Gas emissions, tars, and secondary minerals at the Ruth Mullins and Tiptop coal mine fires

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ABSTRACT

Both the Tiptop and Ruth Mullins coal fires, Kentucky, were reinvestigated in 2009 and 2010. The Tiptop fire was not as active in 2009 and may have been on the path to burning out at the time of the 2009 visit. The Ruth Mullins coal mine fire, Perry County, Kentucky, has been the subject of several field investigations, including November 2009–February 2010 investigations in which we measured gas emissions, collected minerals and tars, and characterized the nature of the fire. Vents exhibiting the greatest gas flux ($> 100,000 \text{ mg/s/m}^2$) are those with the largest amount of condensate minerals and tars. Vents with moderate gas flux ($10,000\text{--}100,000 \text{ mg/s/m}^2$) are less likely to contain condensate minerals, but are collocated with tars, and vents with the lowest flux ($< 10,000 \text{ mg/s/m}^2$) generally lack both minerals and tars. Aliphatic hydrocarbons present in the gases include C1–C9 compounds, and aromatics include BTEX compounds. Diffuse- CO_2 emissions are concentrated along the fracture zones overlying abandoned mine works. The area of peak diffuse flux corresponds to the trend of the collapsed portal that forms vent 5. The greatest vent emissions were also recorded at vent 5. The snow-melt zone mapped in January 2010 overlies the areas of peak diffuse- CO_2 emissions measured in November; together they delineate the zone of active combustion. Comparison of greenhouse gas emissions from the two sources shows that vent emissions exceed diffuse emissions. The highly fractured, quartz-cemented roof rock funnels the majority of emissions toward the vents. Significant decreases are seen in estimates of yearly greenhouse emissions based on data gathered from November 2009 to February 2010, with estimates from November significantly exceeding any previously published estimates. For example, September 2009 estimates from vent 3 alone indicated that $19 \pm 7.5 \text{ T CO}_2/\text{yr}$ were emitted while the November 2009 estimates were $1800 \pm 690 \text{ T/yr}$.

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Barometric pressure was lower in November than September. This implies that there are many factors influencing the seasonal variations in fire emissions and that more frequent monitoring will be necessary to derive accurate estimates of coal fires' contribution to the carbon budget.

1. Introduction

Coal fires destroy valuable energy resources and damage ecosystems; they have the potential to damage infrastructure and adversely impact human health. They are a poorly understood source of both greenhouse gases and particulate matter. Coal fires and their environmental implications have gained worldwide attention (Stracher et al., 2010) and steps are being taken to further quantify the extent and potential impact of many of these fires. Ongoing work in India and China (Jiang et al., 2011; Mishra et al., 2011; Prakash et al., 2011; Wu and Liu, 2011; Prakash et al., 2009; Prakash and Berthelote, 2007; Singh et al., 2007; Zhang and Kuenzer, 2007; Chatterjee, 2006; Prakash and Vekerd, 2004; Gupta and Prakash, 1998) and work in Wyoming (Engle et al., 2011, 2012a) has shown that remote sensing is an extremely valuable tool in monitoring large-scale fires underlying relatively flat strata. Unlike many fires worldwide, the known fires burning in eastern Kentucky do not occur below thin veneers of poorly indurated sediment; they occur in abandoned underground coal mines beneath thick, indurated rocks within a mountainous terrain. The lone exception is the Fishtrap Lake fire, which is visible using MODIS infrared satellite imagery (M. Ruminski, personal communication to Hower et al., 2011). In these settings, ground-based measurements can take the place of remote-sensing in terms of monitoring the extent and migration of the fire. While time consuming, these techniques have the added bonus of providing valuable emissions data necessary for assessing the potential human health and infrastructure impacts. Human health impacts are of especial concern, as many of the fires in Kentucky and worldwide occur near populous areas; indeed, the April 2011 Appalachian Community & Ecosystems Health Summit (<http://www.appsciencesummit.eku.edu/>) identified coal fires as a point source of concern within the spectrum of cradle-to-grave coal resource contaminants. Before this concern can even be addressed, however, much more information is needed on coal fire emissions and dynamics.

Studies of coal fires in Kentucky have concentrated on the six mine fires that are most easily accessible: Laura Campbell (Stracher et al., 2008), Ruth Mullins (Hower et al., 2011; Silva et al., 2011a, 2011b; O'Keefe et al., 2010), Truman Shepherd (O'Keefe et al., 2010; Hower et al., 2013; Dindarloo et al., 2015), Old Smokey (O'Keefe et al., 2011), Tiptop (Hower et al., 2009), and Lotts Creek (Hower et al., 2012; Garrison et al., 2017).⁶ The Ruth Mullins coal mine fire (Fig. 1) is the most studied coal fire in eastern Kentucky. The fire was first visited by Hower, Stracher, and others in March 2007. Following remediation in the spring of 2007, it was thought to be extinguished until smoke was noted on the opposite side of the ridge in September 2007. Hower, O'Keefe, and others visited the site shortly after reports of smoke were received and they were able to see flames and glowing embers on the floor of one abandoned mine shaft and smoke exiting several others. At that time, all abandoned mine portals on the exposed ridge face were intact and no slumping had occurred. Since 2007, the Ruth Mullins site has changed significantly. Large blocks have slumped away from the cliff face and all mine portals have collapsed. Trees have fallen as the roots were burned from the bottom up. In the space of the 10 months of this study, more slumping was apparent, and since the completion of this study, progressive failure of the highwall has continued. This fire has not been extinguished and poses eventual risk to Kentucky Highway (KY) 80, a major four-lane divided regional highway, and possibly the

reclaimed mine on the far side of KY 80. A service station is located near the fire, and while not in any danger from the fire, per se, continued exposure to emissions could impact the employees' health.

The Tiptop coal mine fire (Fig. 1) has been examined on multiple occasions since 2008. Fire flare-ups ignited forest fires on the overlying slopes in fall 2008 and summer 2009. Following both forest fires, remediation of the active burn zone was attempted. This consisted of pushing loose dirt over the exposed mine shafts and auger holes. These efforts were largely unsuccessful in extinguishing the fire, although the later efforts resulted in significantly decreased emissions. This fire is located in a single isolated ridge surrounded by active underground and surface mining operations, directly across a valley from a coal preparation plant. The mining operations are in no danger from the fire, although the health of mine employees and preparation plant workers could potentially be impacted by the emissions.

1.1. Prior work

The Ruth Mullins and Tiptop coal mine fires have been under investigation since the spring of 2007 (Stracher et al., 2008; O'Keefe et al., 2010) and the spring of 2008 (Hower et al., 2009), respectively. These investigations made first-order quantifications of CO₂, CO, and Hg vent gas concentrations using Dräger tubes and an Arizona Instruments Jerome 431-X Mercury Vapor Analyzer. The S-type pitot tube in conjunction with a Flow Kinetics FKT 1 1DP1A-SV flow meter, as was used for the Wyoming studies (Engle et al., 2011, 2012a), was first employed at the Ruth Mullins fire in the spring of 2009, allowing vent emission estimates to be calculated (O'Keefe et al., 2010).

Results from these basic surveys indicate that vent temperatures in both cases range between ambient and extreme (291 - > 300 °C) temperatures, with greatest concentrations of greenhouse gases recorded from the hottest vents. In all cases, Dräger tube-indicated CO concentrations exceeded OSHA 8-h limits (> 50 ppm). In many cases, Dräger tube-indicated CO₂ concentrations also exceeded OSHA 8-h limits of 0.5 vol%, ranging from 0.25–6.0 vol%. The Jerome instrument provided very low elemental Hg vapor concentrations at the Ruth Mullins fire, between 0.009 and 0.560 µg/m³, although still above typical background concentrations of about 1.5 ng/m³. The Jerome instrument provided significantly higher concentrations at the Tiptop fire, ranging from < 9–580 µg/m³. High benzene and other volatile organic compounds (VOCs) were measured at both sites. Initial vent velocity measurements at Ruth Mullins ranged from 0.25–0.95 m/s. Prior to the current work, vent velocity measurements had not been made at the Tiptop mine fire.

These initial analyses allowed us to estimate that Ruth Mullins is emitting roughly 734 T of CO₂, 21 T of CO, and 0.84 T of Hg per year. We expect that overall greenhouse gas emission estimates from the initial survey of Tiptop will be similar, given similar conditions, although Hg emissions are likely higher. When compared to coal-fired power plants and larger fires in the United States (Engle et al., 2011, 2012a; Ide and Orr, 2011), emission estimates from both Ruth Mullins and Tiptop are small. However, when multiplied by the number of fires of this size estimated to be burning in Kentucky alone, a number certainly in the 'tens', these numbers become significant. It is, therefore, necessary to arrive at a better estimate of coal fires' contribution to the North American carbon budget.

⁶ In Kentucky, where possible, coal fires are named for the person who reports them. This is the case for the first three fires noted.

Fig. 1. Location of known coal mine fires in Eastern Kentucky. Inset map shows fire location relative to county outlines. TS = Truman Shepherd; RM = Ruth Mullins; TT = Tiptop; OS = Old Smokey; LC = Laura Campbell; LS = Lotts Creek/Second Creek.

1.2. Justification for further study of the Ruth Mullins and Tiptop coal mine fires

In May 2009, the Kentucky coal fires team joined a national team examining fires in Wyoming (Engle et al., 2011, 2012a). This venture revealed several oversights in previous studies of fires in Kentucky including the effect of vent size on emissions estimates, and the need to complete replicate measurements. The Wyoming studies were the first to compare concentrations of greenhouse gas emissions derived from Dräger Tubes against those generated from an MX6 iBrid multigas analyzer, and to measure concentrations of more than just CO and CO₂ in vent emissions. The i-Brid utilizes IR absorbance for CO₂ and catalytic diffusion analysis for CO and other gases, while the Dräger Tubes rely on colorimetric response to CO and CO₂. The Wyoming study was also the first coal fire study to utilize an Ohio Lumex RA-915+ Zeeman atomic absorption analyzer to measure Hg concentrations. Additionally, the Wyoming study was the first coal mine fire study in the United States to integrate both diffuse and vent emissions measurements to estimate total fire emissions.

From these endeavors, we learned that the Dräger tube measurements did not accurately estimate CO and CO₂ concentrations in vent emissions. Dräger tube measurements of gas concentrations consistently overestimated CO and CO₂ concentrations from small vents and underestimated the same concentrations from large vents, with error ranging $\pm 25\%$. This implies that previously published greenhouse gas emission estimates for the Ruth Mullins fire, which has a high proportion of large vents, are underestimates. The Wyoming studies also demonstrated that other greenhouse gases and toxicants are often significant components of the vent emissions. Notably, CH₄ and H₂S should be monitored and are of use in determining how the coal is burning (smoldering, flaming, etc.). The Jerome Instrument consistently overestimated Hg concentrations; therefore, Hg emissions from both fires may be lower than previously reported. The Jerome analyzer, which relies upon interaction of mercury with gold strips to change the resistance of an electrical circuit, is known to exhibit interferences from several coal combustion products including H₂S, NO₂, and thiol-bearing compounds. The Zeeman atomic absorbance based

Ohio Lumex RA-915+ instrument is free from interference from these same S- and N-bearing compounds, suggesting it may be more appropriate for quantifying Hg in coal fire emissions. Additionally, we found that the inclusion of diffuse emissions measurements using flux chamber-based methods significantly impacted the total greenhouse gas emission estimates for those fires (Engle et al., 2013).

Together these findings prompted us to re-examine the coal mine fires at the Ruth Mullins site and the Tiptop site. The current study aims to:

1. Produce more accurate estimates of greenhouse gas and Hg emissions from both fires by:
 - A. using an MX6 iBrid multi-gas analyzer, rather than Dräger tubes, to estimate gas concentrations,
 - B. determining the diffuse CO₂ emissions at both sites, and
 - C. utilizing the Ohio Lumex Zeeman instrument to measure elemental Hg concentrations;
2. Visit the more accessible Ruth Mullins site repeatedly over a four-month period to determine if vent emissions vary significantly over that period;
3. Collect long-term carbon emission data from one vent at the Ruth Mullins fire site; and,
4. Determine an alternate means of locating the current locus of combustion, as IR imaging is not feasible at either fire site.

The present paper deals with the results of objectives 1, 2, and 4. Results of objective 3 are discussed in Hower et al. (2011).

2. Methods

Emissions from the Tiptop coal fire were studied in November 2009 and compared to previous works. Emissions from the Ruth Mullins coal fire were studied in November 2009, and January, February, and August 2010 and compared to previous works. Studies of both fires utilized ground-based techniques developed by the team during work in Wyoming (Engle et al., 2011, 2012a), significantly expanding upon previous studies and refining estimates of greenhouse gas emissions.

Table 1

Site identification, location, temperature and CO₂ flux from diffuse emission measurement at the Tiptop fire.

Site	Easting (m)	Northing (m)	CO ₂ flux (g/m ² d)	Soil Temp (°C), 10 cm depth	Soil Temp (°C), surface	Group
TTF 01	318,089	4,163,274	6.36	11.9	13.4	Fire
TTF 02	318,092	4,163,253	9.13	15.4	26.4	Fire
TTF 03	318,090	4,163,258	12.78	14.9	25.3	Fire
TTF 04	318,120	4,163,237	8.04	18.5	25.3	Fire
TTF 05	318,122	4,163,246	−2.27	17.1	27.6	Fire
TTF 06	318,120	4,163,264	0.31	18.1	21.9	Fire
TTF 07	318,149	4,163,238	4.60	21.5	20.1	Fire
TTF 08	318,150	4,163,251	8.81	25.4	30.3	Fire
TTF 09A	318,150	4,163,265	4.18	16.2	22.2	Fire
TTF 09B	318,150	4,163,265	6.58	16.1	28.3	Fire
TTF 09C	318,150	4,163,265	4.68	16.4	24.8	Fire
TTF 10A	318,150	4,163,222	4.34	16.6	14.5	Fire
TTF 10B	318,150	4,163,222	3.01	16.4	13.3	Fire
TTF 10C	318,150	4,163,222	5.55	16.1	14.8	Fire
TTF 11	318,181	4,163,240	1.86	31.4	22.7	Fire
TTF 12	318,180	4,163,251	5.11	25.7	27.6	Fire
TTF 13	318,182	4,163,221	2.32	22.9	19.5	Fire
TTF 14	318,193	4,163,206	3.12	18.4	15.8	Fire
TTF 15	318,210	4,163,236	9.85	17.8	22.3	Fire
TTF 16	318,210	4,163,221	3.39	18.5	19.3	Fire
TTF 17	318,210	4,163,210	0.74	17.6	21.7	Fire
TTF 18	318,211	4,163,197	6.75	16.1	16.8	Fire
TTF 20	318,177	4,163,301	4.75	10.9	12.5	Background
TTF 21	318,202	4,163,301	8.75	10.2	10.2	Background
TTF 22	318,216	4,163,305	6.44	11.1	16.4	Background
TTF 23	318,224	4,163,293	−0.61	12.6	16.3	Background
TTF 24 A	318,204	4,163,291	6.88	11.2	13.4	Background
TTF 24 B	318,204	4,163,291	1.67	11.7	10.7	Background
TTF 24C	318,204	4,163,291	1.77	11.3	15.1	Background
TTF 25	318,206	4,163,261	8.96	18.3	26.3	Fire
TTF 26A	318,196	4,163,254	55.62	27.9	23.7	Fire
TTF 26B	318,196	4,163,254	66.16	26.8	23.8	Fire
TTF 26C	318,196	4,163,254	72.04	27.4	21.2	Fire
TTF 27	318,184	4,163,267	6.75	17.5	20.7	Fire
TTF 28	318,179	4,163,261	10.72	19.8	28.0	Fire
TTF 29	318,187	4,163,241	19.78	34.1	35.0	Fire
TTF 30	318,193	4,163,234	12.74	29.3	23.4	Fire
TTF 31	318,177	4,163,236	4.31	31.1	29.1	Fire
TTF 32	318,160	4,163,253	5.93	29.8	26.7	Fire
TTF 33	318,169	4,163,240	22.88	35.1	32.0	Fire

Data available from Engle (2018).

Both fires were visited after the 2009 and 2010 studies but no additional detailed work was conducted.

Coal fire gases are transported to the surface through two primary mechanisms: advection through vents and fractures (vent emissions) and diffusion/convection through overburden (soil emissions). To inventory gases released from a site, both soil and vent emissions are measured and summed. Calculation of diffuse soil emissions requires use of geostatistical interpolation methods. Thus, the study of coal fires involves a significant geospatial component.

The techniques described below were initially field-tested at fires in the Powder River Basin (PRB) of Wyoming and were utilized in this study. Results from ground-based emission measurement methods specifically developed for coal fires were presented by Kolker et al. (2009a, 2009b) and Engle et al. (2011, 2012b, 2013).

Methods for measurement of diffuse gas emissions via flux chambers and extrapolation for coal fires are detailed in Engle et al. (2012b, 2013). Engle et al. (2013) details the sampling design, field chamber design, and geostatistical methods applied to determine estimates from the Ruth Mullin's fire. Using a custom-designed static flux chamber system (Engle et al., 2011), 49 CO₂ flux measurements were made at 37 sampling points at the Ruth Mullins fire, including four points (six

measurements) outside of the active coal fire area. At the Tiptop fire, a total of 40 CO₂ flux measurements were made at 27 locations, including five points (seven measurements) outside of the active coal fire area. Corresponding results are summarized in Table 1 (Engle, 2018). Estimates of the total diffuse emission and uncertainty were scaled across the fire using sequential Gaussian simulation (see Engle et al., 2013 for details); results were corrected for soil respiration-related emissions using the measurements taken outside the active coal fire area.

At each fire site, coordinates of each measurement point for diffuse emissions were imported into ArcGIS® and plotted in WGS 1984 UTM 17 N projection. The image of the CO₂ diffuse emissions generated using the methods of Engle et al. (2013) was imported, georeferenced, and matched to the measurement points for each fire. A Kentucky base map layer was added, as was a dBase topographic file for each quadrangle studied to show the footprint of the fire site in relation to topography. This also allowed an estimate of overburden volume to be calculated, as the combusting coals are contained in near-horizontal strata at an elevation of ca. 430 m.

In January 2010, the perimeter of the zone of melted snow overlying the fire was mapped using a Trex GPS unit. A polygon was generated using these points and overlain on the maps of the diffuse emissions.

For vent emission measurements the gas flow rate, air temperature, relative humidity, and barometric pressure were measured in at least five locations within each vent using a Flow Kinetics FKT 1DP1A-SV flow meter attached to an S-type pitot tube. In the case of large vents, the emission area was broken into smaller areas and five sets of measurements were taken from each. Within each vent area, concentrations of CO₂, CO, CH₄, and H₂S were measured using an Industrial Scientific MX6 iBrid combustion gas analyzer and Hg concentrations were determined using an Ohio Lumex Zeeman atomic absorption spectrometer. The MX6 combustion gas analyzer was calibrated with zero and span standards prior to and after the field campaign; previous work in the PRB has shown that no significant drift is observed in this instrument during a three-day field campaign (Engle et al., 2012a). The Lumex Hg analyzer was calibrated daily using its internal standard. Vent fluxes for specific gases (Q_i) from individual vents were determined by:

$$Q_i = C_i v a \quad (1)$$

where C_i is the concentration of gas i, v is the average velocity of the coal gas exiting the vent, and a is vent area. Results are summarized in Table 2.

Vent gases were sampled for VOCs at selected vent locations. Samples were collected in pre-evacuated, electropolished stainless-steel gas-sampling canisters. Samples were analyzed for carbon-bearing gases (i.e., CO, CO₂, carbonyl sulfide, dimethylsulfide, and carbon disulfide), C1–C7 aliphatic hydrocarbons, and single-ring aromatics (BTX, etc.) on a gas chromatographic system in the Rowland-Blake Group laboratory at the University of California - Irvine. Analytical methods and quality control methods are described in Barletta et al. (2008) and Coleman et al. (2001). Results are summarized in Table 3.

Bulk minerals collected from the Ruth Mullins fire were analyzed chemically at the University of Kentucky Center for Applied Energy Research (CAER) and optically at Morehead State University. Samples for optical analysis were separated from the associated rock, twigs, and roots, crushed to −140 mesh (finer than 106 μm), mounted in Cargille Meltmount® thermoplastic resin, and examined on a Nikon Optiphot® petrographic microscope. Photomicrographs were obtained using a Nikon digital camera. Independent of this study, nanominerals and nanocarbons from this fire were detailed in Silva et al. (2011a, 2011b).

X-ray diffraction (XRD) patterns were used to identify the mineralogy of samples collected at vents 3 and 5 of the Ruth Mullins fire; vent minerals were not observed at the Tiptop fire during any of the sampling events. Mineralogy data were obtained at the University of Georgia, Athens, where the samples were first ground to powder in air

Table 2
Vent area, gas velocity, gas emissions, and gas flux. 2a, Tiptop; 2b, Ruth Mullins.

Active Vent #	Tiptop Mine Fire										Total
	1	2	3	4	5	6	7	8	9	10	
Date	11/17/2009	11/17/2009	11/17/2009	11/17/2009	11/17/2009	11/17/2009	11/17/2009	11/17/2009	11/17/2009	11/17/2009	
North latitude											
West longitude											
Approximate Vent Area (m ²)	0.373	0.390	0.00503	0.00126	0.07660	0.0156	0.206	0.00630	0.00785	0.0840	
Pitot Tube:											
Flow Rate (m/s)	9.48	2.32	1.38	1.54	2.42	1.1	1.255	0.54	0.475	1.04	
Std. Dev. Velocity	1.93	0.716	0.274	0.274	1.102	0.162	0.587	0.364	0.236	0.236	
Temp. (°C)	21.6	27.34	33.02	40.1	31.35	54.28	30.09	40.82	48.9	45.06	
Rel. Humid. (%)	74.56	55.13	64.8	87.4	45.45	36.8	29.4	27.2	27.2	45.2	
ρ (kg/m ³)	1.130	1.111	1.076	1.07	1.087	1.018	1.101	1.06	1.032	1.028	
Baro. Pres. (kPa)	96.445	96.481	96.580	96.564	96.600	96.550	96.552	96.500	96.526	96.472	
I-brid Multigas Analyzer:											
CO ₂ % vol	0.3	0.018	0.28	0.34	0.03	0.092	0.06	0.2	0.314	0.08	
CO ppm	< dl	< dl	273.4	325.6	118.6	112.4	84	200	339.4	99.2	
CH ₄ % vol	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	
H ₂ S ppm	0	0.56	2.84	3.1	1.46	0.96	0.16	1.98	2.52	1.28	
O ₂ % vol	106.02	63.98	21.08	20.9	85.78	21.3	42.7	21.2	20.94	21.2	
Ohio Lumex Analyzer:											
Hg High (ng/m ³)	42	30	–	–	41	6	15	9	10	Present	
Hg Avg (ng/m ³)	35	26	–	–	28	5	12	7	8	–	
CO ₂ emissions (T/yr)	100 ± 21	2 ± 0.62	0.29 ± 0.058	0.12 ± 0.021	0.79 ± 0.36	0.39 ± 0.057	2.1 ± 0.99	0.13 ± 0.085	0.26 ± 0.13	1.4 ± 0.32	110 ± 24
CO emissions (T/yr)	< dl	< dl	0.018 ± 0.0036	0.0073 ± 0.0013	0.2 ± 0.09	0.03 ± 0.0044	0.19 ± 0.088	0.008 ± 0.0054	0.018 ± 0.0088	0.11 ± 0.025	0.58 ± 0.23
CH ₄ emissions (T/yr)	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl
H ₂ S emissions (T/yr)	< dl	0.0048 ± 0.0015	0.00023 ± 0.00015	0.00084 ± 0.00015	0.003 ± 0.0014	0.00031 ± 0.00046	0.00044 ± 0.0002	0.000096 ± 0.000065	0.00016 ± 0.00008	0.0018 ± 0.0004	0.011 ± 0.0038
O ₂ emissions (T/yr)	27,000 ± 5400	5200 ± 1600	16 ± 3.1	5.3 ± 0.95	1600 ± 750	65 ± 9.6	1100 ± 510	9.7 ± 6.5	13 ± 6.2	270 ± 62	35,000 ± 83,000
Hg maximum emissions (kg/yr)	0.0047 ± 0.00096	0.00086 ± 0.00026	–	–	0.00024 ± 0.0011	0.000032 ± 0.000048	0.00012 ± 0.00057	0.00000097 ± 0.00000065	0.00000012 ± 0.00000058	–	0.0059 ± 0.0014
Hg average emissions (kg/yr)	0.0039 ± 0.0008	0.00074 ± 0.00023	–	–	0.00016 ± 0.00075	0.000027 ± 0.000004	0.000098 ± 0.000046	0.00000075 ± 0.00000051	0.00000094 ± 0.00000047	–	0.0049 ± 0.0012
CO ₂ flux (mg/s/m ²)	8900	330	1800	3000	730	770	530	630	1000	540	17,000
CO flux (mg/s/m ²)	< dl	< dl	0.41	0.15	5.8	0.86	7.5	0.46	1.2	3.5	14
CH ₄ flux (mg/s/m ²)	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl	< dl
H ₂ S flux (mg/s/m ²)	< dl	0.0037	0.00022	0.000067	0.0017	0.00018	0.00037	0.000073	0.0001	0.0012	0.011
O ₂ flux (mg/s/m ²)	11,000	1900	7.7	1.9	660	57	940	11	15	190	16,000
Hg maximum flux (ng/s/m ²)	130	8.1	–	–	1.7	0.098	1.8	0.029	0.036	dl	160
Hg average flux (ng/s/m ²)	1.2	0.083	–	–	0.013	0.0089	0.016	0.00025	0.00031	–	1.5
Ruth Mullins Mine fire											
Active Vent #	3	1	2	4	5	6	7	8	9	10	
Date	9/11/2009	11/18/2009	11/18/2009	11/18/2009	11/18/2009	11/18/2009	11/18/2009	11/18/2009	11/18/2009	11/18/2009	
North latitude											
West longitude											

Table 2 (continued)

Ruth Mullins Mine fire										
Approximate Vent Area (m2)	0.466	0.287	0.146	0.466	0.073	0.137	2.41	0.322	1.387	
Pitot Tube:										
Flow Rate (m/s)	1	2.30	0.62	1.90	0.84	3.72	0.38	0.28	2.78	
Std. Dev. Velocity	0.4	0.38	0.12	0.73	0.36	1.08	0.09	0.11	0.51	
Temp. (°C)	24.1	38.88	16.84	56.59	34.01	96.49	16.42	18.04	18.67	
Rel. Humid. (%)	88	29.80	62.60	40.13	79.50	25.15	93.40	65.60	69.15	
ρ (kg/m3)	1.13	1.03	1.15	1.02	1.07	0.89	1.15	1.15	1.14	
Baro. Pres. (kPa)	97.43	97.12	97.14	97.13	97.16	97.16	97.11	97.06	96.92	
I-brid Multigas Analyzer:										
CO2% vol	0.37	4.792	0.528	8.04	5.184	11.792	0.516	1.624	1.108	
CO ppm	20.9	5524.2	663.6	4495.2	5053.8	8235.4	509.8	471	210.4	
CH4% vol	0	0.468	0	0.436	0.522	1.132	0	0	0	
H2S ppm	2.9	11.86	1.34	13.02	9.86	26.84	1.58	1.46	0	
O2% vol	20.9	60.38	20.68	55.14	37.5	72.34	20.88	19.36	84.1	
Ohio Lumex Analyzer:										
Hg High (ng/m3)	–	304	0	> 100	101	> 100	52	69	116	
Hg Avg (ng/m3)	–	< 500	0	< 500	0	< 500	49	49	103	
CO2 emissions (T/yr)	19 ± 7.5	550 ± 92	3.6 ± 0.7	1800 ± 690	49 ± 21	2600 ± 760	35 ± 8.7	12 ± 4.5	360 ± 66	
CO emissions (T/yr)	0.067 ± 0.0-27	41 ± 6.8	0.29 ± 0.0-56	65 ± 25	3 ± 1.3	120 ± 34	2.2 ± 0.55	0.22 ± 0.083	4.4 ± 0.79	
CH4 emissions (T/yr)	0	20 ± 3.3	0 ± 0	36 ± 14	1.8 ± 0.76	92 ± 27	0 ± 0	0 ± 0	0 ± 0	
H2S emissions (T/yr)	0.011 ± 0.0-045	0.11 ± 0.018	0.0007-1 ± 0.000-14	0.23 ± 0.087	0.0072 ± 0.0031	0.46 ± 0.13	0.0083 ± 0.0021	0.00083 ± 0.00031	0 ± 0	
O2 emissions (T/yr)	770 ± 310	5100 ± 850	100 ± 20	9100 ± 3500	260 ± 110	12,000 ± 3400	1000 ± 260	100 ± 39	20,000 ± 3600	
Hg maximum emissions (kg/yr)	–	0.0063 ± 0.0011	0 ± 0	> 0.002-8 ± 0.0011	0.00019 ± 0.000084	> 0.001-6 ± 0.00047	0.0015 ± 0.00038	0.0002 ± 0.00074	0.014 ± 0.0026	
Hg average emissions (kg/yr)	–	< 0.01 ± 0.0017	0 ± 0	< 0.014 ± 0.00053	0 ± 0	< 0.008 ± 0.00023	0.0014 ± 0.00035	0.00014 ± 0.00053	0.013 ± 0.0023	
CO2 flux (mg/s/m ²)	1300	63,000	760	120,000	21,000	610,000	460	1200	7900	
CO flux (mg/s/m ²)	2.1	570	15	1100	110	990	180	25	50	
CH4 flux (mg/s/m ²)	0	1600	0	1500	160	2700	0	0	0	
H2S flux (mg/s/m ²)	0.015	0.087	0.0014	0.13	0.0068	0.16	0.016	0.0014	0	
O2 flux (mg/s/m ²)	270	5400	53	7200	100	15,000	350	50	9100	
Hg maximum flux (ng/s/m ²)	–	190	0	> 87	5.8	> 57	42	5.4	400	
Hg average flux (ng/s/m ²)	–	< 3.4	0	< 4.5	0	< 2.6	0.46	0.045	4.1	
Ruth Mullins Mine fire										
Active Vent #	9	November Totals			1	2	1	2	5	
Date	11/18/2009				1/19/2010	1/19/2010	2/12/2010	2/12/2010	2/12/2010	
North latitude										
West longitude										
Approximate Vent Area (m2)	0.694				0.287	0.146	0.287	0.146	0.137	
Pitot Tube:										
Flow Rate (m/s)	0.96				2	0.36	1.76	0.98	0.38	

Table 2 (continued)

Ruth Mullins Mine fire										
Std. Dev. Velocity	0.28									
Temp. (°C)	18.10	0.36	0.13	0.34	0.30	0.12				
Rel. Humid. (%)	67.20	10.88	0.12	1.05	1.27	1.14				
ρ (kg/m ³)	1.14	69.8	25.4	24.67	36.6	74.6				
Baro. Pres. (kPa)	96.94	5.364	1.25	1.228	1.232	1.23				
I-brid Multigas Analyzer:		98.12	98.12	96.805	96.839	96.81				
CO2% vol	0.558	3.752	1.01	4.288	1.952	0.866				
CO ppm	200.4	4354	0.0622	0	0	0				
CH4% vol	0	0.288	1017.2	1.584	0.114	0.116				
H2S ppm	0.34	7.98	1.92	6.92	1.68	1.84				
O2% vol	42.16	59.06	19.84	57.18	39.06	19.82				
Ohio Lumex Analyzer:										
Hg High (ng/m ³)	59	–	–	–	–	–				
Hg Avg (ng/m ³)	41	–	–	–	–	–				
CO2 emissions (T/yr)	30 ± 9	5400 ± 1700	0.029 ± 0.01	10 ± 2	1.6 ± 0.48	0.23 ± 0.075				
CO emissions (T/yr)	0.69 ± 0.21	240 ± 69	0.0000001-1 ± 0.000000-0039	0 ± 0	0 ± 0	0 ± 0				
CH4 emissions (T/yr)	0 ± 0	150 ± 45	10 ± 3.7	1.4 ± 0.27	0.034 ± 0.01	0.011 ± 0.0037				
H2S emissions (T/yr)	0.0014 ± 0.00042	0.82 ± 0.24	0.000004-2 ± 0.000000-15	0.0013 ± 0.00025	0.00011 ± 0.000032	0.00003-8 ± 0.000012				
O2 emissions (T/yr)	1700 ± 490	49,000 ± 12,000	0.41 ± 0.14	100 ± 19	23 ± 7	3.9 ± 1.3				
Hg maximum emissions (kg/yr)	0.0012 ± 0.00037	> 0.028 ± -	–	–	–	–				
Hg average emissions (kg/yr)	0.00086 ± 0.00025	< 0.047 ± -	–	–	–	–				
CO2 flux (mg/s/m ²)	1400	830,000	6.3	1200	350	54				
CO flux (mg/s/m ²)	23	3100	0.0000097	0	0	0				
CH4 flux (mg/s/m ²)	0	6000	2600	130	3.7	2.9				
H2S flux (mg/s/m ²)	0.0025	0.41	0.0011	0.039	0.0027	0.0011				
O2 flux (mg/s/m ²)	790	38,000	0.51	130	20	1.6				
Hg maximum flux (ng/s/m ²)	34	820	–	–	–	–				
Hg average flux (ng/s/m ²)	0.28	15	–	–	–	–				

Table 3

Aliphatic hydrocarbons and benzene-toluene-ethylbenzene-xylene aromatics in vent emissions at the Ruth Mullins fire.

			Vent 1b	Vent 3a	Vent 6	Vent 9	Vent 1	Vent 3b	Vent 4	Vent 5
			18-Nov-09	18-Nov-09	18-Nov-09	18-Nov-09	12-Jan-10	12-Jan-10	12-Jan-10	12-Jan-10
Carbon monoxide	CO	ppbv	270,000	1,070,000	757,000	63,600	15,600	1,170,000	272	610,000
Carbon dioxide	CO ₂	ppmv	6560	23,700	6560	2110	603	70,500	410	38,200
Carbonyl sulfide	OCS	pptv	266,000	1390	373	5270	4040	90,600	568	78,700
Carbon disulfide	CS ₂	pptv	102,000	634	97	24,300	1460	1550	25	1030
Aliphatic compounds										
Methane	CH ₄	ppmv	415	11	111	421	5	220	2	84
Ethane	C ₂ H ₆	pptv	36,400,000	328,000	8,870,000	1,790,000	215,000	8,740,000	10,700	5,940,000
Ethene	C ₂ H ₄	pptv	1,690,000	175,000	461,000	568,000	21,500	2,590,000	917	1,210,000
Ethyne	C ₂ H ₂	pptv	67,000	7940	22,500	24,200	2820	176,000	828	75,200
Propane	C ₃ H ₈	pptv	8,240,000	54,800	2,180,000	362,000	62,600	1,870,000	4760	1,280,000
Propene	C ₃ H ₆	pptv	889,000	11,700	214,000	31,000	9880	286,000	246	225,000
i-Butane	C ₄ H ₁₀	pptv	781,000	4980	212,000	36,200	23,000	185,000	690	124,000
n-Butane	C ₄ H ₁₀	pptv	2,110,000	12,600	609,000	89,100	21,900	500,000	1650	362,000
trans-2-Butene	C ₄ H ₈	pptv	150,000	333	31,900	1930	1550	15,700	18	24,800
cis-2-Butene	C ₄ H ₈	pptv	105,000	226	22,800	1090	1140	10,100	15	17,200
i-Butene	C ₄ H ₈	pptv	113,000	216	22,800	848	1360	6890	45	15,300
1-Butene	C ₄ H ₈	pptv	129,000	360	26,500	1240	1970	6140	60	15,000
1,3-Butadiene	C ₄ H ₆	pptv	23,800	343	6060	462	299	12,800	dl	8030
2-methyl-1,3-butadiene (isoprene)	C ₅ H ₈	pptv	7670	173	1610	154	116	1710	10	1480
i-Pentane	C ₅ H ₁₂	pptv	527,000	3110	132,000	21,100	68,000	93,900	481	66,100
n-Pentane	C ₅ H ₁₂	pptv	1,020,000	5170	291,000	36,600	14,900	220,000	500	173,000
1-Pentene	C ₅ H ₁₀	pptv	50,900	80	9740	264	526	1350	dl	5220
n-Hexane	C ₆ H ₁₄	pptv	598,000	3010	172,000	18,300	3400	130,000	211	109,000
n-Heptane	C ₇ H ₁₆	pptv	357,000	1590	106,000	9060	5140	88,000	92	74,400
n-Octane	C ₈ H ₁₈	pptv	315,000	1230	69,100	4520	2460	34,200	37	31,400
n-Nonane	C ₉ H ₂₀	pptv	231,000	1080	43,700	2270	2110	20,000	25	20,000
2,3-Dimethylbutane	C ₆ H ₁₄	pptv	36,900	147	9350	1580	449	5150	12	3840
2-Methylpentane	C ₆ H ₁₄	pptv	243,000	1440	66,100	9290	2580	36,400	dl	29,400
3-Methylpentane	C ₆ H ₁₄	pptv	88,300	450	22,700	3840	1090	13,500	39	10,200
2-Methylhexane	C ₇ H ₁₆	pptv	73,300	532	18,500	2920	1270	11,500	80	9970
3-Methylhexane	C ₇ H ₁₆	pptv	83,300	424	18,800	2990	1650	12,400	86	11,400
2,4-Dimethylpentane	C ₇ H ₁₆	pptv	53,500	247	15,700	2060	656	7260	46	5850
Aromatic compounds										
Benzene	C ₆ H ₆	pptv	1,440,000	31,000	328,000	31,200	34,900	1,110,000	744	736,000
Toluene	C ₇ H ₈	pptv	646,000	3180	120,000	2840	37,000	69,500	632	149,000
Ethylbenzene	C ₈ H ₁₀	pptv	101,000	377	15,000	650	3190	5160	107	19,000
m&p-Xylene	C ₈ H ₁₀	pptv	348,000	1380	53,400	2240	8640	15,900	452	54,300
o-Xylene	C ₈ H ₁₀	pptv	145,000	542	19,800	795	3550	4740	140	22,100

with an agate mortar and pestle. Each powder was then mounted on a 40 × 30 mm petrographic glass slide. All powder XRD data were obtained using a Bruker D8 Advance X-ray diffractometer. Instrument operating conditions included the following: CoK α radiation (generated at 40 kV and 40 mA), a 250-mm goniometer radius, 1°/2° primary/scattering slits, 0.3° receiving slit, primary soller slit, and a LynxEye® 192 silicon strip position sensitive detector. Data were collected using a scan rate of 0.1 s per step with a step increment of 0.01° 2 θ .

Diffractogram peaks were externally calibrated with reference to the National Institute of Standards and Technology (NIST) corundum standard, SRM1976. Peak positions were best matched with patterns from the International Centre for Diffractions Data - Powder Diffraction File (ICDD-PDF) using Bruker's Eva® evaluation software. ICDD-PDF card numbers were assigned to our best-fit diffractograms.

Each sample was examined for high-resolution imaging and compositional purposes using Scanning Electron Microscopy/Energy Dispersive X-Ray Spectroscopy (SEM/EDS). Freshly fractured surfaces were prepared and mounted onto aluminum stubs using carbon-coated tape. Data were collected using a Zeiss 1450EP SEM/EDS instrument located in the University of Georgia Center for Advanced Ultrastructural Research (CAUR) (<http://www.uga.edu/caur/>). The instrument is a variable pressure tungsten filament SEM with a sample chamber that allows imaging from high vacuum mode to 2800 Pa. It is equipped with a Debens peltier stage, water injection system, and an Oxford INCA EDS system.

Tar samples were collected in sterile glass jars at the Ruth Mullins

fire and sent to NewFields Environmental Forensics for high-resolution hydrocarbon fingerprinting using a modification of EPA Methods 8015 and 8270C. This was accomplished with a gas chromatograph equipped with a flame ionization detector (GC/FID) for hydrocarbons in the 9 to 44 carbon molecular weight range and a GC equipped with a mass spectrometer (GC/MS) for polycyclic aromatic hydrocarbons (PAHs) with 2 to 7 rings (Stout and Emsbo-Mattingly, 2008; Emsbo-Mattingly and Stout, 2011). The tar results are presented in Table 4.

To investigate possible controls and inter-relationships between conditions and compounds in the vent emissions, data from both sites were examined using principal component analysis (PCA) in Aabel™ 3 (Gigawiz™ Software). Included variables were flow rate, gas temperature, barometric pressure, relative humidity, and log₁₀ concentrations of CH₄, CO, CO₂, and H₂S. A portion of the CH₄ (64%), CO (20%), and H₂S (8%) data were reported below the method detection limit; estimated values were determined using an isometric-log ratio based expectation-maximum-likelihood estimation algorithm (Hron et al., 2010) and subsequently imputed. Eigen decomposition was completed using the covariance matrix of the scaled dataset.

3. Results and discussion

3.1. Tiptop

Based on the vent data collected and presented in Table 2, Tiptop is emitting ± 107.48 T/yr CO₂/yr, ± 0.58 T/yr CO, ± 0.01 T/yr H₂S, little

Table 4

Total extractable hydrocarbons in the C9–C44 range, the U.S. Environmental Protection Agency (EPA) listed polyaromatic hydrocarbons (PAHs) (with the EPA carcinogenic PAHS in *italics*), fluoranthene/pyrene ratio, (Benzo[*b*]fluoranthene + Benzo[*k*]fluoranthene)/ Benzo[*a*]pyrene, and the pyrogenic weathering index.

Compound:	Sample ID:	RM Tar	RM 5A	RM 5D
	Source:	Vent 1, part B	Vent 5, part A	Vent 5, part D
Total Extractable Hydrocarbons (TEH, C9–C44)	mg/kg	639,000	117,000	634,000
EPA PAHs:				
Naphthalene (NO)	mg/kg	10.3	3.08	52.6
Acenaphthylene (AY)	mg/kg	134	0.333	1.77
Acenaphthene (AE)	mg/kg	1.05	0.28	4.27
Fluorene (FO)	mg/kg	25.8	3.32	297
Phenanthrene (PO)	mg/kg	823	144	3820
Anthracene (AO)	mg/kg	1220	28.5	1990
Fluoranthene (FLO)	mg/kg	11,900	146	3900
Pyrene (PYO)	mg/kg	12,900	182	6230
<i>Benzo[<i>a</i>]anthracene (BAO) (tetracene)</i>	mg/kg	19,700	182	5180
<i>Chrysene (CO)</i>	mg/kg	17,900	918	5060
<i>Benzo[<i>b</i>]fluoranthene (BBF)</i>	mg/kg	11,900	585	717
<i>Benzo[<i>k</i>]fluoranthene (BJKF)</i>	mg/kg	13,600	308	438
<i>Benzo[<i>a</i>]pyrene (BAP)</i>	mg/kg	14,700	221	500
<i>Indeno[1,2,3-<i>cd</i>]pyrene (IND)</i>	mg/kg	5130	76.2	55.2
<i>Dibenz[<i>a,h</i>]anthracene (DA)</i>	mg/kg	2490	36.9	28.6
<i>Benzo[<i>g,h,i</i>]perylene (GHI)</i>	mg/kg	3710	172	88.5
Sum of EPA PAHs:	mg/kg	116,000	3010	28,400
	%	18%	3%	4%
FLO/PYO	Unitless	0.922	0.802	0.626
(BBF + BJKF)/BAP	Unitless	1.73	4.04	2.31
Degree of pyrogenic weathering (PWI)		NO < PO < PYO	NO < PO < PYO	NO < PO < PYO

[RM, Ruth Mullins].

to no CH₄ per year, and a maximum of 5.9 g Hg/yr. High CO₂ emissions relative to CO and CH₄ are indicative of near-complete combustion, although the quantities emitted also indicate that relatively little coal is burning. This is not surprising, as the seam has been auger-mined and relatively little coal remains.

Little vent activity has been observed at Tiptop since November 2009.⁷ It is possible that this fire is nearing the end of its lifespan. The Tiptop fire will be limited by the footprint of the ridge it is burning through. It was advancing toward the nose of the ridge in the two years it was monitored, and evidence of past fire activity in the area indicates that it has been advancing in this direction for some time.

A map of interpolated diffuse CO₂ emissions at Tiptop indicates that the main locus of combustion is near the east end of the ridge (Fig. 2), which is adjacent to an area of auger holes. Based on results from 100 sequential Gaussian simulations, background-corrected diffuse CO₂ emissions at Tiptop are estimated at 3.3–17.6 T/yr (5th and 95th percentile, respectively), with a median of 10.3 T/yr. This quantity is significantly smaller than the vent emissions. Total emissions for this fire, based on data from November 2009 indicate that it is producing approximately 118 T/yr of CO₂.

We may see more activity as the burn front reaches the auger holes to the west of its present location (Fig. 3). That will, however, likely be the final phase of the Tiptop fire; with near-complete combustion occurring, it is unlikely that this fire will continue burning once the remaining coal surrounding the auger holes is consumed.

3.2. Ruth Mullins

The Ruth Mullins fire site consisted of (1) three boreholes along state highway KY-80, drilled by the Kentucky Department of Transportation to determine if the seam and/or abandoned mine works

extend beneath the road, and (2) a series of nine vents opening through slumps and slides in the ridge. Along some of these latter vents, rather unusual fire features may be seen, such as tar-coated spider webs and, during the winter months, tar-coated icicles. The Ruth Mullins fire site was visited three times over the course of this study: November 2009, January 2010, and February 2010. The bulk of the data presented in this paper was collected in November 2009; selected vents were visited in January and February 2010, as conditions at the face allowed. The snowmelt polygon was mapped in January 2010.

Based on the November 2009 data, the Ruth Mullins coal mine fire was projected to be emitting ± 5400 T/yr CO₂, ± 240 T/yr CO, ± 150 T/yr CH₄, ± 0.81 T/yr H₂S, and a maximum of 2.7 g/yr Hg (Table 2). The high values of CO and CH₄ relative to CO₂ values indicate that, unlike the Tiptop fire, some degree of incomplete combustion is occurring at the Ruth Mullins fire. During the January and February 2010 sampling trips, only vents 1 and 2 were reliably accessible. Variations in emissions were recorded during those visits (Table 2). The overall vent emissions dropped significantly in January and February. For example, vent CO₂ emissions in January and February of 2010 were > 98% lower than those for November 2009. This indicates that fluctuations in vent emission from coal fires are more complex than previously thought. We hypothesize that the observed variations are driven by complex forcing mechanisms including: 1) seasonal variations including temperature and quantity of moisture entering the system; 2) air pressure variations; 3) collapse of conduits leading to the vents resulting in cessation or reduction in venting from specific locations; and 4) movement of the fire front. It is suspected that while a combination of all four factors is acting on the fire system, the variations are largely driven by factors 1 and 2, based on results of long-term monitoring of CO emissions (Hower et al., 2011).

A map of the diffuse CO₂ emissions recorded above the Ruth Mullins coal mine fire shows that the greatest diffuse emissions occur near the center of the study area (Fig. 4), with a median flux of 5.9 g CO₂/m²d being emitted across the fire. When the fire “melt zone” mapped in January 2010 is overlain atop this image, it shows reasonable

⁷ Hower observed minor activity on a November 2012 trip to the site. He was told that the fire was still active in March 2014 (personal communication with company personnel).

Fig. 2. False color heat maps of showing the mean diffuse CO₂ fluxes from the Tiptop fire for each node in the study based on 100 realizations from sequential Gaussian simulation.

Fig. 3. Auger holes in the coal bed exposed below the sample sites for the Tiptop fire (photos by J. M.K. O'Keefe). Clockwise from left: arrows denote approximate locations of the auger holes; collapsed auger hole; round auger hole.

alignment with the areas of greatest diffuse emissions mapped in November 2009. Together, the two provide a reasonable estimate of the Fall 2009/Winter 2010 location of the fire. The areas of greatest diffuse emissions also correlate well with the trend of collapsed mine portals that were visible during the 2008 visit, locations of which were recorded in field notes at that time (Fig. 4). This suggests that the majority of combustion is occurring along the faces of abandoned mine works. This observation is not unexpected, as more oxygen is likely to be present in these locations and fractures in the overlying rocks are most likely to develop along pre-existing zones of weakness caused by mine roof subsidence. Based on the November 2009 sampling, Engle et al. (2013) estimated total diffuse CO₂ emissions for the Ruth Mullins coal fire of 11–42 T/yr CO₂ (5th and 95th percentile, respectively) with a median of 25 T/yr CO₂, with total CO₂ emissions of approximately 5400 T/yr. The diffuse emissions at Ruth Mullins are, in general, two orders of magnitude lower than the vent emissions. By comparison, in coal fires in Wyoming, vent and diffuse emissions are generally of the same order of magnitude (Engle et al., 2011, 2012a). We think the

Fig. 4. False color heat maps of showing the mean diffuse CO₂ fluxes from the Ruth Mullins fire for each node in the study based on 100 realizations from sequential Gaussian simulation. Also shown are the location of the highwall, the January 2010 snowmelt boundary, and the location of collapsed mine tunnels. Modified from Engle et al. (2013).

Fig. 5. Minerals and tars at the Ruth Mullins fire (photos by J.M.K. O'Keefe). Counterclockwise from lower left: tar-infused salammoniac on twig, salammoniac on rock fragment, minerals on rock face at vent, tar along rock face at vent, tar on spider web, and tar on leaf.

lower diffuse-to-vent emissions at the Ruth Mullins fire are due to two factors: 1) low permeability, thick quartz- and calcite-cemented sandstone and shale overburden is reducing diffusion; and 2) venting is occurring primarily along abandoned mine tunnels and connecting fractures in the overlying rocks produced as tunnel roofs collapse.

Unlike the Tiptop mine fire, the Ruth Mullins mine fire is producing a variety of mineral sublimates on surfaces adjacent to the vent, be they rock or organic (Fig. 5). Most of the minerals are generally white and grow in dendritic, lacy forms. Many are yellowed by co-deposited tars. Minerals are most abundant surrounding the most active vents. In November, this was surrounding vents 3 and 5. By February, little activity was noted at vent 3 and the mineral deposits were largely weathered away. Active deposition was continuing at vent 5.

Analysis of bulk mineral and soil samples collected in November 2009 indicates that the majority of minerals collected from vents 1, 3, and 5 are salammoniac (PDF file #01-073-0365). Analysis of fairly homogeneous samples collected from vents 1 and 3 indicates that epsomite (PDF file #01-072-0696), Mg-sulfate hexahydrate (PDF file #72-1068), gypsum (PDF file#33-0311), muscovite (PDF file#01-072-1503), salammoniac, and quartz (PDF file#46-1045) are present. All but muscovite and quartz are known to be readily soluble in water, indicating that it is likely that these species could be mobilized into the regional ground water. Work by Silva et al., 2011a, 2011b details the mineral forms identified through optical and nanomineralogic techniques, and supports results obtained by powder XRD.

Tars coat a variety of surfaces at the Ruth Mullins coal mine fire (Fig. 5), including ice in the winter months. These tars contain potentially hazardous levels of both petroleum hydrocarbons and PAHs (Table 4). Among the documented health effects of these compounds are hemolytic anemia (Medlineplus, 2012) for naphthalene and cancer (International Agency for Research on Cancer, 2002) for naphthalene and other PAHs, such as benzo[a]pyrene, benz[a]anthracene, chrysene, benzo[b]fluoranthene, benzo[k]fluoranthene, dibenz[a,h]anthracene, and indeno[1,2,3-cd]pyrene (US EPA, 2007). Obvious care should be taken to limit exposure to these tars.

Vent gas emissions contain aliphatic compounds with carbon numbers ranging from C1-C7 (Table 3), and abundant aromatic BTEX compounds, especially benzene and toluene. Concentrations of the

organic compounds vary considerably between vents, such as 0.27 to 1174 ppm CO and 410 to 70,526 ppm CO₂ in vents 4 and 3b, respectively, at the time of the January 2010 sampling. Overall, for the January 2010 analyses, those two vents generally represent the extremes in concentrations for these gases. The VOC concentrations measured in November 2009 are greater than those from the January 2010 dataset. An important caveat in the latter observation is that changes in vent configurations prevented us from sampling the same vents. Therefore, we cannot be certain if variations in emissions reflect, for example, (1) variations due to the selection of vents to be sampled, (2) changes in the position of the active fire front, (3) responses to atmospheric conditions, or (4) some combination of some or all of the variables.

3.3. Examination of patterns in vent data

Principal component analysis of the vent data (three principal components, 74.6% of variance explained) shows that the vent data from the two fires are easily distinguishable with high flow rates for the Tiptop fire, compared with higher concentrations of CH₄, CO₂, and H₂S and higher barometric pressures observed in data for the Ruth Mullins fire (Fig. 6). Inverse relationships between flow rate and gas concentration suggests that at higher gas transport rates, trace gases from the fire are lower. This effect may represent dilution by atmospheric gases when the pressure gradient (either internal or external to the fire) causes increased flow. A linear trend ("A" in the upper panel of Fig. 6) for the Tiptop data in the PC biplots from higher temperature and CO concentrations with lower humidity and flow rates in vents 6, 8, 9, and 10 to lower temperature and CO concentration with higher flow rates in vents 1, 2, and 7 suggests spatial controls on the fire. Of note, CH₄ and CO₂ concentrations appear strongly associated while CO, an intermediate product between the two, appears unrelated. Such findings suggest that the system is not in a steady state and that CO may be rapidly converted to CO₂, and that its lifetime in the fire is rather short. However, CO concentration appears closely linked with vent temperature. More so, volume ratios of CO/CH₄ decrease notably as a function of temperature (Fig. 7) suggesting more CH₄ production and/or more rapid CO oxidation at higher temperatures. Such findings indicate that although the controls on the relative amounts of CH₄, CO, and CO₂ in

Fig. 6. Principal component biplot showing sample scores and parameters loadings for the first three components of the Ruth Mullins and Tiptop fires.

Fig. 7. Plot of the CO/CH₄ volume ratio in coal fire gas vent samples as a function of vent temperature at the Ruth Mullins and Tiptop fires.

coal fires are not well understood, the rate of CO production and loss appears to be a dynamic and important component. Given the large difference in greenhouse gas effect between CH₄ and CO₂, a better understanding of the factors controlling the relative ratio of the two gases in coal fire emissions is needed.

4. Conclusions

The Tiptop fire seemed to be nearing the end of its life at the time of our 2009 visit. At that time, the projected CO₂ emissions from the fire were about 118 T/yr, about 90% of that coming from vents. Principal component analysis of vent chemistry and physical characteristics at this site indicate a spatial transition from high CO concentration and temperature and low velocity gas to higher humidity and velocity gas with lower CO concentration and temperature.

The Ruth Mullins coal mine fire is dynamic. The fire front migrated significantly from 2007 to 2008, and was burning unpredictably along the north side of a ridge through 2010. Emissions variations appear to be at least in part seasonally controlled, but are also controlled by daily “breathing cycles” (Hower et al., 2011). To accurately estimate atmospheric greenhouse and toxic gas contributions by this fire, monitoring vent emissions six times a year is suggested. The combination of diffuse flux measurements and snow-melt patterns, an admittedly seasonally-limited technique, can be used to identify areas of active combustion where other methods are unavailable or unfeasible. Based on these studies, estimates of CO₂ emission from the Ruth Mullins coal mine fire range from 734 to 5400 T/yr. Both values likely represent underestimates, as they only take the winter months into account. The estimates of the emissions of other gases include ± 240 T/yr CO, ± 150 T/yr CH₄, ± 0.81 T/yr H₂S, and a maximum of 2.7 g/yr Hg. Emission estimates for most gases using the new sampling design developed in 2009 produced relatively similar results compared to data collected using the initial setup involving Dräger tubes. A notable exception are the emission estimates for Hg. Emission estimates using the Zeeman atomic absorbance analyzer are 5 orders of magnitude lower than our previous estimates (0.84 T Hg/yr) using the Jerome Instrument, suggesting the latter may have greatly over-estimated Hg concentrations in the vents.

Multivariate examination of vent chemistry and physical parameter data using data for both fires provided further insight. Concentrations of CH₄ and CO₂ are strongly associated but CO, an intermediate product between the two, appears poorly correlated with both. This result

indicates that controls on the CO production and loss rate are dynamic and rapid but not well understood.

Minerals, volatile and aromatic hydrocarbons, and tars found around vents at the coal fire sites contain compounds of concern. Among the aromatic hydrocarbons, benzene and toluene are relatively abundant.

Disclaimer

The use of brand and trade names is for descriptive purpose and does not imply endorsement by the U.S. Government.

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