Emission of Toxic Gases and Condensation Minerals from Burning Coal Waste Heaps in Northern France: Measurements and Analyses

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Abstract
The Nord-Pas-de-Calais region in northern France is well known for its great number of coal waste heaps. One of the problems associated with these residues from coal mining is spontaneous combustion. Spontaneous combustion poses significant safety, geo-technical, and environmental hazards; it is at the origin of gas spots (vents), ground subsidence, surface cavities, noxious gases, secondary minerals, and thermal metamorphosis of rock debris. Gas spots were localized at one site based on field observations and aerial infrared thermography. In-situ gas measurements and analyses were carried out around active spots in two burning coal waste heaps. The gases measured were greenhouse (CO₂ and CH₄) as well as acidic gases (SO₂ and NOₓ), CO, O₂, and H₂O. The proportion of CO₂ (7 %), in particular, was higher than expected. O₂ concentrations ranged between < 1 and 19 %. The ambient air at some spots had to be classified as contaminated or poisonous. Secondary salt efflorescence of single minerals or mineral compounds was observed on carbonaceous shale around gas vents. To a large part, these minerals were deposited as encrustations on rock debris at temperatures of less than 300 °C; they included sulfates (thenardite, bloedite, konyaite, glauberite, aphphtitalite, langbeinite, arcanite,
gypsum, epsomite, hexahydrite, alunogen, kalinite, pickeringite, halorichite, tschermigite, mascagnite, lecontite), halides (salammoniac and halite), native sulfur, and two possibly new unknown minerals. Most of the sulfate minerals were documented for the first time in connection with coal fire emissions; the same holds for fluid inclusions in thenardite crystals. Major chemical components detected in fumarole discharge were SO$_4$, NH$_4$, H$_2$O, Cl, Mg, K, Na, Al, Ca, Fe, Mn, and S. A multitude of different approaches – field observations, optical microscopic examinations, X-ray diffraction, scanning electron microscope observations, energy-dispersive spectrometry, wavelength-dispersive spectroscopy, and total chemical analysis (ICP-MS) – were combined to study the occurrence of secondary minerals.

摘要

癌国北部的 Nord-Pas-de-Calais 地区以其大量的煤矸石堆而著名。煤自然是与这些煤矿开采废弃物有关的重要问题之一。煤自然引起了安全、地质和环境灾害，正是被自然引发了气体排放、地表沉陷、地表洞穴、有害气体、次生矿物和岩石碎屑热变质作用。根据野外观察和航空热红外测量圈定了气体排放位置，还在两个正在燃烧的矸石堆周围气体排放处进行了现场气体测量与分析。所测气体包括了温室气体（CO$_2$和 CH$_4$），及酸性气体（SO$_2$和 NO$_x$）、CO、O$_2$和 H$_2$O。特别是二氧化碳气体浓度的比例（7%）远高于预期值。O$_2$含量介于 1 到 19%。在某些观测点周围空气可归类为污染气体或者有害气体。在气体排放孔周围的不同岩石中可见单矿物或复和矿物的次生盐积物。这些矿物相当大部分在低于 300℃ 时沉积形成岩石碎屑的盖层，包括硫化矿物（芒硝、无水芒硝、白钠镁矾、konyaite、钙芒硝、钾芒硝、无水钾镁矾、单钾芒硝、石膏、泻利盐、六水氢氧化物、毛矾、纤维钾明矾、镁明矾、铁明矾、铵明矾、铵矾、钠铵矾），卤化矿物（氯化铵和岩盐），天然硫磺，可能还有两种未知的矿物。大部分硫酸盐矿物在煤火排放中属第一次有记载，同样在无水芒硝晶体中还发现了流体包体。在矸石堆煤火喷气孔中探测到的主要化学成分是 SO$_4$、NH$_4$、H$_2$O、Cl、Mg、K、Na、Al、Ca、Fe、Mn 和 S。研究中采用多种不同测试方法（野外观测、光学测试、X 光衍射分析、电子显微镜扫描、释能光谱测定、分波长光谱和全成分化学分析（ICP-MS）等方法）相结合进一步研究发现的次生矿物。
1 Introduction
Expanding energy consumption and the discovery of coal in the 17th century had the coal mining industry in northern France thrive over centuries. Underground coal mining activities, however, also produced large amounts of coal waste, which was deposited in heaps (about 600) near coal mines, towns, and roads, with little or no environmental concern. The composition of these coal waste heaps was largely dependent on the mining method and type of equipment used in their construction, and the sequence of tipping. The coal waste heaps in the Nord-Pas-de-Calais region vary in size and in shape. The oldest heaps are elongated; those of the early 20th century are mostly cone-shaped (Figure 1). They consist of shale, sandstone, and coal, deposited in sedimentary basins during the Upper Carboniferous 335 to 295 million years ago. The predominant geological material in most heaps is carbonaceous shale, often constituting over 85% of all waste. Its mineralogical composition may differ, but pyrite occurs in almost all colliery waste material.
Some of the coal waste heaps in the Nord-Pas-de-Calais were later removed for civil works or transformed into leisure areas. Others could not be put to immediate use and continue to spoil the landscape, or worse – pollute the environment. Some of them have undergone spontaneous combustion. Today there remain about 300 coal waste heaps in northern France. Spontaneous combustion is most likely to occur in loosely tipped and hence well aerated heaps with high carbonaceous and pyrite content. Moisture content
Spontaneous coal seam fires: mitigating a global disaster

and grading are important too. At low temperatures, free moisture increases the rate of spontaneous combustion (Cook 1990).

Coal waste heaps are complex structures, made up of a mixture of materials with different reactivities toward oxygen and different broad particle size distribution. Where particles are large, air flux can easily dissipate heat; in fine materials, air stagnates and allows heat to build up gradually. However, stagnant air also means that fires caused by accumulative heating will stop as soon as the oxygen in the material is consumed. Waste distribution in coal waste heaps depends both on the layering of the mined soil as well as on the dumping method used, each resulting in a different overall layering and mixing of materials in the heap. For example, dragline mining will produce a sequence of layers different from that of shovel mining (Carras et al. 1999). Particles of different sizes may be segregated over time as surface material erodes down the slope.

Broadly speaking, coal waste heaps are structures of reactive material which allow gas and heat transport. Oxygen (O$_2$) and water (H$_2$O) vapor are the decisive factors for spontaneous combustion. Fires caused by self-heating are indeed a moderately common occurrence in coal mining. They received considerable attention in the past from the perspective of mine safety, but are now coming under closer scrutiny as a source of greenhouse gases (GHGs). Coal and carbonaceous rock debris react with atmospheric O$_2$ in a heat-generating process. Under certain conditions, the heat accumulates and raises the temperature inside the material. This rise in temperature increases the rate of chemical reaction and thus, again, the rate at which heat is generated. Should the heating remain unchecked, combustion will result.

Spontaneous combustion poses significant safety, geo-technical and environmental hazards; it is at the origin of gas spots (vents), ground subsidence, surface cavities, noxious gases, secondary minerals, and thermal metamorphosis of rock debris (Masalehdani & Potdevin 2004; Mroueh et al. 2005). In places where gas and water vapor is discharged along open cracks and vents, solid minerals condensate on unbaked and baked shale debris.
This paper presents methods and results of in-situ gas measurements and analyses at two burning coal waste heaps in the Nord-Pas-de-Calais region. At one site, gas vents (hot spots) were localized based on field observations and aerial infrared thermography. At both sites, samples were collected and laboratory-tested. Efflorescence salt minerals were identified, too. Texture, composition, and mode of occurrence of these minerals will be presented in another publication.

2 Study Sites
The burning coal waste heaps selected for this study were coal waste heaps nos. 76 and 83, numbered according to the Charbonnages de France for the Nord-Pas-de-Calais region. Heap no. 76 is situated 1.3 km south of the city of Avion. Before road works led to a large-scale clearing in the years following 1993, it used to be cone-like in shape, rising up to 85 m above ground level over an area of 96,000 m$^2$ (Figure 2). At that time, heap no. 76 was estimated to contain 500,000 t of mixed waste materials. Spontaneous combustion here occurred in 1987.

Coal waste heap no. 83 borders the national motorway A21 and lies northeast of the city of Fouquières-les-Lens. It is elongated (tabular), with a ridge as high as 10 m above ground level, running discontinuously over about 82 ha (Figure 3). After a short period of debris clearing from 1992 to 1999, the heap was largely abandoned.
Figure 2: Coal waste heap no. 76, Avion. a) Location map 1:60,000 and aerial photo of site during combustion in 1987 (photo courtesy of S.A. Terrils, 1993). b) Visible gas discharge, 2002.
Figure 3: Coal waste heap no. 83, Fouquières-les-Lens. a) Location map 1:25,000 and aerial photo of site 1:5,000 (Paquette 2002). b) Horizontal fissure and gas vent (35 cm wide, 3 m long), 2005.
3 Detection of Gas Spots (Vents)

Basic visual monitoring at regular intervals is imperative for coal waste heaps with high combustibles content. Fumaroles can be detected in wet weather and gas spots in snowy seasons; changes in vegetation and noxious gas emissions have to be surveyed, too.

Aerial infrared thermography is a common method for surveying coal waste heaps. The advantage of extensive spatial coverage and clear visualization of risk areas, however, is offset by rather high application costs, a pronounced sensitivity towards atmospheric conditions, and the impossibility to follow up on combustion reactions. Field investigations must complement infrared surveys in order to localize gas spots (vents) in burning coal waste heaps in a most efficient and exhaustive manner. Investigations at heap no. 83 combined both approaches (Figure 4a).

For thermographic detection of infrared radiation (3-5 and 8-14 μ), an airborne multispectral numeric scanner of the DEDALUS type was used. Measurements were performed before dawn, at a height of 400 m to ensure a ground resolution of 1 m. Thermal resolution at ground level was 0.25 °C. Images were color-treated to bring out combustion zones in greater depth and different vegetation zones. It showed that coal waste heap no. 83 hosts a number of combustion zones (gas spots) in its flanks. These zones are located upslope; particularly along the heap’s east flanks near the purification station; along the west flank of the Marais de Lengles sector; and at the tip of the southwest flank (sector of Le Tierce) (Figures 4b and 4c).
Figure 4: Coal waste heap no. 83, Fouquières-les-Lens. a) Map of gas spots and location of gas measurements. b) and c) Aerial thermographic infrared analysis 1:5,000 (after Paquette 2002): b) north sector, c) south sector.
4 In-Situ Gas Measurements: Methods of Analysis

As site conditions at heap no. 83 were not optimal (the heap is covered with shrubs and small trees, and contains a number of dangerous vents), gas measurements and analyses at this site were carried out only twice, from a single gas spot in the east flank near the purification station (Figure 4a). Due to technical problems, carbon dioxide (CO$_2$) and carbon monoxide (CO) concentrations could not be measured for either site in the first measurements. At coal waste heap no. 76, gas analyses were carried out at different selected spots as shown in Figure 5c.

A special technique was devised to measure gas emissions in situ at both heaps. For this purpose, a stainless steel chamber was placed over a gas spot (vent), and the gas streaming up from the surface directed into the sampling apparatus through an orifice in the chamber’s casing (Figure 5a). Since water vapor in the gas mix would disturb infrared measurements and harm the high-tech analyzer, it was eliminated by a tangential condenser placed between gas chamber and analyzer. Tangential condensers are very common in these set-ups; they trap water vapor by freezing on dry ice. Upstream to the water trap, a fraction of the gas was channeled into bubblers in order to bind hydrogen sulfide (H$_2$S). Water vapor here was no hazard. At the exit of the water trap, through a bifurcated cold transfer line, the then water-free gas was pumped into the analyzer bay placed in a specially equipped vehicle (a mobile laboratory) for analysis of CO$_2$, CO, hydrocarbons, sulfur dioxide (SO$_2$), nitrogen oxides (NO$_x$), and O$_2$. Again, bubblers served to trap remnant H$_2$S (Figure 5b).
Figure 5: Coal waste heap no. 76, Avion. a) *In-situ* gas measurements. b) Outline of gas sampling device. c) Gas spots selected for gas measurements.
H$_2$S was trapped with a solution of sodium hydroxide (NaOH; 0.5 mol l$^{-1}$), to which N,N-dimethyl-p-phenylenediamine oxalate was later added for examination by UV spectroscopy (absorbance 665 nm). The coloring (methylene blue) caused by this reagent is proportional to the amount of sulfides (S$^{2-}$) in the host solution. Other gases such as CO, CO$_2$, methane (CH$_4$), SO$_2$, nitrogen dioxide (NO$_2$), and nitric oxide (NO) were measured with a complex system composed of the following elements (Figure 6):

- A membrane pump with heated head,
- A heated dust filter for elimination of particles,
- A cooling apparatus for trapping of residual moisture,
- A methane and non-methane hydrocarbon analyzer (FID-model Cosma Graphite 355),
- An oxygen analyzer (based on paramagnetic detection), and
- A non-dispersive infrared analyzer (Hartmann and Braun, Model URAS 100) for CO/CO$_2$, NO/NO$_2$, and SO$_2$.

![Figure 6: Outline of gas analysis system](image)
5 Gas Mineralization: Analytical Methodology

Secondary minerals are a frequent sight along open cracks and fissures with hot gas and/or water discharge; they are reaction products of subsurface combustion of coal and carbonaceous rock debris (Figure 7). Specimens of these minerals were collected at both study sites and placed into containers after 5 minutes of cooling in fresh air. The containers were sealed and brought to a laboratory for analysis. All samples were kept at ambient temperature in a shelter throughout testing. A first series of analyses was performed within a week after collection.

Figure 7: Coal waste heap no. 76, Avion. a) Sulfate mineral crystallizations. b) Gas vent; nipper for indication of scale: 15 cm.
The standard method of sample preparation in whole-sample mineralogy is to grind samples with a mortar and spread the powder obtained on a glass slide. This method was also used in the present study. X-ray diffraction (XRD) data were generated using a Phillips PW1710 diffractometer, with an accelerating voltage of 40 kV and a current intensity of 25 mA. Diffraction patterns were collected over 3-60 °2θ using CuKα radiation at 1°2θ min⁻¹. Peak search for minerals within each x-ray pattern was performed with MACDIFF software version 4.2.2.

Some of the samples provided enough condensate for preparation of thin sections amenable to examination of mineralogical, textural, and morphological features, as well as quantitative mineral composition. Special precautions were taken in sample preparation to account for the salt crystals’ brittleness and high solubility, which, for instance, precluded water use. Polished uncovered sections in a range allowing for both transmitted light viewing and fluid inclusion analysis (60 to 100 and 50 µm) were prepared. The thickness of these sections depended on the granulometry of the samples (fan-shaped). They were placed in purpose-built boxes (15 x 15 x 15 mm), which were subsequently filled with epoxy. After hardening, the faces of the boxes were smoothed down with an abrasive until perfectly flat; they were then coated and left to dry at room temperature for about 24 hours. After drying, the upper faces were again rectified by means of a series of coarse to very fine grain abrasives (sizes: 1200 to 2400 µm). It is imperative to impregnate the samples during this process. After polishing, the samples were fixed on frosted glass wafers, where the sections of interest were leveled with petrol. Final rectification was performed with abrasive paper, and a last polish given with petrol and diamond paste.

Optical studies were carried out using an Olympus BX60 transmitted and reflected light microscope, equipped with software and camera. This special device allowed detection of fluid inclusions in the samples as well as micro-thermometric analysis. The composition of trapped fluids is a direct link to the composition of the vapor which has led to the formation of the crystals in the first place. The results will be presented elsewhere.
Environmental scanning electron microscopy (ESEM) analysis of bulk samples was carried out with a Quanta 200 plus EDS (energy-dispersive spectrometry microanalysis device) to confirm XRD mineral identification results and trace minerals contained in only small concentrations in the sample material. Accelerating voltage here was 15 kV. Samples for mineral phase identification, elemental analysis, and photomicrographs by EDS were carbon-coated; they were used as either uncovered thin sections or crystal chips.

Quantitative electron microprobe (EMP) and wavelength-dispersive spectroscopy (WDS) determination of chemical composition was performed with a Cameca SX50 and SX100 at the CAMPARIS laboratory, Department of Geology, Jussieu, University of Paris VI. Due to the instability and fragility of the minerals, beam power was minimized to 15 kV, current intensity to 5-10 nA, and spot size to 10 µm.

Some efflorescence samples were additionally tested for soluble sulfate condensate composition, which XRD mineralogy alone was not able to determine. Some of them contained trace elements like As, Pb, Zn, and Cu.

Secondary salt efflorescence of single minerals or mineral compounds was observed on carbonaceous shale around gas vents. To a large part, these minerals were deposited as encrustations on rock debris at temperatures of less than 300 °C; they included sulfates (thenardite, bloedite, konyaite, glauberite, aphpthalite, langbeinite, arcanite, gypsum, epsomite, hexahydrite, alunogen, kalinite, pickeringite, halorichite, tschermigite, mascagnite, lecontite), halides (salammoniac and halite), native sulfur, and two possibly new unknown minerals.

Some of the identified minerals are generally held to be the product of volcanic sublimates or evaporates. They have never been described in connection with coal seam fires or burning coal waste heaps.
6 Results of Gas Measurements and Analyses

Gas temperatures and measurement results for \( \text{H}_2\text{S}, \text{SO}_2, \text{NO}_x, \text{CO}, \text{CO}_2, \text{CH}_4, \text{O}_2, \) and \( \text{H}_2\text{O} \) are presented in Table 1 and Figures 8 to 12. Measurements at coal waste heap no. 83 (gas spot E1) showed that gas composition can change within minutes to seconds. During a period of 1 h 45 min, \( \text{SO}_2, \text{CO}, \text{CO}_2, \text{CH}_4, \text{NO}_x, \) and \( \text{O}_2 \) were found to vary between 15 and 25 ppm (\( \text{SO}_2 \)), 20 and 25 ppm (\( \text{CO} \)), 3 % and 7 % (\( \text{CO}_2 \)), 110 and 260 ppm (\( \text{CH}_4 \)), 15 and 25 ppm (\( \text{NO}_x \)), and 13 % and 18 % (\( \text{O}_2 \)), respectively. Gas emissions at this spot were evidently pulsating – a phenomenon directly rooted in or influenced by the zone of combustion and gasification. A strong heterogeneity of temperatures around gas vents was observed at both coal waste heaps.

The temperatures at which the measured gases first appear is unknown, but at the active gas spots (vents) of both coal waste heaps, near surface temperatures were measured in a range from 56 to 255.7 °C and 74.3 to 77.8 °C, respectively (Table 1). The gases could not have been generated at such low temperatures and must undoubtedly stem from hotter internal zones in the coal waste heaps.

Table 1: Gas temperatures and measurement results from coal waste heaps nos. 76 and 83

<table>
<thead>
<tr>
<th>Site, Spot</th>
<th>Gas T (°C)</th>
<th>CO (ppm)</th>
<th>CO(_2) (%)</th>
<th>CH(_4) (ppm)</th>
<th>SO(_2) (ppm)</th>
<th>NO(_x) (ppm)</th>
<th>O(_2) (%)</th>
<th>H(_2)O(^b) (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>76, S1</td>
<td>100.5</td>
<td>ND</td>
<td>ND</td>
<td>80</td>
<td>&lt;5</td>
<td>15-26</td>
<td>ND</td>
<td>100</td>
</tr>
<tr>
<td>76, S2</td>
<td>225.7</td>
<td>ND</td>
<td>ND</td>
<td>47</td>
<td>11</td>
<td>15-26</td>
<td>18-19</td>
<td>ND</td>
</tr>
<tr>
<td>76, S3</td>
<td>99.7</td>
<td>110</td>
<td>7</td>
<td>ND</td>
<td>9.6</td>
<td>26</td>
<td>15-18</td>
<td>3550</td>
</tr>
<tr>
<td>76, S4</td>
<td>56</td>
<td>22</td>
<td>6.13</td>
<td>191</td>
<td>19.8</td>
<td>7.87</td>
<td>14-15</td>
<td>30</td>
</tr>
<tr>
<td>83, E1</td>
<td>74.3</td>
<td>ND</td>
<td>ND</td>
<td>96</td>
<td>20</td>
<td>25</td>
<td>&lt;1</td>
<td>ND</td>
</tr>
<tr>
<td>83, E1(^a)</td>
<td>77.8</td>
<td>20-25</td>
<td>3-7</td>
<td>100-260</td>
<td>15-25</td>
<td>15-25</td>
<td>13-18</td>
<td>68</td>
</tr>
</tbody>
</table>

\(^a\) Second measurement

\(^b\) Condensate water collected

ND = no data
Figure 8: Gas analysis at gas spot S1 of coal waste heap no. 76, Avion.

Figure 9: Gas analysis at gas spot S2 of coal waste heap no. 76, Avion.
**Figure 10:** Gas analysis at gas spot S3 of coal waste heap no. 76, Avion

**Figure 11:** Gas analyses at gas spot E1 (first measurement) of coal waste heap no. 83, Fouquières les-Lens
6.1 Hydrogen sulfide (H$_2$S)

The NaOH bubbler solutions obtained during gas measurements at spots S3 of coal waste heap no. 76 and E1 of coal waste heap no. 83 were analyzed for their UV/visible spectrum as described in Chapter 4. Standard sulfide (S$^{2-}$) solutions have their peak of absorption at 665 nm; the two tested solutions, however, failed to show such a peak (Figure 13). This confirms that H$_2$S was absent, both in the solutions and in the emitted gases. To make sure traces of the gas had not been trapped in the apparatus upstream to the bubblers, the condensate water collected in the cold traps was analyzed, too. Test results here were also negative.
Figure 13: Verification of \( \text{H}_2\text{S} \) at 665 nm wavelength, coal waste heaps nos. 76 and 83

Although \( \text{H}_2\text{S} \) or “stink damp” was not found in gas analysis, it should be noted that, on several occasions during field investigations at both sites, the typical “rotten egg smell” indicative of \( \text{H}_2\text{S} \) hovered over gas spots. It is probable that \( \text{H}_2\text{S} \) in the emission gases had oxidized and precipitated at temperatures higher than what was measurable with our devices, or had escaped from the gases already below surface. \( \text{H}_2\text{S} \) is a reaction product of combustion of elemental sulfur, usually at temperatures above pyrolysis level (Mondragón et al. 2002), provided oxygen is not sufficient for complete oxidation (Bell et al. 2001).

\( \text{H}_2\text{S} \) analysis for spots S3 and S1 revealed that \( \text{NO}_x \) and \( \text{SO}_2 \) had also partly been trapped in the form of nitrate (\( \text{NO}_3^- \)), nitrite (\( \text{NO}_2^- \)), and sulfate (\( \text{SO}_4^{2-} \)). At gas spot S3, 25 ppm \( \text{NO}_x \) and 13.4 ppm \( \text{SO}_2 \) were directly measured by the analyzer; 1 ppm (\( \text{NO}_3^- \)) and 0.61 ppm (\( \text{SO}_4^{2-} \)) were detected in the condensates. Likewise, at gas spot S1, 0.91 ppm \( \text{NO}_3^- \) and \( \text{NO}_2^- \); and 0.05 ppm (\( \text{SO}_4^{2-} \)) were found in the water trap.
6.2 Carbon monoxide (CO)
CO or “white damp” is a colorless toxic gas, whose hazardous nature is aggravated by the fact that it cannot be detected either by taste, smell, or irritation (Bell 1996). CO nonetheless is a good indicator of coal fires because it is released sequentially with increasing temperature during heating (Stracher & Taylor 2004).

The reaction of coal with oxygen is an exothermic process, leading in a first step to the formation of a “coal oxygen complex.” As a chemical phenomenon it has received particular scientific attention (e.g. Schmidt 1945; Sondreall & Ellman 1974; Nordon et al. 1979; Cudmore & Sanders 1984; Nelson 1989; Khan et al. 1990; Chen & Scott 1993; Carras & Young 1994; Krishnaswamy et al. 1996). CO is known to be a result of incomplete combustion of carbon contained in coal. Kim (1973) discovered that CO is not only released from coal but also from carbonaceous shale at relatively high temperatures ($\geq 100 ^\circ C$). CO content in gas discharge from coal fires is above all a function of temperature; this clearly shows in Table 1. The higher the combustion temperature, the higher the CO content (Wang et al. 2002).

CO concentrations at gas spot S3 measured up to 110 ppm, which is significantly higher than the Threshold Limit Value (TLV; see Table 2). All other measurement locations ranked lower (Tables 1 and 2). CO emissions of any concentration must be considered highly dangerous as CO readily combines with hemoglobin in human blood, effectively impeding oxygen uptake. The highest concentration of CO to which man may be exposed continually without adverse effect is 50 ppm (TLV). Above this level it will cause symptoms such as headache, fatigue, or dizziness in healthy individuals if breathed (Grossman et al. 1994). Higher concentrations can of course also contribute to combustion hazards (DEP 2001).
### Table 2: Effects of noxious gases

<table>
<thead>
<tr>
<th>Gas</th>
<th>Concentration by Volume in Air</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(%) (ppm)</td>
<td></td>
</tr>
<tr>
<td><strong>NO₂</strong></td>
<td>0.005 5</td>
<td><strong>Threshold Limit Value</strong></td>
</tr>
<tr>
<td></td>
<td>0.062 62</td>
<td>Least amount causing immediate irritation to throat</td>
</tr>
<tr>
<td></td>
<td>0.077 77</td>
<td>Rapidly fatal after short exposure</td>
</tr>
<tr>
<td><strong>CO</strong></td>
<td>0.005 50</td>
<td><strong>Threshold Limit Value</strong></td>
</tr>
<tr>
<td></td>
<td>0.02 200</td>
<td>Headache after c. 7 h at rest or after 2 h of exertion</td>
</tr>
<tr>
<td></td>
<td>0.04 400</td>
<td>Headache and discomfort with possibility of collapse after 2 h at rest or 45 min of exertion</td>
</tr>
<tr>
<td></td>
<td>0.12 1200</td>
<td>Palpitation after 30 min at rest or 10 min of exertion</td>
</tr>
<tr>
<td></td>
<td>0.20 2000</td>
<td>Unconsciousness after 30 min at rest or 10 min of exertion</td>
</tr>
<tr>
<td><strong>CO₂</strong></td>
<td>0.5 5000</td>
<td><strong>Threshold Limit Value</strong> – Lung ventilation slightly increased</td>
</tr>
<tr>
<td></td>
<td>5.0</td>
<td>Breathing labored</td>
</tr>
<tr>
<td></td>
<td>9.0</td>
<td>Depression of breathing commences</td>
</tr>
<tr>
<td><strong>SO₂</strong></td>
<td>0.0001-0.0005 1-5</td>
<td>Can be detected by taste at lower levels and by smell at upper levels</td>
</tr>
<tr>
<td></td>
<td>0.0005 5</td>
<td><strong>Threshold Limit Value</strong> – Onset of irritation to nose and throat</td>
</tr>
<tr>
<td></td>
<td>0.002 20</td>
<td>Irritation to eyes</td>
</tr>
<tr>
<td></td>
<td>0.04 400</td>
<td>Immediately dangerous to life</td>
</tr>
</tbody>
</table>

**Notes:**

1) Some gases have a synergistic effect, that is their presence augments the effect of others and lowers the concentration at which symptoms normally occur. Also, a gas which is not toxic itself may increase the toxicity of another, for example by increasing the rate of respiration; strenuous work has a similar effect.

2) Of the gases listed, only CO is likely to pose a danger to life; it is the most common and cannot be detected by the human senses, while all other gases become intolerably unpleasant already in concentrations far below the danger level.

Data source: Sumi and Tsuchiya (1971); Anonymous (1973)
6.3 Carbon dioxide (CO$_2$) and methane (CH$_4$)

CO$_2$ is another product of coal oxidation; it is liberated from carboxyl groups which form in a dehydroxylation process (Walker 1999). The complete oxidation of carbon to CO$_2$ is an exothermic reaction (1). The heat generated in this reaction is, under normal circumstances, released into the atmosphere (as pollutant); under these conditions, the ignition temperature for coal lies between 420 and 480 °C. However, under adiabatic conditions, where the heat generated cannot be given off, the minimum temperature at which coal ignites drops dramatically to between 35 and 140 °C, depending on coal rank (Sujanti 1999).

$$ (1) \quad C + O_2 \rightarrow CO_2 \uparrow + 394 \text{ kJ mol}^{-1} $$

CH$_4$ was the principal hydrocarbon emitted from the gas spots (vents) at both study sites (compare profiles of total hydrocarbon (THC) and CH$_4$ in Figures 8 and 11). Here too, a significant variation in concentration was observed at different spots. At coal waste heap no. 76, variance strongly depended on location, ranging from 47 over 80 to 191 % (see Table 1; gas spots S2, S1, and S4). At coal waste heap no. 83, one and the same gas spot (E1) showed different levels of CH$_4$ concentration at different O$_2$ and temperature levels (see Table 1). As a matter of fact, emissions at the latter site were all higher than at the former. Laboratory oxidation tests revealed that CH$_4$ is not emitted from carbonaceous shales but exclusively from coal, at temperatures $\geq 120 \text{ °C}$. Therefore, all CH$_4$ measured in situ must have resulted from coal combustion.

CO$_2$ and CH$_4$ are greenhouse gases (GHGs). Global CO$_2$ emissions are expected to rise to 29.575 million t yr$^{-1}$ by 2010 and 36.102 by 2020. Geo-natural hazards such as spontaneous combustion of coal seams or coal waste heaps are thus not only a significant source of large amounts of toxic gases, but also GHGs. CO$_2$ cannot be eliminated from the combustion process, but it can be significantly reduced (IEA 2000). If the combustion is incomplete, more CH$_4$ is released. According to Havenga (1993), gas emissions from burning coal heaps increase with temperature; if the fire remains unchecked and heat is allowed to build up, the content of CO$_2$ and CH$_4$ in the gas discharge can reach up to 20 % and 2.5 % respectively!
Since the adoption of the Kyoto Protocol to the United Nations Framework Convention on Climate Change (UNFCCC) in 1997, much attention has been directed at quantifying GHG emissions from a variety of sources, including coal mining and coal fires. Scientists have pointed out that controlling these man-made disasters might be a very cost-effective way to meet national emission reduction targets under the Kyoto Protocol. CH$_4$ (mine methane gas) is of greater concern as a GHG since its Global Warming Potential is more than 20 times higher than that of CO$_2$ (Carras et al. 1999; Yoshimura 1999).

Our measurements indicate that CO$_2$ is indeed produced in high quantities at both coal waste heaps; in fact, it is predominant among the emitted gases. CO$_2$ concentrations as high as 7% were detected – this is much higher than the TLV of 5,000 ppm (0.5%) (see Table 2). Apart from their environmental impact, high CO$_2$ concentrations also affect human health if inhaled by people living in the vicinity of burning coal waste heaps. Inhalation of CO$_2$ stimulates respiration and this, in turn, increases inhalation of both oxygen and toxic gases/vapors from the fires. Respiration is pronounced at a concentration of 5%; exposure for 30 minutes will produce signs of intoxication. At more than 7%, unconsciousness results after only a few minutes (ACGIH 1971; Onargan et al. 2003).

Sampled gas emissions from the two study sites varied considerably in CH$_4$ concentration. CH$_4$ is the most easily combustible gas among the emissions from coal waste heaps nos. 76 and 83. 10 years ago, there seems to have been a gas explosion at coal waste heap no. 83 (oral confirmation); this phenomenon may actually reproduce itself around the gas spots (vents) when CH$_4$ exceeds a concentration of 5 to 15% (Yalcin & Gurgen 1995; DEP 2001). This concentration is called Lower Explosion Limit (LEL); it is a function of O$_2$ availability/concentration and ambient temperature. According to Onargana et al. (2003), CH$_4$ at a concentration of 5.5% may trigger off an explosion at as low as 100°C. When concentration falls to 5%, the temperature necessary for explosion rises to 175°C. At 4.5% it is 250°C; and at 3% it is 600°C. At CH$_4$ concentrations below 5% and temperatures below 100°C, there will be no explosion, but simple gas combustion (US EPA 1993). If the CH$_4$ concentration in air is > 14% and O$_2$ con-
centration < 12 %, an explosion is not possible either, due to the high specific heat of CH$_4$ (C$_p$ = 2.254 kJ kg$^{-1}$) (Solid Waste Landfill Guidance 1999). During the study, CH$_4$ levels at both sites remained below the LEL ($\leq$ 260 ppm); they were capped by insufficient O$_2$ and low gas temperatures (Table 1).

### 6.4 Sulfur dioxide (SO$_2$)

SO$_2$ is a colorless, water-soluble toxic gas. It can be detected by taste at concentrations of 0.35 to 1.05 ppm, and has an immediately pungent and irritating odor at concentrations above 3.5 ppm (Rabinovitch et al. 1989).

XRD, petrography, EDS, and SEM observations confirmed the presence of pyrite (FeS$_2$) in some of the carbonaceous shale samples. This mineral is also found in coal. Oxidation tests proved that SO$_2$ was emitted from both coal and carbonaceous shale. This clearly points to a low-temperature oxidation of pyrite (see equations (2) and (3)) – an exothermic process, which is catalyzed in the presence of *thiobacillus ferrooxidans* (Harries & Ritchie 1981; Bannerjee 1985; Speight 1994). Direct oxidation of FeS$_2$ to SO$_2$ gas (equation 4) produces an even greater amount of heat (Chunli 1997):

\[
\text{2FeS}_2 + 7\text{O}_2 + 16\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 + 7\text{H}_2\text{O} + 1324 \text{ kJ mol}^{-1}
\]  

(2)

\[
\text{2FeS}_2 + 7\text{O}_2 + 2\text{H}_2\text{O} \rightarrow 2\text{H}_2\text{SO}_4 + 2\text{FeSO}_4 + 260 \text{ kJ mol}^{-1}
\]  

(3)

\[
\text{4FeS}_2 + 11\text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3 + \text{SO}_2 \uparrow + 3412 \text{ kJ mol}^{-1}
\]  

(4)

As shown in Table 1, in-situ gas measurements yielded varying concentrations of SO$_2$, depending on location. They ranged from the detection limit (< 5 ppm) to 19.8 ppm in coal waste heap no. 76, and 15 to 25 ppm in coal waste heap no. 83 (see also Figures 8, 9, 11, and 12). At gas spot S1, concentrations were especially low, and secondary soluble sulfate minerals were observed on adjacent rock debris (Masalehdani et al. 2004). They may be a result of oxidation due to water vapor. In the presence of water, SO$_2$ can dissolve into an acid aqueous solution (e.g. H$_2$SO$_4$). This solution reacts with the clay minerals in the debris to form the said secondary sulfate-bearing minerals (Masalehdani
et al. 2005). According to Rabinovitch et al. (1989), SO\(_2\) can react with O\(_2\) at ambient temperature to form sulfur trioxide SO\(_3\) (equation 5), which then reacts with water (on moist surfaces) to form sulfuric acid (H\(_2\)SO\(_4\)) (equation 6).

\[
\begin{align*}
(5) & \quad 2\text{SO}_2 + \text{O}_2 \leftrightarrow 2\text{SO}_3 \uparrow \\
(6) & \quad \text{SO}_3 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{SO}_4
\end{align*}
\]

SO\(_2\) is a toxic gas, and exposure to concentrations as low as 15 to 25 ppm has detrimental effects on human health (see Table 2). At this range, SO\(_2\) may cause distress to persons with respiratory ailments (Bell 1996). It may even lead to pulmonary edema when in contact with mucous membranes and the respiratory tract, where it reacts to H\(_2\)SO\(_4\) (ACGIH 1971).

SO\(_2\) is also an atmospheric pollutant with profound impact on the environment as the major cause of acid rain. When deposited, SO\(_2\) can contribute to the acidification of soils and surface waters (de Kluizenaar et al. 2001). Recent peaks in global sulfur emissions have been linked to coal seam fires, for example from China (Lefohn et al. 1999). Uncontrolled emissions of SO\(_2\) from burning coal waste heaps may contribute just as well.

6.5 Nitrogen oxides (NO\(_x\))

The emission of NO\(_x\) (or fuel-NO\(_x\)) from coal waste heaps no. 76 and 83 as observed in our gas measurements (see Table 1) stems from nitrogen (N) bound in coal (coal-N). Coal-N exists in the form of pyridinic-, pyrrolic- and quaternary-N and is released during coal pyrolysis (Kelemen et al. 1994). Xu and Kumagai (2002) showed that during hydropyrolysis of coal, the predominant nitrogen gaseous species produced is ammonia (NH\(_3\)), which evolves from slow-heating pyrolysis; together with small amounts of hydrogen cyanide (HCN), released from decomposition of N-containing rings in coal tar. Most HCN is converted to NH\(_3\) in secondary reactions. Xu and Kumagai also indicated that nitrogen evolution during pyrolysis depends on coal rank and nitrogen content. Bassilakis et al. (1993) suggested three possible pathways for NH\(_3\) formation:
Kambara et al. (1993) demonstrated that NH$_3$ is derived from decomposition of quaternary-N in coal, whereas HCN is a product of pyridinic- and pyrrolic-N break-up.

In-situ measurements and analyses confirmed NO$_x$ presence in the gas discharge of both study sites, in the form of NO$_2$ and NO. Investigation of secondary minerals on rock debris around gas vents at coal waste heap no. 76, however, found mostly NH$_4$-bearing efflorescent salt minerals (salammoniac, mascagnite, lecontite, and tschermigite) (Masselehdani et al. 2004). It is widely held that NH$_3$ gas reacts with atmospheric oxygen to form NO$_x$. The NO$_3^-$ and NO$_2^-$ anions in the condensate water of the analyzer bay mentioned earlier may serve as evidence in this respect. Migration of NO$_3^-$ and NO$_2^-$ into the soil and ground water is a source of environmental pollution (Panov et al. 1999).

NO$_x$ were detected at both coal waste heaps in a range from 7.8 to 26 ppm (see Table 1), which is clearly above the TLV (5 ppm; Table 2). NO$_2$ is a very toxic gas produced in the combustion of cellulose nitrate. NO does not exist in atmospheric air because it is immediately converted to NO$_2$ in the presence of O$_2$. Both are strong irritants, particularly to mucous membrane, and will damage tissues in the respiratory tract by reacting with moisture to nitrous (HNO$_2$) and nitric (HNO$_3$) acids if inhaled (Sumi & Tsuchiya 1971).

NO$_x$ are considered one of the major causes of acid rain worldwide. Their various derivatives are also categorized as GHGs, both in view of their phytotoxic effect and their role in the ozone formation process in the stratosphere. Studies indicate that NO$_x$ increase susceptibility to lung bacterial infections. Extended exposure to concentrations of 1 ppm causes symptoms in pulmonary alveoli similar to pulmonary emphysema. The principal function of NO is that of precursor to NO$_2$, which is insoluble and able to penetrate deep
into the respiratory system. NO$_2$ inhibits the pulmonary defenses and has a phytotoxic effect (Teixeira & Lora 2004).

7 Conclusion

Gas emissions from the two burning coal waste heaps nos. 76 and 83 in the French region of Nord-Pas-de-Calais can be described, in very broad terms, as similar to those from large-scale coal seam fires. The main emission gas is CO$_2$ (7 %), with smaller amounts of NO$_x$ and SO$_2$. Products of incomplete coal combustion, namely CO and CH$_4$, are also present. Other hydrocarbons were not detected.

Carbonaceous shales are the main component of coal waste heaps. They contain pyrite and organic carbon, which contribute to SO$_2$, CO$_2$, and CO formation during combustion. Rock debris is thus a significant source of pollutant gas; it also needs to be considered in calculations of CO$_2$ emissions for climate change scenarios.

NH$_3$ released from fire sites reacts with O$_2$ to form NO$_x$ (NO and NO$_2$) gases, which may precipitate as NO$_3^-$ and NO$_2^-$. Secondary minerals resulting from chemical reactions of these NH$_3$ derivates, such as SO$_4^-$, NH$_4^+$, and NH$_4^+$/SO$_4^-$-bearing minerals, must be studied in more detail as they, too, can act as environmental (air, water, soil) pollutants.

O$_2$ concentrations in a range from < 1 to 19 % were measured at both sites. This is below the stipulations of the International Mining Law, which requires a minimum proportion of 19.5 % oxygen for safe working (Sumi & Tsuchiya 1971). The air above and around some gas spots (vents) had to be classified as contaminated and/or poisonous – burning coal waste heaps, in consequence, should be fenced off to prevent accidents and health hazards. Various gases emitted from the heaps may impact directly on the well-being of people.

As the total amount of GHGs in the atmosphere accumulates, and the global climate heats up ever more noticeably, it becomes imperative to carry out direct and regular
field gas measurements at coal fire sites (i.e. coal seams and coal waste heaps) to identify gas compositions; quantify emission gases, especially GHGs; and indicate the location and extent of active combustion zones.

Precautions must be taken for those working – as scientists or miners – on burning coal waste heaps. The danger of accident and poisoning is omnipresent; suitable working attire is an absolute must (e.g. gas masks).

Further research is required to measure the heat flux in CO₂ discharge from burning coal waste heap no. 83 in Fouquières-les-Lens. Under the Geneva Convention on Long-Range Transboundary Air Pollution (CLRTAP), the parties of the United Nations Economic Commission for Europe (UNECE) have been called upon to report emission data annually to the Steering Body to the Cooperative Program for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe (EMEP). Concordantly, the authors, through this article, are reporting the release of noxious pollutant gases from the two burning coal waste heaps nos. 76 and 83 in northern France.

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