Spontaneous coal fires in heaps and beyond – a forgotten factor of the dynamics of climate change

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Abstract. Spontaneous coal fires are known from both post-coal mining waste-rock heaps and natural geoenvironments. They represent a still not fully scientifically encompassed phenomenon. They are very difficult to be fully contained, thus sustaining long-time emissions in the heaps. Some of them may burn for 70 years and more. As a worldwide issue, both from environmental and human safety point of view, these fires pose a forgotten factor of the dynamics of coal fires, as they add to the worldwide CO_2 emissions' budget. However, CO_2 is just a tip of an iceberg in these emissions, as shown here by the example of the Upper Silesian heaps of Poland.

1 Introduction

1.1 Spontaneous coal fires – general information

Spontaneous coal fires (SCF) pose a global issue that concerns both natural (e.g., coal mines, unexploited coalfields (e.g., [1])) and industrial (post-coal-mining waste-rock heaps, PCWH) [2-4]. They are rarely mentioned as a factor of climate change. Meanwhile, coal (and also bitumen) burning induces formation of fumarole that are analogous to volcanic hydrothermal vents. Examples of such fumaroles from Polish PCWH are shown in Figure 1.

These events are typically linked to self-heating, spontaneous ignition, and combustion of the fuel. Their causes are complex, with key factors including oxidation of organic matter, formation of oxocarbons, the role of coal petrology (maceral composition), the physico-chemical behavior and spatial interactions of coal macerals, and the catalytic or fluxing effects of iron minerals [5-7]. Importantly, in heaps not only coal but also associated barren sedimentary rocks—shales, sandstones, carbonate concretions, and others—may burn and degas [7, 8]. Some well-known cases have, however, been human-induced. One of the most famous examples is the Centralia fire in Pennsylvania, USA, which has been active for over 57 years [4].

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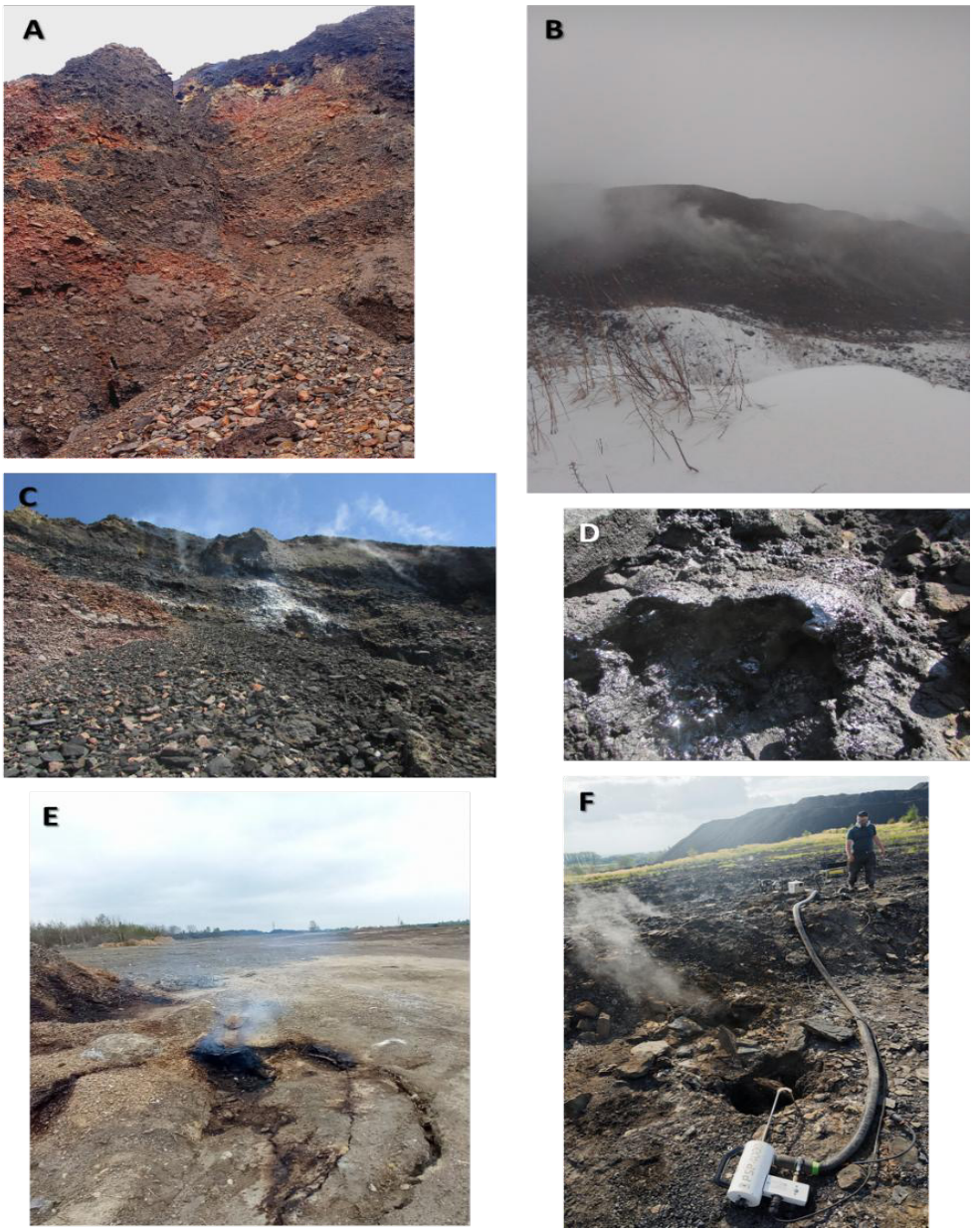

Fig. 1. Examples of coal-fire fumaroles in the Upper Silesian post-mining waste-rock heaps. A – hot (>200 °C surface temperature) gas vent richly encrusted with salammoniac (NH_4Cl), sulfur (S_8) and NH_4-Bi-Pb-Sn-Cd-Ag-Cl-I-Br mineralization; B – another, highly hydrated fumarole in the same heap, winter time; C – hot fumaroles of another heap, richly encrusted by salammoniac covered by orange-red ammonium iodobismuthate – a new mineral; this site strongly resembles La Fossa volcano, Italy; D – shiny coal tar and minor salammoniac freshly desublimed from reduced gases; E – very hot organics-rich fumarole in a fire front; F – *in situ* complex gas analysis of sulfur-encrusted gypsum ($CaSO_4 \cdot 2H_2O$)-rich fumaroles using portable GASMET DX4000 system.

In China and India, both anthropogenic and natural coal fires affect areas spanning many square kilometers. In China, they occur mainly in the northern provinces—Xinjiang, Inner Mongolia, and Ningxia. In Tajikistan, famous lignite fires of the Kukhi-Malik – Ravat – Jijikrut are (Fan-Yagnob Coal Basin) were reportedly observed by Alexander the Great [8], suggesting continuous activity for more than 2000 years.

The PCWH are widespread wherever coal is exploited [4, 6-8, 9-10]. Such heaps typically contain both residual coal and barren rock and undergo intense physicochemical transformations driven by three main processes [8, 11–13]: (1) pyrometamorphism – high-temperature contact metamorphism during the burnout stage, (2) exhalative processes – condensation of hot coal-fire gases (CFG) and their interaction with waste material, analogous to hydrothermal processes; and finally (3) low-temperature supergene alteration – formation of hydrated sulfates of NH_4^+, Mg, Al, Fe, Ca, K, and Na.

1.2 Chemistry of coal burning

Coal burning induces decomposition and simplification of the complex structure of the coal macromolecule that comprises carbon, hydrogen, oxygen, nitrogen, sulfur and some minor elements. Examples of chemical reactions related to this process are given in Figure 2.

1.3 Coal fires versus climate change

The SCF are rarely mentioned as a factor of the climate change and its dynamics. Meanwhile, the north China SCF area is potentially responsible for as much as 2-3% of the yearly, worldwide CO_2 production from fossil fuels burning [1].

Numerous studies of coal-fire gas (CFG) rely on the Gas Chromatography (GC) method and simple analytical tools, thus reporting, e.g., SO_2 as the sole form of sulfur. We have proven that the GC method – especially as not necessarily an *in situ* method – may not be ideal and may not represent the completely true and whole spectrum of the gaseous compounds in the heap emissions. With the sophisticated portable FTIR spectrometer (GASMET DX-4000), used, i.a., in situ, we have shown that this is a large oversimplification, with dimethyl sulfide (DMS), $(CH_3)_2S$, thiophene, C_4H_4S, and occasionally dimethyl disulfide(DMDS), $(CH_3)_2S_2$, being volumetrically more important [14]. One of the major discoveries is also highly probable admixture of SF_6 in concentrations much higher (1.n ppmv) than ones typically measured in natural environment [15].

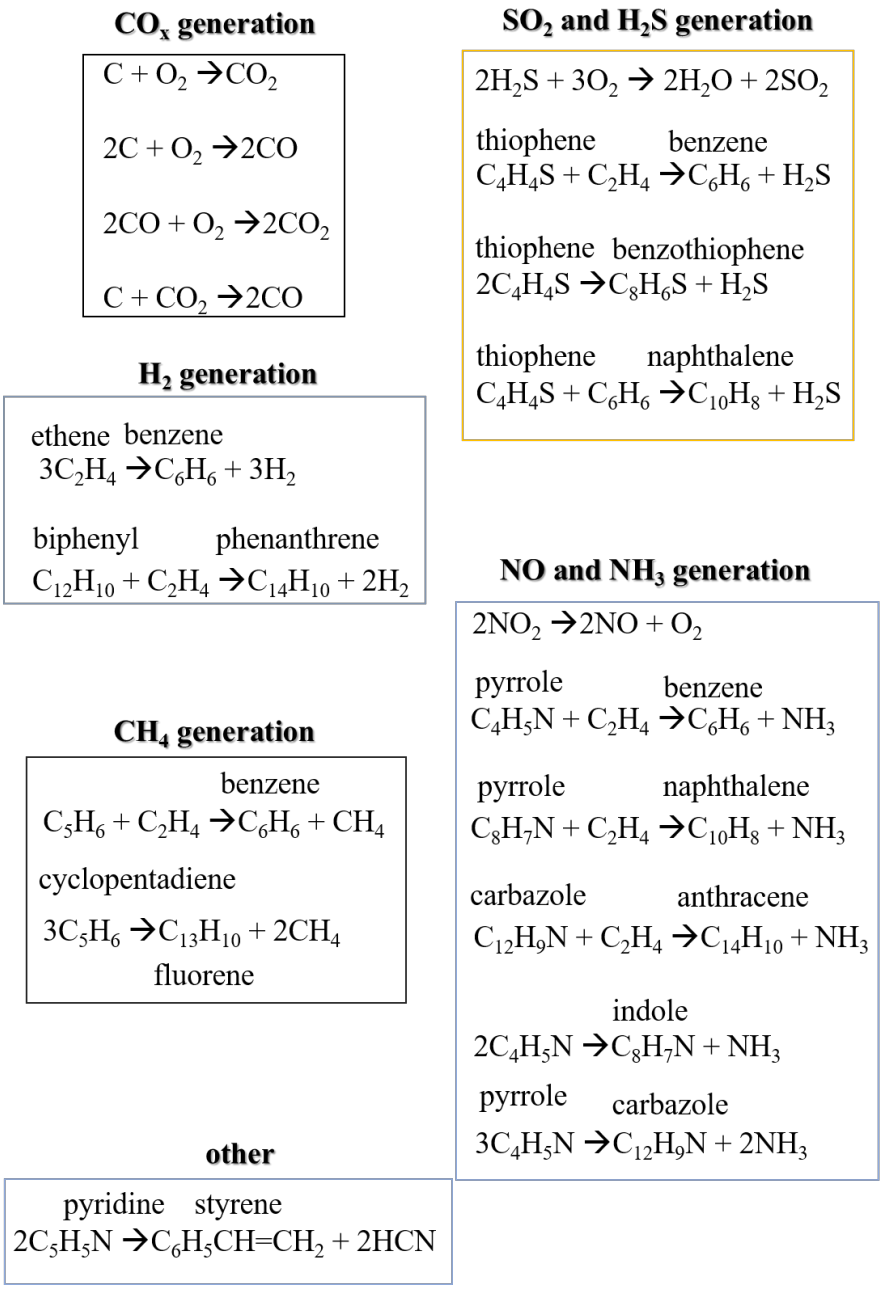

Fig. 2. Examples gas-generation reactions due coal burning (from [7], also given in [13]).

2 Examples from Poland

A few-year-long spatiotemporal study of the gaseous emissions in the Polish PCWH mainly of the Upper Silesian Coal Basin area, that encompassed ~100 fumarolic vents in various objects allowed to deeply dive into both the chemical composition of the local CFG and its variations. We have used a sophisticated *in situ* analysis by the means of the FTIR spectrometry (GASMET DX4000 system) that allows to study hot, chemically aggressive and ash-carrying fumes. An important feature of this system is capability of immediate reporting of both organic and inorganic compounds. The inorganic part not only includes separated NO_x (N_2O, NO, NO_2) but also water and simple gases that do not interact with due to a special heating procedure applied. The method is based on a multi-step approach: (1) precise, certified, fully quantitative analysis of 30+ preselected gases with comparative spectra written in the internal Calibration Library, (2) semi-quantitative analysis of few tens of additional external Library Search, (3) semi-quantitative analysis of numerous additional substances via Spectrum Match, and finally (4) qualitative analysis of residual spectra allowing to pinpoint additional admixing gases. Some of the latter were confirmed by us using Indicatory Tube colorimetric method; they include HCN, I_2, and methyl bromide.

The composition of coal-fire gases (CFG) is highly variable, and no clear correlations within the gas–condensate system have been established to date. Among sulfur-bearing species, thiophene is the most common and abundant, followed by dimethyl sulfide (DMS), while SO_2 and H_2S typically occur only in lesser or minor amounts. Nitrogen-rich gases are dominated by NH_3 and NO_2; the latter can sometimes be present in large quantities. Pyridine is usually trace, but may be strongly enriched in some heaps studied recently by me within a multi-year monitoring that stands for a continuation of the research cited here. This monitoring also allowed to determine >15000 ppmv CO emitted in some very hot (250 – 777 ^oC) fumaroles. Chlorine-rich compounds are numerous, with 1,1-dichloroethane and dichloromethane (DCM) prevailing, followed by vinyl chloride. Other chloroalkanes, chloroalkenes, chlorobenzene, and CCl_4 are usually present in smaller amounts or are absent (or below detection limits). Silicon tetrafluoride (SiF_4) is generally much more abundant than hydrogen fluoride (HF), while freons appear only as trace components. Arsine (AsH_3) is detected in most samples, but always in very low concentrations. Certain oxygen-bearing organics—such as acetic acid, phenol, *o*-cresol, furan, and tetrahydrofuran (THF)—may be absent in some samples, yet occasionally show high enrichment. Additionally, trace gases may include neutral metal hydroxides, hydrides, and carbonyl and nitrosyl complexes, that would serve as important carriers of (semi)metallic elements [14-15].

As much as 65% of the fumaroles researched by [26, 27] have their CFG composition dominated by water; 19% is CO_2-dominant, and the remainder of 17% has other gases as their major component. 31% of these vents show 15-40 vol.% of water, 29% – 0.n-5 vol.%, 20% – 6-15 vol.%, 16% are anhydrous, while just 4% are extremely hydrated with >40 vol.%. In the methane case, 38% vents show >100 ppmv, 15% – >1000 ppmv, and just 1% has extreme contents of >10000 ppmv. Total sulfur-rich gases usually occur in the amounts of >100 ppmv (52% of the vents), 39% of the fumaroles is S-low or S-free, while 9% are enriched with >1000 ppmv. Most (70%) of the fumaroles are low or possibly free in nitrogen-rich gases, but as much as 28% shows >100 ppmv of these; extreme (>1000 ppmv) amounts only concern 2% of the vents. In the chlorine case, the Cl-rich gases at the level of >100 ppmv concern much higher part – 58% of the vents; 29% is low in or free of these, and 13% show >1000 ppmv contents.

Dominance of the S-species of gases is as follows: 32% fumaroles have thiophene as the dominant gaseous S species; 25% – DMS, 23% – SO_2, and 18% – DMDS. In the nitrogen case, 50% cases represent dominance of NH_3, with 23% records of NO_2, 16% of pyridine, 10% of NO, and just 3% of N_2O. The corresponding data values for the Cl-rich gases are as follows: 28% – DCM, 23% – vinyl chloride, 17% – 1,1-dichloroethene, 12% – 1,2-dichloroethane, 10% – dichloropropane, 4% – 1,1-dichloroethane, and 3% for both chlorobenzene and 1,1,1-trichloroethane. It should be noted that in some cases there is a possibility of the dominance of another S-, Cl- and N-rich gases that could not be encompassed by the methods used.

Moderate enrichment of the local CFG, with contents >100 ppmv (but below 1000 ppmv) usually concerns CO_2 (22% of cases), followed by 17% with thiophene, 12% – SO2, 10% – furan + THF collective, 8% – cumene, 7% – (phenol and *o*-cresol), 6% – NO_2, with 5% for both NO, NH_3 and SiF_4.

Extreme enrichment with >1000 ppmv levels usually concerns CO (59% of cases), with 19% for DMS, 11% for DMDS, 7% for NH_3, and 4% for NO_2. A single case of a fumarole with ~15000 ppmv DMS is known.

Typical concentrations of gases measured in 52 fumaroles of 4 PCWH are (mean followed by maximum): in vol.%, CO_2 7.0, 67.2; H_2O 19, 57.5; in ppmv, CO 2690, 26700; N_2O 0.83, 8.7; NO 42, 434; NO_2 41, 16430; NH_3 88, 1715; SO_2 56, 582; HCl 3.8, 58; HF 3.4, 5.1; CCl_4 1.6, 22; SiF_4 65, 1980; AsH_3 0.58, 8.2; methane 457, 82970; ethane 59, 511; ethene 8.2, 92; propane 46, 1446; hexane 38, 921; DCM 214, 5472; 1,1-dichloroethane 139, 2110; 1,2-dichloroethane 91, 573; 1,1-dichloroethene 20, 140; 1,2-dichloropropane 166, 4900; 1,1,1-trichloroethane 7.7, 40; vinyl chloride 289, 1980; chlorobenzene 32, 416; cumene 22, 194; phenol 19, 348; *o*-cresol 73, 1620; furan 31, 130; tetrahydrofuran 195, 2830; thiophene 186, 781; DMS 533, 6780; DMDS 41, 518; acetic acid 54, 7000; formaldehyde 0.82, 5.7; pyridine – 11 ppmv content in a single spot. However, further measurements in few other heaps have shown even larger contents of CO (26700 ppmv), SO2 (671 ppmv), 1,1-dichloroethene (347 ppmv), 1,1,1-trichloroethane (492 ppmv), cumene (264 ppmv), formaldehyde (17 ppmv), and pyridine (232 ppmv).

3 Discussion

As shown above, the SCF can represent an important, though seemingly forgotten component of the complex puzzle that is changing climate dynamics. Even if they do not essentially influence the atmosphere as a whole, they definitely impact it's local parcels. An example of this is a road sign in Łaziska Górne warning against sudden weather changes. It is there due to one of the local, large PCWH, known as "Skalny". Even though this heap was reclaimed a long time ago, the emergence of new fire foci – an almost unpredictable phenomenon – may be a matter of time. This was the case of one of the heaps in Ruda Śląska, where the fire suddenly appeared suddenly after several decades of calm, i.e., since the object was built.

4 Conclusions

Spontaneous coal fires – both of the anthropogenic (mining, heap formation) and natural environments – pose an obvious threat to the local environments. They should also be introduced in discussions of the changes of dynamics of climate change, as they are responsible for continuous, multi-year emissions of numerous gaseous compounds, including

not only the noxious gases but also potent greenhouse gases as CO_2, CH_4, CO, H_2O, freons, N_2O, and SF_6. The presence and abundance of NO_x, NH_3, DMS, DMDS, SO_2, chloroalkanes and chloroalkenes should also be considered. An open question remaining is: are the heap fires influencing only the local atmosphere or beyond?

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