

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, SO₂, and, to a lesser extent, NO₂, CCl₄, ethane, propane, ethene, and thiophene. The latter, and DMS, are confirmed as gaseous S source more frequent and rich than SO₂.

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 O₂, CO₂, CO, NO₂, SO₂, NH₃, PH₃ (phosphine), acetic acid, acetone, propane, benzene, toluene, styrene, *o*-xylene, butadiene, total mercaptans (thiols), methanol, *i*-propanol, trichloroethene (TCE), vinyl chloride, methyl *tert*-butyl ether (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): H₂S (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 I₂ (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 overcome 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 revolatilization, 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 PH₃, 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), (CH₃)₃As, and trimethylstibine (TMS), (CH₃)₃Sb, and also metallic Hg, emitted from algal mats. The same method allowed to Feldmann et al. to detect (via cryo-trapping) trimethylbismuthine, (CH₃)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 HNO₃ and H₂O₂), 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 $\sim 1200^{\circ}\text{C}$ 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, $(\text{NH}_4, \text{K})_2[\text{FeCl}_5(\text{H}_2\text{O})]$ and other chlorides. The second one is responsible for vast, thick sulfate crusts mainly comprising godovikovite-sabieite solid solution, $(\text{NH}_4)(\text{Al}, \text{Fe})(\text{SO}_4)_2$, millosevichite-mikasaite solid solution, $(\text{Al}, \text{Fe})_2(\text{SO}_4)_3$, steklite, $\text{KAl}(\text{SO}_4)_2$, tschermigite, $(\text{NH}_4)\text{Al}(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ (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 $2\text{ }\mu\text{m}$ 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]: H₂O 57.5, 19.3, 12.5, 36.2 vol.%; CO₂ 67.2, 7.63, 6.82, 30.6 vol.%; CO 2690, 694, 21, 347; NO 434, 38, 123, 151; N₂O not observed (n.o.), 0.42, 1.2, 8.7; NO₂ 16430, 116, 24, 191; NH₃ 1715, 646, 14, 98; SO₂ 582, 74, 64, 226; HCl 58, 23, 2.4, 8.9; CCl₄ 22, 1.5, 6.0, 14; HF 4.0, 2.2, n.o., 5.1; SiF₄ 1890, 228, 504, 1980; AsH₃ 8.2, 0.49, 0.18, 0.64; CH₄ 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, GeCl₄, i.e., 3130, 209, 333, and 2098 should be treated with care due to possible coincidence as yet unresolvable by the Calcmets software. Geometric means of the concentration values (Pszów, Rybnik-Rymer, Radlin, Rydułtowy, whole series) are: H₂O 31, 12, 3.0, 21, and 19 ($n_{\text{total}} = 46$); CO₂ 31, 4.0, 0.22, 11, and 7.0 ($n_{\text{total}} = 50$) [vol.]; CO 84, 186, 9.6, 81, and 81 ($n_{\text{total}} = 41$); NO 87, 15, 14, 66, and 42 ($n_{\text{total}} = 24$); NO₂ 334, 38, 14, 42, and 41 ($n_{\text{total}} = 26$); N₂O -, 0.10, 0.66, 4.3, and 0.83 ($n_{\text{total}} = 17$); NH₃ 287, 22, 3.4, 59, and 88 ($n_{\text{total}} = 18$); SO₂ 110, 18, 17, 48, and 56 ($n_{\text{total}} = 31$); HCl 7.4, 4.2, 0.56, 3.0, and 3.8 ($n_{\text{total}} = 46$); CCl₄ 3.2, 0.18, 0.91, 2.5, and 1.6 ($n_{\text{total}} = 51$); HF 4.0, 2.2, -, 3.3, and 3.4 ($n_{\text{total}} = 9$); SiF₄ 16, 114, 94, 182, and 65 ($n_{\text{total}} = 29$); AsH₃ 1.1, 0.19, 0.17, 1.0, and 0.58 ($n_{\text{total}} = 26$); CH₄ 1945, 500, 23, 537, and 457 ($n_{\text{total}} = 47$); ethane 46, 114, 15, 75, and 59 ($n_{\text{total}} = 37$); propane 148, 70, 16, 27, and 46 ($n_{\text{total}} = 27$); hexane 160, 25, -, 15, and 38 ($n_{\text{total}} = 26$); ethene 7.9, 7.3, 11, 8.3, and 8.2 ($n_{\text{total}} = 28$); DCM 230, 119, 160, 295, and 214 ($n_{\text{total}} = 45$); 1,1-DCE 235, 190, 98, 99, and 139 ($n_{\text{total}} = 32$); 1,2-DCE 153, 28, 7.4, -, and 91 ($n_{\text{total}} = 9$); 1,1,1-TCE 5.4, -, 40, 9.5, and 7.7 ($n_{\text{total}} = 19$); 1,2-DCP 1038, 5.7, -, 20, and 166 ($n_{\text{total}} = 9$); 1,1-DCEe 19, 2.6, 31, 25, and 20 ($n_{\text{total}} = 35$); vinyl chloride 329, 38, -, 394, and 289 ($n_{\text{total}} = 32$); chlorobenzene 24, 36, 92, 32, and 32 ($n_{\text{total}} = 12$); cumene 28, 30, 35, 15, and 22 ($n_{\text{total}} = 38$); phenol 14, 36, 3.8, 32, and 19 ($n_{\text{total}} = 32$); *o*-cresol 115, 21, -, 99, and 73 ($n_{\text{total}} = 15$); furan 11, 9.8, 72, 12, and 31 ($n_{\text{total}} = 18$); THF 126, 372, -, 643, and 195 ($n_{\text{total}} = 10$); thiophene 251, 200, 90, 156, and 186 ($n_{\text{total}} = 40$); formaldehyde 3.5, -, -, 0.54, and 0.82 ($n_{\text{total}} = 8$); acetic acid 189, 6.6, 8.1, 83, and 54 ($n_{\text{total}} = 22$); DMS 517, 433, -, 921, and 533 ($n_{\text{total}} = 16$); DMDS 68, 11, -, 31, and 41 ($n_{\text{total}} = 35$); 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, CS₂, freons (CCl₃F, CCl₂F₂, CHClF₂), *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 $\geq 90\%$, 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 $\geq 50\%$ 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, disilane, 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
	40	45	45	45	25	35	35	35	35	60	90	90	82	82	50	82	30	45
T [°C]																		
pFTIR																		
inorganics, vol. %																		
H ₂ O 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 ₂ O	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
SF 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
tp _h	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 ³	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 ₃ Cl	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>i</i> -butane	0.0003			0.002	1.6			3.2	3.5						0.08	0.69	8.3	2.3
<i>n</i> -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>i</i> -butene	0.0001			0.002	0.41			0.32	0.52						0.03	0.04	1.3	0.42
<i>t</i> ⁻² -bu	0.00004			0.001	0.52			1.4	0.50						0.02	0.04	0.59	0.24
<i>c</i> -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>i</i> -pentane	0.001			0.01	0.92			1.8	1.8						0.06	0.35	6.5	1.7
<i>n</i> -pentane	0.0003			0.01	1.1			2.3	1.5						0.06	0.35	6.0	1.9
<i>t</i> -2-pte	bdl			0.002	0.20			0.57	0.19						0.01	0.01	0.36	0.18
<i>c</i> -2-pte	bdl			0.001	0.08			0.23	0.07						0.004	0.003	0.09	0.04
<i>n</i> -heptane	bdl			0.003	0.44			0.84	0.34						0.02	0.07	1.7	0.68
<i>n</i> -octane	bdl			0.002	0.36			0.65	0.10						0.01	0.04	0.64	0.32
<i>n</i> -nonane	bdl			0.0003	0.25			0.40	0.03						0.01	0.01	0.22	0.04
<i>n</i> -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-ErT	bdl			0.0005	0.07			0.10		0.02					0.001	0.003	0.01	0.01
o-ErT	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.

¹A – samples taken from the depth of 0.8–1 m; “a” and “o” – nearby vents; “s” – repeated analysis; “S” – sulfur-mineralized vent.

²DCM – dichloromethane, DCE – dichloroethane, DCEe – 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.

³Notable (>100 ppm) enrichment given in bold.

⁴GC 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 ₂ O 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 ₂ O	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
<i>heterocyclic organic compounds, ppm</i>																	
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
<i>other organic compounds, ppm</i>																	
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 ₃ Cl	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>i</i> -butane	3.3		1.7	0.08	0.005	0.13	2.0	2.6			2.4						1.7
<i>n</i> -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>i</i> -butene	0.06		0.08	0.51	0.002	0.01	0.98	0.38			6.6						0.26
<i>t</i> -2-bu	0.01		0.06	0.16	0.001	0.01	0.78	0.24			2.3						0.07
<i>c</i> -2-bu	0.01		0.03	0.12	0.0005	0.003	0.47	0.18			1.6						0.04
<i>i</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
<i>n</i> -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
<i>t</i> -2-pte	0.12		0.01	0.06	0.001	0.01	0.21	0.08			0.81						0.01
<i>c</i> -2-pte	0.05		0.003	0.03	0.0004	0.002	0.09	0.03			0.39						0.003
<i>n</i> -heptane	0.44		0.18	0.03	0.001	0.01	0.58	0.41			0.93						0.11
<i>n</i> -octane	0.05		0.05	0.03	0.0007	0.004	0.18	0.21			0.57						0.05
<i>n</i> -nonane	0.03		0.46	0.02	0.0003	0.001	0.08	0.15			0.44						0.10
<i>n</i> -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
<i>m/p</i> -X	0.03		0.11	0.28	0.001	0.05	0.34	0.36		3.0							0.17
<i>o</i> -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>i</i> -PrB	0.001		0.02	0.01	bdl	0.001	0.003	0.02		0.71							0.01
<i>n</i> -PrB	0.002		0.01	0.04	0.0001	0.002	0.003	0.02		0.27							0.01
<i>m</i> -EtT	0.01		0.05	0.11	0.0001	0.003	0.01	0.08		0.54							0.05
<i>p</i> -EtT	0.002		0.02	0.05	0.00003	0.001	0.01	0.06		0.38							0.02
<i>o</i> -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.
¹the “A” add denotes samples taken from the depth of 0.8–1 m (below the ground level), while “a” and “o” denote nearby veins; “r” – repeated measurement; “p” – pyrometamorphic zone,
“S” – sulfur-mineralized vent.
²Abbreviations explained under **Table 1**: ViCl – vinyl chloride; furan, pyridine and DMDS were analyzed but were below their detection limits.
³Notable (>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	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	100
pFTIR																	
main components, vol. %																	
H ₂ O 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	21.13
CO ₂	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	0.11	0.79	38.31	33.95	34.75	38.41
inorganics, ppm																	
CO	92	143	166	164	144	1090	1070	1060	1040	172	176	21	21	1220	12600	938	26700
N ₂ O	bdl	bdl	bdl	bdl	bdl	1.3	1.3	1.3	1.2	bdl	bdl	bdl	2.6	bdl	bdl	bdl	bdl
NO	12	15	bdl	bdl	19	bdl	bdl	bdl	bdl	bdl	bdl	100	bdl	bdl	bdl	bdl	bdl
NO ₂	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	66	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	8.3
SO ₂	bdl	15	46	bdl	14	79	59	58	53	39	47	129	172	bdl	bdl	bdl	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	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	4.0
HF	0.19	bdl	bdl	1.1	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	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	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	880
propane	192	72	bdl	bdl	85	34	37	37	39	208	215	11	12	233	bdl	257	bdl
hexane	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	bdl	38	69	39	64
ethene	bdl	bdl	bdl	2.3	bdl	26	26	24	8.5	bdl	bdl	bdl	bdl	18	19	21	21
DCM	30	19	11	28	20	181	191	191	189	36	39	173	143	92	142	46	82
1,1-DCE	12	bdl	bdl	bdl	bdl	103	102	102	104	bdl	bdl	11	2.4	bdl	bdl	bdl	bdl

vent¹	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	bdl	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
<i>o</i> -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
<i>heterocyclic organic compounds, ppm</i>																		
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
<i>other organic compounds, ppm</i>																		
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 ₃ Cl	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	0.004	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>i</i> -butane	0.002						0.001			0.15	0.06	0.01	0.03	0.53	0.03			
<i>n</i> -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>i</i> -butene	bdl						0.002			0.09	0.37	0.0003	0.0005	0.24	0.01			
<i>t</i> -2-bu	0.001						0.001			0.09	0.20	0.0001	0.0003	0.28	0.02			
<i>c</i> -2-bu	0.001						0.001			0.06	0.14	0.0001	0.0001	0.16	0.01			
<i>i</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>i</i> -pentane	0.003						0.001			0.10	0.04	0.002	0.01	0.34	0.01			
<i>n</i> -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			
<i>t</i> -2-pte	0.0002						0.0004			0.04	0.04	0.0002	0.001	0.09	0.01			
<i>c</i> -2-pte	0.0001						0.0003			0.02	0.02	0.0001	0.0002	0.04	0.002			
<i>n</i> -heptane	0.001						0.001			0.12	0.07	0.001	0.01	0.33	0.01			
<i>n</i> -octane	0.0002						0.001			0.10	0.05	0.0001	0.001	0.18	0.004			
<i>n</i> -nonane	0.0003						0.0003			0.08	0.03	0.00004	0.001	0.07	0.003			
<i>n</i> -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				
<i>m</i> / <i>p</i> -X	0.001						0.002		0.07	0.15	0.002	0.002	0.34	0.01				
<i>o</i> -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>i</i> -PrB	0.0002						bdl		0.002	0.004	0.00002	0.0002	0.003	0.001				
<i>n</i> -PrB	0.0004						0.0004		0.01	0.01	0.0001	0.0003	0.02	0.001				
<i>m</i> -EtT	0.001						0.0002		0.01	0.02	0.0003	0.001	0.04	0.003				
<i>p</i> -EtT	0.0004						0.0001		0.004	0.01	0.0001	0.001	0.02	0.001				
<i>o</i> -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.
¹The "A" add denotes samples taken from the depth of 0.8–1 m (below the ground level), while "a" and "o" denote nearby vents; "γ" – repeated measurement; "p" – pyrometamorphic zone, "s" – sulfur-mineralized vent.
²Abbreviations explained under Table 1; ethane, furan and acetic acid were analyzed but were below their detection limits.
³Notable (>100 ppm) enrichment given in bold.

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

8.3; SO₂, 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; CCl₄, —, —; 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; —, —; SiF₄, 6.3, 1.3; 31, 3.5; 21, 16; 3.2, 1.7; 48, 4.6; 28, 19; AsH₃, 0.17, 0.09; 1.7, 0.38; 1.7, 0.75; 3.4, 1.7; 0.40, 0.20; 2.9, 1.1; CH₄, 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, 7.2; 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-DCE, 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: H₂O 9.5, CO₂ 3.83 [vol.%], CO 350, NO 20, NO₂ 54, N₂O 0.51, NH₃ 7.5, SO₂ 72, HCl 2.5, CCl₄ 2.3, HF 0.26, SiF₄ 4.5, AsH₃ 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), SO₂, 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 NO₂, CCl₄, 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, AsH₃, 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: CH₃Cl (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 H₂O, CO_x, NO_x, HCl, SO₂, NH₃, 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 CO₂, COS, CS₂, S₂, S₈, SO₂, AsH₃, HCl, HF, HBr, CHCl₃, NO₂, 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, C₂H₇O₂B borane, trimethylsilane, butytrimethylsilane, or undecanoic acid 11-chloro- and 11-fluorotrimethylsilyl esters.

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