AN IMPROVED TGA METHOD FOR RESPIRABLE COAL MINE DUST AND COMPARISON TO RESULTS BY SEM-EDX

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ACADEMIC ABSTRACT

It has long been known that chronic exposures to high concentrations of respirable coal mine dust can lead to the development of lung diseases such as Coal Worker's Pneumoconiosis, commonly referred to as "black lung", and silicosis. Since the mid-1990s, an alarming resurgence of diseases has been documented in central Appalachia, where underground mining often necessitates significant extraction of rock strata along with the thin seams of coal. These circumstances have prompted concern over if or how changing dust composition might be a factor in contemporary disease prevalence.

Until now, the total mass concentration and quartz mass fraction of respirable dust have been regulated and monitored in US coal mines. Unfortunately, however, these two metrics alone do not paint a full picture of dust composition. Earlier work in the author's research group established a preliminary thermogravimetric analysis (TGA) method for coal mine dust. The method is intended to allow estimation of three key mass fractions of the dust from separate sources: coal from the coal strata being mined; non-carbonate minerals from the rock strata being mined or drilled; and carbonates that are primarly sourced from application of rock dust products to the mine floor or ribs. However, accuracy of the preliminary method was substantially limited by poor dust recovery from the fibrous filter media used for sample collection.

This thesis includes two studies: The first study aims to establish an improved TGA method. It uses smooth polycarbonate (PC) filters for dust sampling and a modified thermal ramping routine. The method is verified using laboratory-generated respirable dust samples. In the second study, the improved TGA method is used to analyze 75 respirable mine dust samples, collected in 15 US mines. Replicate samples are also analyzed by scanning electron microscopy using energy dispersive X-ray (SEM-EDX).

TGA and SEM-EDX results are compared to gain insights regarding the analytical methods and general trends in dust composition within and between mines.

AN IMPROVED TGA METHOD FOR RESPIRABLE COAL MINE DUST AND COMPARISON TO RESULTS BY SEM-EDX

Eleftheria Agioutanti

GENERAL AUDIENCE ABSTRACT

It has long been known that chronic exposures to excessive respirable coal mine dust can lead to the development of lung diseases such as Coal Worker's Pneumoconiosis ("Black Lung") and silicosis. Disease rates in central Appalachia have shown an alarming and unexpected increase since the mid-1990s, despite declining dust concentrations evident from regulatory compliance monitoring data. Clearly, there is a need to better understand coal mine dust composition, which will require additional analytical methods.

Thermogravimetric analysis (TGA) has been proposed as one possible method, because it should allow estimation of three key dust components from separate sources: coal from the coal strata being mined; non-carbonate minerals from the rock strata being mined or drilled; and carbonates from application of rock dust products to the mine floor and ribs. However, preliminary work with TGA showed limited accuracy, mostly due to sampling materials.

In this thesis, two studies were performed. The first study aims to establish an improved TGA method using smooth, polycarbonate (PC) filters. The second study demonstrates the method on a large number of mine dust samples, and compares the results to those gained by an alternative method that uses electron microscopy.

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I am very thankful I have such a great group of friends in Blacksburg that each one of them with their unique way contributed in beautiful memories the past two years.

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TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

PREFACE

Respirable coal mine dust has been identified as a serious occupational health hazard. Prolonged exposures can lead to the development of lung diseases such as Coal Worker's Pneumoconiosis and silicosis, and eventually Progressive Mass Fibrosis (PMF) which is the most severe and rapidly progressive form of disease. Respirable dust monitoring data available since 1989 (Figure 0-1) show a decline in the average total dust and quartz concentrations. Unexpectedly though, disease prevalence began to increase in the mid-1990s, especially in parts of the Appalachia. Figure 0-2 shows the percentage of all Federal Black Lung Benefits Act program (BLBA) claimants with a PMF diagnosis since 1970, with a marked increase in central Appalachian coal miners since the 1990s.

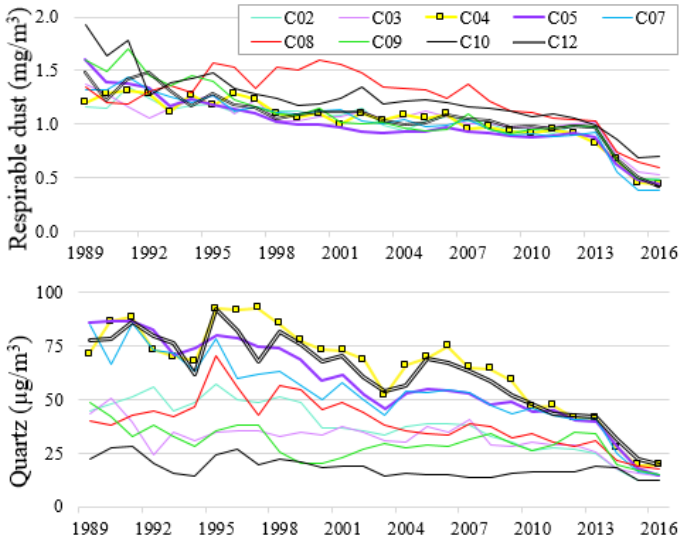

Figure 0-1 (Taken from Frost et al 2019.) Annual averages by MSHA coal district for a) respirable dust concentration, and b) respirable silica concentration. The dataset was retrieved from MSHA (2017) and includes all valid quartz (i.e., silica) samples collected for compliance monitoring between 1989-2016. With few exceptions, each sample also has a (total) respirable dust mass concentration and average mining height associated with it. The data was filtered to exclude non-underground operations, and then sorted by district and sampling data. The plots show a simple average of all available data points in a given district each year. Total sample counts across all districts per year ranged from n=423 (1989) to n=12660 (2000), with a mean value of n=4175. Total sample counts in any individual district per year ranged from n=17 (districts 3, 8 and 10 in 1989) to n=4148 (district 5 in 2000), with a mean value of n=463.

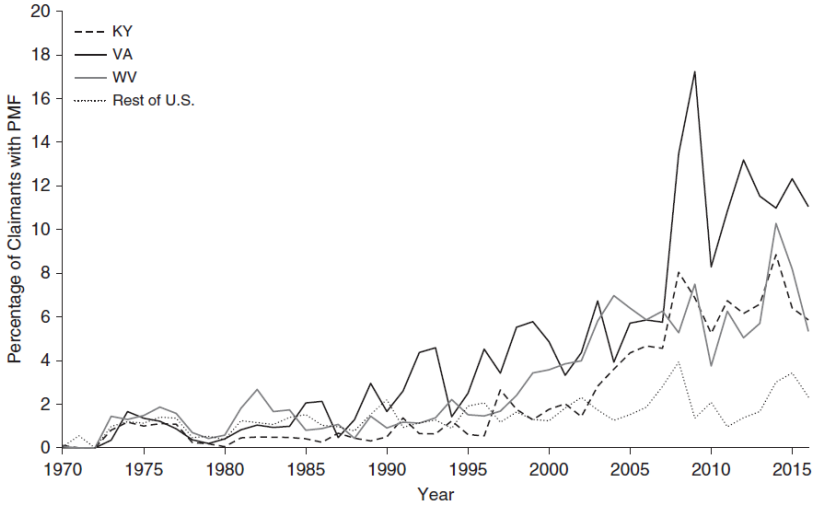

Figure 0-2 (Taken from Almberg et al., 2018.) Percentage of claimants for Federal Black Lung Program benefits who received a determination of progressive massive fibrosis (PMF) during their claim process in the central Appalachian states of Kentucky, Virginia, and West Virginia compared with the rest of the United States, 1970–2016. Data restricted to those miners with between 5 and 60 years of coal mine employment. Data source: U.S. Department of Labor, Office of Workers' Compensation Programs, Division of Coal Mine Workers' Compensation.

The apparent disagreement between respirable dust monitoring data and disease rates has resulted in calls to better understand dust composition (National Academies of Sciences, Engineering, and Medicine, 2018). Previous work in the author's research group authors and focused on development (e.g., see Scaggs, 2016) and application (e.g., Phillips et al., 2017) of a preliminary Thermogravimetric Analysis (TGA) method for respirable coal mine dust characterization. That method was based on sample collection using fibrous filter media, i.e., polyvinyl chloride (PVC) or mixed cellulose ester (MCE), which are compatible with conventional gravimetric dust sampling in coal mines. However, low dust recovery from such media posed a clear obstacle for TGA accuracy.

The work presented in this thesis is intended to develop an improved TGA method using PC filters and then compare the results to those from an electron microscopy using energy dispersive X-ray (SEM-EDX) analysis. A comparison of the two methods was carried out in the end to obtain more comprehensive information of dust composition. TGA is relatively simpler and faster mass based method that yields estimates of three dust fractions of interest: coal, carbonates and non-carbonates. On

the other hand, SEM-EDX is a particle level analysis that is more complicated and time consuming, but provides more comprehensive data.

This study is divided into 3 Chapters with an introduction that precedes the first two chapters. The overall objective is to advance the existing knowledge regarding respirable dust characterization by improving an already existing laboratory methodology for TGA analysis and comparing the results from this mass based analysis to a particle level analysis.

More specifically, in Chapter 1, bulk materials of coal shale and rock dust are used for creating lab generated samples and developing a methodology for dust characterization with Thermogravimetric analysis. TGA analysis estimates the total mineral fraction in a respirable dust sample which is composed of coal, carbonates, and non-carbonate minerals. The chapter ends with a subsection on the method validation.

In Chapter 2, the methodology developed in Chapter 1 is applied to 75 respirable dust area samples obtained from a sampling campaign carried out in 15 different underground coal mines in the norther and central Appalachian, Mid-western and Western regions. The TGA mass fraction results are compared to results from an alternative method using scanning electron microscopy with energy dispersive X-ray (SEM-EDX).

Chapter 3 reports the overall conclusions of the study and highlights future work that can be carried out. By completing this study, the goal was to gain more information regarding comprehensive characterization of coal dust along with the advantages and limitations of the analytical techniques used here.

1 Chapter 1. An Improved TGA Method for Respirable Coal Mine Dust

Eleftheria Agioutanti, Cigdem Keles, Emily Sarver

Abstract

It has long been known that chronic exposures to respirable coal mine dust can cause occupational lung diseases such as Coal Worker's Pneumoconiosis and silicosis. The dust composition can play an important role in determining health outcomes, and it can vary significantly depending on source materials (e.g., coal and rock strata being mined, rock dust products being applied in the mine). For regulatory compliance purposes, total mass concentration and quartz mass fraction of respirable dust are monitored in US coal mines, but the whole composition of the dust is not typically determined. Previous work in our research group has indicated that thermogravimetric analysis (TGA) can be used to estimate the coal and total minerals mass fractions in respirable dust samples. With sufficient sample mass, carbonates and non-carbonate minerals fractions can also be differentiated, which may help to distinguish dust sources. However, that earlier work focused on samples collected on fibrous filter media, which limited dust recovery and method accuracy. Here, we present an improved TGA method using smooth, polycarbonate (PC) filters.

1.1 Introduction

It is well established that respirable dust exposures in coal mines can cause a number of occupational lung diseases such as Coal Workers' Pneumoconiosis (CWP, often called "black lung") and silicosis (Laney et al., 2012; Joy, 2012; Suarthana et al., 2011; OSHA, 2010; NIOSH, 2008; Castranova and Vallyathan, 2000; Seixas et al, 1995; Organiscak et al., 1990) Diagnosis of lung disease in coal miners is most often based on radiography and occupational history; and the diagnosis can range from simple CWP to complicated CWP, which is often termed progressive mass fibrosis (PMF) and has been frequently associated with respirable silica exposures (Laney and Weissman, 2014; Petsonk et al., 2013). Across the US, prevalence of CWP declined significantly following the passage of the 1969 Federal Coal Mine Health and Safety Act in the late 1960s (NIOSH, 2008). In the mid-1990s, however, disease rates

began to rise unexpectedly, particularly in central Appalachia (CDC, 2012; Wade et al, 2011; Suarthana et al., 2011; Laney and Attfield, 2010; NIOSH, 2008; Colinet et al. 2010).

Since that time, a number of epidemiologic studies have shed light on this new era of CWP, which has been characterized by regional hotspots of very severe and rapidly progressive disease, even among relatively young miners (Graber et al., 2017). For example, a cluster of 60 cases of progressive massive pneumoconiosis (PMF), was reported in 2016 out of single clinic in eastern KY (Blackley et al., 2016). In 2018, an even larger cluster of PMF, 146 miners, was identified between three clinics in Virginia (Blackley, 2018b). These isolated findings have been underscored by trends observed in data from Federal Coal Workers' Health Surveillance Program and the Federal Black Lung Benefits Act program (BLBA) (Almberg et al., 2018).

Based on the radiographic evidence, respirable silica has emerged as primary culprit in the resurgence of PMF (Blackley et al., 2018a, 2016). However, the available dust monitoring data does not provide clear evidence from the mine environment. For demonstration of regulatory compliance, only the mass concentration of total respirable dust and the mass fraction of quartz (i.e., silica) in that dust are monitored in US coal mines. Doney et al. (2019) recently summarized this data from 1982-2017 and found that, while mines in central Appalachia consistently had higher quartz fractions than mines in other regions, they had lower total dust concentrations; and both metrics generally trended downward over the 35 years with available data. Thus, although relatively higher silica concentrations might have explained elevated disease prevalence in this region decades ago, the documented trends in silica concentrations does not seem to explain the more recent and dramatic resurgence of disease. One possibility is that monitoring data does not tell the complete story of exposure, in terms of sampling frequency and/or important dust composition factors (National Academies of Sciences, Engineering, and Medicine, 2018).

In general, there are three major sources of respirable dust in coal mines: the coal strata being mined, the surrounding rock strata being mined or drilled (e.g., for roof bolting), and rock dust products that are being applied to mitigate explosibility hazards (Sarver et al., 2019; National Academies of Science, Engineering and Medicine, 2018). Rock dust application is required in US mines, and products must meet specifications in terms of both their content and particle size (Colinet and Listak, 2012). They are often made from high quality (i.e., calcium carbonate-rich, silica-limited) limestone that is finely ground. A fourth component of respirable

dust in some coal mines is diesel particulates – although, due to their size (i.e., generally smaller than some coal or mineral dust), they may not contribute significant mass to the total respirable content (Sarver et al., 2019; Birch and Noll, 2004).

Regarding the rock strata-sourced dust, Central Appalachian mines are often characterized by their thin seam heights, which frequently means extracting significant roof and/or floor rock (e.g., shales, slates, sandstones) along with the coal. Many have speculated that such mining conditions might influence dust characteristics and contribute more silica (Laney and Attfield, 2010; Pollock et al., 2010; Schatzel, 2009 CDC, 2006 and 2007; Antao et al., 2005; Page and Organiscak, 2002). In addition to silica, rock extraction is expected to generate other mineral dusts, especially silicates (e.g., Johann-Essex et al., 2017a, 2017b). Notably, in recent studies of PMF among coal miners that included lung tissue pathology, findings have indicated high abundances of silicates (Jelic et al., 2017; Cohen et al., 2016).

1.1.1 Thermogravimetric Analysis of Respirable Coal Mine Dust

In order to explore the variability of respirable coal mine dust composition, our research group began pursuing thermogravimetric analysis (TGA) in 2015 (Scaggs et al., 2015). TGA basically tracks the weight change of a sample with temperature in a controlled environment. Because coal and the major carbonate mineral of interest (i.e., calcium carbonate) tend to lose weight in characteristic temperature regions, and the non-carbonate minerals of interest (i.e., silica and silicates) tend to be inert in these regions, evaluation of a dust sample's weight with temperature can theoretically be used to determine its coal, carbonate and non-carbonate minerals mass fractions (Figure 1-1). TGA is well-established for determining the content of ash-forming minerals in bulk coal samples, in which case it is often termed "proximate analysis" (Mayoral et al. 2001; ASTM, 1993). It has also recently been used to look at coal and limestone mass fractions in total airborne dusts from a coal mine (Barone et al., 2016). With regard to a TGA application for respirable coal mine dust, progress until now can be briefly summarized as follows.

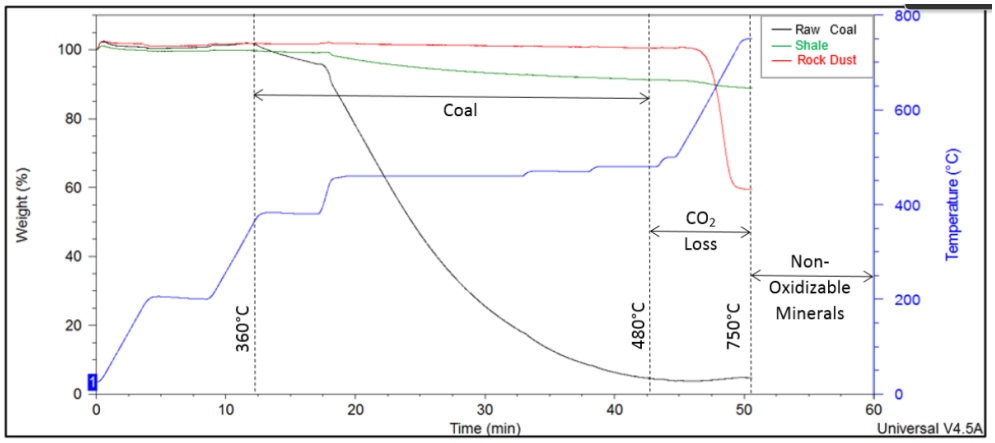

Figure 1-1 Representative thermograms for the raw coal, rock dust, and shale materials used to develop the TGA method (Taken from Scaggs et al. 2016).

Scaggs et al. (2015) initially considered a direct-on-filter TGA method, with the intention of gaining additional data from filter samples that are typically collected for gravimetric and quartz analysis (i.e., by MSHA's Standard P7 Method (MSHA,2014)). Because such samples are currently collected on polyvinyl chloride (PVC), this media was considered for the direct-on-filter method. Mixed cellulose ester (MCE) was also considered as potentially attractive because it is classified as virtually ash-less. However, experimental work quickly showed that combustion of the (relatively high weight) filter material itself would provide too much interference for interpretation of (relatively low weight) dust sample behavior. Other filter media (e.g., polytetrafluoroethylene or PTFE, polycarbonate or PC, and glass fiber) were also deemed incompatible with a direct-on-filter TGA approach, either due to their temperature stability, hygroscopicity, or interference with a subsequent quartz analysis. Thus, the focus turned to a dust-only TGA approach.

Scaggs (2015) developed a dust-only TGA method for a set of respirable coal mine dust samples that had been collected on PVC and MCE filters in a group Appalachian mines. The sample preparation involved dust recovery from the filters by sonication in deionized water; evaporation of the water; and dust transfer to the TGA sample pan by resuspension in a small volume of isopropyl alcohol. Then, the sample was slowly heated in air with isotherms at key temperatures to drive off moisture, volatiles and filter residue (i.e., before 360 °C); promote complete oxidation of coal (i.e., at or before 480°C); and promote complete decomposition of calcium carbonate (i.e., between 480-750°C). Based on analysis of empty TGA pans and blank

filters, corrections were developed for any internal drift of the TGA instrument itself and interference of filter residue with the sample weight loss, respectively. Based on analysis of real rock dust material, a correction was also developed for a minor amount of premature weight loss (i.e., before 480 °C).

Using composite samples of respirable dust that were generated in the laboratory from well-characterized coal, rock dust and shale materials, Scaggs (2015) showed that the final method for PVC or MCE generally produced accurate results for estimating coal and non-coal (i.e., total minerals) mass fractions. Moreover, with sufficient weight of sample recovered to the TGA pan, carbonate and non-carbonate minerals could be distinguished. Consistent with these findings were those from a study by Phillips et al. (2017), which applied Scaggs' (2015) TGA method to 106 filters from the aforementioned set of available mine dust samples. The TGA results were compared to estimates of coal, carbonate and non-carbonate mineral mass fractions derived from analysis of replicate filter samples (one for each TGA sample) by scanning electron microscopy with energy dispersive X-ray (SEM-EDX). Of the 106 paired TGA and SEM-derived results, 86 were deemed to be in good agreement when comparing coal and non-coal fractions, and 47 were in good agreement for carbonate; and agreement markedly improved with recovered sample mass for the TGA.

However, Scaggs (2016) and Phillips et al. (2017) observed that dust recovery from the PVC and MCE filters was generally low. Not only will limited TGA sample mass tend to magnify errors associated with the method, but the fibrous nature of these filter media may also mean that the recovered dust is not necessarily representative of the entire sample collected with the filter. For example, dust from different sources could have different size distributions, which might result in disproportionate collection of particles within the filter fibers versus on the filter surface (i.e., from where most recovery presumably occurs).

Building on the lessons learned from earlier work in our group, especially by Scaggs (2015), an improved TGA method for respirable coal mine dust samples is presented here. The improved method still represents a dust-only approach with the aim of determining the coal, carbonate and non-carbonate mass fractions of a sample. However, it is developed for use with smooth (i.e., non-fibrous) filters as the sampling media, and modifies the sample preparation and TGA thermal program.

1.2 Experimental Details

In order to develop and verify the improved TGA method for a respirable coal mine dust application, three major phases of experiments were conducted to: 1) characterize the dust from source materials in terms of their thermal behavior; 2) characterize interferences from the sample preparation procedure and develop appropriate corrections; and 3) apply the thermal routine and data corrections to composite dust samples in order to verify the method. Each phase of experiments is described in later sections. First, the TGA instrument, dust source materials, and respirable dust sample collection and preparation procedures are described.

1.2.1 TGA Instrument

As in the earlier work by Scaggs (2015), a Q500 Thermogravimetric Analyzer (TA Instruments, New Castle, DE) was used for all TGA experiments. The Q500 employs a microbalance with 0.1μg resolution, and its vertical furnace eliminates some thermal influence on the balance (Cheng et al., 2010). The instrument used here is equipped with an auto sampler, which provides the ability to run up to 16 separate samples in sequence. Here, sample sets were limited to 8 pans based on use of gas cylinders, which have to be periodically replaced. The first and last pans (i.e., pans 1 and 8) were always run blank, and pans 2-6 were used for dust samples. Periodically, experiments were run with all 8 pans being blanks to check internal drift of the instrument.

Platinum TGA sample pans, which are inert across a wide temperature range, were used for this work. Pans were cleaned prior to each use using an open flame from a butane torch for at least twenty seconds, and this procedure was repeated until the pans showed constant weight. Before each experiment, all pans were tared empty in the TGA instrument and weights were also recorded using the microbalance as a check. The specific pan sequence was maintained throughout all experiments to improve data corrections related to internal drift of the TGA instrument.

1.2.2 Dust source materials

The dust source materials used in this work included three bulk samples provided by industry partners: a bituminous clean coal product (i.e., low-ash, low sulfur), a limestone rock dust product, and shale rock that was hand-picked from the run-of mine material at an

underground operation in central West Virginia. The rock dust product was already a powder; the coal and shale were pulverized in the laboratory to produce powders. Since none of the materials were pure, it was expected that the coal would contain some small fraction of minerals, the rock dust would contain some non-carbonate minerals, and the shale would have some coal or other organic matter associated with it, that will be attributed to coal for this study. For this TGA application, carbonate minerals are assumed to be calcium carbonate ($CaCO_3$). Indeed, carbonates in US coal mines are expected to be primarily sourced from rock dust products, which are frequently made from high quality limestone.

1.2.3 Respirable dust collection and sample preparation

From each of the three powdered dust source material samples, respirable dust was generated in the laboratory in a sealed enclosure. The dust was made airborne by using compressed air pulses. Respirable sized particles of a given material were sampled on to 37-mm PC filters[1], which were located inside plastic cassettes along with a filter support pad. The cassettes were attached to 10-mm Dorr-Oliver cyclones. The dust-laden air was drawn through the cyclones and then the sampling cassettes using Escort ELF personal sampling pumps, set at a flowrate of 2.0 L/min. At this flow, the cyclone yields a d_{50} particle cut size of approximately 4 μm and a top size of 10 μm.

During respirable dust collection, the goal was to densely load the PC filters with a given material type (i.e., to collect significant mass). This dust was then used to make samples for the TGA experiments, either by scooping it (with a small stainless steel spatula) directly onto a TGA pan for the dust characterization experiments; or onto a clean PC filter for the experiments to establish data corrections and verify the final method. At that point, the weight of any given dust material added to a pan or PC filter was measured using a microbalance (Sartorius MSE6.6S, Gottingen, Germany). For composite samples, weight measurements were made and the spatula was cleaned after addition of each dust component. It is noted that the approach of directly placing respirable dust onto the PC filters, instead of collection from

[1] Both PC and PTFE filters were considered for this work. PC was ultimately chosen based on several factors, including: both media are compatible with isopropyl alcohol, which is proposed for sample preparation; preliminary experiments demonstrated that PC was easier to handle without tearing during sample preparation; filter cost is substantially lower for PC filters.

the airborne material inside the dust enclosure, was used here to provide control over sample masses (i.e., which could not reliably be done in the dust enclosure).

For respirable dust samples placed directly to a TGA pan, no further preparation was required – and the samples were generally analyzed immediately after the pans were loaded to avoid mass losses. For dust samples transferred onto PC filters, the dust was recovered by placing the filter in a clean glass tube with conical bottom, and submersing it in 5 -10 ml of isopropyl alcohol. (To minimize the required alcohol volume, 15 mL tubes were used and the filter was loosely rolled, dust-side in, to place into the tube.) The tube was placed in an ultrasonic bath for 3 minutes at 30°C to dislodge the dust, and then the filter was carefully removed from the tube. Next, the tube was centrifuged for 10 minutes at 2500 rpm in order to settle the dust. A volumetric pipette was then used to pipette the suspended in isopropanol dust from the tube into a clean tared TGA pan and the pan was placed in a fume hood for the isopropanol to evaporate completely. These two steps were repeated until no dust could be seen in the tube using a microscope. Finally, the pan containing the dust was weighted on the microbalance to determine the amount of mass recovered from the laboratory procedure. The microbalance data served also as a check for TGA instrument measurements.

1.3 Experiments to characterize thermal behavior of dust from source materials

The aim of experiments conducted during this phase was to confirm the thermal routine for the TGA method, and establish the temperature region(s) of interest from which weight loss data can be used to determine the sample mass fractions of coal, carbonate and non-carbonate minerals. The thermal routine is shown in Table 1-1 and was adapted from Scaggs (2015). The basic premise is that sample weight loss in three separate regions of interest should correspond to three separate sample constituents. First, moisture, volatiles and any residue from sample preparation should be lost between ambient to 200°C; then, coal oxidation will occur between 200-480°C; and finally, thermal decomposition of calcium carbonate (to CO_2 + CaO) will occur between 480-800°C, such that the weight loss in this region corresponds to the CO_2 release. The final sample weight will include non-carbonate minerals and the CaO produced from carbonate decomposition.

Table 1-1 Steps in TGA routine for respirable coal mine dust

Region of Interest	Thermal Step	Temperature (°C)	Description of Sample Mass
	Initiate routine in air	Ambient	Initial sample mass
"PC"	Ramp 50°C/min to 200°C, isotherm for 5 min	Ambient-200°C	Mass loss due to moisture, volatiles, and residue (e.g., from the PC filter) associated with sample preparation
"Coal"	Ramp 20°C/min to 480°C, isotherm for 50 min	200-480°C	Mass loss due to coal decomposition, premature CO_2 release and secondary PC filter residue oxidation
"CO_2"	Ramp 20°C/min to 800°C, isotherm for 5 min	480-800°C	Mass loss due to major CO_2 release
	Cool in N_2 for 16 min	800°C-Ambient	Final sample mass (recorded at beginning of step)

First, a total of 35 single-material samples (i.e., 12 of the clean coal and rock dust material and 11 of shale) were prepared and analyzed. The samples were prepared by placing the respirable dust directly onto the TGA pan, and effort was made to cover a wide range of sample masses (Table 1-2). Then, 16 composite samples (i.e., two or more of the dust materials) were prepared and analyzed (Table 1-3).

Table 1-2 Weights of 36 single-material samples prepared directly on TGA pans (no filter).

Sample	Coal (μg)	Sample	Shale (μg)	Sample	Rock dust (μg)
1	49	13	56	24	51
2	50	14	61	25	58
3	70	15	62	26	80
4	77	16	79	27	115
5	83	17	108	28	135
6	100	18	158	29	146
7	123	19	187	30	318
8	133	20	246	31	371
9	152	21	267	32	457
10	216	22	312	33	496
11	327	23	411	34	649
12	598			35	783

Table 1-3 Weights of each source material in 16 composite dust samples prepared directly on TGA pans (no filter).

Sample	Coal (μg)	Shale (μg)	Rock Dust (μg)	Total dust (μg)
1	51	0	56	107
2	74	0	92	166
3	72	77	57	206
4	72	180	0	252
5	0	138	121	259
6	0	222	46	268
7	36	175	68	279
8	48	0	257	305
9	152	0	155	307
10	103	105	131	339
11	299	0	80	379
12	241	59	81	381
13	311	0	70	381
14	265	0	188	453
15	122	139	279	540
16	238	252	223	713

Figure 1-2 shows representative thermograms for the single-material samples. In general, each material behaved as expected within the three distinct temperature regions of weight loss described in Table 1-1. Figure 1-2 also shows representative thermograms for the residue from a prepared blank PC filter, which will be discussed later, and a blank "empty" pan. (Thermograms for all samples are shown in Appendix A, Figures A-1 to A-4). As mentioned above, the empty pan behavior is due to internal mechanical drift of the TGA instrument during

the thermal routine and must be used to correct all sample results. Briefly, this is done by subtracting from any given sample results the corresponding empty pan results in each temperature region of interest. For example, if a sample is analyzed in pan 2, the empty pan 2 results are used for the data correction. As mentioned earlier, empty pan runs were conducted periodically (a total of 21 set of runs) to be sure that the instrument drift was stable; across these runs, all results for a given pan were averaged to yield the final corrections for that pan. Moreover, pans 1 and 8 were always analyzed empty in sample runs as a check (i.e., that their behavior was consistent with pans 1 and 8 during empty pan runs).

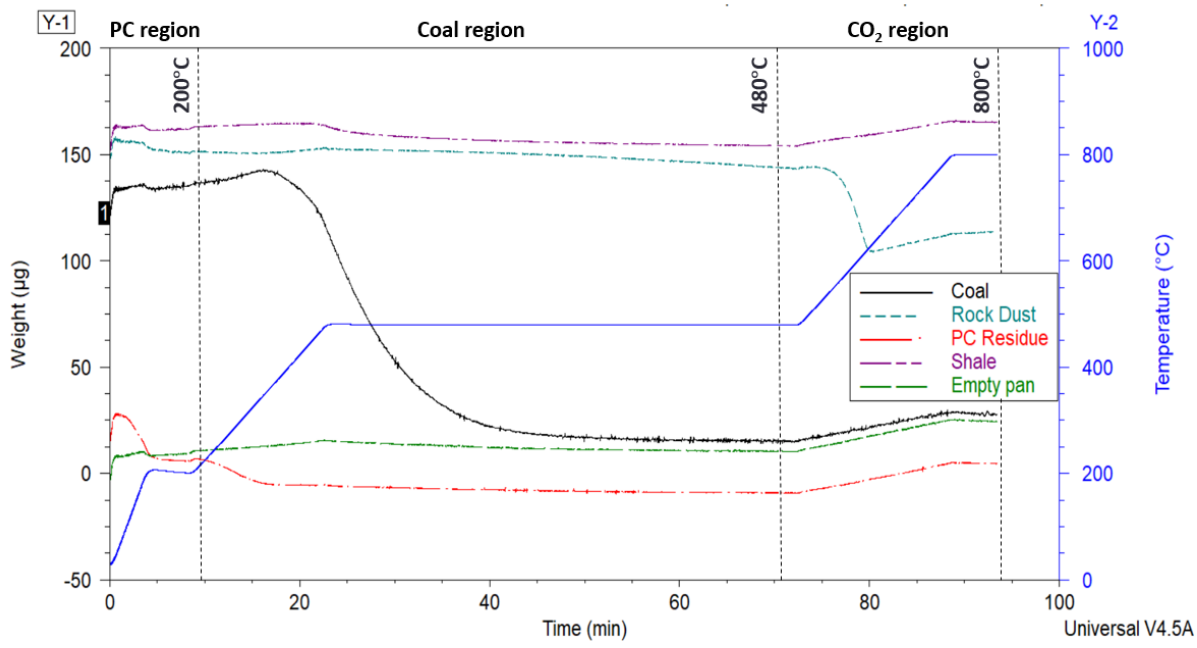

Figure 1-2 Thermograms for respirable dust generated from clean coal, shale, and rock dust, and placed directly on the TGA pan (no filter). Results are also shown for a blank PC filter and empty pan for comparsion

After correcting for the instrument drift, Table 1-4 shows the weight loss in each temperature region for the single-material samples, and the final residue at 800°C. As expected, the clean coal appears to have a minor (non-carbonate) impurity (i.e., 4%, on average). Likewise, the shale appears to have minor impurities of both coal and carbonates (i.e., 6 and 2%, respectively on average).

Table 1-4 Weight losses for single-material respirable dust samples in each temperature region. For each material, results represent the mean weight loss (N=12 for clean coal and rock dust and N=11 for shale).

	Mean % (Stdev %)			
Dust Material	0-200°C	200-480°C	480-800°C	Residue at 800°C
Clean Coal	0 (1)	96 (1)	0 (0)	4 (1)
Shale	0 (1)	6 (1)	2 (2)	92 (2)
Rock Dust	0 (2)	4 (1)	37 (2)	59 (2)

From Table 1-4, it is evident that the carbonate-rich rock dust material releases most of its CO_2 in the expected region (i.e., 480-800°C). This is termed the "major CO_2 release" (or $CO_{2(2)}$) and can be simply computed as the weight loss in this region ($W_{480\text{-}800°C}$, Equation 1.1). However, there also is a minor weight loss in the coal region (i.e., 200-480°C). Since the rock dust material used here surely did not contain coal, this is attributed to premature CO_2 release is termed $CO_{2(1)}$. (Rock dust is assumed to be composed only of $CaCO_3$). To develop a correction for the TGA data, the Langumuir relationship between $CO_{2(1)}$and $CO_{2(2)}$can be used (Figure 1-3, Equation 1.2). Then, the total CO_2 ($CO_{2(Total)}$, Equation 1.3) can be used to stoichiometrically determine the original carbonate mass (M_{CB}) and the resulting oxide mass (M_{CaO}) upon carbonate degradation. Since most rock dust products are made from high quality limestone, Equations 1.4 and 1.5 assume stoichiometry for calcite ($CaCO_3$), which degrades to 44% CO_2 and 56% CaO (oxide). Finally, the masses of coal (M_{coal}) and non-carbonate minerals (M_{NCB}) can be determined using Equations 1.5-1.7.

$$CO_{2(2)} = W_{480-800°C} \qquad \textit{(Equation 1.1)}$$

$$CO_{2(1)} = \frac{39.35 \times CO_{2(2)}}{269.39 + CO_{2(2)}} \qquad \textit{(Equation 1.2)}$$

$$CO_{2(Total)} = CO_{2(1)} + CO_{2(2)} \qquad \textit{(Equation 1.3)}$$

$$M_{CaO} = \frac{0.56 \times CO_{2(Total)}}{0.44} \qquad \textit{(Equation 1.4)}$$

$$M_{CB} = \frac{CO_{2(Total)}}{0.44} \qquad \textit{(Equation 1.5)}$$

$$M_{coal} = W_{200-480°C} - CO_{2(1)} \quad \textit{(Equation 1.6)}$$

$$M_{NCB} = W_{@800°C} - CaO \quad \textit{(Equation 1.7)}$$

After accounting for the impurities in the clean coal and shale materials, and the premature CO_2 release from the rock dust, the composition (i.e., % coal, non-carbonates and carbonate) of respirable dust from each source material was determined (Table 1-5). These values serve as the basis for establishing "expected" compositions for composite dust samples generated from these source materials. To interpret the "observed" TGA results for the same sample, Equations 1.5-1.7 can be used to determine the carbonate, coal and non-carbonates mass fractions.

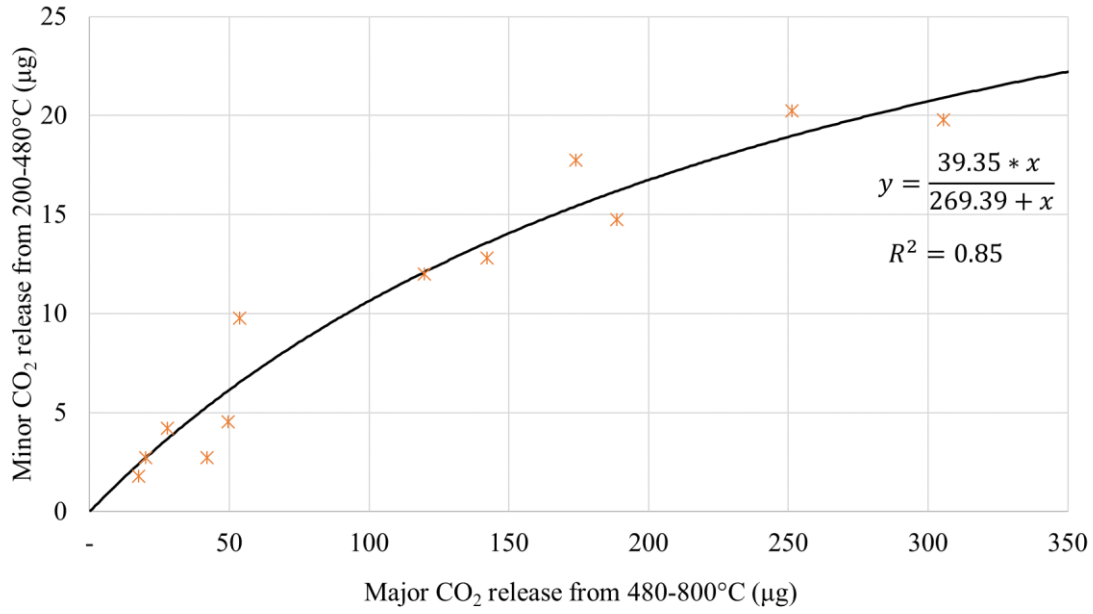

Figure 1-3 Langmuir relationship between the minor (premature) CO_2 release in the 200-480 °C range and the major CO_2 release in the 480-800°C range.

Table 1-5 Respirable dust composition of each source material.

	Mean %		
Material	Coal	Carbonate	Non-Carbonates
Clean Coal	96%	0%	4%
Shale	6 %	5%	89 %
Rock Dust	0%	91%	9%

To validate the proposed computations, the 16 composite dust samples shown in Table 1-3 were analyzed. Figure 1-4 shows example thermograms, and compares the expected and observed results for all samples. The expected results are based on the mass of each dust component in a given sample (i.e., determined from the measured mass of each material included in the sample and the material composition from Table 1-5); and the observed results were computed from the TGA data using Equations 1.5-1.7. The error % shown on the y-axis in Figure 1-5 represents the difference between the observed and expected results for a given dust component in a given sample. For example, if the TGA-derived result for coal was 25% and the expected result was 35%, the error value is shown as -10%. For all 16 composite samples, the error lies within ±10%, including for relatively low sample masses.

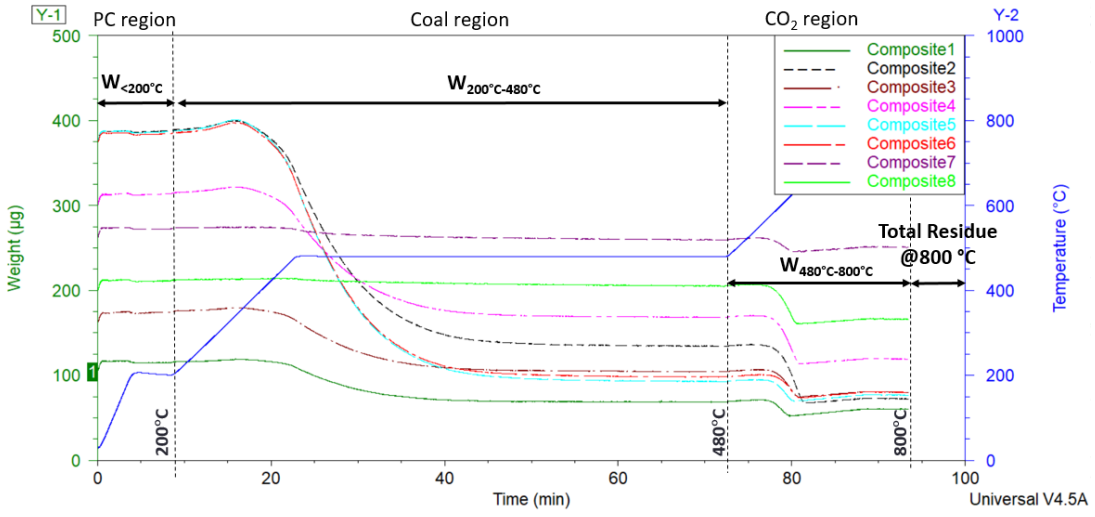

Figure 1-4 Example thermograms for eight composite dust samples (no filter).

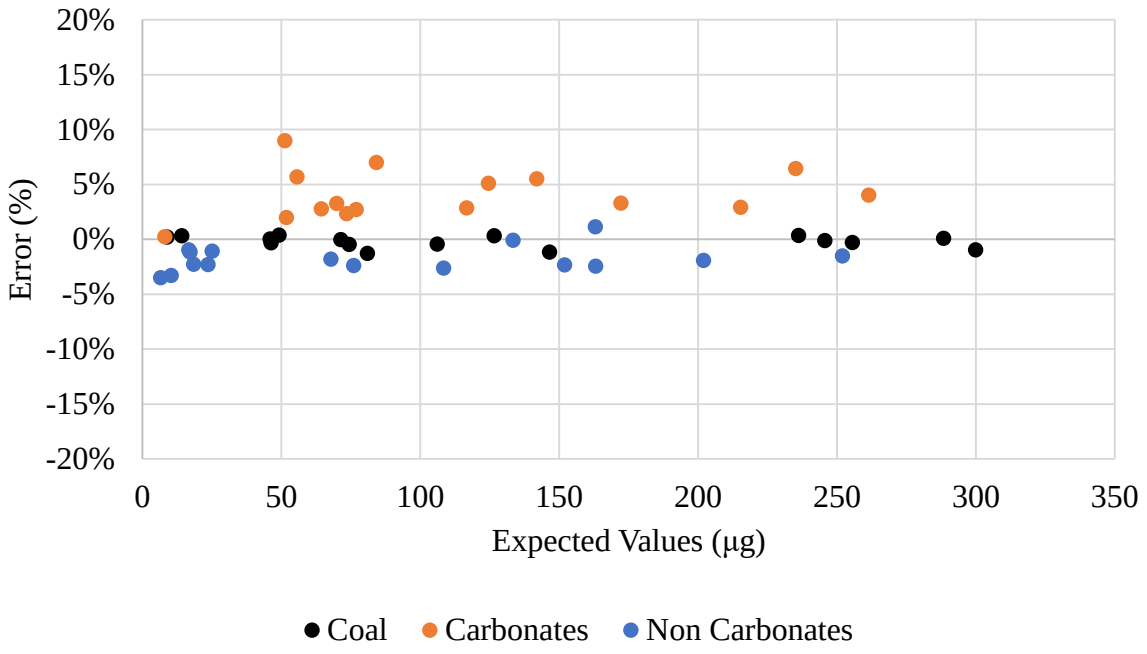

Figure 1-5 Error between observed and expected coal, carbonates and non-carbonates % values for composite dust samples made by placing variable masses of clean coal, shale and rock dust directly on a TGA pan. Error is computed as TGA-derived % - measured %.

1.4 Experiments to characterize interferences from the sample preparation procedure and develop appropriate corrections

To understand the thermal behavior of filter (or other) residue yielded by the filter-sample preparation procedure, 24 blank PC filters (37-mm, 0.4µm pore size) were prepared per section 1.2.3 and the contents of the resulting isopropyl alcohol suspension were analyzed. Representative thermograms for the blank PC filters are shown in Figure 1-6, and indicate an initial weight loss from ambient-200°C, which is termed F_1 (Equation 1.8). A secondary weight loss of the filter residue is also evident in the coal region (i.e., 200-480°C) and is termed F_2. Figure 1-7 shows that F_2 can be reasonably predicted from F_1 using a Langmuir relationship (Equation 1.9). Finally, a small amount of residue (F_3) is present at the final temperature of 800°C; this value is taken as a constant 5µg (Equation 1.10) based on the mean value observed from all blank PC filters analyzed here following empty pan correction (5±2µg).

$$F_1 = W_{ambient-200°C} \qquad \textit{(Equation 1.8)}$$

$$F_2 = \frac{29.10 \times F_1}{3.32 + F_1} \qquad \textit{(Equation 1.9)}$$

$$F_3 = 5\mu g \qquad \textit{(Equation 1.10)}$$

After incorporating the sample preparation (i.e., filter) corrections, the final equations for determining coal, non-carbonates and carbonate masses from TGA results are shown as Equations 1.11-1.13.

$$M_{coal(F)} = W_{200-480\,C} - CO_{2(1)} - F_2 \qquad \textit{(Equation 1.11)}$$

$$M_{CB(F)} = \frac{CO_{2(total)}}{0.44} \qquad \textit{(Equation 1.12)}$$

$$M_{NCB(F)} = W_{@800\,C} - M_{CaO} - F_3 \qquad \textit{(Equation 1.13)}$$

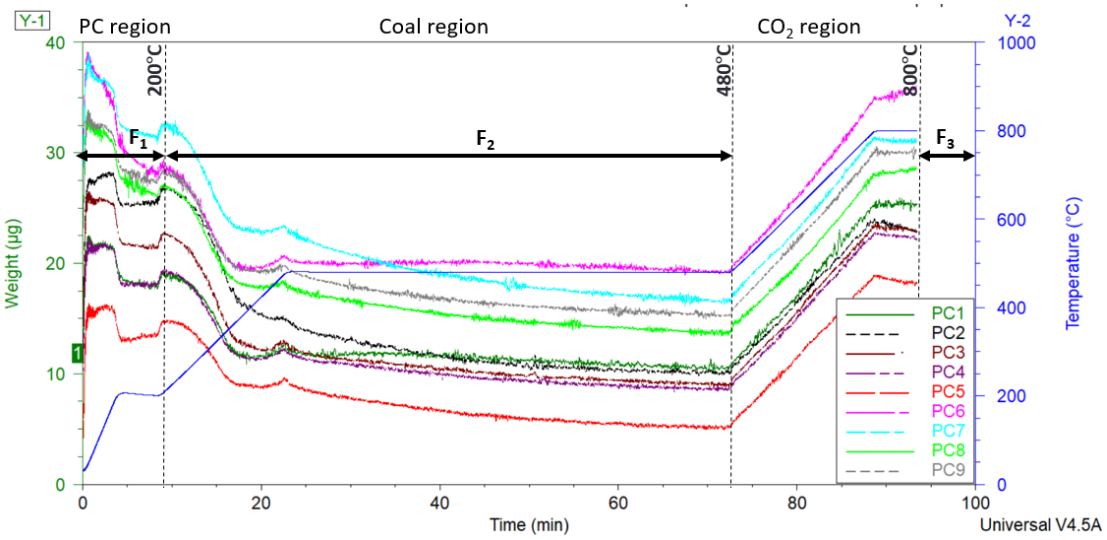

Figure 1-6 Example thermograms for nine blank PC filters.

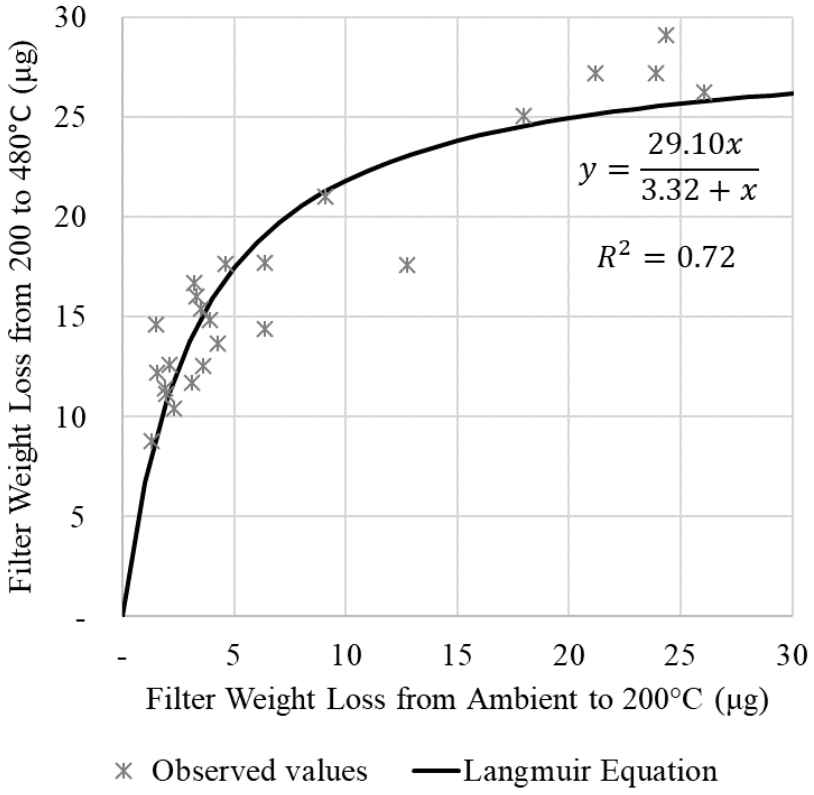

Figure 1-7 Langmuir relationship between the filter weight loss in the ambient-200°C range and the filter weight loss in the 200-480°C range.

As a preliminary verification for Equations 1.11-1.13, 31 single-material dust samples were made on PC filters, then put through the sample preparation procedure and analyzed (Table 1-6). Dust recovery for each sample was calculated from Equation 1.14, where initial dust weight is defined as the total weight of dust placed on the PC filter during (i.e., sum of clean coal, shale and rock dust). Recovery was observed to be very good across a wide range of sample weights, especially when compared to recoveries from fibrous PVC (40 ± 22%) and MCE filters (52 ± 20%) observed by Scaggs (2016). However, it should be noted that recovery from filter samples of airborne dust collected using a sampling pump (i.e., as would occur for field sampling) might be lower that the recoveries observed here, where dust was simply placed onto the filter. This is because more particle-filter interaction is expected to occur in the former case, as particles are pulled onto the filter surface by the airflow through the filter. Figure 1-8 shows representative thermograms for the single-material samples prepared on filters. Figure 1-9a-c compare the expected and observed results for each dust component. Even with the required filter corrections, the error still generally lies within ±10%.

$$Dust\ Recovery = \frac{M_{coal(F)} + M_{CB(F)} + M_{NCB(F)}}{Initial\ Dust\ Weight} \qquad (Equation\ 1.14)$$

Table 1-6 Initial weight of respirable materials on PC filters

Sample	Initial Coal weight (µg)	Dust Recovery from coal experiments	Sample	Initial Shale weight (µg)	Dust Recovery from shale experiments	Sample	Initial Rock Dust weight (µg)	Dust Recovery from rock dust experiments
1	139	111%	1	84	108%	1	92	157%
2	163	65%	2	90	130%	2	174	102%
3	192	171%	3	153	99%	3	182	99%
4	236	67%	4	173	93%	4	228	164%
5	270	100%	5	198	85%	5	228	114%
6	311	87%	6	201	73%	6	230	104%
7	328	56%	7	242	99%	7	294	83%
8	360	85%	8	274	100%	8	352	93%
9	425	108%	9	283	108%	9	377	94%
10	507	52%	10	333	99%	10	437	91%
			11	360	72%			

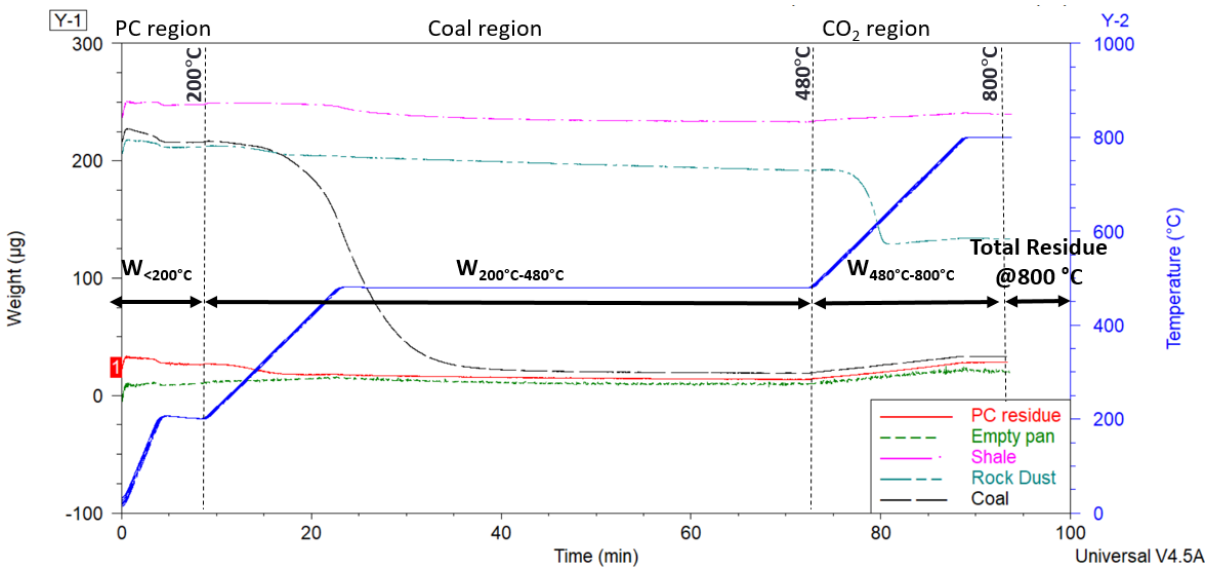

Figure 1-8 Example thermograms of clean coal, rock dust, and shale materials on PC filters. Results for a blank PC filter (labeled PC residue) and empty pan are also shown for comparison.

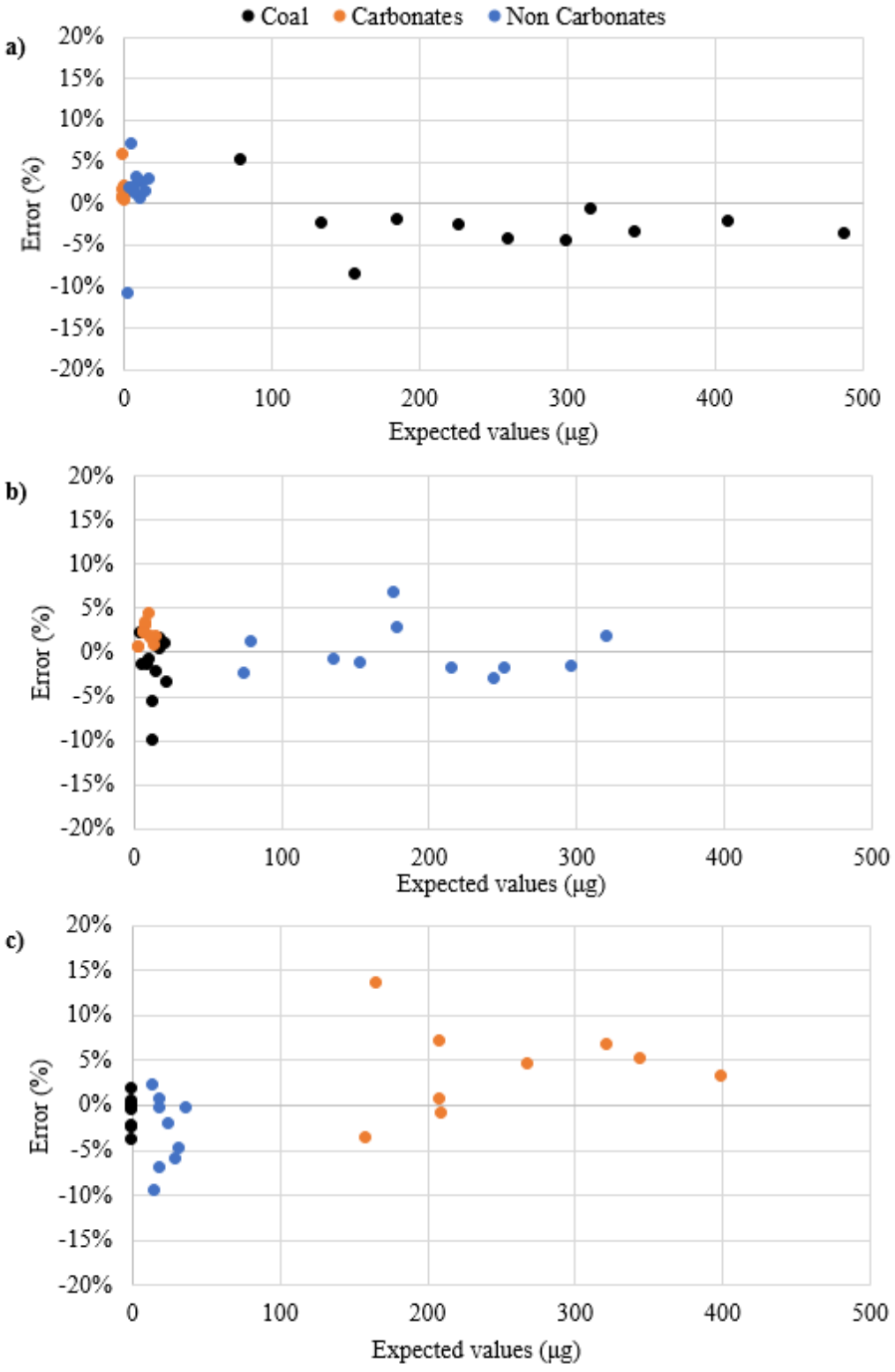

Figure 1-9 Error between observed and expected coal, non-carbonates and carbonates % values for single-material samples prepared on PC filters using a) clean coal, b) shale and c) rock dust. Error is computed as TGA-derived % - measured %.

1.5 Experiments to Verify the Improved TGA Method

In order to verify the improved TGA method and computations established above, the final phase of experiments included 36 composite dust samples made on the PC filters (Table 1-7). Each sample contained respirable dust generated from two or three of the source materials (i.e., clean coal, rock dust and shale), and total sample weights ranged from 95-1,319μg. Average dust recovery (calculated from Equation 1.14) was 97% (±10%), which again demonstrates the superiority of the smooth PC filters used here as opposed to the fibrous media used in earlier work (Scaggs, 2016; Phillips et al., 2017). Recoveries that are significantly higher than 100% are likely related to errors associated with the data corrections.

Examples of representative thermograms for the composite dust samples on filters are shown in Figure 1-10; and a comparison of the observed and expected results is shown in Figure 1-11 (data given in Table A-1, Figure A-8, Appendix A). For all 36 samples, the error for all three components was within ±20%; and for 32 samples it was within ±10% (i.e., all but samples 11, 14, 15 and 24 in Table 1-7). Notably, three of the four samples that showed one or more component errors greater than ±10% contained dust from just two source materials. Samples 11 and 24 did not contain shale, but did contain a relatively small amount of clean coal and a relatively larger amount of rock dust; and they were the only such samples in the entire set. The TGA results from these two samples showed overestimation of coal and underestimation of carbonate. This may mean that the premature CO_2 loss was underestimated in these samples. On the other hand, sample 15 contained no clean coal, but relatively similar amounts of shale and rock dust – as did samples 6, 22 and 33. However, the TGA results for sample 15 overestimated coal and underestimated both non-carbonates and carbonate. This might simply be an anomalous result.

To examine the component errors as a function of sample mass, Table 1-8 shows mean errors across the whole range of component expected masses, and it also shows the results when only masses less than or greater than 100μg are considered. Overall, results indicate that the improved TGA method tends to predict all three component masses very well over the entire mass range investigated here. Across this range, there is a slight underestimation of non-carbonates, which may mean that the final filter correction (F_3) needs further consideration, or that the stoichiometric assumptions made here for calcite are slightly off. When looking at the mean errors for expected masses below and above 100μg, it appears that trends for coal and

carbonate tend to shift somewhat. Specifically, at low masses, these components are slightly overestimated, whereas they are slightly underestimated at higher masses. However, it is worth noting that the results are clearly affected by the four aforementioned samples with relatively higher errors. If these were excluded from the analysis, the results would clearly show a reduced margin of error with increasing sample mass.

Table 1-7 Single material weights in composite respirable dust experiments on Polycarbonate (PC) filter experiments

Sample	Clean Coal (μg)	Shale (μg)	Rock Dust (μg)	Total Dust Weight (μg)	Dust Recovery from experiments
1	48	0	47	95	84%
2	31	65	0	96	117%
3	47	83	0	130	95%
4	107	34	0	141	96%
5	70	75	0	145	118%
6	0	71	89	160	90%
7	91	0	88	179	93%
8	30	99	59	188	90%
9	39	150	35	224	88%
10	0	183	61	244	84%
11	73	0	172	245	83%
12	135	51	68	254	119%
13	76	77	121	274	100%
14	38	72	166	276	77%
15	0	152	166	318	119%
16	98	137	97	332	99%
17	95	113	136	344	85%
18	131	123	95	349	94%
19	142	79	131	352	94%
20	139	86	135	360	104%
21	103	267	0	370	98%
22	0	200	177	377	91%
23	50	236	121	407	118%
24	68	0	348	416	99%
25	73	249	121	443	95%
26	0	264	213	477	107%
27	285	307	0	592	95%
28	0	300	348	648	96%
29	328	332	0	660	96%
30	142	408	260	810	99%
31	487	0	334	821	103%
32	516	0	407	923	103%
33	0	451	489	940	103%

34	0	621	333	954	94%
35	428	321	324	1073	101%
36	354	507	458	1319	100%

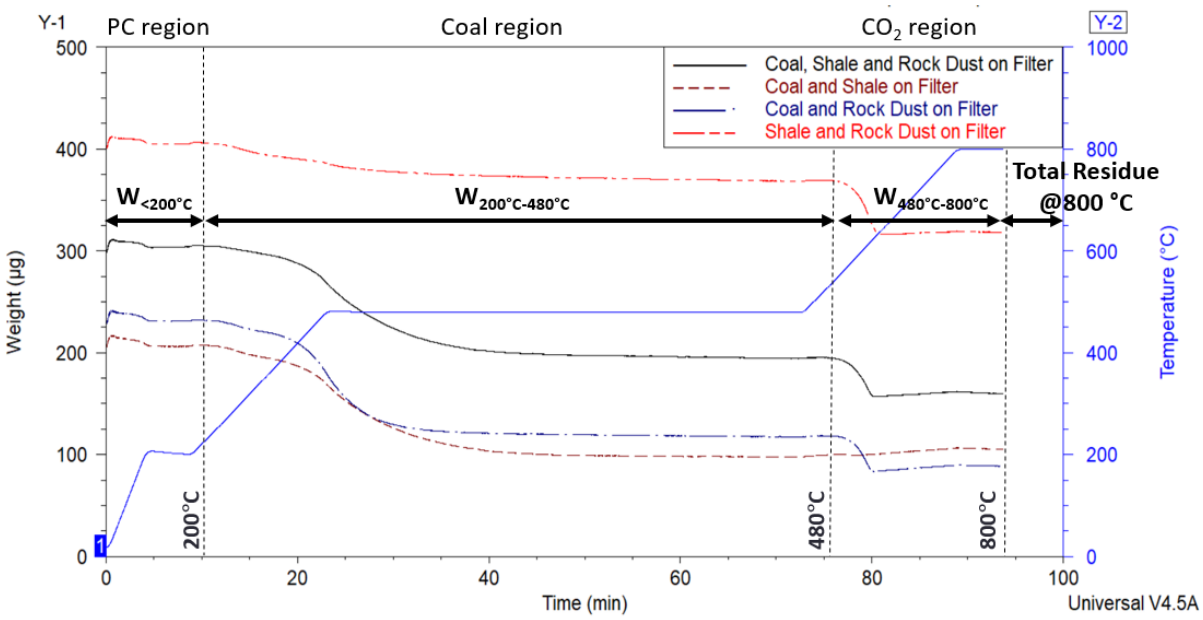

Figure 1-10 Example thermograms of composite dust samples on PC filters.

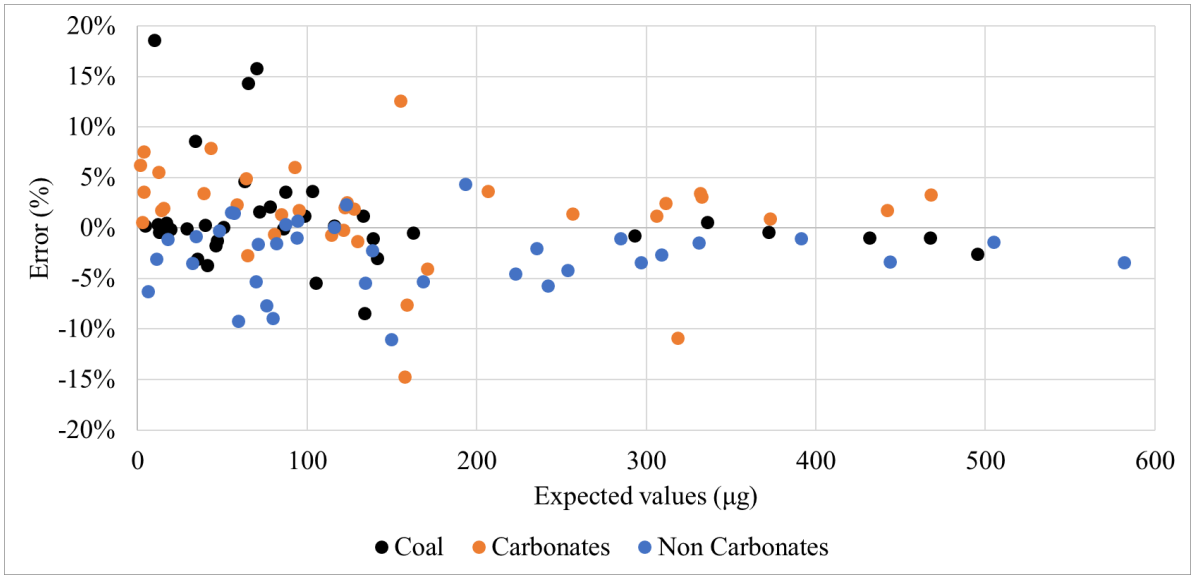

Figure 1-11 Error between observed and expected coal, non-carbonates and carbonates % values for composite dust samples prepared on PC filters. Error is computed as TGA-derived % - gravimetric %.

Table 1-8 Summary statistics for errors when determining coal, non-carbonates and carbonate mass % in composite dust samples prepared on PC filters. The mean error represents the average difference between the observed component % (i.e., based on TGA data) and the expected component % (i.e. based on the measured weights of each component as samples were prepared). Statistics are also shown when considering expected component masses less than and greater than 100μg.

	Coal	Non-Carbonates	Carbonates
		Entire mass range	
Mean Error	1%	-2%	1%
Std. Deviation	6%	3%	5%
Upper 95% Mean	3%	-1%	3%
Lower 95% Mean	-1%	-4%	0%
N	36	36	36
		C*omponent mass* <100 μg	
Mean Error	3%	-2%	3%
Std. Deviation	6%	4%	3%
Upper 95% Mean	5%	-1%	5%
Lower 95% Mean	0%	-4%	2%
N	22	16	17
		C*omponent mass* >100 μg	
Mean Error	-2%	-2%	0%
Std. Deviation	3%	3%	6%
Upper 95% Mean	0%	-1%	3%
Lower 95% Mean	-3%	-4%	-3%
N	14	19	20

1.6 Conclusions

Considering the need of understanding dust characteristics to explain the uptick in respiratory diseases the last years, the dust only TGA method described in this chapter, along with the sample preparation corrections, allow for an accurate estimation of coal, carbonate and non-carbonate minerals mass fractions in composite dust samples with weights ranging from about 90-1300μg. Higher dust recoveries than before were achieved and therefore a more representative sample was analyzed with TGA. However, the term recovery here should be used while bearing in mind that respirable dust was not directly collected using the train of sampling equipment, rather it was scooped on to a clean PC filter. The results from this study also reveal that PC filters can be used successfully as a filter media for dust sampling since filter degradation was not so high during the laboratory methodology.

The small sample sizes were not a limitation in this study since dust mass fractions could be accurately predicted with an overall error of less than ±19%. In general, the accuracy of the results increased with increasing sample mass. This outcome was expected though since TGA analysis is a mass based method and results are influenced by the mass of the dust on the filter.

Future work should also focus on using TGA analysis on field dust samples to help reveal major sources of respirable dust. Being able to accurately characterize respirable dust obtained from an area sample could be a powerful tool to observe any anomalies in dust composition in key locations (i.e. cutting more rock than coal). Moreover, comparing TGA results from different mines and mine regions can be very helpful for revealing general and regional trends in dust composition.

1.7 Acknowledgements

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2 Chapter 2 Respirable coal mine dust composition: a comparison of results as determined by thermogravimetric versus electron microscopy analysis

Abstract

The prevalence of occupational lung disease amongst Appalachian coal miners has risen sharply since the mid-1990s. The appearance of this disease known as Coal Worker's Pneumoconiosis (CWP or "Black Lung"), along with its most advanced form referred to as Progressive Massive Fibrosis (PMF), contradicts the documented decline in conventional respirable dust metrics available from routine regulatory monitoring. In order to better understand health outcomes, there is a clear need to better understand dust composition. For this purpose, several analytical methods have been proposed. This paper focuses on the use of thermogravimetric analysis (TGA) to examine 75 respirable dust samples collected from 15 underground coal mines throughout the US. The TGA results were classified into three mass fractions – coal, carbonate, and non-carbonate minerals – and were compared with results derived from analysis by scanning electron microscopy with energy dispersive X-ray (SEM EDX). This work demonstrated that the two methods can generally produce comparable results, however, key differences in their underlying principles should be considered. The SEM method provides very detailed particle characteristics and can be used to understand particle toxicity and/or lung and particle interaction, but it is cost and time rigorous. On the other hand, the TGA method is less sensitive, but it's much easier and cheaper. In addition, the TGA method provides useful information on the three mass fractions that are largely tied to three main dust sources in most underground coal mines. The results from both methods allowed discussion of dust composition within and between mines.

2.1 Introduction

The resurgence of coal worker's pneumoconiosis (CWP), often called "black lung", among US miners in central Appalachia has been documented extensively over the past two decades (Antao et al, 2005; CDC, 2006; CDC 2007; Laney, et al, 2010; Suarthana et al, 2011; Wade et al, 2011; Laney et al 2012; Laney and Weissman, 2014; Blackley et al., 2016; Blackley et al., 2018a and b; Almberg et al, 2018). It is well-known that this disease is caused by chronic exposure to respirable coal mine dust (CDC, 2011; Castranova and Vallyathan 2000), which has been federally regulated in the US since 1969 (Federal Coal Mine Health and Safety Act of 1969 Public Law 91-173). The regulation requires compliance dust monitoring in coal

mines, and also provides for voluntarily health surveillance of miners and benefits for those affected by debilitating disease. However, the recent resurgence of disease has been perplexing because the available data on dust exposures and health outcomes appear in rather stark contrast. Specifically, while respirable dust and quartz (i.e., silica) concentrations have been generally trending downward since the 1970s, prevalence of CWP, which was also on a downward trend, reversed in the late 1990s. In central Appalachia, the most severe and rapidly progressive forms of disease are now at their highest documented prevalence rate (Blackley et al., 2016).

The radiographic findings point to silica exposure a primary cause of disease in many cases (Blackley et al., 2018a,b; Blackley et al., 2016; Laney and Weissman, 2014; Laney and Attfield, 2010; Schatzel, 2009; Castranova and Vallyathan, 2000; Wade 2011), and pathologic evidence has also suggested that other minerals like silicates could be factors (Jelic et al., 2017; Cohen et al., 2016). Unfortunately, conventional dust monitoring has only focused on total respirable dust and silica – so historical data is not available to provide insights to other dust constituents. Concluding that the whole composition of dust is likely important in understanding the underlying factors to contemporary disease, a 2018 study by the National Academies of Science, Engineering and Medicine recommended a more comprehensive characterization of respirable coal mine dust.

To investigate dust composition, a number of analytical methods could be considered. For the past several years, the authors' research group has been working with two techniques that can be used to fractionate dust into particular compositional categories. The first method involves thermogravimetric analysis, and is aimed at determining the mass fractions of coal, carbonates and non-carbonate minerals in a respirable dust sample (Scaggs, 2016; Scaggs et al., 2015;). The general idea is that three fractions may be quite useful in understanding sources of dust: coal should generally be associated with the coal strata being mined and handled; carbonates should generally be associated with application of rock dust (i.e., usually limestone) to the mine surfaces; and non-carbonate minerals should generally be associated with drilling, mining or handling of rock strata that surrounds the mined coal seam(s).

The second method involves dust analysis by scanning electron microscope with energy dispersive X-ray (SEM-EDX). In this case, individual particles are sized and classified into predefined mineralogy classes, including: carbonaceous, which is generally attributed to coal;

carbonates, which is again attributed to rock dusting; and alumino-silicates and silica, which are generally attributed to the rock-strata sourced dust (Sarver et al., 2019; Johann-Essex et al., 2017a and 2017b). A small number of particles are often also classified as heavy minerals or "other", though these cannot be easily attributed to specific dust source.

2.2 Comparing TGA- and SEM-derived dust compositions

Given the significant overlap between the TGA and SEM-EDX compositional categories, a comparison between their respective results seems prudent both for evaluating the methodologies, and gaining insights about dust characteristics. Phillips et al. (2017) conducted a preliminary comparison using 106 respirable dust sample pairs that had been collected in eight coal mines in northern and central Appalachia. In each pair, one sample was collected onto a polyvinyl chloride (PVC) or mixed-cellulose ester (MCE) filter, and the dust was recovered for TGA (per Scaggs, 2016); due to the fibrous nature of the PVC and MCE media, the recovered dust mass was relatively small for some samples. The other sample in each pair was collected onto a polycarbonate (PC) filter for direct analysis by SEM-EDX (per Johann-Essex et al., 2017a). The SEM results, which were originally published by Johann-Essex et al. (2017b), were normalized in the Phillips et al. 2017 study to exclude particles in the heavy minerals and "other" classes, such that the dust could be partitioned between just three categories: carbonaceous, carbonates, and alumino-silicates + silica. Then, particle number fractions were converted into estimated mass fractions using particle dimensions measured by SEM, and assumed thickness and specific gravity values (i.e., specific to each particle class per Sellaro et al., 2015). Finally, the TGA-derived mass fractions (i.e., % coal, carbonates, or non-carbonate minerals) were compared to the analogous SEM-derived fractions (i.e., % carbonaceous, carbonates, or alumnio-silicates+silica).

Using a matching criterion of ±25% (i.e., the difference between TGA and SEM result for a given category must be within 25% of each other), Phillips et al. 2017 found that 86 (of the total 106) sample pairs were in agreement for coal %. Moreover, these TGA and SEM results indicated that the abundance of coal in the mine dust samples was relatively low, even in sampling locations that might be expected to have significant coal dust (e.g., near the mining face, or adjacent to the feeder breaker). When considering all three composition categories (i.e., coal %, carbonates %, non-carbonate minerals %), Phillips et al. 2017 found that 47 of the sample pairs were in agreement. Carbonate and non-carbonate minerals mass fractions were

generally correlated within a given mine or mine region, with the larger mines (i.e., in northern Appalachia) tending to have more carbonates and the smaller mines (i.e., in central Appalachia) tending to have more non-carbonates. These findings were generally consistent with observations of heavy rock dusting in the larger mines and mining more rock strata in the smaller mines.

Phillips et al. (2017) additionally noted that, overall, agreement between the TGA- and SEM-derived results was correlated with recovered dust mass for TGA, and so it was concluded that increased recovery should increase accuracy of the TGA results. This was also a primary conclusion of Scaggs (2016), based on laboratory work to develop the original TGA method used by Phillips et al. (2017). To that end, the authors have recently sought to develop an improved TGA method for respirable coal mine dust (Chapter 1). This method uses a modified dust recovery procedure as part of the sample preparation, and was developed for dust collected onto smooth PC filters. It was verified earlier using laboratory-generated dust samples.

The improved TGA method was recently used to analyze 75 mine dust samples collected in 15 US coal mines. Again, replicate samples were collected and analyzed by SEM-EDX. Here, the TGA- and SEM-derived results are compared and discussed to gain further insights on dust compositions, as well as the analytical methods.

2.3 Experimental Details

2.3.1 Dust Sample Collection

Between January and August 2018, respirable dust samples were collected in the 15 study mines, which represent four distinct regions: three mines in northern Appalachia (NA, MSHA districts 2 and 3), eight in central Appalachia (CA, MSHA districts 4, 5 and 12), two in the mid-western Illinois coal basin (MW, MSHA district 8) and two in the western coal basin (W, MSHA district 9). Table 2-1 provides summary information about each mine.

Table 2-1 Key characteristics for 15 mines sampled in the present campaign

Mine No.	Region	Seam Thickness (ft)	Total Mining Height (ft)	Roof Strata	Floor Strata	Production (10^6 tons/yr)	Typical Dust Concentration	Typical Quartz Percentage
Mine 10	CA	3.33 - 3.75	5.83 - 6.25	shale and lam. sandstone	shale	0.51	low to moderate	low to moderate
Mine 11	CA	2.5	4 - 4.33	shale	shale	0.5	low to moderate	low to moderate
Mine 12	CA	2.5 - 5	6.25 - 6.67	shale and sandstone	shale	1.6	low	low to moderate
Mine 13	CA	5 - 5.83	5.83 - 6.67	sandstone and shale	shale	1.4	low	low
Mine 14	CA	2.08 - 3.33	5 - 6.25	shale	shale	0.22	low to moderate	low to moderate
Mine 15	CA	3 - 3.83	6.5	shale	shale	0.77	low to moderate	low to moderate
Mine 16	NA	9	7	shale	coal w/ high-sulfur part.	1.5	low to moderate	low
Mine 17	NA	5 - 5.83	6.67 - 7.5	shale	shale	3.4	low to moderate	low to moderate
Mine 18	NA	2.33 - 2.67	5 - 5.83	shale	fire clay	N/A	low to moderate	low to moderate
Mine 19	MW	5.83 - 6.67	6.25 - 7.5	shale and limestone	fire clay	2.5	low to moderate	low to moderate
Mine 20	MW	5.83 - 6.25	5.83 - 6.67	shale	fire clay	1.5	low to moderate	low
Mine 21	CA	2.5 - 3.33	6.5	shale and sandstone	shale	0.43	low to moderate	low to moderate
Mine 22	CA	2.5	4.58	shale	shale and sandstone	0.19	low to moderate	low to moderate
Mine 23	W	20	14	shale	shale	4.8	low to moderate	low
Mine 24	W	6	7-8	shale and sandstone	sandstone	3.8	low	low to high

All samples were collected by the authors' research team, using standard equipment that included an Escort ELF personal sampling pump (calibrated to a flow rate of 2 L/min) with a 10-mm Dorr-Oliver cyclone. This sampling train removes particles larger than 10 μm, and yields a d_{50} of about 4 μm. During each sampling event, a set of 5-6 samples were collected using a hanger (typically hung from a roof bolt) that allowed side-by-side positioning of the cyclone inlets (Figure 2-1). Three samples from each set are relevant to the work reported here (i.e., a sample for TGA, SEM, and gravimetric analysis). Samples for TGA and SEM were collected directly onto 37-mm PC filters (0.4 μm) in closed, two-piece cassettes. For gravimetric analysis (i.e., to determine the total dust mass collected), samples were collected onto pre-weighed PVC filters (weights were measured using a Sartorius MSE6.6S, Gottingen, Germany microbalance).

In total, there were 75 sampling events, each of which lasted between 2-4 hr. In each mine, an effort was made to sample in five key locations: in the intake (including the headgate of the longwall), in the return (including near the tailgate of a longwall), just downwind of an active roof bolter, just downwind of mining (i.e., by a continuous miner or along the longwall face), and adjacent to the feeder breaker or along the main belt conveyor. A general schematic representation of these locations is shown in Appendix B, Figure B-1. Following each sampling event, dust cassettes were carefully transported to Virginia Tech for analysis. The PVC samples were re-weighed, and the total dust weight was determined by difference with the filter pre-weights.

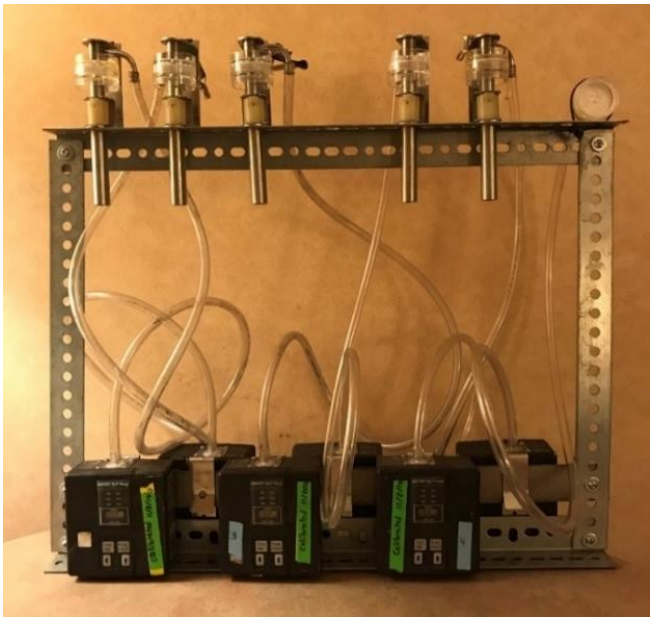

Figure 2-1 Field sampling equipment that included 10mm Dorr-Oliver cyclones and ELF pumps

2.3.2 TGA and SEM Analysis

TGA samples were prepared and analyzed per the method described in Chapter 1. Briefly PC filters with respirable dust were placed in clean glass tubes and submersed in isopropyl alcohol. The tubes were placed in an ultrasonic bath and then in a centrifuge in order to settle the dust. Next, the suspended in isopropanol dust from the tube was pipetted into a clean tared TGA and after complete evaporation of the isopropanol, the pan containing the dust was weighted on the microbalance to determine the amount of mass recovered from the laboratory procedure. The mass recovered from the PC filters versus the mass that was calculated from pre and post weighing of the PVC filters is shown displayed in Appendix B (Figure B-2). It should be taken into account that in the field samples, respirable dust was collected directly on the filter while in the lab generated experiments respirable dust was scooped from densely loaded PC filters for better control. Dust recoveries calculated for field samples might be therefore, somewhat lower.

From the resulting thermogram for each sample (e.g., see Figure 2-2), the observed weight loss in specific temperature regions of interest were used to compute the coal (C), carbonate (CB) and non-carbonate minerals (NCB) mass fractions. For this, Equations 2.1 – 2.10 were used:

$$CO_{2(1)} = \frac{39.35 \times CO_{2(2)}}{269.39 + CO_{2-2}}$$ *(Equation .2.1)*

$$CO_{2(2)} = W_{480°C - 800°C}$$ *(Equation .2.3)*

$$CO_{2(Total)} = CO_{2(1)} + CO_{2(2)}$$ *(Equation .2.4)*

$$F_1 = W_{ambient - 200°C}$$ *(Equation .2.5)*

$$F_2 = \frac{29.10 * F_1}{3.32 + F_1}$$ *(Equation .2.6)*

$$F_3 = 5\mu g$$ *(Equation .2.7)*

$$M_{CaO} = \frac{0.56 \times CO_{2(Total)}}{0.44}$$ *(Equation 1.5)*

$M_{coal(F)} = W_{200C-480°C} - F_2 - CO_{2(1)}$ *(Equation .2.8)*

$M_{CB(F)} = \frac{CO_2(Total)}{0.44}$ *(Equation .2.9)*

$M_{NCB(F)} = Total\ Residue_{@800\ C} - M_{CaO} - F_3$ *(Equation .2.10)*

Where:

- $CO_{2(1)} = premature\ CO_2\ release$
- $CO_{2(2)} = CO_2\ release\ in\ the\ rock\ dust\ region\ of\ interest$
- $F_1 = filter\ residue\ loss\ in\ the\ PC\ region, from\ ambient\ to\ 200°C$
- $F_2 = filter\ residue\ loss\ in\ the\ coal\ region\ from\ 200 - 480°C$
- $F_3 = non\ oxidizable\ filter\ residue\ at\ the\ end\ of\ the\ TGA\ run$
- $W_{\text{ambient}-200°C} = the\ total\ weight\ loss\ between\ ambient\ and\ 200°C$
- $W_{200-480°C} = the\ total\ weight\ loss\ between\ 200 - 480\ °C$
- $W_{480-800°C} = the\ total\ weight\ loss\ between\ 480 - 800\ °C$
- $Total\ Residue_{@800\ C} = non\ oxidizable\ materials\ at\ the\ end\ of\ TGA\ run$
- $M_{coal(F)} = mass\ fraction\ of\ coal\ with\ the\ filter\ correction$
- $M_{CB(F)} = mass\ fraction\ of\ carbonates\ with\ the\ filter\ correction$

- $M_{NCB(F)} = mass\ fraction\ of\ non\ carbonates\ with\ the\ filter\ correction$

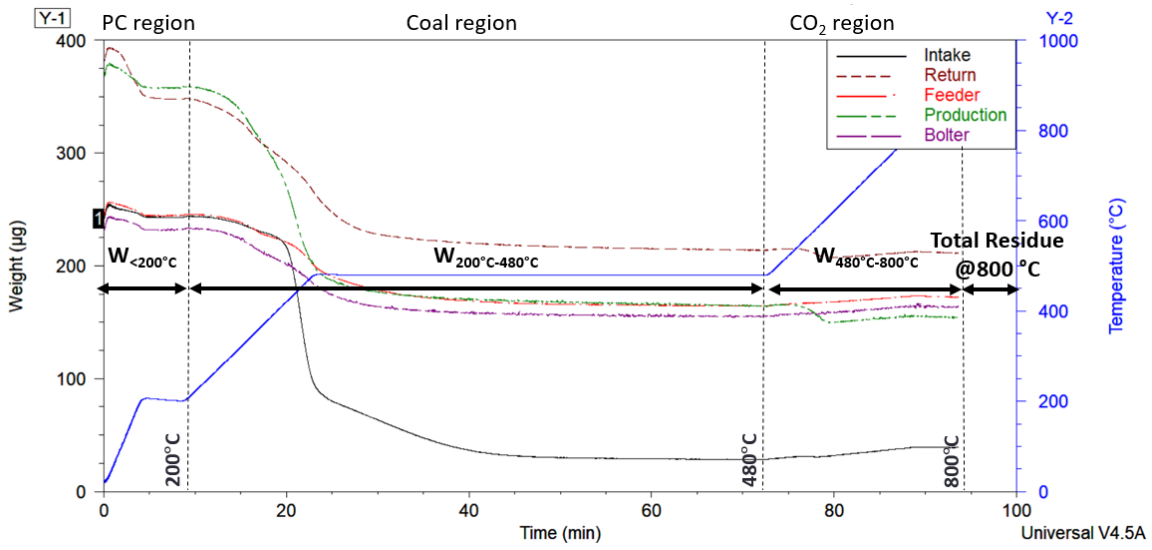

Figure 2-2 Example thermograms of dust samples collected in key locations of a particular mine.

SEM-EDX samples were prepared and analyzed using the method described in Johann-Essex et al. (2017a). Briefly, a 9-mm circular sub-section was cut from each sample collected for SEM work, and sputter coated with Au/Pd. Then, the sample was analyzed using an FEI Quanta 600 FEG environmental scanning electron microscope (ESEM) (Hillsboro, OR, USA), equipped with a backscatter electron detector (BSD) and a Bruker Quantax 400 EDX spectroscope (Ewing, NJ, USA). Bruker's Esprit software version 1.9.4 was used to establish the routine. All work was done at 1000x magnification, and other key instrument settings included a high vacuum mode, voltage of 15 kV, a working distance of 12.5 mm, and a spot size of 6.5 m.

The SEM-EDX analysis was done using a computer-controlled routine, which uses multiple frames (i.e., areas of analysis) to collect representative data across the sample. The analysis begins in the center of the sample, and then proceeds through a series of pre-defined frame locations. In each frame, individual particles are identified and sized using a binary (black background, white particle) SEM image; then, the first 50 particles (moving in horizontal rows from left to right, top to bottom) are analyzed by EDX (using a secondary electron detector). Based on their elemental spectra, each particle is classified into one of six

mineralogy categories (i.e., carbonaceous, carbonates, alumino-silicates, silica, heavy minerals or other). The SEM-EDX work was limited to particles in the 1-10 μm range.

Like in the Phillips et al. (2017) study, SEM-EDX results were used to estimate mass fractions of carbonaceous, carbonate, and alumino-silicate + silica dust in each sample; and for the purpose of comparing to the TGA results, these three mass fractions were then called coal, carbonate and non-carbonate minerals, respectively. To convert the SEM-EDX particle data into mass data, the dimensions and mineralogy classification for each particle were used. The SEM determined the length of each particle (L in μm, which is the longest visible dimension) and its intermediate dimension (I in μm, which is the longest length visible that is perpendicular to L in μm). Then, the short dimension (S in μm, which is the height of the particle as it sits on the PC filter) was estimated using Equation 2.11 and assumed *S:I* ratio for each mineralogy class per Sellaro et. al (2015). The values for *S:I* ratio are shown in Table 2-2. Next, a spherical diameter (d_s) and mass (m_s) could be calculated, in μg, for each particle using Equations 2.12-2.14. Specific gravity (SG) values were also assumed for each mineralogy class per Sellaro et al. (2015), and are given in Table 2-2. Based on the water density (ρ_{water}) which is assumed to be 1g/cm^3 the density (ρ) was calculated in g/cm^3 for Finally, all particle masses in a given category (i.e., coal, carbonate, non-carbonates) were summed for each sample.

$S = (S{:}\,I\ ratio) \times I$	*(Equation.2.11)*
$d_s = \left(\frac{S^2}{L \times I}\right)^{1/3} \times L$	*(Equation.2.12)*
$\rho = SG \times \rho_{water}$	*(Equation 2.13)*
$m_s = \frac{4}{3} \times \pi \times SG \times \rho_{water} \times \left(\frac{d_s}{2}\right)^{1/3} \times 10^{-6}$	*(Equation.2.14)*

Table 2-2 Assumed values for S and SG per Sellaro et al. (2015).

Dust Classification	S:I Ratio	Specific Gravity (SG)
Carbonaceous	0.6	1.4
Alumino-silicate	0.4	2.5
Quartz (i.e., silica)	0.7	2.6
Carbonate	0.7	2.7

2.4 Results and Discussion

2.4.1 TGA- versus SEM-derived Mass Fractions

A table of TGA- and SEM-derived coal, non-carbonate minerals, and carbonate mass fraction results for all 75 samples is provided in Table B-1(Appendix B). Figure 2-3 shows the difference between the TGA and SEM results for coal, non-carbonate minerals, and carbonates as a function of the total dust mass (i.e., as measured on the PVC sample replicate). From these plots, a few key observations can be made. First, the intake samples generally had some of lowest dust masses and yielded some of the highest discrepancies between the TGA and SEM results. (Table 2-3 shows summary statistics for all samples and all samples except those taken in the intake.) Second, with the exception of samples collected in the intake airway, the carbonate results are generally in very good agreement. Third, there is a general tendency of the SEM to underestimate the coal mass fraction, and accordingly overestimate the non-carbonates fraction, versus the TGA – and, again, the discrepancy is highest for intake samples.

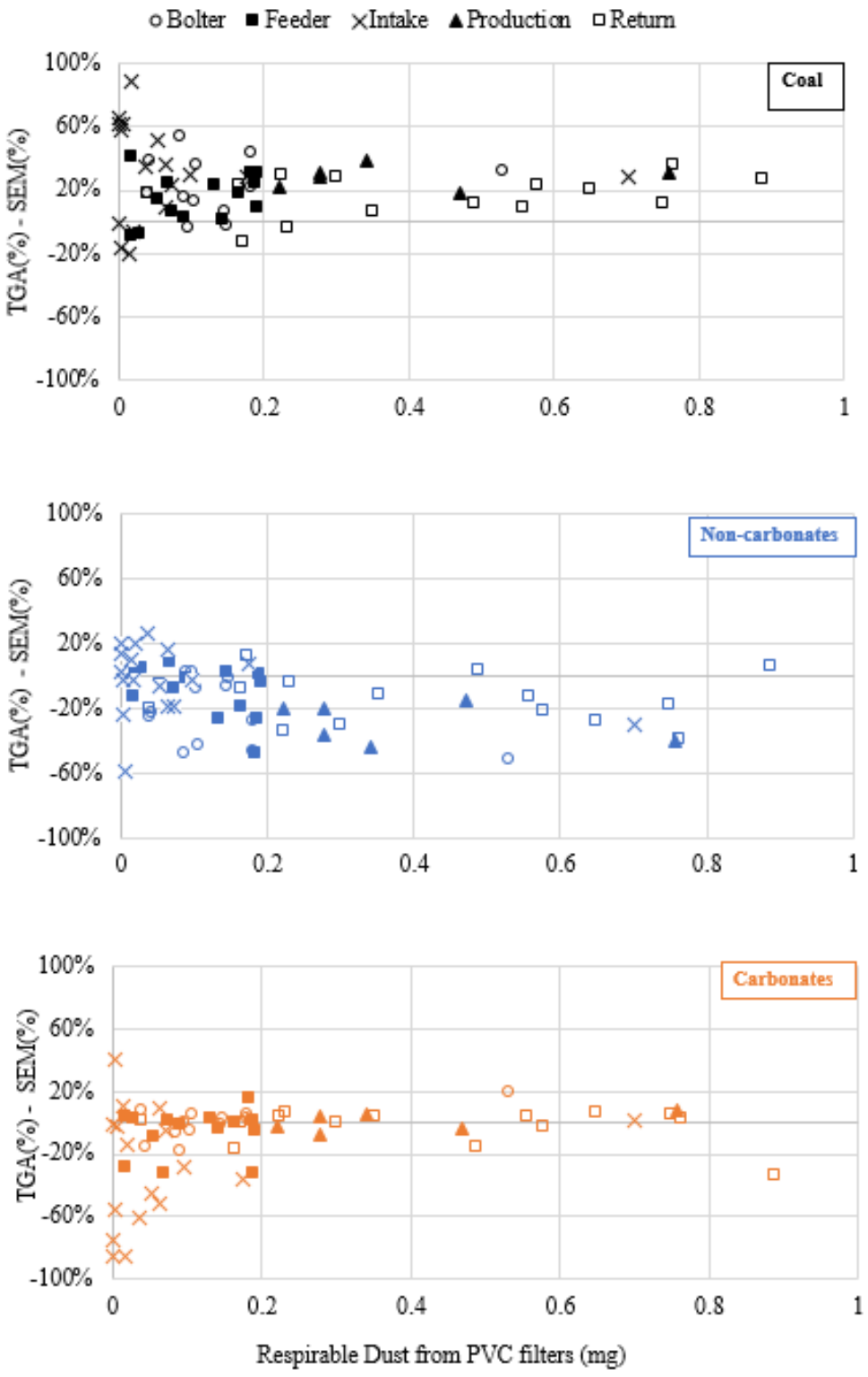

Figure 2-3 Difference between TGA and SEM % vs dust weight (i.e., determined from PVC replicate filters) for a) coal b) non-carbonates and c) carbonates for key locations in underground coal mines (12 dust samples from each plot are not included because the Dust weight from PVC weight was > 1mg but are displayed in Figure B-3, Appendix A)

Table 2-3 Summary statistics for comparison between TGA- and SEM-derived results for intake dust samples, and all samples except the ones collected in the intake. The mean difference (i.e., TGA%-SEM%) is shown for each dust component (i.e., coal, non-carbonates, or carbonate).

	Intake (N=19)			All other locations (N=56)		
	Coal	Non-carbonates	Carbonates	Coal	Non-carbonates	Carbonates
Mean Difference	30%	-6%	-25%	19%	-20%	1%
Std Dev	29%	22%	37%	20%	20%	15%
Upper 95% Mean	44%	4%	-8%	24%	-14%	5%
Lower 95% Mean	17%	-16%	-41%	13%	-25%	-3%

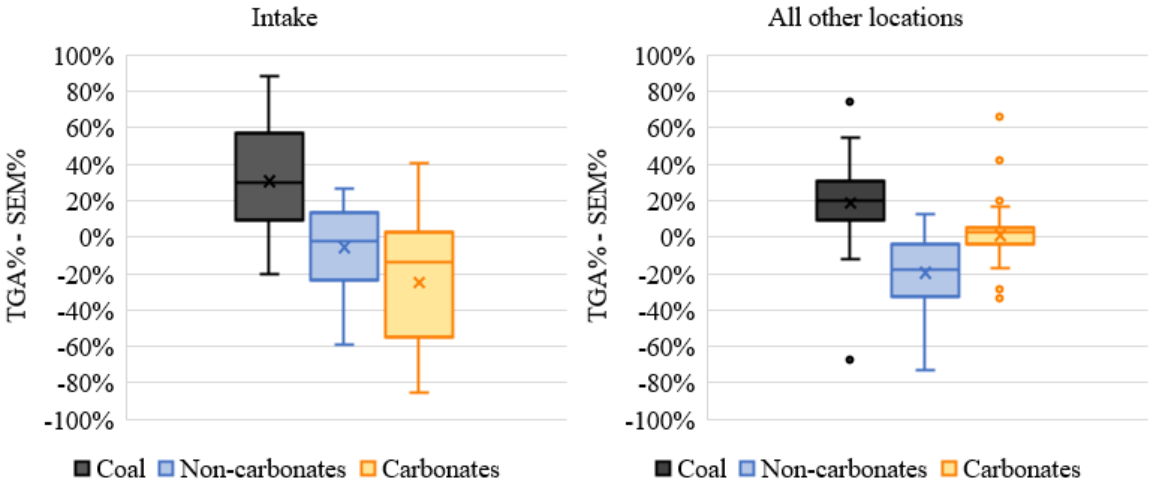

Figure 2-4 Box and whisker plots for comparison between TGA- and SEM-derived results for intake and all other location samples.

While low sample mass is one possible factor in the discrepancy between the TGA and SEM results for intake samples, it is probably not the only factor. Indeed, the carbonate results were in much better agreement for other low-mass samples collected in different locations (e.g., near the feeder breaker). Another likely factor is the presence of significant diesel particulates in these samples, which the TGA may attribute to the coal mass fraction. Sarver et al. (2019) recently found that intake samples, collected in a different set of underground coal mines, were commonly dominated by diesel particulates that occur in the submicron range. Since particles in this range were not included in the SEM-EDX analysis conducted here, they do not contribute to the estimated dust mass fractions derived from SEM; rather, only the dust particles in the supramicron range were considered. However, Sarver et al. showed that the ratio of sub- to supramicron particles could be as high as 200:1. Considering a case where most of the

submicron particles are diesel particulates, while most of the dust particles are carbonates, the TGA results would be expected to show relatively highly fractions of coal and relatively low fractions of carbonates as compared to the SEM-derived results.

Regarding the discrepancy between TGA and SEM results for coal and non-carbonate minerals fractions, again, there might be multiple contributing factors. As discussed above, exclusion of diesel particulates from the SEM analysis might explain some of the overestimation of coal by the TGA for low mass samples. However, this probably does not explain the trend for higher-mass samples. For these, other explanations should be considered. First, a number of assumptions were made to convert the particle-level SEM data to mass fractions. An underestimation, for example, in the assumed specific gravity value for coal could lead to underestimation of the coal mass fraction. Moreover, short dimension might be underestimated for coal or it might be overestimated for non-carbonates, especially for silicates.

Perhaps more impactful are the criteria used to classify particles using the EDX data. While these criteria were developed and verified using respirable dust particles generated from high-purity materials (Johann-Essex et al., 2017a) that were examined using identical SEM-EDX settings to those used here, some limitations should be noted. Fundamentally, the EDX response can be influenced by particle heterogeneity, but particle homogeneity is assumed in order to classify particles. This means that a coal dust particle which has minor impurities or is "occluded" by a surface layer of mineral might be classified as a mineral dust particle even though most of its mass is coal. As described by Johann-Essex et al. (2017a), the classification as coal versus mineral is determined by the threshold limits (on the EDX spectral peaks) for various key elements such as Al and Si (which are used to classify alumino-silicates and silica) or Ca and Mg (which are used to classify carbonates). Changes to these thresholds could cause some particles to be moved from the coal class to a mineral class, or vice versa. In coal mine dust samples, it seems plausible that alumino-silicate (i.e., clay mineral) occlusion or impurities could occur for coal particles, since these minerals are commonly contained in the rock strata surrounding the coal seam, or within the coal itself. Carbonate occlusion seems less likely since most carbonates are attributed to application of rock dusting products, and thus are not expected to be in contact with or ingrained within the coal particles.

The phenomenon of dust particle occlusion is well-established for respirable crystalline silica, and is of interest in the context of toxicity. Epidemiological and toxicity studies have suggested that silica particles occluded with clay minerals may be less harmful than free silica particles (Chen et al, 2015, Leung et al 2012). To study in real mine dust samples, Harrison et al. (1997) actually used SEM-EDX. By varying the accelerating voltage of the SEM, they were able to examine the core versus the surface of silica particles, and show that occluded particles have significantly more Al on their surfaces. A follow-up study by the authors' research group recently used the same approach to examine occluded silica in dust samples from nine coal mines in Appalachia (Frost et al., 2019). However, to date, occlusion of coal particles has not been widely considered.

To demonstrate the influence of classification criteria on the SEM-derived coal and non-carbonate minerals mass fractions in the mine dust samples included in this study, a modified set of criteria were applied to the SEM-EDX results (Table 2-4). By simply lowering the Al, Si, Ca and Mg thresholds for the alumino-silicates, silica and carbonates classes, coal % is significantly reduced while non-carbonates % is significantly increased – with little change in the carbonate %. If these new SEM-EDX results are compared to the TGA, the apparent overestimation of coal and underestimation of non-carbonates by the TGA are exaggerated (Table 2-4). On the other hand, modifying the classification criteria to increase the Al, Si, Ca and Mg thresholds, should yield better agreement between the SEM- and TGA-derived results. While this basic analysis underscores the sensitivity of the SEM technique, it is important to note that for a given set of classification criteria, the difference between TGA- and SEM-derived results is quite consistent. For instance, a comparison between the upper and lower 95% confidence intervals in Table 2-4 reveals that the interval widths are the same for both sets of criteria. Moreover, the interval widths are narrow (i.e., 11% or less for all three component categories

Table 2-4 Summary of statistics regarding TGA- and SEM-derived coal, carbonate and non-carbonate mass fractions for all samples when using the Johann-Essex et al. (2017a) classification criteria and modified criteria with reduced elemental thresholds.

	Johann-Essex et al. (2017a) criteria (N=75)			Modified criteria (N=75)		
	Coal	Non-carbonates	Carbonates	Coal	Non-carbonates	Carbonates
Mean	22%	-16%	-6%	25%	-21%	-4%
Standard Dev.	23%	21%	25%	22%	20%	25%
upper 95% CI	27%	-11%	0%	30%	-17%	1%

lower 95% CI	16%	-21%	-11%	20%	-26%	-10%

2.4.2 Dust Composition by Mine Region and Sampling Location

Using the TGA- and SEM-derived results, some observations about dust composition can also be made on the basis of mine region and sampling location. Figure 2-5 shows the coal, non-carbonates, and carbonate mass fractions by mine region, with intake and all other samples shown separately. In order to eliminate any bias of the results based on fact that the number of samples in each location and/or mine was not consistent, sample results were averaged by location in each mine, and then all mine averages were used to come up with a regional average. (A different representation of the data in is shown from Figure B-4 to Figure B-7 in Appendix B, where the SEM (%) results are plotted against the TGA(%) results for all four different regions.)

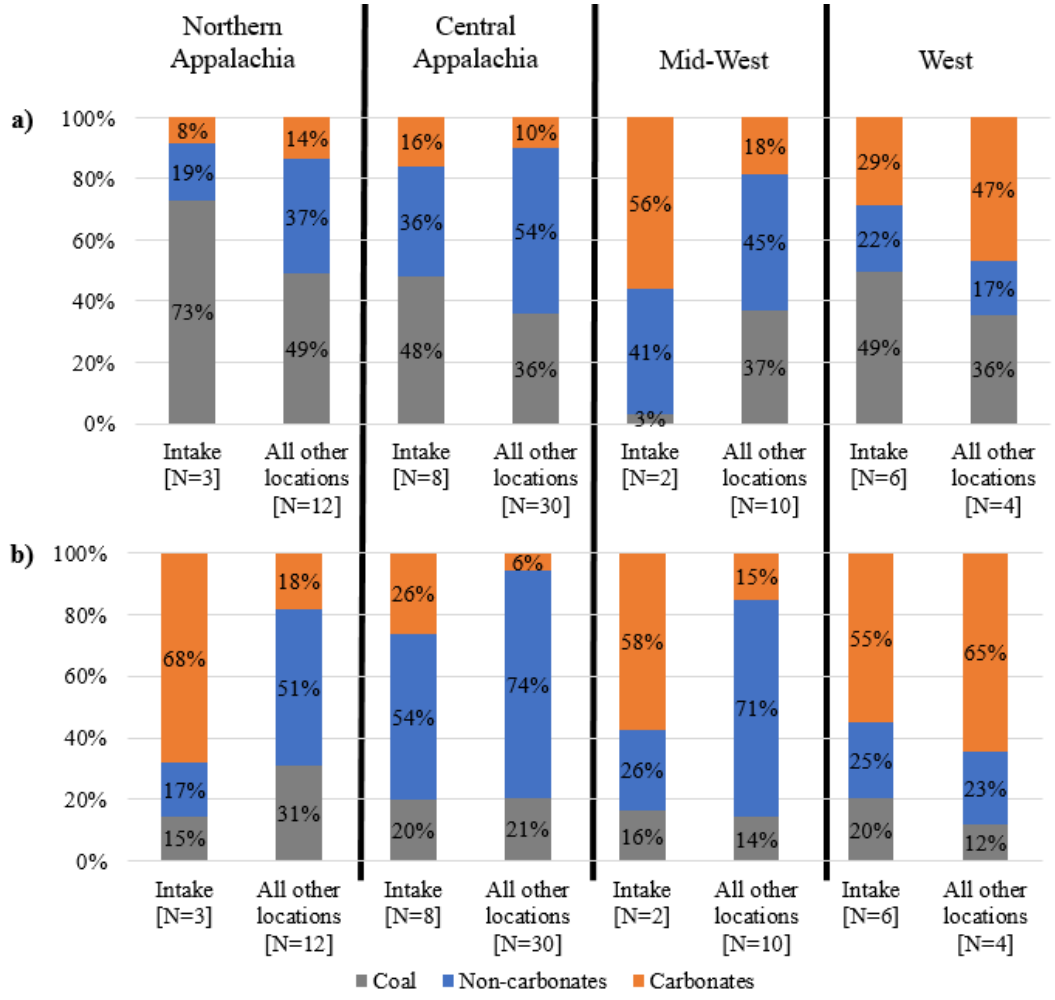

Figure 2-5 Mass fraction average percentages of coal, non-carbonates and non-carbonates from a) TGA and b) SEM analysis in different regions

Based on SEM-derived results for intake samples, where dust generated from mining activities is expected to be limited, it appears that the carbonates were relatively high in NA, MW and W mines, and lower in CA mines. This is consistent with anecdotal observations of much heavier rock dusting in non-CA mines, which tend to be somewhat larger operations. The W mines appear to have significant rock dust in non-intake samples as well. Comparing TGA and SEM results for intake samples, the MW mines appear to be much less affected by diesel particulates than mines in other regions. As speculated above, when diesel particulates represent a significant fraction of the dust mass, it is expected that the TGA results should show a substantial increase in coal %, and decrease in carbonate %, relative to the SEM results; this is evident in the NA, CA and W intake samples, but not in the MW intake samples.

To gain insights about the non-intake samples, it is useful to compare the ratios of coal and non-carbonates (i.e., which are expected to be mostly influenced by mining activities in the coal and rock strata). From this view, it is clear that the proportion of coal dust is relatively low across all regions, whereas the proportion of non-carbonates is relatively high. This observation has also been noted in other studies of NA and CA mines (i.e., Johann-Essex et al., 2017b; Phillips et al., 2018; Sarver et al., 2019). However, the NA and W mines do exhibit higher coal to non-carbonates ratios than CA and MW mines, which is consistent with the relative coal seam thicknesses and total mining heights shown in Table 2-1; the NA and W mines tend to cut less rock and the CA and MW tend to cut more rock. As discussed earlier, CA mines are often characterized as “thin-seam” (e.g., Schatzel, 2009; Pollock et al., 2010).

Aside from the intake samples, results can also be grouped and discussed based on sampling location (Figure 2-6). (To construct Figure 2-5, sample results were averaged by mine first in order to eliminate bias due to different numbers of samples collected in each mine.) Based on the TGA results, the highest coal appears to be in the feeder location, which is consistent with findings by Johann Essex et. al 2017b based on particle mineralogy distributions for mines located in the CA and NA regions; and mass fraction results from a preliminary TGA method developed by Scaggs 2016 and presented in Phillips et.al 2017. Near a feeder, raw coal is broken into smaller pieces and dropped onto a moving conveyor. This procedure probably generates dust that is more associated with coal than non-coal fractions.

The highest non-carbonates were seen in the production location, which is probably where a lot of rock strata is being cut along with the coal (Pollock et. al, 2010). The highest percentages of carbonates appear on the intake and these results suggest that rock dusting activities in this location, contribute significant to carbonate minerals. In addition, the high coal mass fraction that appears in the intake and the bolter location can be probably attributed to the presence of DPM.

Samples collected near bolter or production areas are not expected to contain high percentages of carbonates since in these locations rock dusting activities are not common. The TGA results are consistent with these expectations. Samples collected in the return areas had the highest carbonates apart from the intake. These results are probable since in some mines rock dusting in the return was very common. The fact that relatively high non-carbonate values were observed in all locations apart from the intake, indicates that these particles might be generated from production or bolter areas and then moved throughout the mine.

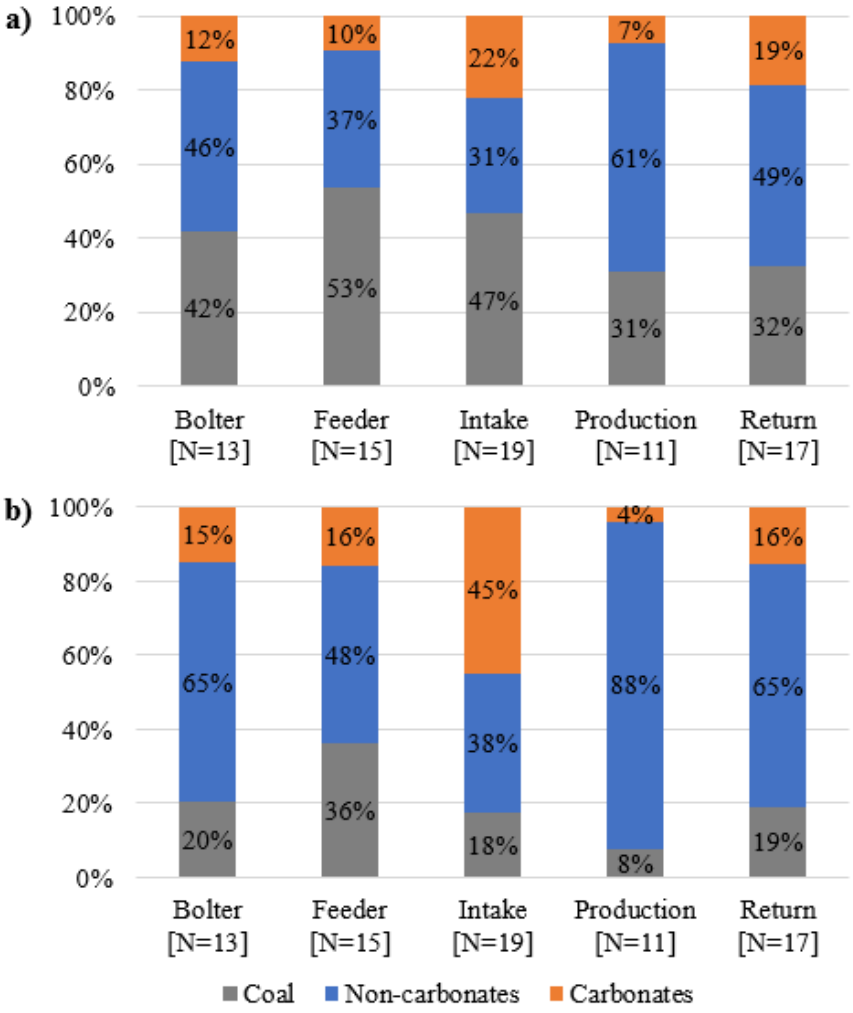

Figure 2-6 Mass fractions average percentages of coal, non-carbonate and carbonate from a) TGA and b) SEM analysis in different locations

2.5 Conclusions

In this chapter, the improved TGA method described in Chapter 1 was used to analyze 75 respirable dust samples collected in 15 US coal mines. The resulting dust mass fractions for coal, non-carbonates and carbonates were compared to those derived from SEM-EDX analysis of replicate samples. Aside from samples collected in mine intake airways, the TGA and SEM results were generally comparable. The carbonate mass fractions tended to agree very well between the two methods, and the SEM consistently underestimated coal and overestimated the non-carbonates with respect to the TGA. This is likely an artifact of key differences between the two techniques. While the TGA works by tracking characteristic changes in sample mass

that are attributed to a given component (e.g., coal), the SEM-EDX works by classifying individual particles into component bins. Depending on the threshold limits of the classification criteria, the SEM method can be quite sensitive to impurities or occlusions on particles. Thus, careful consideration should be given to selection of analytical method(s) for analysis of respirable coal mine dust (or similar) samples.

Also, regional trends based on the TGA results reveal that, in each region the intake samples differed greatly from the other locations. Not taking into account the submicron particles in the SEM analysis (presence of DPM that cannot be detected with the SEM) was a probable explanation in this case, along with the very low masses on the intake samples.

Furthermore, TGA dust sample results from regions in the NA, CA, MW and W, revealed that the highest non-carbonates to coal mass fraction ratio appears in the CA which is consistent with previous studies (Johann-Essex et. al 2017, Phillips et.al 2017) whereas the lowest non-carbonates to coal ratio is reported in the West region which is expected since the seams mined in those regions are thicker.

TGA results based on key locations revealed that the highest non-carbonates to coal ratios were seen in the production location, while the lower ratios were observed in the feeder location. The carbonates were low in all locations. The higher carbonate percentages were observed in the intake and the return indicating that the rock dusting activities contribute in the respirable dust fraction. In the other locations, carbonates might be related to drilling or cutting strata. Relatively high non-carbonate values were observed in all locations apart from the intake, and these results might be important from a health perspective, especially because silicates and silica –contained in the rock strata play a major role in occupational lung diseases.

Overall, the TGA provides a good understanding of mass fractions, but the SEM can be used to perhaps understand particle surfaces and impurities – which might be important for understanding toxicity as mentioned in Chapter 3.

2.6 Acknowledgements

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access and logistical assistance to our research team for dust sampling. Views presented here reflect those of the authors and not necessarily any funding source or research partners.

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3 Chapter 3 Conclusions and Future Work

The purpose of the work described in this thesis was to develop and apply an improved TGA method to accurately characterize respirable coal mine dust.

Development of the method included bulk sample analysis with TGA of coal shale and rock dust-materials commonly found in underground coal mines- and determination of temperature regions of interest where the materials may oxidize or thermally decompose. The clean coal, shale and rock dust used in this study were pulverized if needed and lab generated samples were made using Dorr-Oliver cyclones and Escort ELF personal sampling pumps. These lab-generated samples were used for single materials on PC filters experiments, correction for filter residue and premature decomposition of carbonates and method verification.

For the continuation of the work carried out in Chapter 1, there are some topics that could be further addressed. First, possible adjustments could be made to filter residue and premature CO_2 release corrections by increasing the number of samples used to confirm and optimize these corrections, and possibly decreasing sonication time. Anecdotal observations during the work in Chapter 1 indicated that sonication time for more than 3 minutes, and at temperatures over 30°C, can lead to higher filter degradation, which is undesirable. While PC filters were pursued in this study, future research should also consider the use of PTFE as an alternative sampling media. Despite the higher cost of the PTFE filters, they may prove superior in terms of inertness, which could aid in decreasing interferences from sample preparation.

As far as it concerns the TGA method implementation, a field sampling campaign was carried out in three mines in northern Appalachia, eight in central Appalachia, two in the mid-western Illinois coal basin and two in the western coal basin. 75 respirable dust samples were collected in key locations where coal miners usually work, and that are exposed to concentrations of respirable dust.

TGA results based on region indicate that the highest non-carbonate to coal ratio occurs (as far as it concerns all locations apart from the intake) in the CA region, followed by the W, NA and MW. The CA region has long been known as a hot spot for lung diseases (CDC, 2012; Wade et al, 2011; Suarthana et al., 2011; Laney and Attfield,

2010; NIOSH, 2008; Colinet et al. 2010). Furthermore, TGA results based on location, showed that the highest non-coal to coal occurs in the production followed by the return, the bolter, the intake and the feeder.

Results from the TGA analysis were then compared to results from an already developed SEM-EDX method and a notable disagreement was revealed for the coal and non-carbonate mass fractions between the four mining regions, as well as for the five key location in the mines where samples were collected. More specifically, results seem to indicate that there is a consistent overestimation of coal and underestimation of non-carbonates when using the TGA method versus the SEM method. It should be noted that the terms "overestimation" and "underestimation" are used in a relative sense here, and should not be understood to imply that the TGA method is necessarily better than the SEM method; indeed, these two methods constitute two very different approaches to dust characterization.

Although considerable progress has been accomplished for respirable dust characterization, little is known still about the relative toxicity of these dust constituents or whether the source material makes any meaningful difference. Leung et al. (2012) addressed this issue briefly by presenting a detailed description of a silica response mechanism in the lung and highlighting that the surface condition of silica particles is one important factor that controls the severity of this response mechanism. Wallace et al. (1990) showed that the surface condition of the particles can be determined by using scanning electron microscope with energy dispersive x-ray spectroscopy (SEM-EDX) to analyze elements of interest at two accelerating voltages (i.e., 20 and 5kV). The 20kV electron beam should penetrate into the core of the silica particle and produce elemental spectra accordingly, whereas the spectra produced at the lower voltage should be more influenced by the particle surface. The Si/(Si+Al) ratio decreases significantly from 20 to 5kV for occluded particles but should not change much for non-occluded particles.

Future work should involve SEM analysis of respirable coal mine dust field samples including both the supra and submicron range along with changes in the accelerating voltage to understand if impuritie occur more on the surface or the core of the particle.

With a simultaneous TGA and SEM analysis of respirable coal mine dust field samples can reveal valuable information about the dust composition. TGA can be used to quantify the contribution of each mass fraction which is linked to three major dust sources and SEM can analyze in depth particle characteristics. The combination of those methods can contribute to advancing knowledge related to dust composition and toxicity

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APPENDIX A

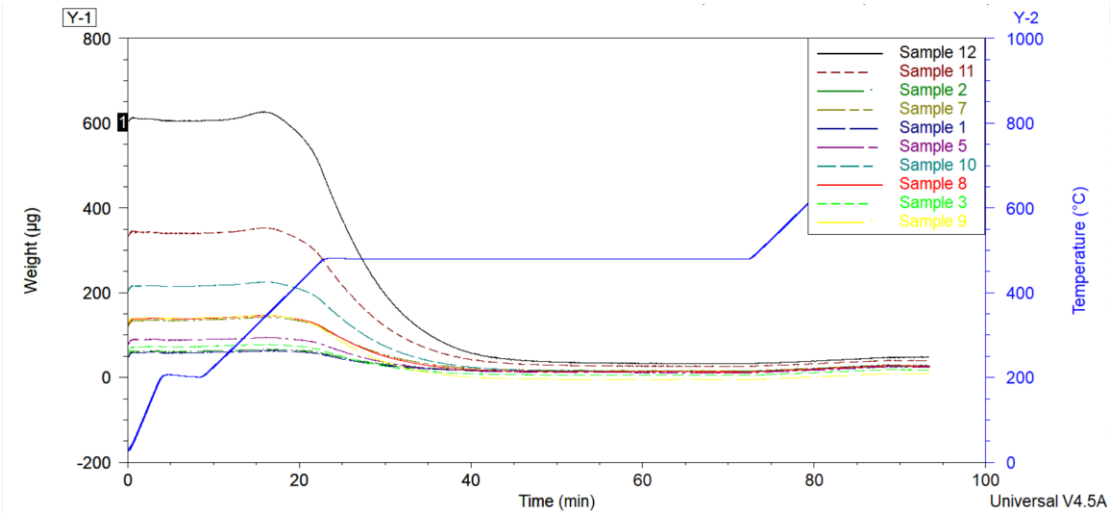


Figure A-1 Thermograms of single material (coal) (only 10 thermograms could be plotted per diagram)

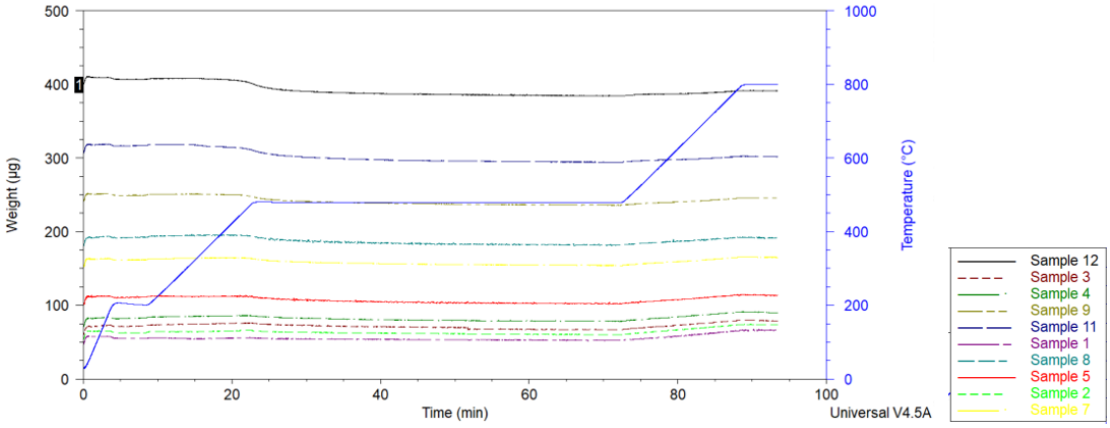


Figure A-2 Thermograms of single material (shale) (only 10 thermograms could be plotted per diagram)

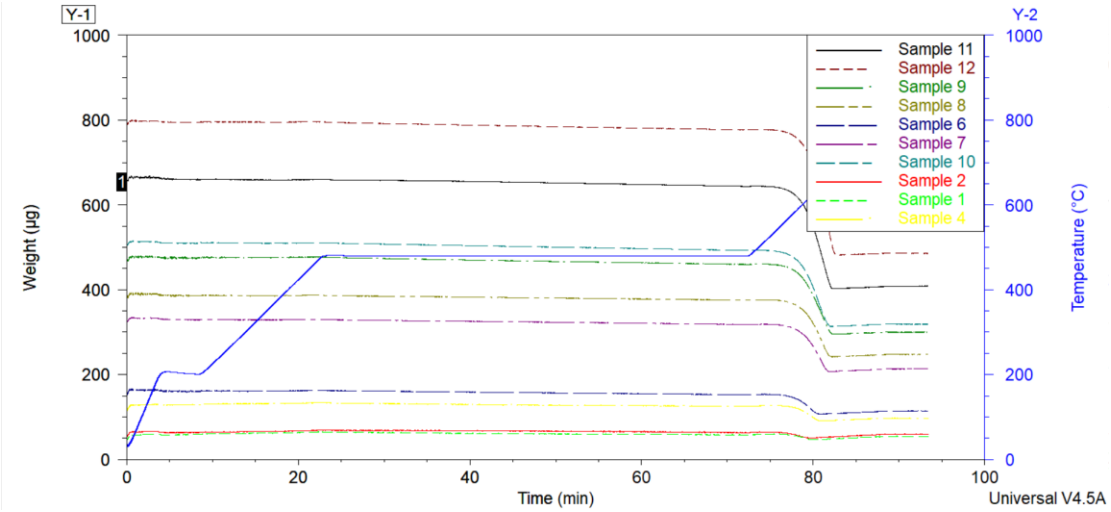


Figure A-3 Thermograms of single material (rock dust) (only 10 thermograms could be plotted per diagram)

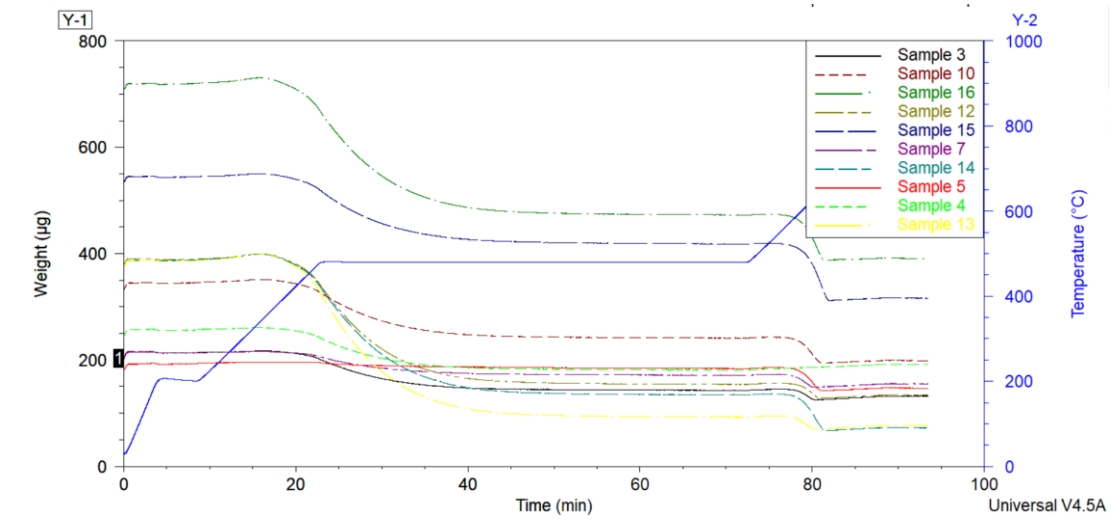


Figure A-4 Thermograms of composite dust experiments (only 10 thermograms could be plotted per diagram)

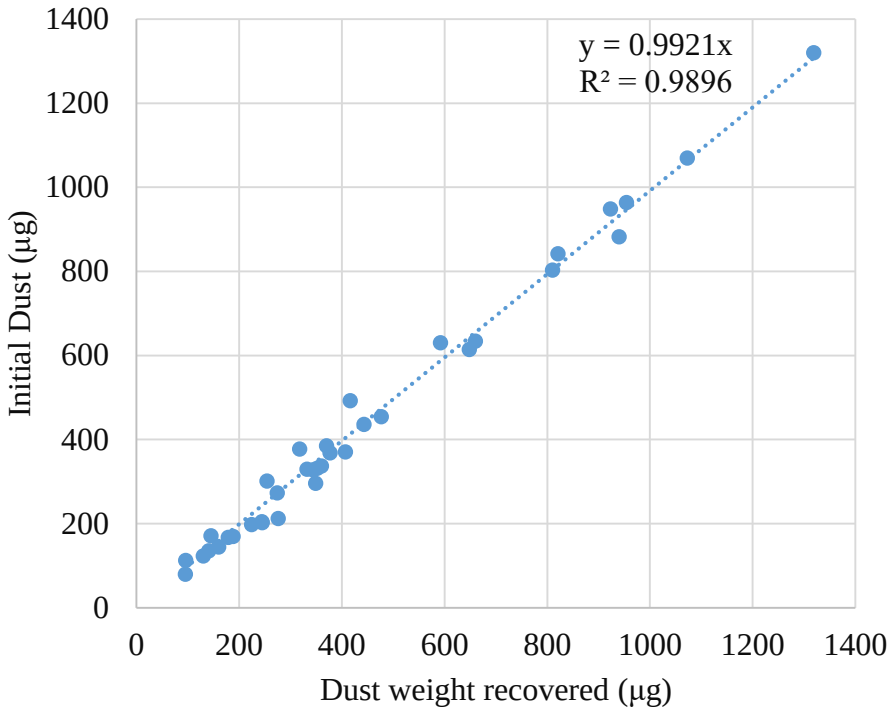


Figure A-5 Initial dust on the PC filter vs dust weight recovered from the laboratory methodology.

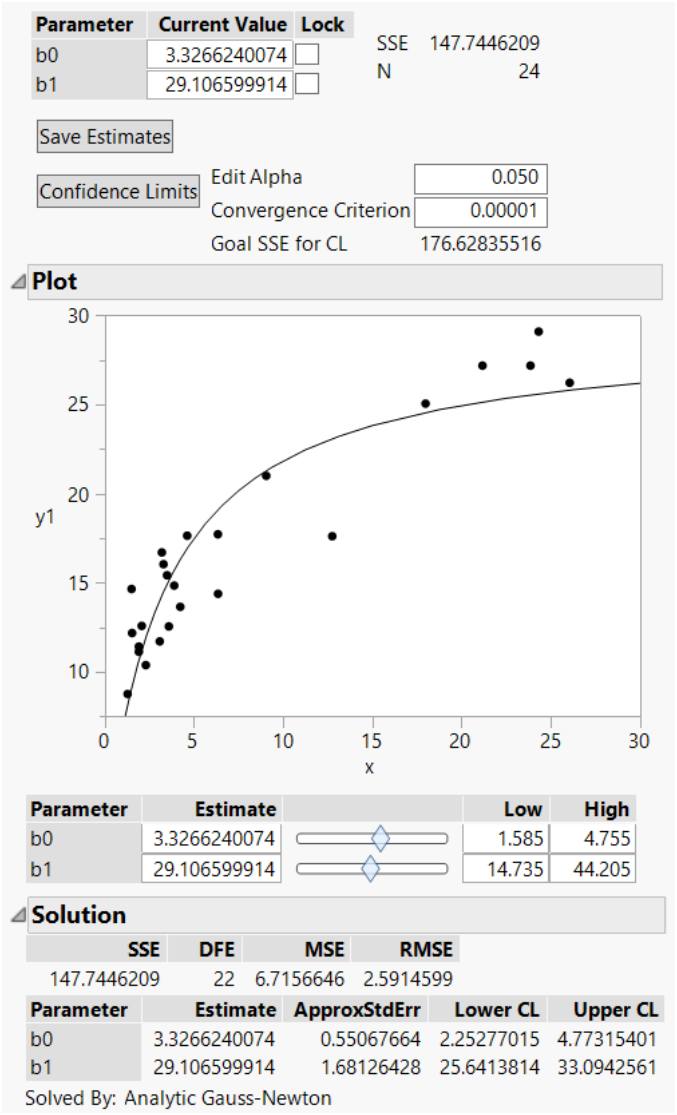


Figure A-6 Summary statistics for the Langmuir model for the filter correction.

Parameter	Current Value	Lock
b0	39.359311383	
b1	269.93976707	

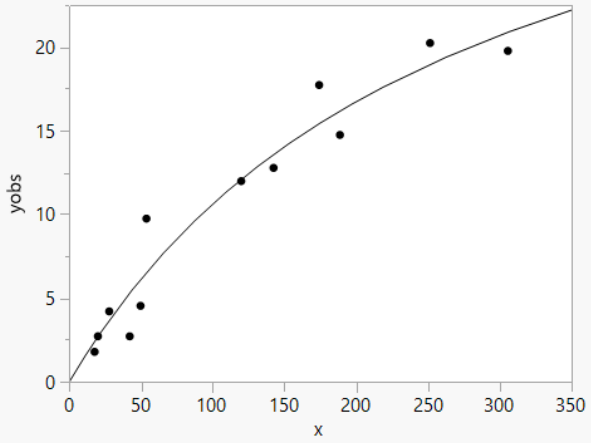
SSE 31.072911989
N 12

Save Estimates

Confidence Limits

Edit Alpha 0.050
Convergence Criterion 0.00001
Goal SSE for CL .

Plot



Parameter	Estimate		Low	High
b0	39.359311383		0.5	39.4093
b1	269.93976707		1	270.04

Solution

SSE	DFE	MSE	RMSE
31.072911989	10	3.1072912	1.762751

Parameter	Estimate	ApproxStdErr
b0	39.359311383	9.07534797
b1	269.93976707	104.865388

Solved By: Analytic Gauss-Newton

Figure A-7 Summary statistics for the Langmuir model for the premature CO_2 correction

Table A-1 Error between observed and expected coal, non-carbonates and carbonates % values for the 36 composite dust samples prepared on PC filters. Error is computed as TGA-derived % - gravimetric %.

Sample	Clean Coal (μg)	Shale (μg)	Rock Dust (μg)	Clean Coal Error (%)	Non-carbonates Error (%)	Carbonates Error (%)	Total Dust Weight
1	48	0	47	-2%	-6%	8%	95
2	31	65	0	9%	-9%	1%	96
3	47	83	0	0%	-8%	8%	130
4	107	34	0	-5%	-1%	6%	141
5	70	75	0	2%	-5%	4%	145
6	0	71	89	0%	-2%	1%	160
7	91	0	88	4%	-3%	-1%	179
8	30	99	59	-3%	1%	2%	188
9	39	150	35	-1%	-2%	3%	224
10	0	183	61	0%	-5%	5%	244
11	73	0	172	16%	-1%	-15%	245
12	135	51	68	1%	1%	-3%	254
13	76	77	121	2%	-1%	-1%	274
14	38	72	166	-4%	-9%	13%	276
15	0	152	166	19%	-11%	-8%	318
16	98	137	97	4%	-5%	2%	332
17	95	113	136	1%	0%	-1%	344
18	131	123	95	-8%	2%	6%	349
19	142	79	131	-3%	0%	3%	352
20	139	86	135	-1%	-1%	2%	360
21	103	267	0	0%	-6%	6%	370
22	0	200	177	0%	4%	-4%	377
23	50	236	121	5%	-5%	0%	407
24	68	0	348	14%	-4%	-11%	416
25	73	249	121	0%	-2%	2%	443
26	0	264	213	0%	-4%	4%	477
27	285	307	0	-1%	-1%	2%	592
28	0	300	348	0%	-3%	3%	648
29	328	332	0	1%	-3%	2%	660
30	142	408	260	0%	-1%	1%	810
31	487	0	334	-1%	0%	1%	821
32	516	0	407	-3%	2%	1%	923
33	0	451	489	0%	-3%	3%	940
34	0	621	333	0%	-3%	3%	954
35	428	321	324	-1%	-1%	2%	1073
36	354	507	458	0%	-1%	2%	1319

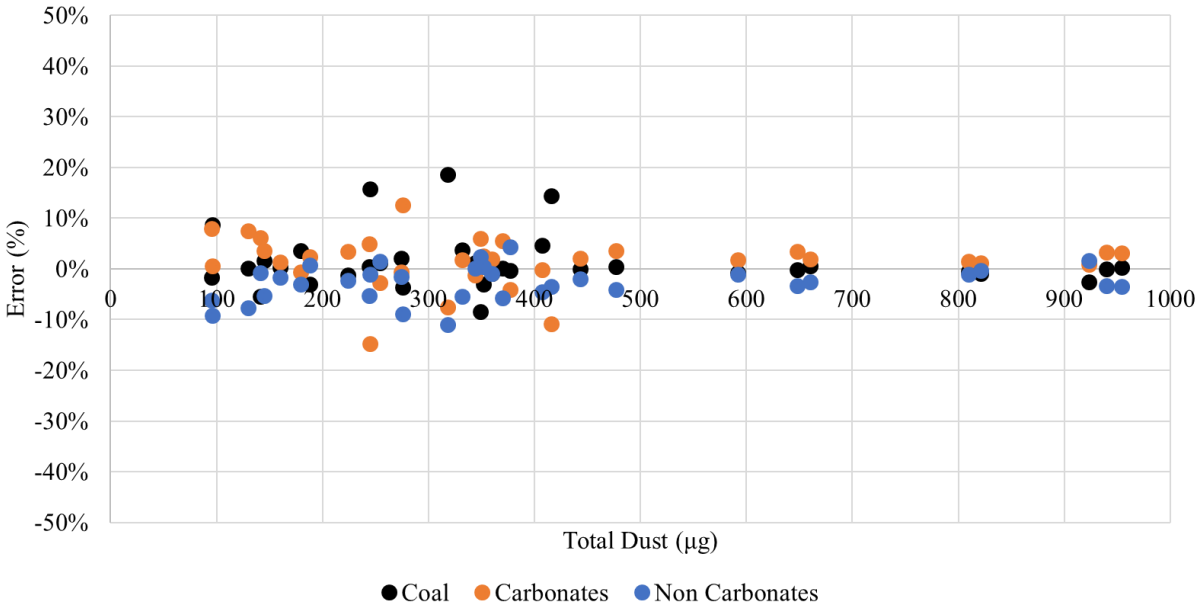


Figure A-8 Error between observed and expected coal, non-carbonates and carbonates % values for composite dust samples prepared on PC filters versus total dust.

APPENDIX B

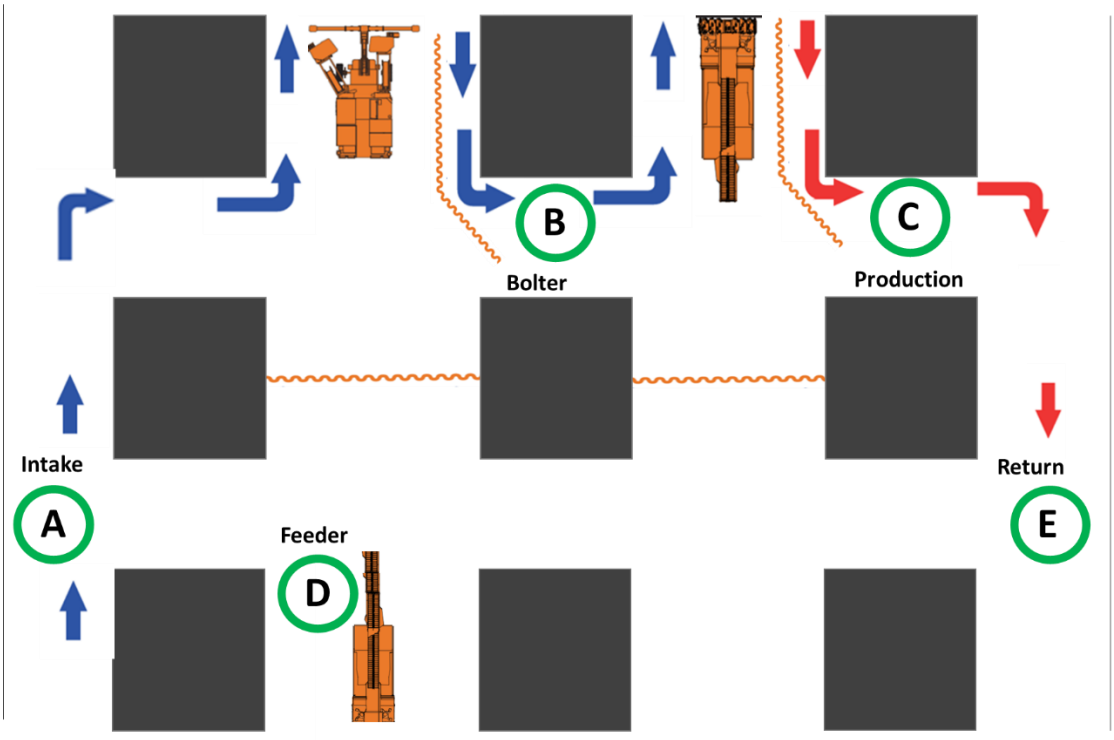


Figure B-1 Schematic representation of a room and pillar mine and key locations of sampling. Solid orange lines between pillars represent ventilation curtains.

Table B-1 Mass fraction results (reported as %) based on the TGA and SEM analysis using both the Johann-Essex et al. (2017a) and modified classification criteria.

			Results based on SEM analysis with modified criteria			Results based on SEM with Johann-Essex et.al 2017 criteria			Results based on TGA analysis			
Mine	Region	Code	Coal	Non-carbonates	Carbonates	Coal	Non-carbonates	Carbonates	Coal	Non-carbonates	Carbonates	PVC dust weight (mg)
10	CA	Bolter	24%	76%	0%	28%	72%	0%	25%	71%	4%	0.148
10	CA	Bolter	3%	97%	0%	5%	95%	0%	27%	68%	5%	0.181
10	CA	Feeder	16%	84%	1%	18%	81%	1%	42%	55%	3%	0.132
10	CA	Feeder	10%	90%	0%	13%	87%	0%	44%	40%	16%	0.183
10	CA	Intake	18%	77%	5%	23%	72%	4%	85%	14%	2%	0.005
10	CA	Production	0%	100%	0%	0%	100%	0%	23%	74%	3%	1.494
10	CA	Return	34%	65%	1%	44%	55%	1%	62%	35%	3%	0.038
11	CA	Bolter	1%	98%	2%	1%	96%	3%	37%	54%	9%	0.106
11	CA	Feeder	30%	63%	7%	37%	57%	6%	54%	39%	7%	0.164
11	CA	Production	0%	100%	0%	0%	100%	0%	11%	84%	5%	1.153
11	CA	Return	0%	100%	0%	0%	100%	0%	12%	82%	6%	0.749
12	CA	Bolter	34%	44%	22%	43%	39%	18%	55%	32%	13%	0.103
12	CA	Feeder	50%	34%	15%	62%	24%	14%	76%	19%	5%	0.054
12	CA	Intake	9%	91%	0%	10%	90%	0%	29%	66%	5%	1.077
12	CA	Return	0%	100%	0%	0%	100%	0%	21%	72%	7%	0.649
13	CA	Bolter	0%	100%	0%	0%	100%	0%	14%	81%	6%	2.535
13	CA	Feeder	34%	17%	49%	48%	13%	40%	78%	14%	8%	0.189
13	CA	Intake	5%	10%	85%	5%	7%	87%	39%	34%	27%	0.035
13	CA	Intake	27%	65%	8%	35%	55%	10%	63%	25%	13%	0.701
13	CA	Return	0%	93%	7%	0%	95%	5%	74%	22%	4%	7.347
13	CA	Return	63%	35%	2%	76%	21%	4%	8%	22%	70%	1.297
14	CA	Bolter	13%	84%	3%	16%	80%	4%	34%	55%	11%	0.039
14	CA	Feeder	2%	98%	0%	3%	94%	3%	28%	67%	5%	0.187
14	CA	Intake	7%	36%	57%	9%	26%	64%	67%	24%	9%	0.002
14	CA	Production	0%	100%	0%	0%	100%	0%	9%	86%	5%	4.348
15	CA	Bolter	17%	75%	8%	24%	65%	11%	31%	59%	10%	0.145
15	CA	Feeder	51%	29%	20%	56%	24%	20%	49%	29%	23%	0.028
15	CA	Intake	9%	5%	87%	10%	4%	86%	76%	24%	0%	0.001
15	CA	Production	12%	83%	5%	14%	76%	11%	32%	60%	7%	0.47
15	CA	Return	8%	92%	0%	11%	88%	1%	17%	77%	6%	0.351
16	NA	Bolter	49%	28%	23%	57%	20%	23%	72%	23%	5%	0.089
16	NA	Feeder	48%	44%	8%	59%	34%	7%	65%	26%	9%	0.073
16	NA	Production	34%	59%	7%	46%	45%	9%	68%	25%	7%	0.221
16	NA	Return	65%	25%	9%	75%	16%	10%	62%	28%	10%	0.172
17	NA	Bolter	7%	44%	49%	9%	38%	52%	47%	16%	37%	0.043
17	NA	Intake	35%	55%	10%	39%	51%	10%	62%	32%	6%	0.072
17	NA	Intake	3%	9%	88%	5%	6%	89%	93%	3%	4%	0.016
17	NA	Production	4%	96%	0%	4%	96%	0%	35%	60%	5%	0.277
17	NA	Return	0%	100%	0%	0%	100%	0%	35%	61%	3%	0.763
17	NA	Return	13%	10%	77%	19%	7%	73%	31%	11%	58%	0.489
18	NA	Bolter	33%	59%	8%	36%	56%	9%	32%	59%	10%	0.096
18	NA	Feeder	29%	40%	31%	31%	34%	35%	71%	22%	6%	0.018
18	NA	Intake	6%	9%	85%	7%	6%	87%	68%	20%	12%	0.001
18	NA	Production	1%	99%	0%	1%	99%	0%	40%	55%	6%	0.34
18	NA	Return	28%	70%	1%	33%	65%	1%	29%	62%	9%	0.231
19	MW	Bolter	11%	87%	2%	13%	81%	6%	57%	34%	9%	0.181
19	MW	Feeder	0%	100%	0%	0%	99%	0%	48%	46%	6%	2.608
19	MW	Intake	16%	51%	33%	21%	41%	38%	0%	51%	49%	0.014
19	MW	Production	16%	74%	10%	21%	55%	24%	50%	34%	16%	0.277
19	MW	Return	8%	84%	8%	16%	65%	19%	45%	35%	20%	0.299
19	MW	Return	13%	86%	0%	18%	81%	1%	47%	48%	5%	0.223
20	MW	Bolter	0%	99%	0%	0%	99%	1%	32%	47%	21%	0.53
20	MW	Feeder	26%	38%	36%	30%	31%	39%	32%	33%	35%	0.143
20	MW	Feeder	20%	51%	29%	27%	47%	26%	37%	42%	21%	0.191
20	MW	Intake	8%	17%	75%	12%	11%	77%	6%	31%	63%	0.019
20	MW	Production	0%	100%	0%	0%	100%	0%	32%	60%	8%	0.758
20	MW	Return	8%	89%	3%	10%	77%	13%	33%	56%	11%	0.577
21	CA	Bolter	5%	78%	18%	6%	72%	22%	61%	24%	16%	0.085
21	CA	Feeder	12%	85%	3%	13%	83%	4%	16%	81%	3%	0.089
21	CA	Intake	9%	86%	5%	12%	83%	5%	20%	65%	15%	0.063
21	CA	Production	0%	100%	0%	0%	100%	0%	8%	88%	4%	1.415
21	CA	Return	0%	100%	0%	0%	100%	0%	9%	87%	4%	0.557
22	CA	Feeder	65%	34%	1%	70%	29%	1%	61%	34%	5%	0.018
22	CA	Intake	39%	49%	12%	43%	44%	13%	27%	20%	53%	0.003
22	CA	Production	0%	100%	0%	0%	100%	0%	34%	50%	16%	1.23
23	W	Intake	60%	18%	22%	71%	10%	20%	70%	11%	18%	0.1
23	W	Intake	3%	5%	92%	5%	2%	93%	35%	0%	65%	0.097
23	W	Intake	8%	6%	87%	12%	3%	86%	40%	9%	50%	0.176
23	W	Return	1%	5%	94%	2%	2%	95%	29%	9%	62%	0.888
24	W	Feeder	37%	26%	37%	47%	11%	42%	71%	19%	10%	0.068
24	W	Intake	0%	100%	0%	1%	99%	0%	31%	66%	3%	1.547
24	W	Intake	12%	32%	56%	17%	23%	60%	68%	16%	16%	0.052
24	W	Intake	10%	21%	69%	17%	12%	71%	53%	28%	20%	0.063
24	W	Return	13%	67%	20%	18%	50%	32%	42%	43%	15%	0.165
24	W	Return	0%	83%	17%	0%	71%	29%	12%	17%	71%	5.361

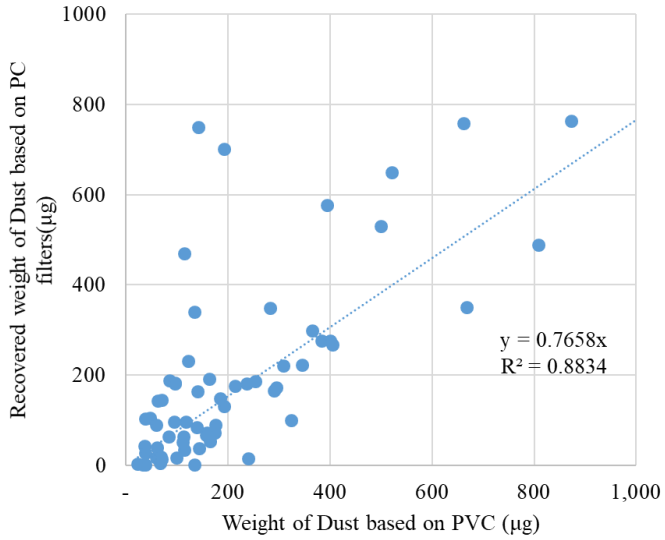


Figure B-2 Recovered weight of dust vs weight of dust based on PVC filters from mine samples.

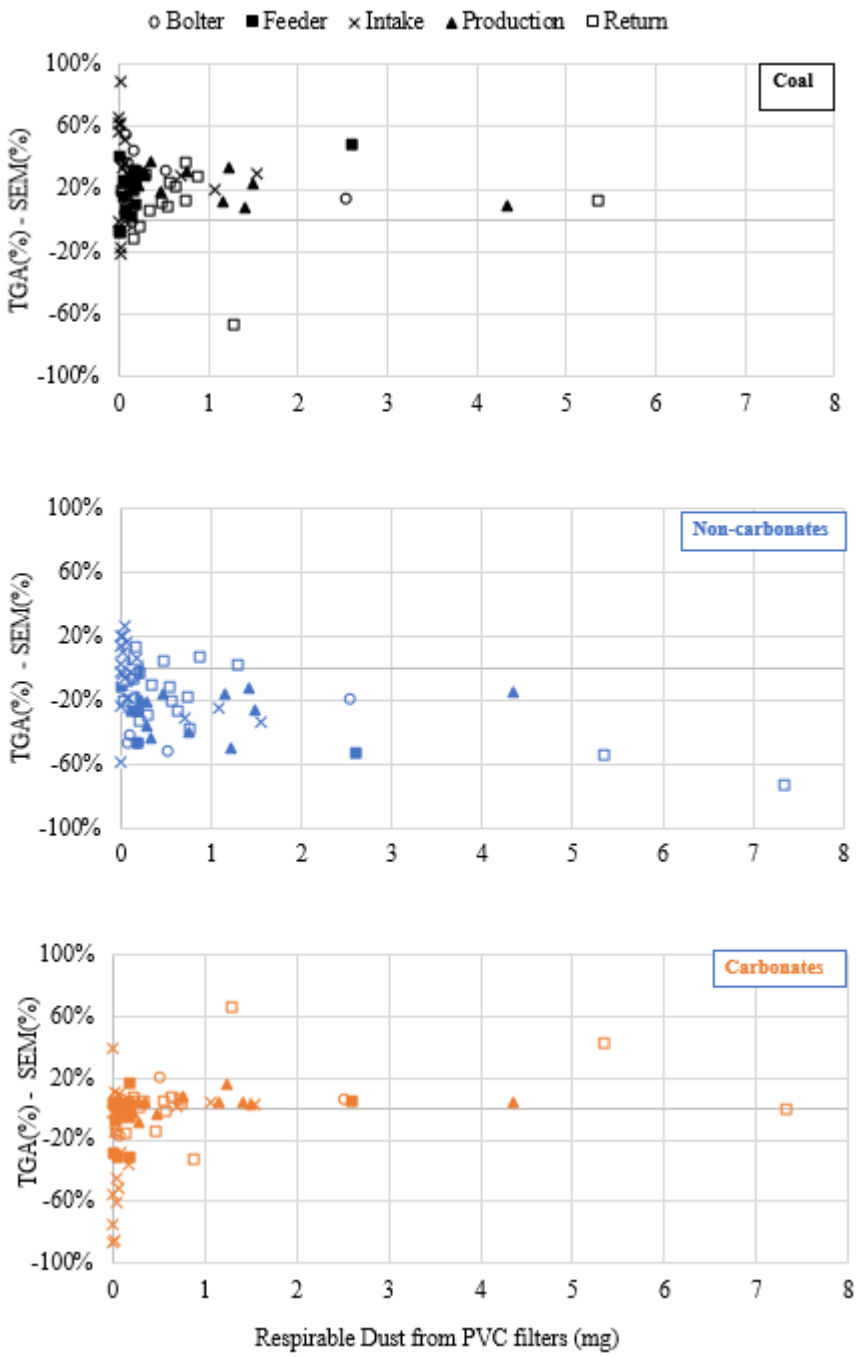


Figure B-3 Difference between TGA and SEM % vs dust weight (i.e., determined from PVC replicate filters) for a) coal b) non-carbonates and c) carbonates for key locations in underground coal mines

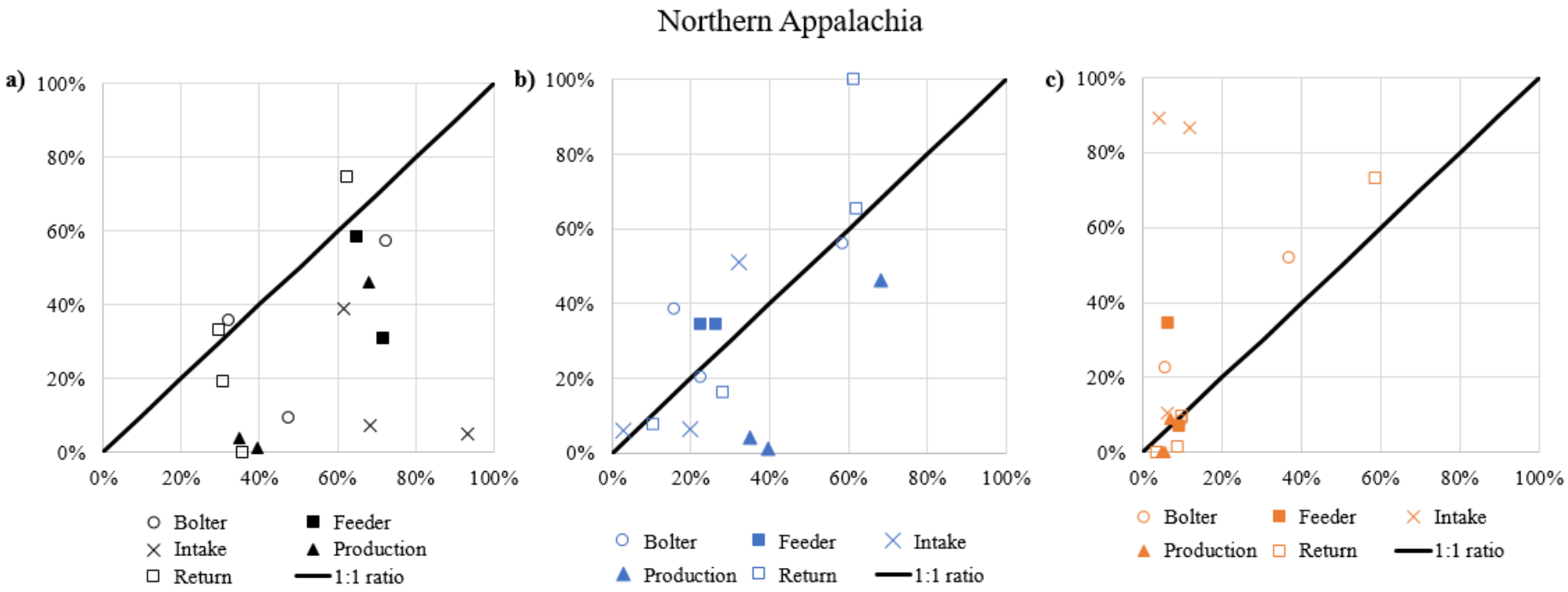


Figure B-4 Mass fractions (%) of SEM vs TGA (%) for a) coal b) non-carbonates and c) carbonates in Northern Appalachia region

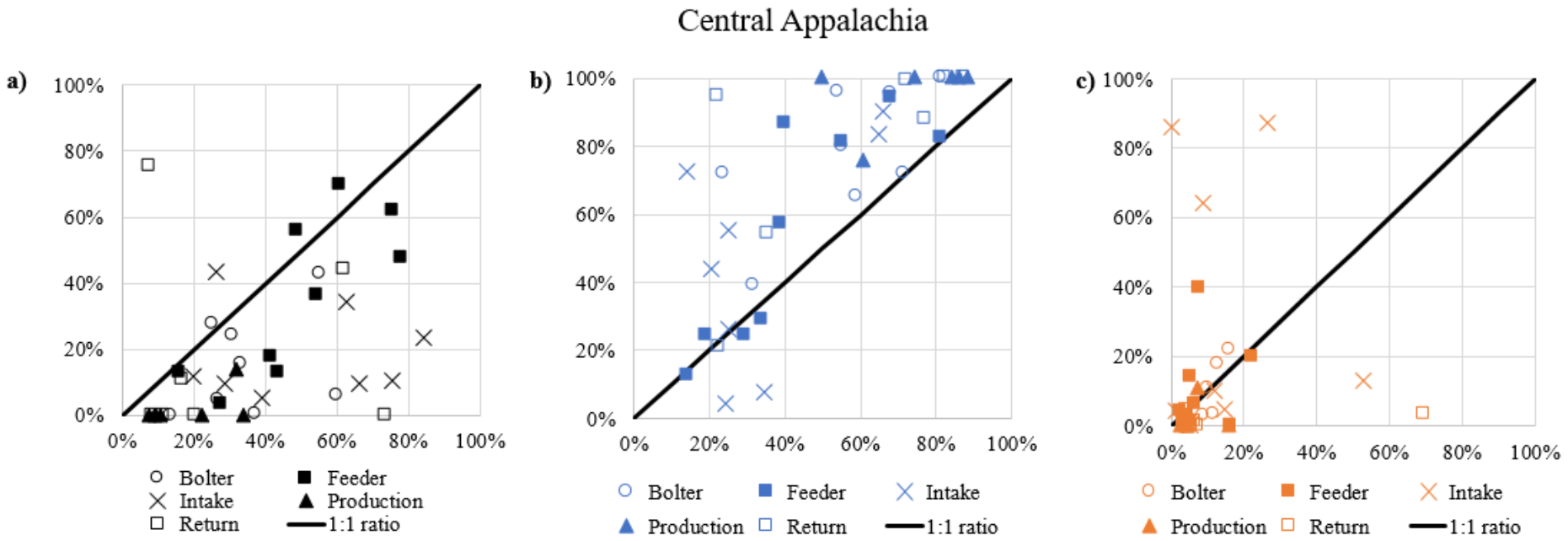


Figure B-5 Mass fractions (%) of SEM vs TGA (%) for a) coal b) non-carbonates and c) carbonates in Central Appalachia region

Figure B-6 Mass fractions (%) of SEM vs TGA (%) for a) coal b) non-carbonates and c) carbonates in Mid West region

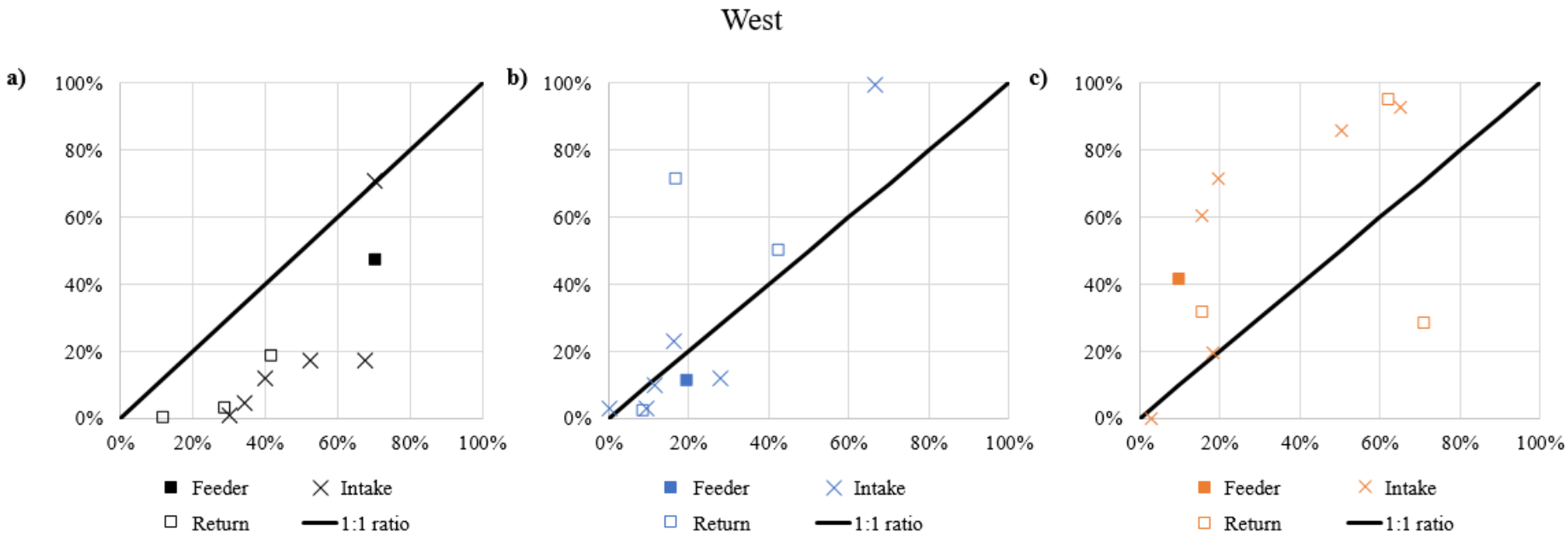


Figure B-7 Mass fractions (%) of SEM vs TGA (%) for a) coal b) non-carbonates and c) carbonates in West region