (*n* = 4), 4.2 (1.4) for tetrachloroethene (*n* = 31 (9)), 7.2 (5.9) for HCN (*n* = 47 (33)), 293 for isocyanic acid (*n* = 18), 1.2 for trimethylamine (*n* = 3), 47 (47) for acrylonitrile (*n* = 12 (9)), 15 (12) for formic acid (*n* = 35 (7)), 62 (28) for acetaldehyde (*n* = 50 (45)), 9.4 for propionaldehyde

(*n* = 4), 37 for 2-ethylhexylaldehyde (*n* = 3), 23 (28) for acrolein (*n* = 13 (9)), 21 for acetone (*n* = 22), 5.2 for diethylether (*n* = 10), 6.8 for 2-ethoxyethanol (*n* = 10), 7.7 for 2-ethoxyethyl acetate (*n* = 20), 4.8 for butyl acetate (*n* = 8), 5.1 for methyl metacrylate (*n* = 9), 12 for MEK (*n* = 8), 2.0 for MIBK (*n* = 5), 2.7 for MTBE (*n* = 4), 0.37 (0.41) for COS (*n* = 16 (13)), 72 (40) for PH_3 (*n* = 28 (10)), and 1.1 for SF_6 (*n* = 10). As such, acetaldehyde, HCN, PH_3, tetrachloroethene, ethanol, benzene, COS, methanol, acetylene, and 1,3-butadiene, isocyanic acid, acrolein, and likely acetone and 2-ethoxyethyl acetate seem to be the most frequent admixing gases in the BCWH exhausts studied.

The third operation mode is qualitative analysis of residual spectra, as thoroughly described in both my previous papers. This method allowed to list proposals of additional, very interesting, admixing gases, many of which were likely first documented in the nature. They include neutral hydroxides of Ca, Mg, Al, Fe(II), Fe (III), Zn, Cu; nitrosyls and carbonyls of Ti, V, Mn, Fe, Ag, Mo, Fe, Cu; hydrides of Al, Cu, Zn, Ge, Mo, Sb, and Hg; nitriles, azo and related compounds (azacyclopropenylidene, dicyanoacetylene, cyanogen isocyanate, cyanogen *N*-oxide, diazomethyl radical, hydrogen isocyanide, isocyanic acid, *m*-hydroxybenzonitrile, phenylnitrene radical; 2,4,6-trinitrene-1,3,5-triazine); amines (methyl(nitrosomethyl)amine); hypobromous and hydroiodic acids; hydrocarbons and halocarbons (cyclohexene, dibenz[*a*,*h*]anthracene, difluorovinylidene, hexachlorobenzene, hexachloroethane, 5-methyl-1,3-didehydrobenzene, pentacene, phenanthrene, triphenylene); nitrosyl chloride and iodide, phosgene; organoboron compounds (fluoroisocyanatoborane) and compounds like CBrO and B_2O_2; organosulfurs (thiirene, thioacetaldehyde, thioxoethenylidyne radical), organophosphorus compounds (methylphosphine), and organosilicons (difluorosilane, disinale, silanenitrile, tribromosilane), organoiodine compounds (iodosomethane – an I^{3+}-bearing compounds; iodocyanoacetylene), $HAlCl_2$, ClO_2^*, and dimeric NO, to mention some. Due to multiple coincidence possible these results should, however, be treated with care.

4. New *in situ* FTIR gas analysis results of the USCB heaps

Results presentation within this chapter has its main goal in enlarging the span of the knowledge on the concentration range of various (major and minor) components of the BCWH combustion gases, both by pFTIR and GC methods. **Table 1** shows data from Czerwionka-Leszczyny (18, that is, 10 vents / vent zones from zone CLD and 8 from the CL one). **Table 2** juxtaposes data for 10 additional, differently mineralized vents from the Radlin heap (RD), with that from a BCWH in Bytom (BTM, 7 vents / vent zones). **Table 3**, in turn, juxtaposed data for vents in a BCWH in Świętochłowice (SWC, 11 vents / vent zones), "Starzykowiec" heap in the Chwałowice part of Rybnik (RCH, 1 vent, surface and deep part), and "Ruda" heap in Zabrze-Biskupice (ZBB, 5 vents / vent zones). In total, data for additional 53 vents is reported. As in the case of the data presented in Kruszewski et al. [6, 12], gases were probed at the surface and from deeper parts of the vents, whenever possible. Temperatures were measured using an IR pyrometer.

Following are values describing maximum and geometric-mean concentrations of gaseous species as detected within fumarolic vents of the CLD, CL, RD, BTM, SWC, and ZBB sites (whole-series-maximums are underlined): H_2O, 18.12, 14.74; 7.30, 2.83; 27.14, 23.04; 11.15, 9.83; 6.42, 4.68; 25.63, 23.19; CO_2, 2.85, 2.29; 27.00, 0.20; 29.89, 20.85; 8.12, 6.05; 38.41, 33.89 [vol.%]; CO, 135, 110; 163, 9.4; 2430, 1002; 3590, 2675; 1090, 303; 26700, 3257; NO, 112, 96; 10, 6.4; 7.3, 7.3; –, –; 19, 15; –, –; NO_2, 44, 22; 368, 155; 2.0, 2.0; 1430, 1430; –, –; 66, 45; N_2O, 3.5, 2.3; 0.06, 0.02; 4.4, 4.4; 2.8, 2.8; 1.3, 1.3; –, –; NH_3, 21, 7.7; 30, 2.5; 19, 7.1; 65, 55; 4.1, 2.4; 8.3,

vent [1]	**CLD1**	**CLD1o**	**CLD2**	**CLD3**	**CLD5**	**CLD5S**	**CLD5o**	**CLD6o**	**CLD6o2**	**CLD7**	**CLdA**	**CLdAr**	**CLdU**	**CLd**	**CL1**	**CLdo**	**CL2a**	**CL2aA**
T [°C]	40	45	45	45	25	35	35	35	35	60	90	90	82	82	50	82	30	45
									pFTIR									
									inorganics, vol.%									
H_2O [2]	9.77	12.21	12.22	12.27	16.43	17.36	16.88	17.62	17.65	18.12	2.68	2.65	2.57	2.58	0.75	2.62	6.10	7.30
CO_2	1.96	2.32	2.34	2.40	1.90	2.26	2.08	2.39	2.54	2.85	0.03	0.03	0.03	0.03	bdl	0.03	18.00	27.00
		inorganics, ppm																
CO	bdl	bdl	bdl	bdl	**135** [3]	**101**	**101**	**132**	94	**103**	6.4	3.1	bdl	0.98	bdl	1.5	145	163
N_2O	2.8	3.4	3.5	3.5	bdl	bdl	bdl	bdl	bdl	0.57	0.02	0.04	0.06	0.01	bdl	0.02	bdl	bdl
NO	64	**107**	**112**	**112**	bdl	bdl	bdl	bdl	bdl	bdl	6.9	9.9	bdl	9.7	1.6	10	bdl	bdl
NO_2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	11	44	bdl	bdl	bdl	bdl	bdl	bdl	**368**	65
NH_3	4.4	3.9	3.6	3.7	10	15	21	10	11	9.4	bdl	1.0	0.23	1.4	bdl	1.4	18	30
SO_2	4.2	bdl	bdl	bdl	bdl	87	bdl	bdl	20	120	bdl	bdl	bdl	1.9	bdl	2.4	**119**	**671**
HCl	0.04	bdl	0.24	0.57	11	10	10	8.7	7.6	6.6	1.5	0.76	0.08	0.58	0.01	0.63	6.5	5.8
CCl_4	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	6.6
HF	bdl	bdl	bdl	bdl	bdl	0.62	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.03
SiF_4	bdl	0.06	0.21	0.16	3.7	5.3	3.8	3.4	6.3	4.6	2.2	1.9	1.9	2.1	1.1	2.1	20	31
AsH_3	bdl	0.08	0.17	0.15	0.03	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.16	bdl	bdl	bdl	0.20	**1.7**
									aliphatic and aromatic hydrocarbons and their derivatives, ppm									
CH_4	26	31	31	31	**244**	**259**	**262**	**251**	**253**	**248**	4.5	4.8	6.8	4.6	0.51	4.8	**811**	**2950**
ethane	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	30	bdl
propane	6.9	3.8	4.4	4.4	34	42	36	bdl	40	37	bdl	4.2	3.1	13	11	8.2	bdl	**729**
hexane	1.8	0.20	0.31	0.35	2.6	4.6	2.3	7.0	4.6	11	bdl	bdl	bdl	bdl	bdl	bdl	**152**	17

vent [1]	**CLD1**	**CLD1o**	**CLD2**	**CLD3**	**CLD5**	**CLD5S**	**CLD5o**	**CLD6o**	**CLD6o2**	**CLD7**	**CLdA**	**CLdAr**	**CLdU**	**CLd**	**CL1**	**CLdo**	**CL2a**	**CL2aA**
ethene	bdl	bdl	bdl	bdl	bdl	1.3	bdl	bdl	3.7	6.6	2.2	bdl	1.3	bdl	1.9	bdl	37	79
DCM	17	10	16	15	73	**104**	71	141	57	20	52	65	56	50	18	51	**368**	**159**
1,1-DCE	bdl	bdl	bdl	bdl	bdl	bdl	bdl	7.2	bdl	bdl	bdl	5.1	bdl	7.4	bdl	7.2	17	12
1,2-DCE	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	77	bdl
vent	**CLD1**	**CLD1o**	**CLD2**	**CLD3**	**CLD5**	**CLD5S**	**CLD5o**	**CLD6o**	**CLD6o2**	**CLD7**	**CLdA**	**CLdAr**	**CLdU**	**CLd**	**CL1**	**CLdo**	**CL2a**	**CL2aA**
1,1,1-TCE	bdl	bdl	bdl	bdl	**99**	bdl	bdl	bdl	bdl	21	bdl	bdl	bdl	6.4	bdl	6.5	**417**	bdl
1,2-DCP	bdl	bdl	bdl	bdl	bdl	bdl	bdl	31	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	56	bdl
1,1-DCEe	4.3	5.3	4.4	4.8	57	77	54	63	43	68	35	45	49	48	25	57	**226**	**347**
ClB	bdl	bdl	bdl	bdl	20	bdl	18	39	bdl	bdl	15	14	22	6.0	6.0	6.3	bdl	**186**
cumene	4.4	6.3	6.4	5.5	29	30	31	29	34	31	6.1	1.3	7.6	1.9	2.4	1.7	**399**	bdl
phenol	2.4	4.4	4.2	4.0	29	bdl	29	28	17	17	4.6	3.2	7.0	bdl	2.9	bdl	bdl	bdl
o-cresole	0.29	bdl	0.41	0.37	19	46	17	20	23	24	1.9	2.2	0.28	7.1	0.81	6.9	66	10
heterocyclic organic compounds, ppm																		
furan	bdl	0.14	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
THF	0.29	bdl	1.3	0.18	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	**177**
py	bdl	bdl	bdl	bdl	bdl	7.1	bdl	bdl	bdl	bdl	0.27	2.3	6.3	12	23	12	86	bdl
tph	bdl	bdl	bdl	bdl	**192**	**137**	**191**	bdl	**127**	**103**	bdl	bdl	bdl	bdl	8.3	bdl	bdl	**173**
other organic compounds, ppm																		
fm	0.11	bdl	bdl	bdl	12	7.0	6.0	5.3	5.3	5.7	0.58	1.2	0.47	0.42	0.45	0.42	13	13
DMS	bdl	13	7.7	11	62	6.9	27	33	31	51	bdl	0.15	bdl	bdl	bdl	bdl	**893**	**165**
DMDS[)]	12	23	32	28	**99**	**104**	40	7.0	85	5.6	3.5	37	31	36	17	36	bdl	bdl

GC – additional compounds, *ppm*																	
vent	**CLD1**	**CLD1o**	**CLD2**	**CLD3**[4]	**CLD5**	**CLD5S**	**CLD5o**	**CLD6o**	**CLD6o2**	**CLD7**	**CLdA**	**CLdAr**	**CLdU**	**CLd**	**CL1**	**CLdo**	**CL2a**	**CL2aA**
CH_3Cl	0.002			0.001	0.003			0.002		0.005					0.002	0.08	0.03	0.01
ethyne	0.001			0.001	0.001			0.001		0.01					0.003	0.01	0.01	0.0002
propene	0.0002			bdl	1.7			5.2		1.4					0.09	0.51	0.36	0.09
i-butane	0.0003			0.002	1.6			3.2		3.5					0.08	0.69	8.3	2.3
n-butane	0.001			0.002	2.4			5.4		3.6					0.15	1.1	12	3.9
1-butene	0.0001			0.001	0.14			0.40		0.13					0.02	0.03	0.08	0.03
i-butene	0.0001			0.002	0.41			0.32		0.52					0.03	0.04	1.3	0.42
t^{-2}-bu	0.00004			0.001	0.52			1.4		0.50					0.02	0.04	0.59	0.24
c-2-bu	0.00003			0.0005	0.29			0.80		0.23					0.01	0.02	0.17	0.06
vent	**CLD1**	**CLD1o**	**CLD2**	**CLD3**	**CLD5**	**CLD5S**	**CLD5o**	**CLD6o**	**CLD6o2**	**CLD7**	**CLdA**	**CLdAr**	**CLdU**	**CLd**	**CL1**	**CLdo**	**CL2a**	**CL2aA**
i-pentane	0.001			0.01	0.92			1.8		1.8					0.06	0.35	6.5	1.7
n-pentane	0.0003			0.01	1.1			2.3		1.5					0.06	0.35	6.0	1.9
t-2-pte	bdl			0.002	0.20			0.57		0.19					0.01	0.01	0.36	0.18
c-2-pte	bdl			0.001	0.08			0.23		0.07					0.004	0.003	0.09	0.04
n-heptane	bdl			0.003	0.44			0.84		0.34					0.02	0.07	1.7	0.68
n-octane	bdl			0.002	0.36			0.65		0.10					0.01	0.04	0.64	0.32
n-nonane	bdl			0.0003	0.25			0.40		0.03					0.01	0.01	0.22	0.04
n-decane	bdl			0.0001	0.16			0.20		0.003					0.001	0.002	0.03	0.04
2,3-DMBu	bdl			0.01	0.07			0.13		0.16					0.003	0.02	0.58	0.14
2-MPT	bdl			0.01	0.41			0.76		0.75					0.02	0.11	3.0	0.82

vent	CLD1	CLD1o	CLD2	CLD3	CLD5	CLD5S	CLD5o	CLD6o	CLD6o2	CLD7	CLdA	CLdAr	CLdU	CLd	CL1	CLdo	CL2a	CL2aA
3-MPT	0.0001			0.005	0.16			0.30		0.30					0.01	0.05	1.3	0.34
cpt	bdl			0.001	0.19			0.42		0.26					0.01	0.05	1.0	0.30
benzene	0.0004			0.002	2.1			3.3		0.06					0.05	0.27	1.1	0.41
toluene	0.001			0.02	2.0			3.4		0.01					0.02	0.11	0.05	0.02
EtB	0.0001			0.003	0.27			0.43		0.01					0.01	0.02	0.12	0.05
m/p-X	0.0003			0.01	1.3			1.9		0.19					0.02	0.09	0.06	0.22
o-X	0.0002			0.003	0.39			0.53		0.03					0.01	0.03	0.02	0.01
styrene	0.001			0.0001	bdl			bdl		bdl					bdl	bdl	bdl	bdl
i-PrB	bdl			0.0002	0.03			0.05		0.03					0.001	0.001	0.06	0.03
n-PrB	bdl			0.0005	0.06			0.08		0.02					0.001	0.002	0.02	0.01
m-EtT	0.0001			0.001	0.18			0.24		0.06					0.004	0.01	0.01	0.01
p-EtT	bdl			0.0005	0.07			0.10		0.02					0.001	0.003	0.01	0.01
o-EtT	bdl			0.0005	0.08			0.10		0.02					0.003	0.002	0.01	0.01
1,3,5-TMB	0.0001			0.001	0.14			0.19		0.07					0.003	0.005	0.01	0.005
1,2,4-TMB	0.0001			0.002	0.27			0.32		0.05					0.01	0.01	0.04	0.03
1,2,3-TMB	0.0001			0.001	0.10			0.10		0.02					0.004	0.003	0.06	0.05

Values in parentheses denote overrun of the upper measurement range.
[1]*"A" – samples taken from the depth of 0.8–1 m; "a" and "o" - nearby vents; "r" – repeated analysis; "S" – sulfur-mineralized vent.*
[2]*DCM – dichloromethane, DCE – dichloroethane, DCEe – dichloroethene, TCE – trichloroethane, DCP – dichloropropane, ClB – chlorobenzene, THF – tetrahydrofuran, py – pyridine, tph – thiophene, fm – formaldehyde, DMS – dimethyl sulfide, DMDS – dimethyl disulfide;* t(c)*-2-bu –* trans(cis)*-2-butene,* c(t)*-2-pte –* cis(trans)*-2-pentene, DMBu – dimethylbutane, MPT – methylpentane, cpt – cyclopentane, EtB – ethylbenzene, X – xylene, PrB – propylbenzene, EtT – ethyltoluene, TMB – trimethylbenzene; vinyl chloride, acetic acid, isoprene, and 1,3-butadiene were analyzed but were below their detection limits.*
[3]*Notable (>100 ppm) enrichment given in bold.*
[4]*GC data for a nearby vent.*

Table 1.
Results of the pFTIR and GC gas analyses of BCWH in Czerwionka-Leszczyny.

vent[1]	**RD07**	**RD07A**	**RD08N**	**RD08NA**	**RD08kr**	**RD08krA**	**RD08o**	**RD11L**	**RD11U**	**RD11o**	**BTM1**	**BTM1A**	**BTM1o**	**BTM1o2**	**BTM1o3**	**BTM1o4**	**BTM2**
T [°C]	60	90	133	187	77	107	76	76	76	76	115	144	73	150	79	115	60
pFTIR																	
main components, vol. %																	
H_2O[2]	19.99	24.62	26.02	18.26	27.14	22.25	26.61	16.94	24.80	26.65	6.92	9.94	10.41	10.67	11.15	11.02	9.43
CO_2	25.00	29.89	20.21	13.94	26.16	21.32	21.24	11.96	21.14	24.64	4.08	5.43	5.52	5.25	7.58	8.12	7.49
inorganics, ppm																	
CO	**1580**	**2430**	**923**	**502**	**1110**	**813**	**832**	**673**	**1030**	**1100**	**1730**	**2830**	**3090**	**2640**	**3090**	**3590**	**2210**
N_2O	bdl	bdl	bdl	bdl	bdl	bdl	bdl	4.4	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.8
NO	bdl	bdl	bdl	bdl	bdl	bdl	7.3	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
NO_2	bdl	2.0	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	**1430**	bdl	bdl
NH_3	9.2	9.2	5.5	6.9	12	19	5.0	1.8	3.1	16	42	60	60	61	62	65	41
SO_2	**388**	**311**	bdl	57	bdl	**193**	bdl	79	bdl	bdl	86	**139**	**147**	**139**	**532**	**378**	**281**
HCl	4.5	3.1	6.1	2.9	2.5	2.6	6.2	bdl	5.0	2.3	2.7	3.3	3.6	5.4	19	15	6.3
CCl_4	6.3	5.1	10	4.4	6.8	6.9	3.2	7.4	11	7.8	bdl	bdl	bdl	bdl	1.1	bdl	bdl
HF	0.12	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.59	0.07	1.1	bdl	bdl	bdl
SiF_4	15	13	21	16	15	15	18	17	14	13	1.7	1.8	1.7	0.95	bdl	3.2	bdl
AsH_3	bdl	**1.3**	0.93	0.49	**1.2**	**1.4**	0.56	**1.7**	bdl	0.11	0.81	**2.9**	**1.3**	**2.0**	0.79	**2.8**	**3.4**
aliphatic and aromatic hydrocarbons and their derivatives, ppm																	
methane	**3190**	**3470**	**1120**	**713**	**1120**	**1160**	**1140**	**500**	**1120**	**1150**	**285**	**437**	**421**	**359**	**808**	**819**	**554**
ethane	bdl	**142**	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	**281**	bdl	bdl
propane	**387**	**601**	**202**	bdl	**291**	**230**	**213**	bdl	**195**	**249**	bdl	bdl	bdl	bdl	**694**	**242**	bdl
hexane	71	**139**	70	53	90	67	71	53	64	76	88	**148**	**160**	**309**	**608**	**543**	**138**
ethene	bdl	0.71	12	5.4	9.3	7.6	12	12	3.1	6.9	4.7	16	17	39	84	78	35

vent[1]	**RD07**	**RD07A**	**RD08N**	**RD08NA**	**RD08kr**	**RD08krA**	**RD08o**	**RD11L**	**RD11U**	**RD11o**	**BTM1**	**BTM1A**	**BTM1o**	**BTM1o2**	**BTM1o3**	**BTM1o4**	**BTM2**
DCM	8.3	18	**126**	29	**104**	25	**111**	**94**	**102**	34	11	68	74	84	bdl	bdl	bdl
1,1-DCE	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	16	bdl	bdl	bdl
1,2-DCE	39	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	38	bdl	bdl	bdl
vent	**RD07**	**RD07A**	**RD08N**	**RD08NA**	**RD08kr**	**RD08krA**	**RD08o**	**RD11L**	**RD11U**	**RD11o**	**BTM1**	**BTM1A**	**BTM1o**	**BTM1o2**	**BTM1o3**	**BTM1o4**	**BTM2**
1,1,1-TCE	29	15	21	33	29	36	bdl	21	bdl	bdl	bdl	bdl	1.0	bdl	59	bdl	20
1,2-DCP	**124**	**384**	75	42	**264**	**175**	**224**	**108**	**251**	**248**	bdl	bdl	39	bdl	**568**	bdl	**519**
1,1-DCEe	81	30	**195**	**101**	**164**	**123**	**176**	**155**	**189**	**162**	bdl	11	11	bdl	24	28	bdl
ViCl	**416**	**96**	**276**	**187**	**248**	**283**	**269**	bdl	**203**	**278**	38	29	47	63	**137**	**205**	**359**
ClB	bdl	bdl	bdl	bdl	11	bdl	74	bdl	77	62	62	46	61	**112**	73	**206**	bdl
cumene	**94**	**126**	**119**	36	**101**	**108**	**123**	**105**	**114**	90	38	46	50	**264**	**117**	bdl	**107**
phenol	bdl	15	49	bdl	21	1.6	51	bdl	11	17	18	39	42	47	60	67	35
o-cresole	37	65	25	40	34	50	26	39	30	31	27	46	48	53	81	73	76
heterocyclic organic compounds, ppm																	
THF	43	**96**	bdl	3.1	bdl	9.3	8.7	4.1	6.1	12	bdl	bdl	bdl	**232**	bdl	bdl	**293**
tph	**164**	**257**	**337**	**385**	**363**	**369**	**344**	**301**	**556**	**391**	63	bdl	bdl	bdl	**689**	**201**	**388**
other organic compounds, ppm																	
fm	bdl	bdl	2.6	1.4	2.0	2.0	5.5	1.4	1.3	1.6	0.74	0.77	0.91	1.2	**17**	**17**	2.1
acac	bdl	9.1	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	2.2	bdl	35	9.9	50
DMS	**131**	**126**	47	**401**	bdl	16	70	**255**	27	15	**172**	**219**	**243**	**1540**	**1370**	**1200**	bdl
GC – additional compounds, *ppm*																	
vent	**RD07**	**RD07A**	**RD08N**	**RD08NA**	**RD08kr**	**RD08krA**	**RD08o**	**RD11L**	**RD11U**	**RD11o**	**BTM1**	**BTM1A**	**BTM1o**	**BTM1o2**	**BTM1o3**	**BTM1o4**	**BTM2**
CH_3Cl	0.001		0.05	1.4	0.03	0.03	0.02	0.01			0.10						0.02
COS	7.4		0.78	2.6	0.88	0.16	2.1	0.43			1.3						0.98

vent	RD07	RD07A	RD08N	RD08NA	RD08kr	RD08krA	RD08o	RD11L	RD11U	RD11o	BTM1	BTM1A	BTM1o	BTM1o2	BTM1o3	BTM1o4	BTM2
ethyne	0.01		0.01	0.001	0.003	0.003	0.002	0.04			0.002						0.004
propene	0.47		0.91	0.93	0.01	0.03	3.8	1.5			8.5						0.62
i-butane	3.3		1.7	0.08	0.005	0.13	2.0	2.6			2.4						1.7
n-butane	8.7		3.6	0.21	0.01	0.03	4.6	3.4			5.9						2.6
1-butene	0.01		0.02	0.13	0.003	0.005	0.24	0.13			1.6						0.05
i-butene	0.06		0.08	0.51	0.002	0.01	0.98	0.38			6.6						0.26
t-2-bu	0.01		0.06	0.16	0.001	0.01	0.78	0.24			2.3						0.07
c-2-bu	0.01		0.03	0.12	0.0005	0.003	0.47	0.18			1.6						0.04
i-pentane	2.0		0.77	0.04	0.004	0.09	1.2	1.1			1.2						0.80
vent	**RD07**	**RD07A**	**RD08N**	**RD08NA**	**RD08kr**	**RD08krA**	**RD08o**	**RD11L**	**RD11U**	**RD11o**	**BTM1**	**BTM1A**	**BTM1o**	**BTM1o2**	**BTM1o3**	**BTM1o4**	**BTM2**
n-pentane	3.3		1.1	0.07	0.005	0.06	2.1	1.2			1.7						0.91
isoprene	bdl		0.002	0.03	0.0003	0.001	0.02	0.01			0.13						0.003
1,3-budi	bdl		bdl	0.02	0.0002	bdl	bdl	bdl			0.03						bdl
t-2-pte	0.12		0.01	0.06	0.001	0.01	0.21	0.08			0.81						0.01
c-2-pte	0.05		0.003	0.03	0.0004	0.002	0.09	0.03			0.39						0.003
n-heptane	0.44		0.18	0.03	0.001	0.01	0.58	0.41			0.93						0.11
n-octane	0.05		0.05	0.03	0.0007	0.004	0.18	0.21			0.57						0.05
n-nonane	0.03		0.46	0.02	0.0003	0.001	0.08	0.15			0.44						0.10
n-decane	0.003		0.02	0.01	0.0001	0.0002	0.02	0.11			0.60						0.01
2,3-DMB	0.12		0.04	0.003	0.0002	0.004	0.09	0.08			0.08						0.06
2-MPT	0.64		0.22	0.01	0.001	0.02	0.53	0.43			0.33						0.28
3-MPT	0.26		0.10	0.02	0.001	0.001	0.22	0.17			0.11						0.17
cpt	0.70		0.25	0.01	0.0004	0.003	0.40	0.27			0.22						0.20

vent	RD07	RD07A	RD08N	RD08NA	RD08kr	RD08krA	RD08o	RD11L	RD11U	RD11o	BTM1	BTM1A	BTM1o	BTM1o2	BTM1o3	BTM1o4	BTM2
benzene	5.3		3.2	4.3	0.13	0.46	5.5	33			21						1.3
toluene	0.16		0.27	0.66	0.005	0.13	1.6	0.53			7.6						0.27
EtB	0.01		0.08	0.08	0.0003	0.02	0.09	0.10			3.6						0.06
m/p-X	0.03		0.11	0.28	0.001	0.05	0.34	0.36			3.0						0.17
o-X	0.01		0.05	0.13	0.0004	0.01	0.18	0.15			1.1						0.07
styrene	0.001		0.01	0.005	0.00003	0.001	0.01	0.01			0.14						0.003
i-PrB	0.001		0.02	0.01	bdl	0.001	0.003	0.02			0.71						0.01
n-PrB	0.002		0.01	0.04	0.0001	0.002	0.003	0.02			0.27						0.01
m-EtT	0.01		0.05	0.11	0.0001	0003	0.01	0.08			0.54						0.05
p-EtT	0.002		0.02	0.05	0.00003	0.001	0.01	0.06			0.38						0.02
o-EtT	0.004		0.02	0.04	0.00005	0.001	0.01	0.05			0.25						0.02
1,3,5-TMB	0.01		0.02	0.05	0.0001	0.001	0.01	0.11			0.38						0.02
1,2,4-TMB	0.01		0.08	0.17	0.0001	0.003	0.02	0.13			1.0						0.05
1,2,3-TMB	0.01		0.05	0.07	0.0001	0.001	0.01	0.14			0.55						0.04

Values in parentheses denote overrun of the upper measurement range.
[1]the "A" add denotes samples taken from the depth of 0.8–1 m (below the ground level), while "a" and "o" denote nearby vents; "r" – repeated measurement; "P" – pyrometamorphic zone, "S" – sulfur-mineralized vent.
*[2]Abbreviations explained under **Table 1**; ViCl – vinyl chloride; furan, pyridine and DMDS were analyzed but were below their detection limits.*
[3]Notable (>100 ppm) enrichment given in bold.

Table 2.
Results of the pFTIR and GC gas analyses of the "Marcel" mine BCWH in Radlin (RD, second gas study) and a heap in Bytom (BTM).

vent [1]	**SWC1**	**SWC1r**	**SWC1oP**	**SWC1oSW**	**SWC1oB**	**SWC2**	**SWC2o**	**SWC2o2**	**SWC2o3**	**SWC3**	**SWC3A**	**RCH1**	**RCH1A**	**ZBB1**	**ZBB1A**	**ZBB2**	**ZBB2o**	**ZBB3**
T [°C]	45	45	100	100	45	180	180	65	65	43	300	30	49	150	210	86	86	100
pFTIR																		
main components, vol. %																		
H_2O[2]	2.47	3.91	4.38	4.29	3.98	6.42	6.37	6.24	6.37	4.43	4.50	7.28	7.81	25.63	22.56	25.53	21.52	21.13
CO_2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.11	0.79	38.31	33.95	34.75	25.77	38.41
inorganics, ppm																		
CO	92	**143**	**166**	**164**	**144**	**1090**	**1070**	**1060**	**1040**	**172**	**176**	21	21	**1220**	**12600**	**938**	**952**	**26700**
N_2O	bdl	bdl	bdl	bdl	bdl	1.3	1.3	1.3	1.2	bdl	bdl	bdl	2.6	bdl	bdl	bdl	bdl	bdl
NO	12	15	bdl	bdl	19	bdl	bdl	bdl	bdl	bdl	bdl	**100**	bdl	bdl	bdl	bdl	bdl	bdl
NO_2	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	66	bdl	bdl	31
NH_3	1.5	3.1	4.1	3.1	3.0	bdl	bdl	bdl	bdl	2.0	1.4	12	bdl	8.3	bdl	bdl	bdl	8.3
SO_2	bdl	15	46	bdl	14	79	59	58	53	39	47	**129**	**172**	bdl	bdl	bdl	**123**	bdl
HCl	0.48	0.73	2.9	2.7	0.94	8.4	8.3	8.3	8.3	3.7	3.9	0.71	1.2	4.3	1.2	5.6	5.9	4.9
CCl_4	0.57	0.03	0.06	bdl	0.11	bdl	bdl	bdl	bdl	0.34	0.34	bdl	bdl	6.0	8.5	8.5	8.2	4.0
HF	0.19	bdl	bdl	1.1	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl
SiF_4	bdl	0.08	2.4	2.5	0.18	48	48	47	47	3.0	3.5	0.42	bdl	25	15	28	26	10
AsH_3	0.04	0.09	0.40	bdl	0.28	bdl	bdl	bdl	bdl	0.38	0.37	bdl	bdl	0.88	**2.9**	0.19	bdl	**2.9**
aliphatic and aromatic hydrocarbons and their derivatives, ppm																		
methane	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	9.8	12	**1110**	**740**	**1130**	**1130**	**880**
propane	**192**	72	bdl	bdl	85	34	37	37	39	**208**	**215**	11	12	**233**	bdl	**257**	**277**	bdl
hexane	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	38	69	39	40	**64**
ethene	bdl	bdl	bdl	2.3	bdl	26	26	24	8.5	bdl	bdl	bdl	bdl	18	19	21	23	21
DCM	30	19	11	28	20	**181**	**191**	**191**	**189**	36	39	**173**	**143**	92	**142**	46	76	82
1,1-DCE	12	bdl	bdl	bdl	bdl	**103**	**102**	**102**	**104**	bdl	bdl	11	2.4	bdl	bdl	bdl	bdl	bdl

vent [1]	SWC1	SWC1r	SWC1oP	SWC1oSW	SWC1oB	SWC2	SWC2o	SWC2o2	SWC2o3	SWC3	SWC3A	RCH1	RCH1A	ZBB1	ZBB1A	ZBB2	ZBB2o	ZBB3
1,2-DCE	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	59	bdl	bdl	60
1,1,1-TCE	bdl	bdl	1.8	bdl	bdl	**492**	**447**	**444**	**436**	bdl	bdl	63	bdl	23	bdl	26	65	bdl
vent	**SWC1**	**SWC1r**	**SWC1oP**	**SWC1oSW**	**SWC1oB**	**SWC2**	**SWC2o**	**SWC2o2**	**SWC2o3**	**SWC3**	**SWC3A**	**RCH1**	**RCH1A**	**ZBB1**	**ZBB1A**	**ZBB2**	**ZBB2o**	**ZBB3**
1,2-DCP	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	54	67	61	bdl	**214**	**114**	bdl
1,1-DCEe	7.2	bdl	27	21	bdl	**287**	**274**	**272**	**272**	30	33	**206**	**221**	**166**	**130**	**191**	**176**	56
VC	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	**323**	**145**	**365**	**299**	**97**
ClB	9.5	bdl	bdl	51	bdl	19	22	39	24	8.3	7.7	bdl	24	bdl	73	bdl	bdl	67
cumene	bdl	bdl	bdl	bdl	bdl	66	64	62	50	bdl	bdl	42	39	90	16	**128**	92	**153**
phenol	4.9	bdl	0.45	9.7	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	20	11	34	bdl	36
o-cresole	2.4	1.6	5.6	2.5	1.4	13	13	12	13	6.2	7.1	56	52	30	22	39	63	16
heterocyclic organic compounds, ppm																		
THF	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	36	bdl	32	21	bdl
py	**178**	**202**	19	**168**	**206**	bdl	bdl	bdl	bdl	**231**	**232**	bdl	bdl	bdl	bdl	bdl	bdl	bdl
tph	bdl	**146**	26	bdl	**149**	**260**	**204**	**200**	**194**	**151**	**141**	bdl	bdl	**496**	bdl	**448**	**282**	bdl
other organic compounds, ppm																		
fm	1.8	0.21	7.1	5.7	0.31	7.4	7.5	7.5	9.4	2.8	3.1	1.6	1.9	bdl	1.2	2.8	bdl	2.2
DMS	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	23	17	65	**153**	60	**148**	**120**
DMDS	**380**	**289**	bdl	16	**293**	bdl	bdl	bdl	bdl	**322**	**321**	7.1	12	bdl	bdl	bdl	bdl	bdl
GC – additional compounds																		
vent	**SWC1**	**SWC1r**	**SWC1oP**	**SWC1oSW**	**SWC1oB**	**SWC2**	**SWC2o**	**SWC2o2**	**SWC2o3**	**SWC3**	**SWC3A**	**RCH1**	**RCH1A**	**ZBB1**	**ZBB1A**	**ZBB2**	**ZBB2o**	**ZBB3**
CH_3Cl	0.001						0.06			0.01	0.04	0.001	0.001	2.0	0.21			
COS												0.003	0.01	2.1	0.45			
ethyne	0.001						0.0004			0.02	0.24	0.0001	0.004	0.02	0.02			

vent	SWC1	SWC1r	SWC1oP	SWC1oSW	SWC1oB	SWC2	SWC2o	SWC2o2	SWC2o3	SWC3	SWC3A	RCH1	RCH1A	ZBB1	ZBB1A	ZBB2	ZBB2o	ZBB3
propene	bdl						0.01			0.65	1.6	0.001	0.001	1.6	0.03			
i-butane	0.002						0.001			0.15	0.06	0.01	0.03	0.53	0.03			
n-butane	0.004						0.002			0.55	0.27	0.01	0.13	2.0	0.07			
1-butene	bdl						0.001			0.05	0.18	0.0002	0.0002	0.17	0.02			
i-butene	bdl						0.002			0.09	0.37	0.0003	0.0005	0.24	0.01			
t-2-bu	0.001						0.001			0.09	0.20	0.0001	0.0003	0.28	0.02			
c-2-bu	0.001						0.001			0.06	0.14	0.0001	0.0001	0.16	0.01			
i-pentane	0.003						0.001			0.10	0.04							
vent	**SWC1**	**SWC1r**	**SWC1oP**	**SWC1oSW**	**SWC1oB**	**SWC2**	**SWC2o**	**SWC2o2**	**SWC2o3**	**SWC3**	**SWC3A**	**RCH1**	**RCH1A**	**ZBB1**	**ZBB1A**	**ZBB2**	**ZBB2o**	**ZBB3**
i-pentane	0.003						0.001			0.10	0.04	0.002	0.01	0.34	0.01			
n-pentane	0.002						0.001			0.29	0.14	0.005	0.03	0.96	0.03			
isoprene	bdl						bdl			0.003	bdl	0.001	0.00005	0.01	0.001			
1,3-budi	bdl						0.0001			0.01	0.04	bdl	bdl	bdl	0.01			
t-2-pte	0.0002						0.0004			0.04	0.04	0.0002	0.001	0.09	0.01			
c-2-pte	0.0001						0.0003			0.02	0.02	0.0001	0.0002	0.04	0.002			
n-heptane	0.001						0.001			0.12	0.07	0.001	0.01	0.33	0.01			
n-octane	0.0002						0.001			0.10	0.05	0.0001	0.001	0.18	0.004			
n-nonane	0.0003						0.0003			0.08	0.03	0.00004	0.001	0.07	0.003			
n-decane	0.0003						0.0003			0.06	0.02	0.00004	0.001	0.04	0.0002			
2,3-DMBu	0.02						bdl			0.01	bdl	0.0001	0.001	0.02	0.001			
2-MPT	0.26						0.001			0.05	0.03	0.001	0.004	0.15	0.003			
3-MPT	9.9						0.0002			0.02	0.01	0.0003	0.001	0.07	0.001			
cpt	0.0005						0.0002			0.04	0.01	0.0005	0.003	0.10	0.002			

vent	SWC1	SWC1r	SWC1oP	SWC1oSW	SWC1oB	SWC2	SWC2o	SWC2o2	SWC2o3	SWC3	SWC3A	RCH1	RCH1A	ZBB1	ZBB1A	ZBB2	ZBB2o	ZBB3
benzene	0.0001						0.03			0.50	1.7	0.003	0.46	12	33			
toluene	0.01						0.005			0.22	0.41	0.002	0.002	2.7	0.01			
EtB	0.0004						0.001			0.03	0.04	0.001	0.001	0.09	0.004			
m/p-X	0.001						0.002			0.07	0.15	0.002	0.002	0.34	0.01			
o-X	0.001						0.001			0.03	0.06	0.001	0.001	0.13	0.005			
styrene	bdl						bdl			0.003	bdl	0.00002	0.0003	0.02	0.0004			
i-PrB	0.0002						bdl			0.002	0.004	0.00002	0.0002	0.003	0.001			
n-PrB	0.0004						0.0004			0.01	0.01	0.0001	0.0003	0.02	0.001			
m-EtT	0.001						0.0002			0.01	0.02	0.0003	0.001	0.04	0.003			
p-EtT	0.0004						0.0001			0.004	0.01	0.0001	0.001	0.02	0.001			
o-EtT	0.0002						0.0001			0.01	0.01	0.0001	0.0004	0.02	0.001			
1,3,5-TMB	0.001						bdl			0.01	0.01	0.0001	0.0004	0.01	0.001			
1,2,4-TMB	0.001						0.0004			0.02	0.03	0.0005	0.001	0.05	0.01			
1,2,3-TMB	0.0004						0.0002			0.01	0.01	0.0002	0.001	0.03	0.004			

Values in parentheses denote overrun of the upper measurement range.
[1]The "A" add denotes samples taken from the depth of 0.8–1 m (below the ground level), while "a" and "o" denote nearby vents; "r" – repeated measurement; "P" – pyrometamorphic zone, "S" – sulfur-mineralized vent.
*[2]Abbreviations explained under **Table 1**; ethane, furan and acetic acid were analyzed but were below their detection limits.*
[3]Notable (>100 ppm) enrichment given in bold.

Table 3.
Results of the pFTIR and GC gas analyses of a BCWH in Świętochłowice (SWC), "Starzykowiec" heap of the "Chwałowice" mine in Rybnik (RCH), and "Ruda" heap in Zabrze-Biskupice (ZBB).

8.3; SO_2, 120, 31; 671, 25; 388, 160; 532, 202; 79, 40; 123, 123; HCl, 11, 2.4; 6.5, 0.58; 6.2, 3.6; 19, 6.1; 8.4, 3.0; 5.9, 3.8; CCl_4, –, –; 6.6, 6.6; 11, 6.5, 1.1, 1.1; 0.57, 0.15; 8.5, 6.8; HF, 0.62, 0.62; 0.03, 0.03; 0.12, 0.12; 1.1, 0.36; 1.1, 0.46; –, –; SiF_4, 6.3, 1.3; 31, 3.5; 21, 16; 3.2, 1.7; 48, 4.6; 28, 19; AsH_3, 0.17, 0.09; 1.7, 0.38; 1.7, 0.75; 3.4, 1.7; 0.40, 0.20; 2.9, 1.1; CH_4, 262, 107; 2950, 16; 3470, 1238; 819, 491; –, –; 1130, 984; ethane, –, –; 30, 30; 142, 142; 281, 281; –, –; –, –; propane, 42, 15; 729, 15; 601, 275; 694, 410; 215, 77; 277, 255; hexane, 11, 1.8; 152, 51; 139, 73; 608, 225; –, –; 69, 48; ethene, 6.6, 3.2; 79, 6.9; 12, 6.0; 84, 27; 26, 13; 23, 20; DCM, 141, 36; 368, 69; 126, 47; 84, 46; 191, 51; 142, 82; 1,1-DCE, 7.2, 7.2; 17, 8.9; –, –; 16, 16; 104, 67; –, –; 1,2-DCE, –, –; 77, 77; 39, 39; 38, 38; –, –; 60, 59; 1,1,1-TCE, 99, 46; 417, 26; 36, 25; 59, 11; 492, 150; 65, 34; 1,2-DCP, 31, 31; 56, 56; 384, 159; 568, 226; –, –; 214, 114; 1,1-DCEe, 77, 21; 347, 67; 195, 123; 28, 17; 287, 66; 191, 132; vinyl chloride, –, –; –, –; 416, 235; chlorobenzene, 39, 24; 186, 15; 77, 44; 206, 81; 51, 18; 73, 70; cumene, 34, 16; 399, 5.7; 126, 97; 264, 81; 66, 81; 153, 60; 153, 76; phenol, 29, 10; 7, 4.2; 51, 16; 67, 41; 9.7, 2.8; 36, 23; *o*-cresol, 46, 5.8; 66, 3.6; 65, 36; 81, 54; 13, 5.3; 63, 30; furan, 0.14, 0.14 (no records for other sites); THF, 1.3, 0.41; 177, 177; 96, 12; 293, 261; –, –; 36, 29; thiophene, 192, 146; 173, 38; 556, 332; 689, 241; 260, 143; 496, 397; formaldehyde, 12, 3.7; 13, 1.2; 5.5, 2.0; 17, 2.3; 9.4, 3.0; 2.8, 1.9; acetic acid, –, –; –, –; 9.1, 9.1; 50, 14; –, –; –, –; DMS, 62, 21; 893, 28; 401, 69; 1540, 534; –, –; 153, 101; DMDS, 104, 28; 37, 21; –, –; –, –; 380, 194; –, –; ad pyridine, 7.1, 7.1; 86, 7.3; –, –; –, –; 232, 144; –, – [ppm]. As compared to these vents, the one at the RCH site. The geometric mean concentrations for the whole range are: H_2O 9.5, CO_2 3.83 [vol.%], CO 350, NO 20, NO_2 54, N_2O 0.51, NH_3 7.5, SO_2 72, HCl 2.5, CCl_4 2.3, HF 0.26, SiF_4 4.5, AsH_3 0.53, methane 201, ethane 106, propane 58, hexane 29, ethene 11, DCM 54, 1,1-DCE 17, 1,2-DCE 53, 1,1,1-TCE 37, 1,2-DCP 127, 1,1-DCEe 60, vinyl chloride 165, chlorobenzene 30, cumene 36, phenol and *o*-cresol and THF 13, furan 0.14, thiophene 200, formaldehyde 2.2, acetic acid 13, DMS 65, DMDS 39, and pyridine 29.

5. Discussion

In general, the data provided for additional vents from additional BCWH probed allows to enlarge the span of the maximum observed values of only some compounds. They include (with excess in parentheses) CO (10x), SO_2, 1,1,1-TCE (12x), 1,1-DCEe (2.5x), cumene (2x), formaldehyde (3x), and pyridine (21x). Higher than previously observed geometric mean values are also observed for NO_2, CCl_4, ethane (2x), propane, ethene, and thiophene. This is clearly seen in the case of the latter two compounds, with more frequent positive determinations than within the previous studies. Similar levels of geometric means are found for HCl, AsH_3, chlorobenzene, phenol, and DMDS. As formerly observed, concentration ranges are usually extremely variable. Cumene is a good example of a compound with very high maximum but very low geometric mean. So is true, though less clearly, for, e.g., *o*-cresol. Some compounds often show large contents but single records. For many BCWHs there are large discrepancies between the geometric mean values and maximums, while for less number of the objects studied the amounts emitted are at very steady level. Some constituents, like vinyl chloride and even methane, may show very high concentrations (>100 ppm) but may be "absent" (below detection limits) at other BCWHs or vents. As explained in the former papers, this results from very high dynamics of the local combustion processes. The *ex situ* GC values obtained are, again, usually much lower than those observed by *in situ* FTIR, thus confirming their uncertain and, possibly, semi-quantitative value. On the other hand, two compounds not observed within the previous GC data are now determined: CH_3Cl (chloromethane or methyl chloride) and cyclopentane.

At the time of the BCWH gas analyses the author could not find paper showing the usage of FTIR for environmental studies. Stockwell et al. [27] used this method to measure H_2O, CO_x, NO_x, HCl, SO_2, NH_3, methane, acetylene, ethene, propane, formaldehyde, formic acid, methanol, acetic acid, HCN, furan, glycolaldehyde, and HONO (the latter also initially reported in [6]) in biomass emissions, though in a Fire Lab at Missoula Experiment. A more *in situ* type of work, engaging airborne FTIR, is by Yokelson et al. [28] who measured African savanna fires, with 14 compounds analyzed.

It is noteworthy that numerous organic and organo(semi)metallic compounds (or similar ones) detected in the BCWHs exhausts are also detected in volcanic fumaroles (mainly via GC, or modeled, as summarized by Wahrenberger [29]) or algal emissions (by GC–MS; [30]). Examples of interesting species include CO_2, COS, CS_2, S_2, S_8, SO_2, AsH_3, HCl, HF, HBr, $CHCl_3$, NO_2, propanal, methanol, acetaldehyde, 1,1,2-trichlorotrifluoroethane, hexafluoropropene, tetrachloroethene, vinyl chloride, *i*-butene, hexane, octane, octane, butadiene, benzene, toluene, α-pinene, *i*- and *n*-propanol, methylacrolein, MEK, acetone, 1,4-dioxane, dimethyldifluorosilane, thioformaldehyde, ethylthiophene, trimethylborane, methylphosphine, and uncertain [*N*-(phenyl-2-pyridinylmethylene)benzeneamine-*N*,*N*′]-irontricarbonyl and silver benzoate; geosmin, cyclopentane, cyclohexane, acetic acid, acetamide, glucopyranose, dibutyl phthalate, cholest-5-en-22-one, benzaldehyde, hydrazine, 8-amino-2-naphthalenol, ethanethioimide, thiourea, 1,3-oxathian-2-one, tetrahydro-2,5-dimethylthiophene, 6-methylbenzo[*b*]thiophene, 3,3,5,5,-tetramethyl-1,2,4-trithiolane, thiirane, $C_2H_7O_2B$ borane, trimethylsilane, butytrimethylsilane, or undecanoic acid 11-chloro- and 11-fluorotrimethylsilyl esters.

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