

**DIESEL PARTICULATE MATTER
SAMPLING METHODS: STATISTICAL COMPARISON**

By

**Winthrop F. Watts, Jr., Ph.D.
University of Minnesota
Department of Mechanical Engineering
Center for Diesel Research**

And

**Gurumurthy Ramachandran, Ph.D.
University of Minnesota
School of Public Health
Department of Environmental Health**

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ABSTRACT

One objective of the Diesel Emission Evaluation Program is the evaluation of diesel aerosol measurement methodologies. Three sampling methods are used in mines to determine the concentration of diesel particulate matter (DPM). The methods are the size selective method (SS), the respirable combustible dust method (RCD), and the elemental carbon method (EC). The statistical analysis described in this report compares the three methods to determine the limitations and potential applications of each.

The objectives of the report are:

- to review existing information on interferences, sampling and analytical biases, limits of detection, and other limitations of the existing methods for measuring DPM concentrations;
- to assemble available data and compare the methods with respect to their specificity, sensitivity and detection limits, and accuracy;
- to recommend appropriate conditions for and uses of each method, and to identify needs for further research.

1. INTRODUCTION

Diesel exhaust is a complex mixture of noxious gases and diesel particulate matter (DPM). DPM consists of nonvolatile, elemental carbon (EC), adsorbed or condensed hydrocarbons referred to as organic carbon (OC), sulfates, and trace quantities of metallic compounds (HEI, 1995). Total carbon (TC) is composed of EC + OC.

Attention has focused on the potential carcinogenicity of DPM and the potential health impact on miners. In 1988, the National Institute for Occupational Safety and Health (NIOSH) recommended that whole diesel exhaust be regarded as a "potential occupational carcinogen", and stated that reductions in workplace exposure would reduce cancer risks (NIOSH, 1988). In 1989, the International Agency for Research on Cancer declared that "diesel engine exhaust is probably carcinogenic to humans" (IARC, 1989).

There is a considerable difference in recommended or established allowable concentrations for DPM in the workplace. In 1995, the American Conference of Governmental Industrial Hygienists (ACGIH) added DPM to the Notice of Intended Changes for 1995-96 with a threshold limit value (TLVTM) recommendation of 0.15 mg/m³ (ACGIH, 1995). DPM < 1.0 µm in size remains on the ACGIH Notice of Intended Changes in 1999 but with a reduction in the proposed TLV to 0.05 mg/m³ (ACGIH, 1998). DPM limits are already in place in Canada and Europe. British Columbia, New Brunswick, Quebec, and Ontario have adopted a 1.5-mg/m³ level for respirable combustible dust (RCD)¹. The Federal Republic of Germany has

¹ Health, Safety and Reclamation Code for Mines in British Columbia, 1997, section 6.22.2(3); Regulation

adopted technical exposure limits (TRK)² for the general workplace, tunneling and mining. For the general workplace, the TRK is 0.1 mg/m³ EC or 0.15 mg/m³ total carbon (TC) when the sample contains > 50 % organic material. For mining and tunneling the TRK is 0.3 mg/m³. The standard for mining is being revised. In Switzerland the standard is 0.2 mg/m³ of TC (SUVA, 1997).

The U. S. Mine Safety and Health Administration (MSHA) recently proposed a DPM permissible exposure limit for noncoal mines based upon TC (MSHA, 1998). An interim standard of 0.4 mg/m³ TC would take effect 18 months after the publication of the final rule. Five years later the standard would be lowered to 0.16 mg/m³ of TC. Total carbon would be determined using NIOSH method 5040.

As might be expected, several sampling and analytical methods are used to determine DPM concentrations in the workplace. Each of these methods measures a different portion of diesel particulate matter and in some cases, such as EC, only a portion of the DPM is measured. Replicated simultaneous samples of DPM aerosols, using these different methods, have been gathered as part of research projects conducted for various purposes. These data were not always obtained explicitly to compare methods. However, the body of data makes such comparison possible over a broad range of DPM concentrations and under a variety of different mining conditions.

The objectives of this analysis are:

- *to review existing information on interferences, sampling and analytical biases, limits of detection, and other limitations of the existing methods for measuring DPM concentrations;*
- *to assemble available data and compare the methods with respect to their specificity, sensitivity and detection limits, and accuracy;*
- *to recommend appropriate conditions for and uses of each method, and to identify needs for further research.*

2. BACKGROUND

Measuring diesel aerosol in the workplace is challenging due to the physical characteristics and chemical complexity of the aerosol. DPM has a mass median diameter of 0.2 µm, with 90% of the particles being < 1.0 µm in diameter. It is composed primarily of OC, EC, adsorbed and condensed hydrocarbons, and sulfate (IARC, 1989). The proportion of OC to EC varies depending upon a number of factors, such as fuel, engine type, duty cycle, engine maintenance, operator habits, use of emission control devices, and lube oil consumption. In

respecting occupational health and safety in mines, 1998, section 102.(1)(a) and 102.(1.1); Schedule VI Sampling and Analysis Protocol for Respirable Combustible Dust (RCD). Regulations for Mines and Mining Plants, Ontario Regulation 854/90, 1997, section 183.1(5).

² TRGS 900, "Grenzwerte in der Luft am Arbeitsplatz "Luftgrenzwerte""; TRGS 901, "Begründungen und Erläuterungen zu Grenzwerten in der Luft am Arbeitsplatz", Bundesarbeitsblatt May, 1998.

general, non-extractable EC accounts for a greater fraction of DPM mass than OC (Perez and Williams, 1989).

Two sampling methods are routinely used in underground mines to collect DPM samples for analysis; these are respirable dust sampling and size selective sampling. Three analytical methods are used to quantify DPM in collected samples; these are gravimetric analysis, RCD analysis and EC analysis. Combining the sampling and analytical methods yields three methods to quantify DPM, which are referred to as 1) respirable dust sampling with RCD analysis, 2) size selective sampling with gravimetric or EC analysis³, and 3) respirable dust sampling with EC analysis (Watts, 1995; Cantrell and Watts, 1996). Each of these is described briefly below.

2.1. Respirable Combustible Dust (RCD)

The RCD method was developed in Canada to estimate DPM concentrations in non-coal mines (Hews and Rutherford, 1973; Rutherford and Elliot, 1977; Maskery, 1978). Recent publications have described the method as currently used by the Canada Center for Mineral and Energy Technology (CANMET) in detail (Gangal *et al.*, 1990; Gangal and Dainty, 1993). RCD is composed of all combustible materials collected on a filter including; drill oil mist, the soluble organic fraction of DPM, EC and other combustible material collected on the filter such as carbonaceous material found in the ore dust. Thus, only a portion of RCD is attributable to diesel exhaust aerosol.

In the RCD method, respirable dust is collected on a 25 or 37 mm, 0.8 μm silver membrane or pre-combusted, glass fiber filter after passing air through a 10 mm Dorr-Oliver cyclone at flow rate of 1.7 l/min. Flow is controlled using a personal sampling pump. The cyclone is a respirable dust preclassifier with a 50% cut point of 4.0 μm . Respirable dust is determined gravimetrically by weighing the silver membrane or glass fiber filter before and after the sample is collected. RCD is determined gravimetrically from the amount of material removed from the silver membrane by controlled combustion at 400 °C (500 °C for the glass fiber filter) for one to two hours. A correction is made for the loss of mass of the silver membrane due to combustion.

CANMET conducted studies on errors associated with the RCD method. These studies are summarized in detail elsewhere (Gangal and Dainty, 1993). The studies investigated the weight loss of combusted blank filters, determined the filtration efficiency of several filters and

³The EC analysis referred to here is NIOSH method 5040 (NIOSH, 1998). This method provides information on EC, organic carbon (OC) and TC. EC is considered a specific marker or surrogate for DPM exposure. However, EC is not a measure of total DPM exposure because the OC portion is excluded. TC has also been used as a measure of DPM exposure (DFG, 1993; SUVA, 1997; MSHA, 1998). The NIOSH method allows the identification of some non-diesel sources of OC, thus allowing the TC estimate to be corrected for these contributions. The coulometric method used in Germany (Dahmann, *et al.*, 1996) is similar to the NIOSH method but provides slightly different information.

evaluated the performance of two cyclones. The major findings are summarized below.

- 25-mm silver membrane (SM) filters lost less mass when combusted than glass fiber (GF) filters. After combusting the filters twice at 500 °C the 0.8 µm SM filter mass loss was approximately one third that of the corresponding GF filter (0.06 mg and 0.17 mg). Table 1 summarizes the predicted error associated with the blank loss under various sampling conditions.
- The smaller the filter pore sizes the greater the mass loss. In addition, smaller pore size filters have unacceptably high-pressure drops for the sampling pumps, particularly under humid conditions.
- CANMET’s experience suggests that either the 0.8 µm 25 mm GF or SM filters are suitable for RCD measurement as long as a correction is applied for the loss of filter mass upon combustion. SM filters have the added advantage of being useful for quartz analysis. GF fiber filters are inexpensive.

Table 1. - Predicted error in RCD analysis associated with blank filter mass loss

Sampling conditions			RCD error, %	Comments
Time, hr	Flow rate, lpm	Mass, mg		
4	1.7	0.70	± 3.8	Correction for uncombusted FG blank loss included
4	1.7	0.70	± 1.9	Correction for pre-ashed FG blank loss included
4	4.0	0.24	± 5.6	Correction for pre-ashed FG blank loss included
4	1.7	0.70	± 3.8	Correction for both pre-ashed and uncombusted SM blanks loss included
4	4.0	0.24	± 11.1	Correction for both pre-ashed and uncombusted SM blanks loss included

Source: Gangal and Dainty, 1993.

2.2. Size Selective Sampling (SS)

The SS method is based on a body of literature developed by the University of Minnesota, and the U.S. Bureau of Mines (Marple, *et al.*, 1986; Rubow, *et al.*, 1990a,b; McCartney and Cantrell, 1992 and Cantrell, *et al.*, 1987, 1990a,b, 1992). These studies showed that submicrometer aerosols found in coal mines were primarily diesel in origin. The difference in the aerodynamic diameter particle size between combustion and mechanically

generated aerosols can be used to separate diesel aerosol from noncombustion aerosols in the collecting process. Respirable aerosol sampling at 1.7 lpm has a 50-pct cutpoint at 4.0 μm and collects a fraction of particles up to 10 μm in size. Diesel aerosol has a mass median aerodynamic diameter of 0.2 μm , and 90 % of the particles are less than 1.0 μm in size. Thus, respirable aerosol sampling collects all diesel and nondiesel aerosol particles falling in the respirable size range. The respirable and diesel fractions may be separated using inertial impaction on greased, aluminum foil substrates. Inertial impaction removes nearly all (> 90 %) nondiesel particles and a small percentage (< 15 %) of large diesel particles. The submicrometer diesel aerosol is collected on a filter downstream of the impaction substrate. Gravimetric analyses determine the mass fraction in each size range. Another advantage this method has over traditional respirable dust sampling is that it separates large particles that are predominately nondiesel in origin, but still allows the respirable fraction to be calculated.

The SS sampler was originally designed for use in coal mines, which use diesel haulage vehicles equipped with water scrubbers. Scrubbers effectively remove diesel aerosol larger than 0.8 μm , thus tailoring the remaining aerosol size distribution and minimizing the amount of diesel aerosol not captured on the filter. The SS sampling method is also used in metal and nonmetal mines where scrubbers are seldom used. In this situation, approximately 10 - 15 % of the total diesel aerosol is not accounted for (Cantrell *et al.*, 1990b), because it is larger than 0.8 μm in size and is removed on the aluminum foil substrate.

The SS sampler can be used in conjunction with the EC method if a pre-combusted, glass fiber filter is used to collect the submicrometer material. This is an advantage over other aerosol measurement techniques, which either do not collect a submicrometer sample or destroy the sample during analysis.

The University of Minnesota, U.S. Bureau of Mines, Mine Safety and Health Administration and the National Institute for Occupational Safety and Health have designed SS diesel aerosol samplers. The sampler used in recent work conducted by the Center for Diesel Research is a Bureau of Mines modification of a sampler originally designed by the University of Minnesota (Rubow, *et al.*, 1990b). It was redesigned to reduce manufacturing costs (McCartney *et al.*, 1992).

The first stage of this sampler is a 10 mm Dorr-Oliver cyclone. A four-nozzle inertial impactor with a 0.8 μm cut point follows the cyclone. The impaction surface consists of a 37-mm oiled, aluminum substrate that is used to collect respirable dust larger than 0.8 μm . Air is drawn through the sampler at 1.7 l/m using a personal sampling pump⁴. DPM, which is primarily smaller than 0.8 μm , passes through the central exit of the impaction surface and is collected on a polyvinyl chloride filter mounted within an MSA filter cassette [or a pre-combusted glass fiber filter if the EC method is to be used]. The amount of DPM is determined gravimetrically from the MSA filter. The mass of respirable dust is determined gravimetrically

⁴ If the flow rate changes the cutpoints for the cyclone and impactor change.

from the combined mass of material collected on the MSA filter and the aluminum substrate.

The collection efficiencies of the impactors used in the Bureau and University samplers were measured as a function of aerosol size using mono-dispersed polystyrene latex particles ranging in size from 0.56 to 1.10 μm . Details of the test protocol are available elsewhere (McCartney and Cantrell, 1992). The 50-pct-collection efficiency point ($E_{50 \text{ pct}}$) for the Bureau impactor was $0.79 \pm 0.01 \mu\text{m}$ with a σ_g of 1.18 ± 0.05 , indicating a sharp cut. The σ_g is defined as the square root of the ratio of the particle diameter corresponding to the 84.1% collection efficiency to the diameter at an efficiency of 15.9%. The University impactor had an $E_{50 \text{ pct}}$ cut point of $0.77 \pm 0.03 \mu\text{m}$ and a σ_g of 1.07 ± 0.04 . These experimental results agree well with previous experimental findings where the University impactor had an $E_{50 \text{ pct}}$ of $0.76 \pm 0.05 \mu\text{m}$ and a σ_g of 1.15 ± 0.05 (Marple, *et al.*, 1991).

2.3. Elemental Carbon

DPM is chemically complex. It is composed of soluble organic hydrocarbons, sulfate, EC and traces of other compounds. In general, EC accounts for about 50% of the mass of DPM, but this percentage varies depending upon engine duty cycle, fuel quality, aftertreatment device and other factors.

Various techniques have been used for the analysis of carbonaceous aerosol. These methods provide estimates for TC that is in general agreement. An interlaboratory comparison of methods for the analysis of carbonaceous aerosols (Countess, 1990) showed that agreement between laboratories for TC was within 20% for all samples. However, there were large interlaboratory differences in the OC to EC ratio for all samples, with the largest differences occurring in the automotive and wood smoke dominated reference samples. Unlike the case for TC, there are no reference standards for speciation of different carbon types in complex carbonaceous aerosols. Methods that speciate EC and OC are considered operational in the sense that the method itself defines the analyte (Cadle and Groblicki, 1982).

NIOSH (Birch and Cary, 1996; NIOSH, 1998) has refined the thermal-optical method that was originally and adopted for atmospheric aerosols (Johnson, *et al.*, 1981; Cadle and Groblicki, 1982; Hering, *et al.*, 1990). This technique is a sensitive measure of the EC portion of DPM. It has a working range of 6 - 630 $\mu\text{g}/\text{m}^3$ with a limit of detection of about 2.0 $\mu\text{g}/\text{m}^3$ for a 960 L air sample collected on a 37-mm filter with a 1.5- cm^2 punch from the filter. If a lower limit of detection is desired, a larger sample volume and/or a 25-mm filter may be used. If a 1920-L sample is collected on a 25-mm filter then the lower limit of detection is 0.4 $\mu\text{g}/\text{m}^3$ (NIOSH, 1998).

The method also determines the presence of organic carbon (OC) and total carbon⁵ is

⁵The Federal Republic of Germany uses the coulometric method to determine EC and TC. The method is described by Dahmann, *et al.*, (1996) and is different from NIOSH method 5040.

determined by summation (EC + OC). Since EC is a product of combustion and is composed of inert graphitic carbon it is a specific marker of diesel exhaust aerosol in many occupational settings where other combustion aerosols are not present. However, the OC portion of the collected aerosol is subject to interferences from other organic aerosols not associated with diesel exhaust, such as drill oil mist, hydraulic fluids, coal dust, cigarette smoke and other organic material also contribute OC aerosol. This is similar to the situation observed for RCD analysis with the exception that in some cases the NIOSH method can identify the interfering compounds and a correction factor can be applied to improve the TC estimate.

Samples for EC are collected with or without an inertial preselector to remove particles > 0.8 µm that may interfere with analysis. The simplest sampling train consists of a 10 mm Dorr-Oliver cyclone followed by a 37 mm precombusted Pallflex, ultra pure quartz fiber filter mounted in a 37 mm plastic cassette. Alternatively, the 0.8 µm size selective impactor described above is followed by the Dorr-Oliver cyclone. In this situation, DPM, which is primarily smaller than 0.8 µm, passes through the central exit of the impaction surface and is collected on the Pallflex filter. This is advantageous because, large mechanically generated aerosol such as coal dust is not collected on the Pallflex filter and cannot interfere with EC analysis. A disadvantage of the Pallflex quartz fiber filter is the tendency to adsorb organic vapor, thus increasing the mass on the filter and the amount of OC. Dynamic blanks must be used to correct for this sampling artifact. Blanks can consist of multiple quartz filters in the same cassette or the use of a non-adsorbing material such as a filter made of Teflon in front of a quartz filter.

3. COMPLETED STUDIES

Recent underground mine studies (Watts, *et al.*, 1997, 1998; Grenier, *et al.*, 1998) have collected data that can be used to compare the RCD, SS, and EC methods to determine advantages, disadvantages and limitations. These data are reanalyzed in this report to estimate specificity, sensitivity and detection limits, and accuracy. A brief review is included for each study to serve as background for the ensuing statistical analysis.

3.1. 1996 Creighton Mine Study

In 1996, UMN, Inco and NIOSH collaborated to evaluate the three sampling methods (Watts, *et al.* 1997, Cantrell, *et al.* 1998). The study was carried out in a non-producing section of Inco's Creighton mine, Sudbury, Canada. Sampling was performed on a mucking operation employing two diesel scoops. One vehicle was operated, while the other served as a backup in case the operating scoop malfunctioned. The scoop moved muck between two drifts where ventilation airflow was carefully regulated. Samples were collected in triplicate at three locations upwind and downwind of scoop activity and on the scoop.

All samplers and pumps were mounted in baskets, one sampler for each method in each basket, and three baskets per site. Pumps were calibrated underground to a flow rate of 1.7

l/min \pm 2% using a Gilibrator (Gilian Instruments, Clearwater, FL) at the beginning, middle and end of each week. The average of the pre- and post-calibration was used to determine the sample flow rate. Both INCO and UMN technicians weighed the SS substrates and filters. Each technician weighed the substrate and filter before and after sample collection on a different microbalance. The difference between the post-weight and pre-weight mass is the mass collected during sampling. This mass is used to calculate sample concentrations. In addition, the UMN technician pre- and post-weighed all SS samples in a temperature and humidity controlled environment at the University. RCD analysis was performed at the INCO laboratories, Sudbury, ON using the method developed by Maggs, Grigg, and Maskery in the mid-1970s (Hews and Rutherford, 1973, Rutherford, et al. 1977, Maskery, 1998). The EC samples were collected without the 0.8 μ m impactor and were analyzed by Sunset Laboratories, Inc., Forest Grove, OR using NIOSH method 5040.

The major findings of this study were:

- There was no significant difference between the RCD and SS sampling methods. RCD measurements made using 0.8 μ m silver membrane filters were more closely correlated with the SS method than were measurements made using 5.0 μ m silver membrane filters.
- The TC concentration was strongly correlated with results from the RCD and SS sampling measurement methods. Approximately 50% of the total carbonaceous aerosol carbon was composed of elemental carbon.

3.2. 1997 Creighton Mine Study

In 1997, DEEP funded a study of biodiesel fuel at the Creighton mine (Watts, *et al.*, 1998). The goal of the investigation was to determine the impact of a blended biodiesel fuel and oxidation catalyst on exhaust emissions and air quality. The study characterized the concentration of DPM and exhaust gas emissions in a non-producing test section. During the first week of the evaluation a diesel-powered scoop was operated on low sulfur, number 2-diesel fuel (D2). During the second week the scoop was operated on a 58 % (by mass) blend of soy methyl ester (SME) biodiesel fuel and a low sulfur D2. During both weeks the scoop was equipped with a pair of identical, advanced design diesel oxidation catalysts (DOC). Data were collected in such a way as to allow comparison of the three sampling methods, but the comparison was not within the scope of the research program.

Arrays of SS, RCD, and EC samplers were co-located in baskets upwind (air intake), downwind (air exhaust) and on the diesel scoop, one sampler for each method in each basket, three baskets per site⁶. All samples were collected in triplicate over 10 days for a total of 270 samples (3 samples x 3 sample types x 3 sample locations x 10 days = 270 samples). The EC samples were collected without the 0.8 μ m impactor.

⁶These sampling locations were nearly the same locations used in the 1996 Creighton study.

Twenty additional EC samples were used to assess aerosol stratification at the down wind location. Three laboratories analyzed the EC samples; NIOSH, CANMET and IGF in Germany⁷. NIOSH analyzed every sample while the other two labs analyzed a subset of samples. NIOSH and CANMET used NIOSH method 5040 while IGF used the coulometric method (ZH 1.120/44, 1995) developed by Dr. Dahmann.

SS, RCD, and SS samplers were operated at a flow rate of 1.7 l/m. Pumps (MSA, Pittsburgh, PA) were calibrated in the test section's underground refuge shelter at the beginning, middle and end of each week. Gilibrators were used for pump calibration.

The University of Minnesota analyzed all SS samples gravimetrically. Inco analyzed the RCD samples as discussed previously. All EC samples (137) were analyzed by NIOSH using NIOSH method 5040 (NIOSH, 1996).

Results obtained from the SS, RCD and EC samples demonstrated that the combination of the blended biodiesel fuel and DOCs decreased TC by 21.4 ± 0.98 %. EC was reduced by 28.6 ± 0.87 % and OC was reduced 6.0 ± 3.32 % although the OC reduction was not statistically significant. Gas sampling demonstrated a slight, but statistically insignificant, increase in NO₂ concentrations measured at the downwind location and a corresponding decrease in NO emissions, which was also statistically insignificant. SO₂ levels were low during both weeks of testing.

3.3. 1997 Brunswick Mine Study

In 1997, DEEP funded a project to determine the impact of high sulfide ore dust on the three sampling methods (Grenier, *et al.*, 1998). This study also evaluated the three methods for measuring worker exposure to DPM. Previous sampling in Canadian mines had uncovered cases where RCD samples were rejected because of suspected interference between sulfide ore dust and the RCD method. The hypothesis was that oxidation of sulfide minerals on the filter caused the sample to gain mass during the ashing process. The first goal of the project was to investigate the impact of the presence of respirable sulfides on the RCD method. The second goal was to compare the three methods under high DPM and mixed sulfide mineral dust and DPM conditions.

The study took place at Noranda's Brunswick Mine. This is a lead-zinc mine in a massive sulfide ore body. Two sites were sampled, the 725-2 and the 125-5. The 725-2 sub-level was used to compare the three sampling methods during the first week of the study. The second week was conducted at the 725-2 location in a mixed diesel/mineral dust atmosphere to evaluate the impact of respirable sulfide ore dust on the RCD method. Sampling was conducted in a similar fashion as the studies described above with intake, vehicle and exhaust sampling

⁷ A comparison of these data was published by Birch, M., Dahmann, D., and Fricke, H. 1999. Comparison of two analysis methods for monitoring diesel particulate levels in mines. *J. Environ. Monit.* 1:541-544.

locations. The test vehicle was a Wagner ST8B scooptram powered by a Detroit Diesel Series 60, DDEC III, 325 hp engine that had received regular preventive maintenance. The vehicle was equipped with an ECS 12 DM oxidation catalyst. Fuel sulfur content was 0.044 wt%. The ventilation air requirement was 23,725 cfm (11.2 m³/s).

A total of 525 DPM samples were collected (315 RCD, 105 SS and 105 EC/OC samples). The samples were equally divided between the three sampling locations and between the two weeks. The EC samples were collected without the 0.8 µm impactor. Further details on this study are available elsewhere (Grenier, *et al.*, 1998).

The study did not find evidence linking the presence of sulfide minerals to interference with the RCD method. The study concluded that the SS, RCD and TC performed well and that as long as the PELs remain above 0.6 mg/m³ the gravimetric methods can be used in sulfide mines. Below these levels methods such as the NIOSH 5040 thermo-optical method should be considered.

4. TYPES OF MEASUREMENTS AVAILABLE AND STATISTICAL ANALYSIS

The first objective was to assemble the available field data in a format conducive to appropriate statistical analyses, perform these analyses in so consistent a manner as the various data sets permit, and use the results to compare the methods (SS, RCD, EC and TC) with respect to their (a) specificity, (b) sensitivity, (c) accuracy and (d) detection limits. In essence, this constitutes a meta-analysis of the available data and provides information over a broader range of mining conditions and DPM concentrations than any of the individual studies.

- (a) *Specificity*, or *selectivity*, refers to the extent to which DPM can be measured by a particular method without interference due to the presence of other substances. In the presence of interferant thought to affect one measurement method but not another, the average effect of the interferants will be modeled as the intercept of the calibration curve relating the two measurement methods.
- (b) *Sensitivity* refers to the smallest change in DPM concentration that can be measured by a particular method at a specified confidence level. To determine sensitivity the slopes of the calibration curves relating measurement methods, along with their associated standard errors were used. The EC method was selected as the reference measurement method.
- (c) Measurement *precision* is expressed as the coefficient of variance (standard deviation divided by the mean) of repeated measurements of the same aerosol. For each method, the relationship between DPM loading and measurement precision was investigated.
- (d) The *limit of detection* for the method is derived by multiplying a confidence coefficient (reflecting the level of confidence desired for establishing that a minimum level of DPM is actually present) by the ratio of the method's imprecision (as expressed by the standard

deviation of repeated measurements of the same aerosol) to its sensitivity.

Systematic differences in DPM measurements were used to evaluate relative biases in the methods, including those attributable to known interferences. These systematic differences were combined with the variability of replicated measurements to assess the accuracy of each method under various conditions. Confidence intervals were calculated for all differences observed between methods, and any such differences were tested for statistical significance.

4.1. In-mine Data Used For The Statistical Analysis

Data used in this analysis are summarized in tables 2-4.

Table 2. Sampling matrix for 1996 Creighton study

Sample Type	Number of test days	Number of daily samples by location		
		Upwind	Vehicle	Downwind
RCD 0.8 μm	8	3	3	3
Size Selective	8	3	3	3
Elemental carbon	8	3	3	3
Total carbon	8	3	3	3

Table 3. Sampling matrix for 1997 Creighton study

Sample Type	Number of test days	Number of daily samples by location		
		Upwind	Vehicle	Downwind
RCD 0.8 μm	11	3	3	3
Size Selective	11	3	3	3
Elemental carbon	11	3-6	3	3-6
Total carbon	11	3-6	3	3-6

Table 4. Sampling matrix for Brunswick study

Sample Type	Number of test days	Number of daily samples by location		
		Upwind	Vehicle	Downwind
RCD 0.8 μm	10	3	3	3
Size Selective	10	3	3	3
Elemental carbon	10	3	3	3
Total carbon	10	3	3	3

Respirable Combustible Dust: Only measurements made with 0.8 μm silver membrane filters were used in the analysis. Appendix 1 summarizes the valid RCD measurements

collected in the three studies. For each sampling day, measurements were made in triplicate at three locations - upwind and downwind of the scoop activity and on the scoop vehicle.

Size Selective Sampling: Appendix 2 summarizes the valid SS measurements collected in the three studies. For each sampling day, measurements were made in triplicate at three locations - upwind and downwind of the scoop activity and on the scoop vehicle. For each set of three measurements at a location, we calculated the average mass gain, flow rate, and calculated concentration, and the coefficients of variance of the mass gain on the filter, the flow rate and the calculated concentration. For the 1996 Creighton study, three sets of gravimetric analyses were done. Only the gravimetric analysis done at the University of Minnesota⁸ were used.

Elemental Carbon (EC), Total Carbon (TC): Appendices 3 and 4 summarize the valid EC and TC measurements collected in the three studies. As in the case of RCD and SS measurements, for each sampling day, measurements were made in triplicate at three locations - upwind and downwind of the scoop activity and on the scoop vehicle. For each set of three measurements at a location, we calculated the average mass gain, flow rate, and calculated concentration, and the coefficients of variance of the mass gain on the filter, the flow rate and the calculated concentration.

Table 5 presents summary statistics for each of the measurement methods combining data from all three studies. The number of samples (N) shown in the table differs for each of the measurements because only portions of data sets were excluded. For instance, if a mass measurement was handled inappropriately causing an erroneous mass to be measured only the mass was excluded, as the pump flow rate would not have been affected.

One data anomaly in the Brunswick data set is worth mentioning: while all the measurements were made at a flow rate with a nominal or target value of 1.7 lpm, the actual flow rate values were not available. The concentration values were calculated from these target values. Therefore, during our analysis, the coefficient of variance of flow rate for measurements was taken to be zero. The authors of this study have informed us that their standard operating procedures required that pumps be pre- and post-calibrated to $1.7 \text{ lpm} \pm 5\%$, but they routinely did better than that with electronic calibrators aiming for a range of 1.69 lpm to 1.71 lpm. Therefore, while our estimates of the total CV in flow rate might be an under-estimate, the effect is rather small and will not affect the conclusions of this study.

⁸ Pre and post-weights were done at the University of Minnesota.

Table 5. Summary statistics for each measurement type for all three studies combined.

Respirable Combustible Dust							
N of cases	73	72	76	76	73	78	78
	Mass (µg)	CV of mass gain (%)	Flow Rate (lpm)	CV of Flow Rate (%)	Conc. (µg/m ³)	CV of conc. (%)	Sampling Time (min)
Minimum	13.34	0.00	1.62	0.00	21.89	0.00	134.0
Maximum	606.67	50.00	1.73	9.27	1228.38	50.00	442.67
Mean	207.70	12.88	1.70	1.27	398.21	14.14	318.06
Standard Deviation	117.60	13.09	0.02	1.80	258.43	14.68	59.85
Size Selective Sampling							
N of cases	79	80	53	51	79	78	90
	Mass (µg)	CV of mass gain (%)	Flow Rate (lpm)	CV of Flow Rate (%)	Conc. (µg/m ³)	CV of conc. (%)	Sampling Time (min)
Maximum	753.00	70.33	1.82	10.09	1468.93	70.33	442.67
Mean	225.65	17.10	1.71	2.25	421.42	15.67	315.10
Standard Deviation	129.42	16.99	0.04	2.44	237.48	15.71	63.55
Elemental Carbon							
N of cases	90	86	90	86	90	86	90
	Mass (µg)	CV of mass gain (%)	Flow Rate (lpm)	CV of Flow Rate (%)	Conc. (µg/m ³)	CV of conc. (%)	Sampling Time (min)
Maximum	315.07	62.34	1.79	14.18	617.78	97.91	444.00
Mean	79.18	17.08	1.69	3.46	148.50	17.55	314.56
Standard Deviation	59.60	16.73	0.05	3.82	112.23	18.33	64.02
Total Carbon							
N of cases	90	86	90	86	90	86	90
	Mass (µg)	CV of mass gain (%)	Flow Rate (lpm)	CV of Flow Rate (%)	Conc. (µg/m ³)	CV of conc. (%)	Sampling Time (min)
Maximum	460.72	60.78	1.79	14.18	903.38	91.37	444.00
Mean	137.79	15.89	1.69	3.46	264.17	16.40	314.56
Standard Deviation	97.44	14.94	0.05	3.82	181.99	16.75	64.02

5. ERRORS AND VARIABILITY IN THE MEASUREMENT PROCESS

The four most common sources of uncertainty in industrial hygiene sampling are statistical sampling, interferences, reproducibility of the measurement, and variability of blank levels (Watson et al., 1995; Baron and Heitbrink, 1993).

Statistical sampling error arises because only a portion of the air is measured at a few locations for a limited period of time. The sample is assumed to be representative of the air in the area under study. In the case of diesel aerosol, this assumption may not always be justified. Diesel exhaust exits the tailpipe in a hot gas stream. Over time and distance, the aerosol is mixed in the ventilation air stream. Aerosol stratification occurs if the aerosol is not thoroughly mixed. This results in different concentrations of aerosol being measured at different locations within the same vertical plane. Thus, it is expected that the aerosol concentration measured on the scoop vehicle would be more variable than far upstream or downstream of the scoop, since the aerosol would have less time to become completely mixed near the vehicle.

Besides the error due to spatial differences, variability or imprecision of diesel exhaust concentration measurements is caused by (a) weighing errors, and (b) variability in the flow rate. For concentrations measurements derived from gravimetric measurements, the concentration is calculated as:

$$C = \frac{M}{Q \cdot t} \quad (1)$$

where M is the mass collected on the filter, Q is the flow rate of the pump, and t is the sampling time. The precision of a measurement is defined as the standard deviation of repeated measurements of the same aerosol. The precision in the concentration C_i is related to the precision in the measurement of M_i and Q_i (assuming that the errors in determining sampling time t are negligible) by the following relationship:

$$\left(\frac{\sigma_C}{\bar{C}_i} \right)^2 = \left(\frac{\sigma_M}{\bar{M}_i} \right)^2 + \left(\frac{\sigma_Q}{\bar{Q}_i} \right)^2 \quad (2)$$

where \bar{C}_i , \bar{M}_i , and \bar{Q}_i are the arithmetic averages of the i^{th} set of replicates. This expression is

an approximation and assumes that the errors made in the determination of M and Q are independent, and σ_Q is small. A mathematical justification of this is given in Appendix 5. Thus the coefficient of variation (standard deviation of repeated measurements divided by the mean value of those measurements) of the concentration is given by

$$\begin{aligned} CV_C^2 &= CV_M^2 + CV_Q^2 \\ &= \left(\frac{\sigma_M}{\bar{M}_i} \right)^2 + \left(\frac{\sigma_Q}{\bar{Q}_i} \right)^2 \end{aligned} \quad (3)$$

Equations (2) and (3) are true for RCD and Size Selective measurements. For the case of elemental and total carbon measurements, it has been reported that

$$CV_M^2 = \frac{K^2}{M}, \quad (4)$$

i.e., the coefficient of variation is inversely proportional to the square root of the carbon loading, and $K = \frac{\sigma_M}{\sqrt{M}}$. Therefore for the case of EC and TC, Equation (2) needs to be modified by using Equation (4) for the first term on the right hand side.

The approach developed by Kogut et al. (1997) to estimate CV_C directly from multiple simultaneous measurements of the same aerosol was used in this analysis. As indicated by the summary statistics in Table 5 and the more complete data in Appendices 1-4, roughly 70 to 90 sets of measurements (for each of the methods) were made over a broad range of aerosol concentrations. Imprecision of an aerosol concentration measurement refers to the variability of measurements as they deviate from the average time-weighted concentration within a set of replicates. This will be evaluated for the four measurement methods. The estimates of CV_C in Appendices 1-4 are based on at most 3 to 6 replicates, and thus they are not reliable estimates of the true CV_C . Since the aerosol concentrations varied considerably between measurement sets, we can estimate CV_C as a function of filter loading and flow rate. While σ_M^2 and σ_Q^2 can be estimated from Equation (2) using linear regression using $\left(\frac{1}{\bar{M}_i} \right)^2$ and $\left(\frac{1}{\bar{Q}_i} \right)^2$ as the independent variables, Kogut et al. (1997) point out that, in practice, more stable estimates can be obtained through non-linear regression. Thus, σ_M^2 and σ_Q^2 can be estimated by non-linear regression using $(\bar{M}_i)^2$ and $(\bar{Q}_i)^2$ as the independent variables and an estimate of CV_C as the dependent variable in the following model:

$$CV_{ci} = \left[\left(\frac{\sigma_M}{\bar{M}_i} \right)^2 + \left(\frac{\sigma_Q}{\bar{Q}_i} \right)^2 \right]^{1/2} + \varepsilon_i \quad (5)$$

where CV_{ci} is the sample coefficient of variation observed in the i^{th} set of measurements and ε_i is the residual regression error (the difference between estimated and true values of CV_c for the i^{th} set. It should be kept in mind that Equation (5) is applicable for RCD and SS measurements. For EC and TC measurements, we need to use:

$$CV_{ci} = \left[\left(\frac{K^2}{\bar{M}_i} \right) + \left(\frac{\sigma_Q}{\bar{Q}_i} \right)^2 \right]^{1/2} + \varepsilon_i \quad (6)$$

where, as before, $\sigma_M = K\sqrt{M}$. To obtain a sense of the relative contributions of CV_M^2 and CV_Q^2 , we plotted these against \bar{M}_i and \bar{Q}_i respectively for the four types of measurement methods. These are shown in Figures 1-8. It is clear that imprecision in weighing is the major contributor to total variability (as much as 60-70%), and the imprecision in flow rate measurements is minor in comparison (less than 5-10%). The plots of CV(weight gain) versus weight gain show a decrease in the CV with increase in weight gain. This is because the weight gain is calculated by subtracting pre-exposure weights from post-exposure weights. Since the weight gain is a very small percent of the total mass being weighed, weighing errors can be assumed to be independent of sampling time and quantity of dust collected, leading to a decrease in the CV of weight gain with increase in weight gain. The plots of CV(flow rate) versus flow rate show no such trend. This is because flow rate is supposed to be set to a fixed value of 1.7 lpm, and the variability in flow rate is distributed randomly around this central value.

In Figures 1, 3, 5, and 7 measurements are grouped according to whether or not they were made in the vicinity of the scoop vehicle. All these plots show a higher CV for measurements made near the vicinity of the scoop vehicle compared to measurements made upwind or downwind of the vehicle. This is because spatial variability is likely to be more near a vehicle. This was the case for all four types of measurements.

To account for this contribution to total variability, the regression model was modified by including the effect of location of sampling (near the vehicle or away from the vehicle) for each of the three studies. The revised model (for RCD and SS measurements) is now given as:

$$CV_{c_i} = \left[\left(\frac{\sigma_M}{\overline{M}_i} \right)^2 + \left(\frac{\sigma_Q}{\overline{Q}_i} \right)^2 + vehicle x \left(\begin{array}{l} Creighton1996 * Veh1 \\ + Creighton1997 * Veh2 + Brunswick * Veh3 \end{array} \right) \right]^{1/2} + \varepsilon_i \quad (7)$$

where *vehicle* is a categorical variable which takes a value of 1 when the measurement location is near a vehicle and 0 otherwise, *Creighton1996*, *Creighton1997*, and *Brunswick* are categorical variables denoting each study (taking values of 0 or 1), and *Veh1*, *Veh2*, and *Veh3* are regression coefficients that describe the effect of sampling location in each study. A similar model for EC and TC measurements is given as:

$$CV_{c_i} = \left[\left(\frac{K^2}{\overline{M}_i} \right) + \left(\frac{\sigma_Q}{\overline{Q}_i} \right)^2 + vehicle x \left(\begin{array}{l} Creighton1996 * Veh1 \\ + Creighton1997 * Veh2 + Brunswick * Veh3 \end{array} \right) \right]^{1/2} + \varepsilon_i \quad (8)$$

Results of nonlinear regression analyses for the four methods are shown in Tables 6-9. These tables contain estimates of σ_M and σ_Q , the percent contribution of the sampling location to total variability, along with the standard error of the regression estimate, σ_ε . The tables also show the symmetric Wald 95% confidence intervals for the estimates of the parameters.

Table 6. Results of 70-point regression analysis for RCD measurements ($R^2_{adj} = 0.5$).

Parameter	Least Squares Estimate	Asymptotic Standard Error	Wald 95% Confidence Interval
σ_M (μg)	6.96	0.80	(5.35,8.56)
σ_Q (LPM)	0.10	0.04	(0.02,0.17)
<i>Veh 1</i> (percent)	4.38	7.98	(-11.57,20.32)
<i>Veh 2</i> (percent)	17.59	3.45	(10.70,24.49)
<i>Veh 3</i> (percent)	11.91	3.92	(4.08,19.74)
σ_ε (percent)	10.39	NA	NA

Table 7. Results of 75-point regression analysis for SS measurements ($R^2_{adj} = 0.29$).

Parameter	Least Squares Estimate	Asymptotic Standard Error	Wald 95% Confidence Interval
σ_M (μg)	13.05	0.12	(12.81, 13.29)
σ_Q (LPM)	0.17	0.003	(0.16, 0.18)
<i>Veh 1</i> (percent)	10.13	0.91	(8.35,11.91)
<i>Veh 2</i> (percent)	2.22	1.64	(-0.99,5.43)
<i>Veh 3</i> (percent)	5.47	0.75	(3.99,6.94)
σ_ε (percent)	14.38	NA	NA

Table 8. Results of 85-point regression analysis for EC measurements ($R^2_{adj} = 0.2$).

Parameter	Least Squares Estimate	Asymptotic Standard Error	Wald 95% Confidence Interval
σ_M (μg)	$0.49 \times \sqrt{EC \text{ loading}}$	$0.006 \times \sqrt{EC \text{ loading}}$	$(0.47 \times \sqrt{EC \text{ loading}}, 0.50 \times \sqrt{EC \text{ loading}})$
σ_Q (LPM)	0.18	0.003	(0.17, 0.185)
<i>Veh 1</i> (percent)	32.35	0.38	(31.59,33.10)
<i>Veh 2</i> (percent)	14.91	0.40	(14.12,15.69)
<i>Veh 3</i> (percent)	2.94	1.42	(0.16,5.72)
σ_ϵ (percent)	16.8	NA	NA

Table 9. Results of 84-point regression analysis for TC measurements ($R^2_{adj} = 0.2$).

Parameter	Least Squares Estimate	Asymptotic Standard Error	Wald 95% Confidence Interval
σ_M (μg)	$0.40 \times \sqrt{TC \text{ loading}}$	$0.014 \times \sqrt{TC \text{ loading}}$	$(0.37 \times \sqrt{TC \text{ loading}}, 0.42 \times \sqrt{TC \text{ loading}})$
σ_Q (LPM)	0.22	0.003	(0.211, 0.222)
<i>Veh 1</i> (percent)	29.12	0.47	(28.19,30.05)
<i>Veh 2</i> (percent)	10.65	0.50	(9.66,11.63)
<i>Veh 3</i> (percent)	2.95	1.61	(-0.21,6.12)
σ_ϵ (percent)	14.8	NA	NA

From Tables 6 and 7, we see that the weighing imprecision for the SS method is almost twice that for the RCD technique.

In Figures 9a, 10a, 11a, and 12a, the values of CV_c predicted by the regression equations, and the observed values of CV_c are plotted against the filter loading for each of the four measurement methods. The effect of sampling location on measurement imprecision is clearly seen for all four methods in these figures. Figures 9b, 10b, 11b, and 12b show the corresponding residual plots as a function of filter loading. The residuals are the differences between predicted and observed values of CV_c . These figures show enough diagnostic information to show that the data support the model reasonably well.

6. SENSITIVITY, SPECIFICITY AND LIMITS OF DETECTION

NIOSH prefers the EC measurement to be the reference method because it is subject to the least amount of interferences/biases. Figures 13-15 plot the RCD, SS, and TC measurements against the EC measurements that were made simultaneously at the same locations. The figures also show the results of linear regressions.

Ordinary least squares regression overestimates the intercepts, and hence a weighted least squares procedure was adopted. For example, in the model comparing RCD measurements with EC measurements,

$$RCD_i = \beta_0 + \beta_1 \times EC_i + \varepsilon_i \quad (9)$$

it is assumed that the errors ε_i are independent with constant variance. While the independence assumption is justifiable, we can see from Figure 13 that the variability of the errors is smaller for small values of EC than it is for large values of EC. The same is true for SSS and TC measurements. Thus it might be appropriate to give higher weights to observations with small EC values. Therefore, we chose the weights to be equal to variances of the ε_i . Thus, the weighted least squares procedure minimizes the expression

$$\sum_i \frac{1}{EC^2} (RCD_i - \beta_0 - \beta_1 \times EC_i)^2. \quad (10)$$

Table 10 shows the slopes and intercepts of the regression lines for the three calibration curves, along with their associated standard errors. The intercepts can be interpreted as the *specificity* of the measurement method. For instance, in the case of RCD vs. EC, the intercept of 25.5 ($\mu\text{g}/\text{m}^3$) means that the RCD method will give this reading when the EC method reads zero. This may be due to interferants that affect the RCD measurement method but not the EC method.

Table 10. Slopes and intercepts of the regression lines for the three calibration curves, along with the associated standard errors.

Calibration	Slope, m \pm Standard error	Intercept, b ($\mu\text{g}/\text{m}^3$) \pm Standard error	R_{adj}^2
RCD vs. EC	2.059 ± 0.173	25.5 ± 3.6	0.68
SS vs. EC	1.68 ± 0.153	96.6 ± 1.04	0.62
TC vs. EC	1.588 ± 0.10	14.76 ± 0.487	0.72

Table 11 provides estimates of the interferences to which RCD, SS, and EC are susceptible as presented by Cantrell and summarized by Watts, 1996. Such interferences pertain to both the specificity and accuracy of the methods, but the statistical methods used to obtain these estimates have not been published in detail. Our estimates shown in Table 10 suggest that except for SS, they are in the range proposed by Cantrell.

Table 11. - Comparison of method interferences.

Analytical Method	Interferences	Source Range, $\mu\text{g}/\text{m}^3$
SS	Atmosphere	1 - 30
	Coal/Ore	3 - 80
RCD*	Oil Mist	0 - 50
	Ore	0 - 10
EC	Atmosphere	0.5 - 2
	Coal/Ore	5 - 15

The slopes of the calibration curves shown in table 10 can be interpreted as the *sensitivity* of the method in relation to the EC method. It refers to the smallest change in DPM concentration that can be measured by a particular method at a specified confidence level.

The limit of detection is defined as the lowest mass or concentration level that can be determined to be statistically different from a blank. Assume that the measurements are distributed approximately normally. Let S_t represent the total value measured for the sample, S_b the value for the blank, and σ the standard deviation for the measurements. The analyte signal is the difference ($S_t - S_b$). It can be shown that for normal distributions, $(S_t - S_b) > 0$ at the 99% confidence level when that difference $(S_t - S_b) > 3\sigma$. Since we have chosen the EC measurements to be the reference measurements, all other measurement methods need to be converted to this reference. This is done using the calculated sensitivity of the method. The limit of detection for the method is thus derived by multiplying a confidence coefficient (reflecting the level of confidence desired for establishing that a minimum level of DPM is actually present) by the ratio of the method's imprecision (as expressed by the standard deviation of repeated measurements of the same aerosol) to its sensitivity. Thus,

$$LOD = 3.0x \left(\frac{\sigma_M}{m} \right) \quad (11)$$

Table 12 presents LODs for RCD, SS and TC derived from field measurements.

Table 12. Limits of detection for RCD, SS, and TC methods from field data.

Method	LOD (μg)	LOD ($\mu\text{g}/\text{m}^3$)
RCD	10.14	10.56
SS	23.3	24.3
TC (at 23 $\mu\text{g}/\text{m}^3$)	4.4	4.6

The above analysis treats the EC method as the reference method against which the other three methods are compared. The EC method itself has an estimated limit of detection in the laboratory of 0.15 µg of elemental carbon per cm² of filter, which translates to a concentration of 2 µg/m³ for a 37-mm filter, assuming sampling at 2 l/min for 8 hours (Birch and Cary, 1996). If we assume that the LOD for OC is similar to that for EC, then the LOD for TC that we have calculated from field data are remarkably close to the laboratory values.

It has been proposed that for the SS method, if the sampling flow rate is 2 L/min and gravimetric analysis is to within 0.005 mg (5 µg), then for an 8-hour sampling time, then the aerosol concentration for the fraction of aerosol less than 0.8 µm should have a theoretical limit of detection of 15 µg/m³ ±50% with a confidence level of 95 percent (Cantrell and Watts, 1997). The results of this analysis based on field data yields a somewhat higher number for the limit of detection of the SS method (24.3 µg/m³).

Similarly, the RCD method is a gravimetric method with a reported detection limit of 0.02 mg (20 µg), which corresponds to a concentration of roughly 21 µg/m³. This again is slightly higher than the value we obtained of 10.56 µg/m³.

7. DISCUSSION

The EC, RCD and SS methods measure different portions of the mine aerosol and comparisons between the methods must take this into account. The EC method measures elemental, organic and total carbon. Elemental carbon is produced under the conditions of high temperature combustion and is a sensitive and specific marker of diesel exhaust but it does not measure total DPM exposure unless an estimate of the organic carbon is included. Unfortunately, there are other sources of organic carbon other than diesel exhaust such as oil mist, blasting fumes and cigarette smoke. The RCD method measures total carbon and is subject to similar interferences plus carbon in the ore and as discussed in the 1998 Brunswick mine study sulfide ore dust may interfere with the measurement. The SS method is subject to interferences or losses due to the particle size. Some diesel aerosol may be lost because it is larger than the 0.8-µm and nondiesel aerosol < 0.8 µm is collected. All the methods are affected to some extent by adsorption of organic vapors either onto the filter as the case with ultra pure quartz fiber filters or onto the particulate collected by the filters. We believe that some of these problems are illustrated in this study as discussed below.

As mentioned previously, the level of interference determined in this analysis is higher than previously reported by Cantrell as shown in Table 11 for RCD. According to Table 11 the total interference expected for the RCD method ranges from 0 - 60 µg/m³. In this study we found when compared to EC the interference to vary between 21.9 – 29.1 µg/m³ as shown in Table 10. Part of this difference can be accounted for by the vehicle data that shows more spatial variability.

We are most familiar with the Creighton studies conducted in 1996 and 1997. During

the 1996 and 1997 studies, there was a hydraulic oil leak on the scoop that sprayed an oil mist onto deck near the sampling baskets. After a day of sampling, the baskets and samplers located on the scoop were frequently covered with hydraulic oil. The investigators believe that oil droplets formed under this condition were generally large nonrespirable particles that were removed by the cyclones on the samplers. However, gaseous volatile material and a few small oil droplets may have passed through the cyclone. The gaseous material may have adsorbed to the particulate matter collected on the filter and the small oil droplets may have collected on the filter. No correction was made for this potential contamination.

During the 1997 study at Creighton, there was also a period of time when excess fuel from the fuel tank overflowed onto the hot surface of the diesel oxidation catalyst. This created very high concentrations of smoke for short periods of time that would have had a major impact on the SS, EC and RCD measurements collected on the scoop because there was little opportunity for dilution. Again no attempt was made by the investigators to correct for this problem. This problem would have also affected the TC and SS data as the smoke would have been collected by the SS and EC samplers and included in the measurement of diesel aerosol as either aerosol $< 0.8 \mu\text{m}$ or organic carbon. These possible interferences help explain the least squares estimates shown in tables 7 – 10 and point out the need for careful assessment of potential sources of interference so that estimates of exposure can be corrected.

From Table 11 it can be seen that the level of interference for the SS method would be expected to vary from 4 – $120 \mu\text{g}/\text{m}^3$. This compares to $96 \mu\text{g}/\text{m}^3$ shown in table 10 as determined by our analysis. Our predicted level of interference is in the same range as predicted in Table 11.

There is no direct comparison between Tables 10 and 11 for EC, but we report about twice as much interference for TC as Cantrell reported for EC.

The most sensitive marker of diesel exhaust is EC. Regulations for DPM are reducing allowable level of DPM in mines. Mines are reducing concentrations of DPM underground through the use of improved engine technology, higher quality diesel fuel, better aftertreatment devices, increased ventilation, lower allowable levels, and other methods. As levels decrease the need to use EC as the measure of exposure will increase because the other methods lack the necessary sensitivity to determine exposure. However, unless care is taken to determine correct the OC measurement for non-diesel sources and to included dynamic blanks to correct for OC adsorbed by the ultra pure quartz fiber filter then the OC carbon and subsequent TC measurements will be inflated.

Future research should focus on further defining the sources of error in the three methods with the major emphasis being placed upon the EC method. A laboratory study designed to introduce potential interferences both singly and in combination should be followed by several field studies in different types of mines.

8. SUMMARY

One objective of the Diesel Emission Evaluation Program is the evaluation of diesel aerosol measurement methodologies. Three sampling methods are used in mines to determine the concentration of DPM. The methods are the SS method, the RCD method, and the EC method. The statistical analysis described in this report compares the three methods to determine the limitations and potential applications of each.

The level of interference determined in this analysis is in the same range as previously reported by Cantrell. According to Cantrell the total interference expected for the RCD method ranges from 0 - 60 $\mu\text{g}/\text{m}^3$. In this study we found when compared to EC the interference to vary between 21.9 – 29.1 $\mu\text{g}/\text{m}^3$. Part of this difference can be accounted for by the vehicle data that shows more spatial variability.

According to Cantrell the level of interference for the SS method would be expected to vary from 4 – 120 $\mu\text{g}/\text{m}^3$. This compares to about 98 $\mu\text{g}/\text{m}^3$ as determined by our analysis. Our predicted level of interference is somewhat higher but some of the same factors affecting the RCD measurements would also affect the SS measurement and account for this difference.

The most sensitive and specific marker of diesel exhaust is EC, but TC provides the best estimate of total DPM exposure because EC accounts for only about 50 % of the total exposure. However, unless care is taken to determine correct the OC measurement for non-diesel sources and to included dynamic blanks to correct for OC adsorbed by the ultra pure quartz fiber filter then the OC carbon and subsequent TC measurements will be inflated.

9. FIGURES

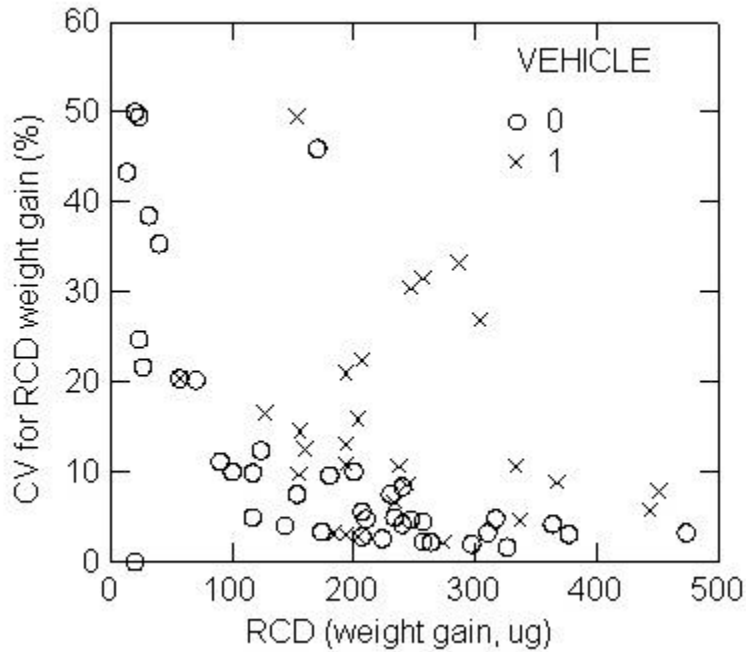


Figure 1. Coefficient of variance as a function of weight gain for RCD measurements. Measurements are grouped according to whether they were made in the proximity of a scoop vehicle or not. The circles (o) refer to data obtained upwind or downwind of the vehicle while the crosses (x) refer to data obtained very near the scoop vehicle.

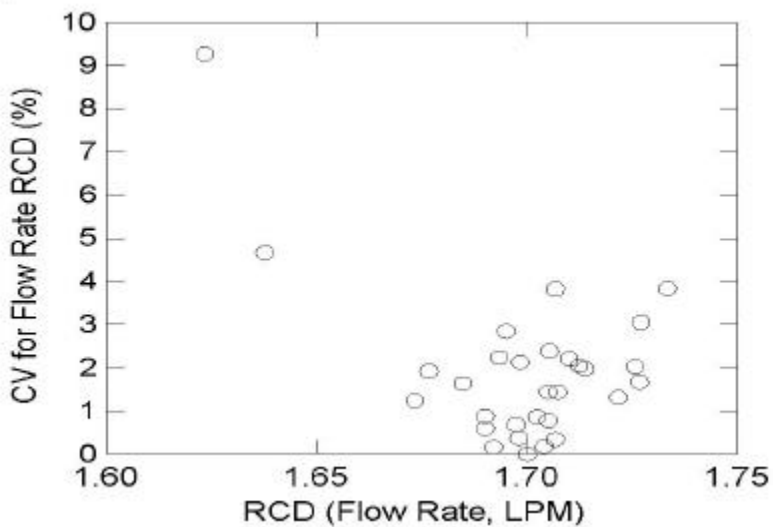


Figure 2. Coefficient of variance as a function of flow rate for RCD measurements.

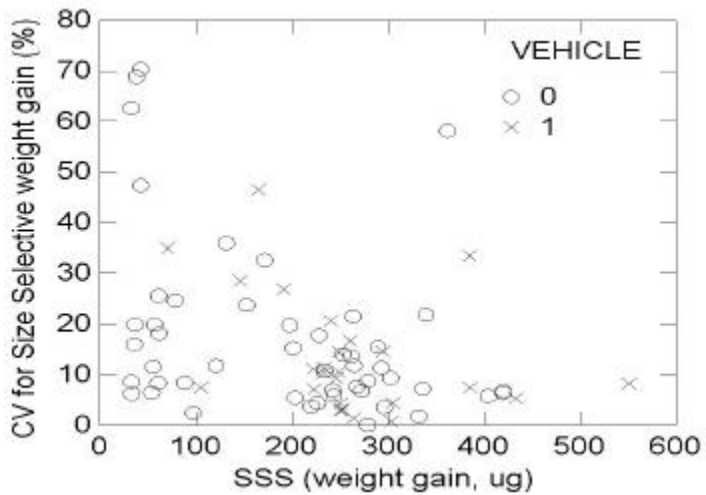


Figure 3. Coefficient of variance as a function of weight gain for SS measurements. Measurements are grouped according to whether they were made in the proximity of a scoop vehicle or not. The circles (o) refer to data obtained upwind or downwind of the vehicle while the crosses (x) refer to data obtained very near the scoop vehicle.

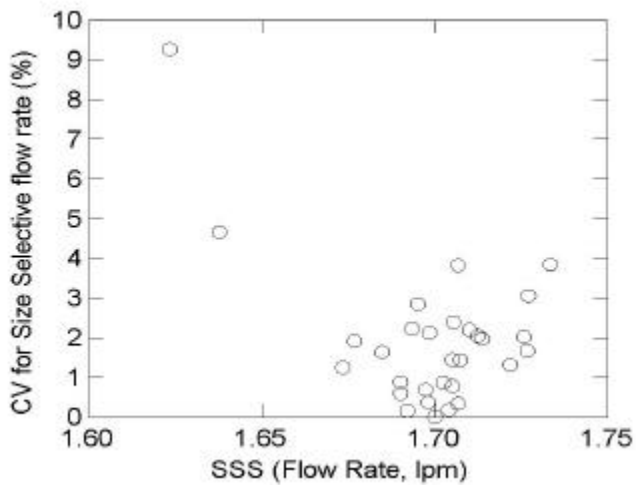


Figure 4. Coefficient of variance as a function of flow rate for SS measurements.

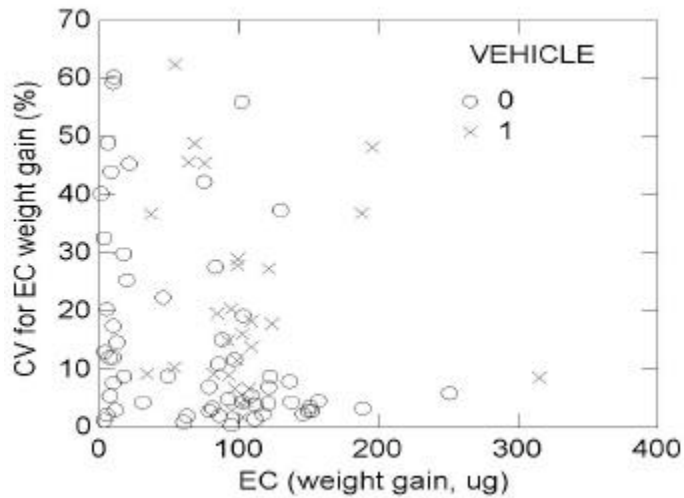


Figure 5. Coefficient of variance as a function of weight gain for EC measurements. Measurements are grouped according to whether they were made in the proximity of a scoop vehicle or not. The circles (o) refer to data obtained upwind or downwind of the vehicle while the crosses (x) refer to data obtained very near the scoop vehicle.

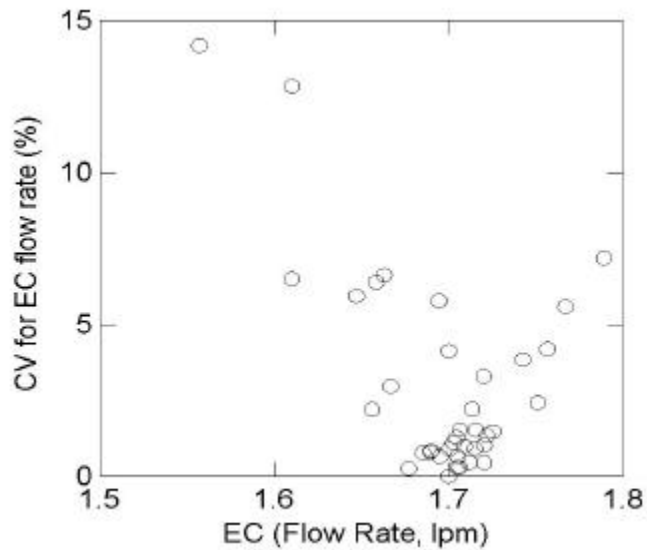


Figure 6. Coefficient of variance as a function of flow rate for EC measurements.

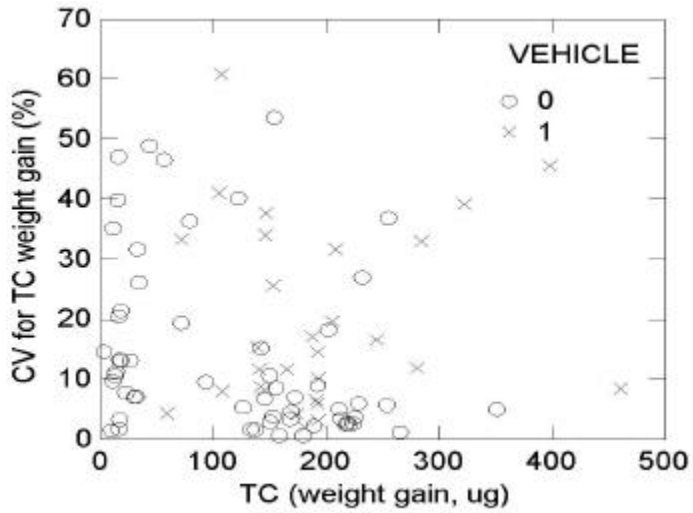


Figure 7. Coefficient of variance as a function of weight gain for TC measurements. Measurements are grouped according to whether they were made in the proximity of a scoop vehicle or not. The circles (o) refer to data obtained upwind or downwind of the vehicle while the crosses (x) refer to data obtained very near the scoop vehicle.

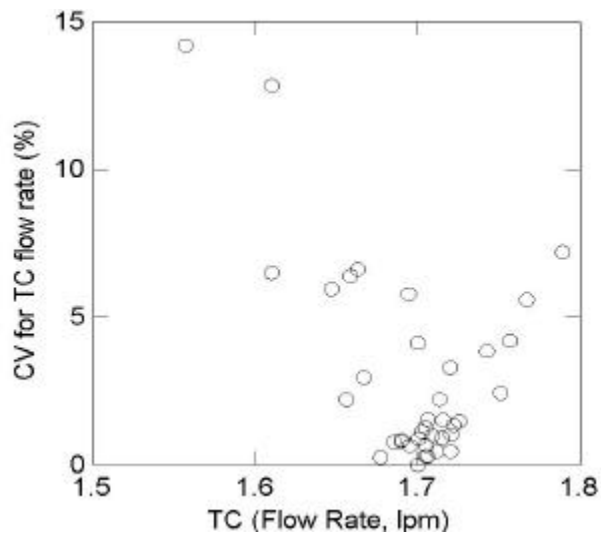


Figure 8. Coefficient of variance as a function of flow rate for TC measurements.

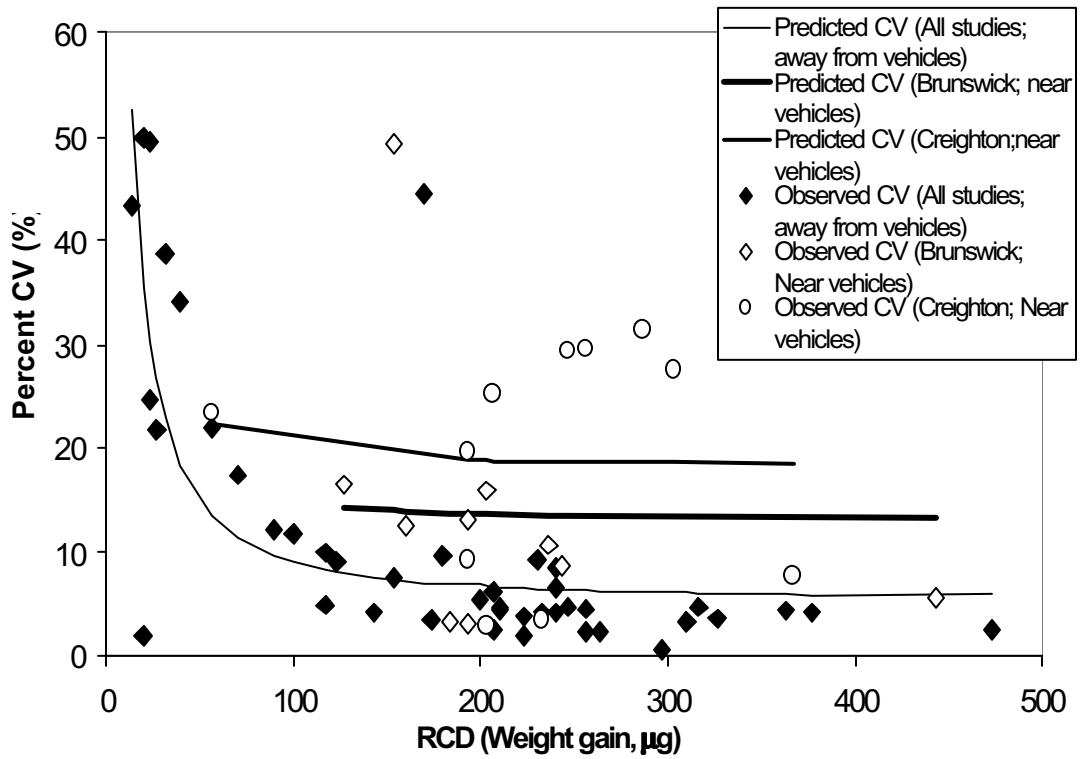


Figure 9a. Predicted and observed imprecision in RCD concentration measurement as a function of weight gain. The predicted curves are stratified by sampling near or away from scoop vehicles.

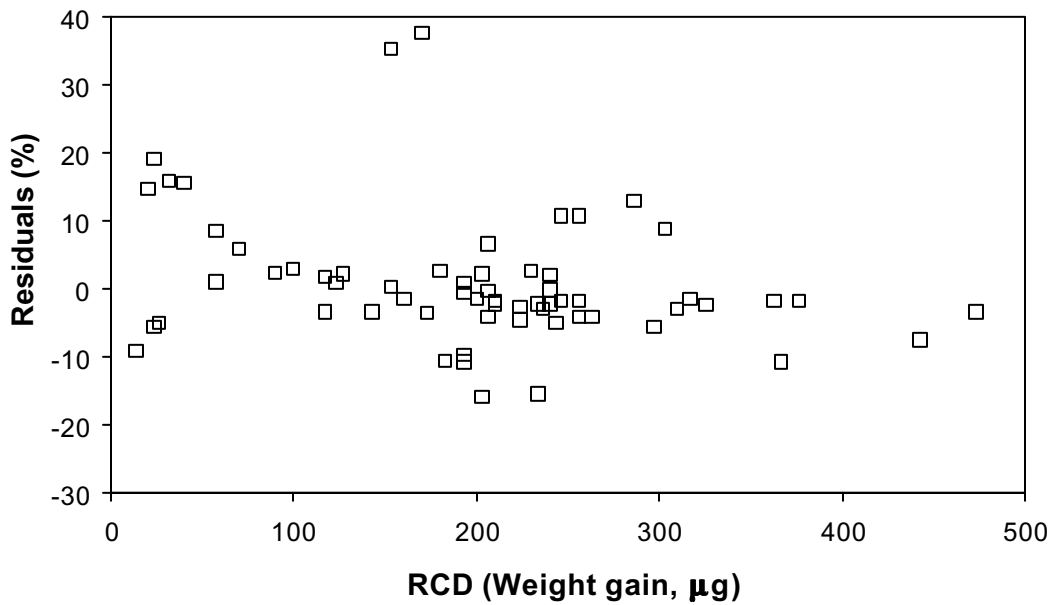


Figure 9b. Residuals between predicted as observed CV for RCD measurements as a function of weight gain.

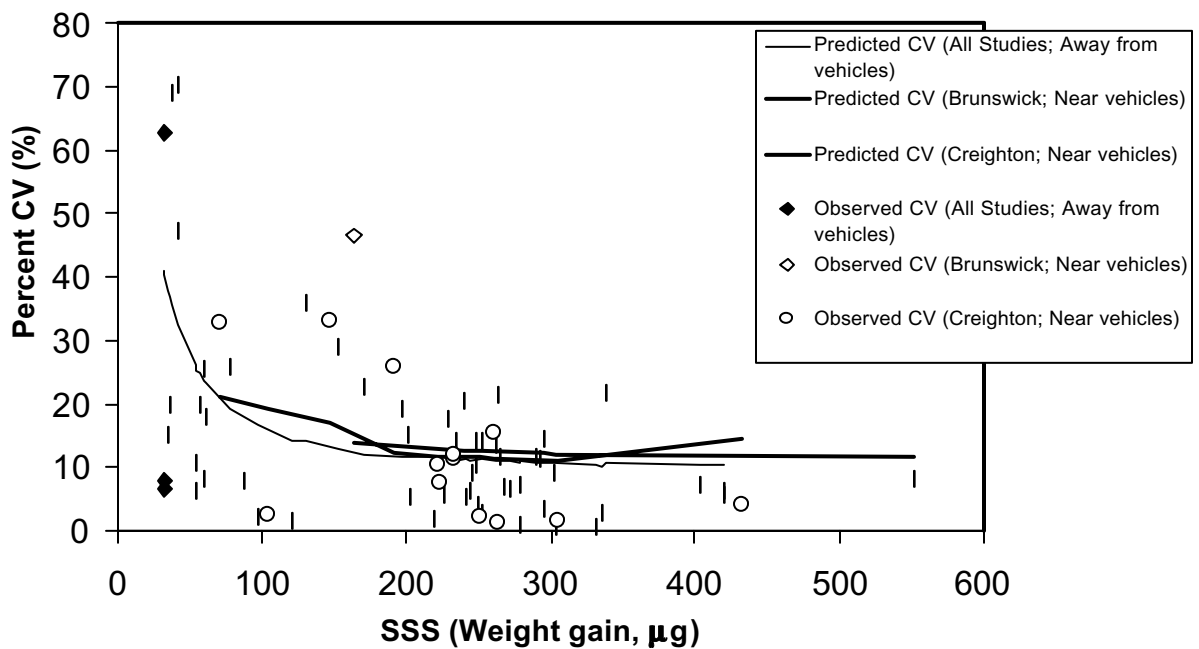


Figure 10a. Predicted and observed imprecision in SSS concentration measurement as a function of weight gain. The predicted curves are stratified by sampling near or away from scoop vehicles.

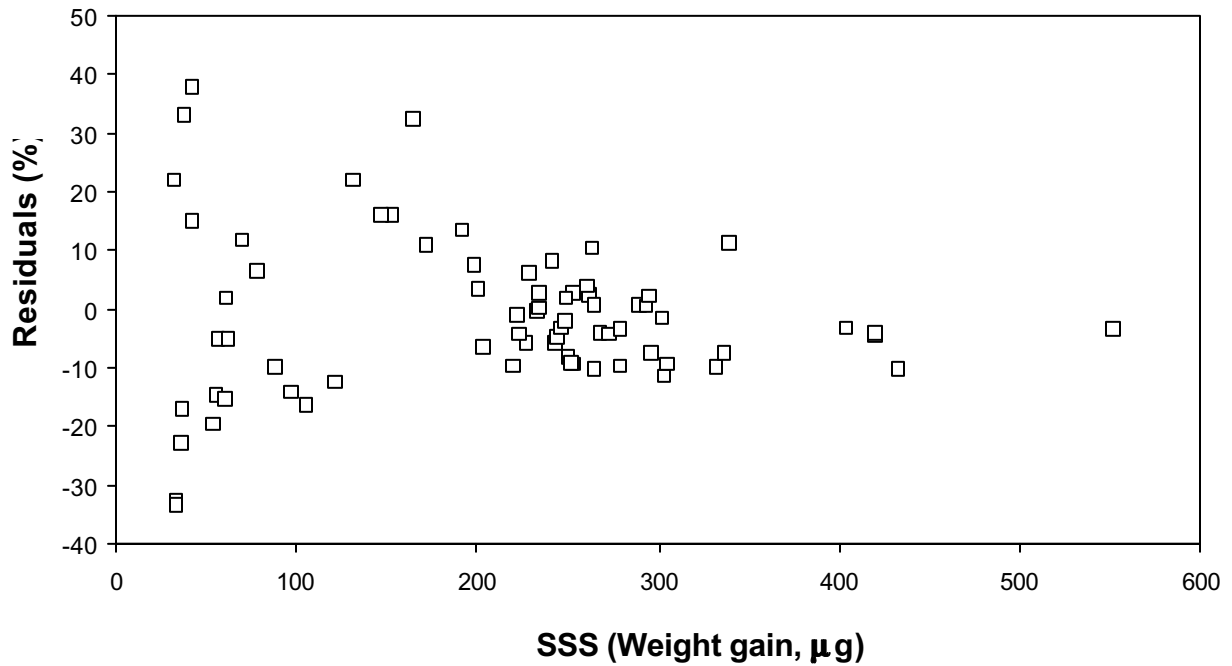


Figure 10b. Residuals between predicted as observed CV for SSS measurements as a function of weight gain.

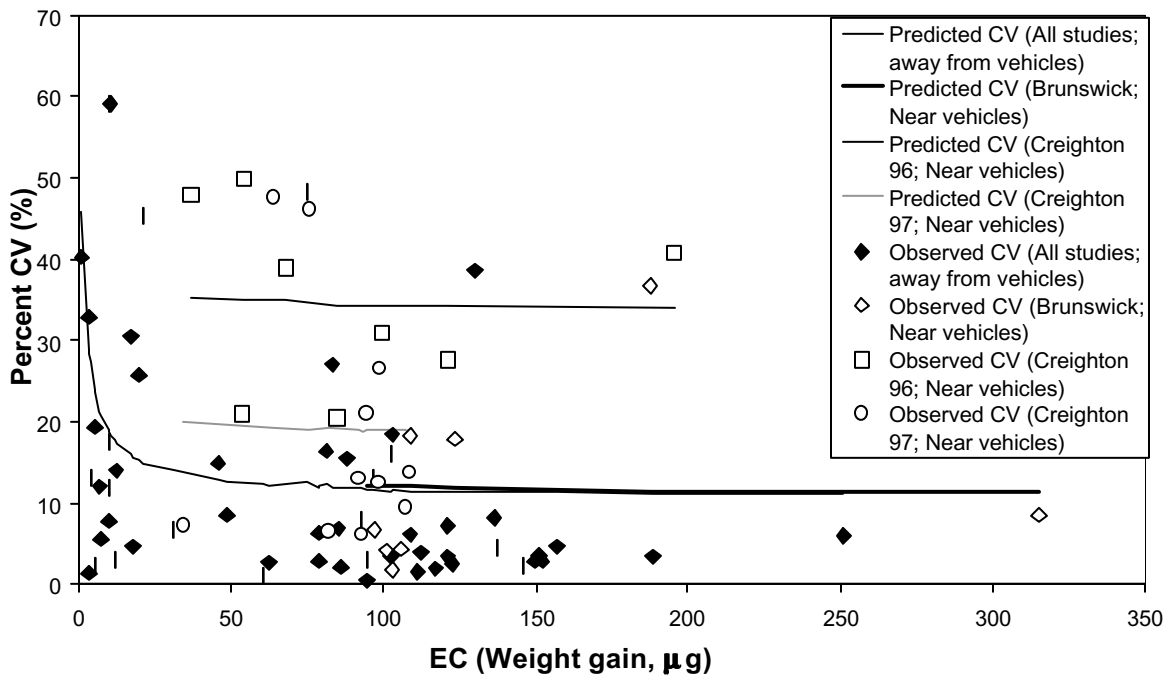


Figure 11a. Predicted and observed imprecision in EC concentration measurement as a function of weight gain. The predicted curves are stratified by sampling near or away from scoop vehicles.

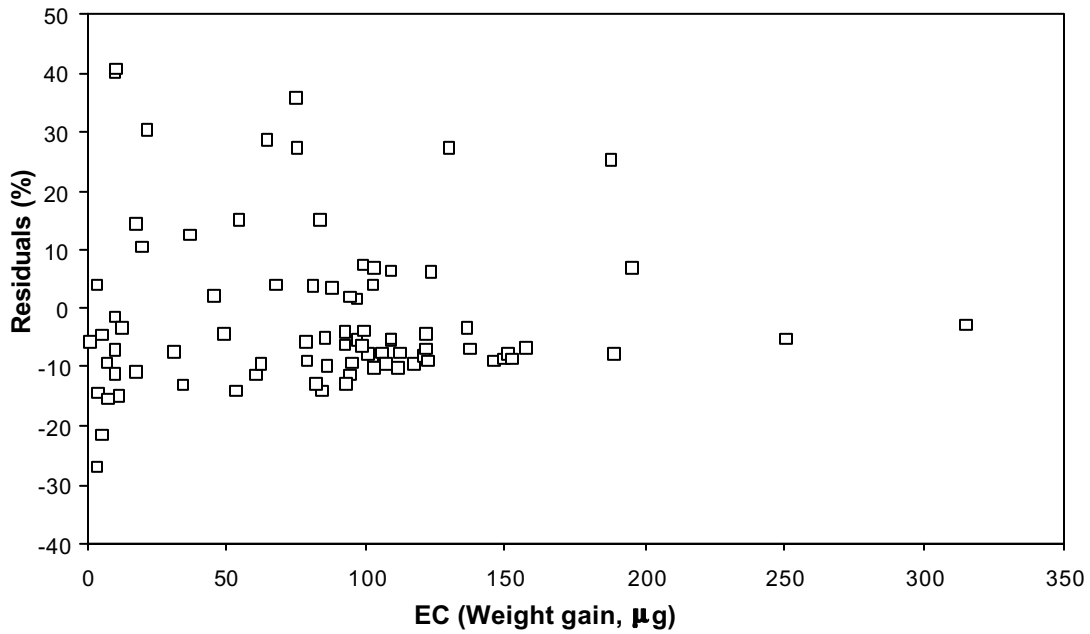


Figure 11b. Residuals between predicted as observed CV for EC measurements as a function of weight gain.

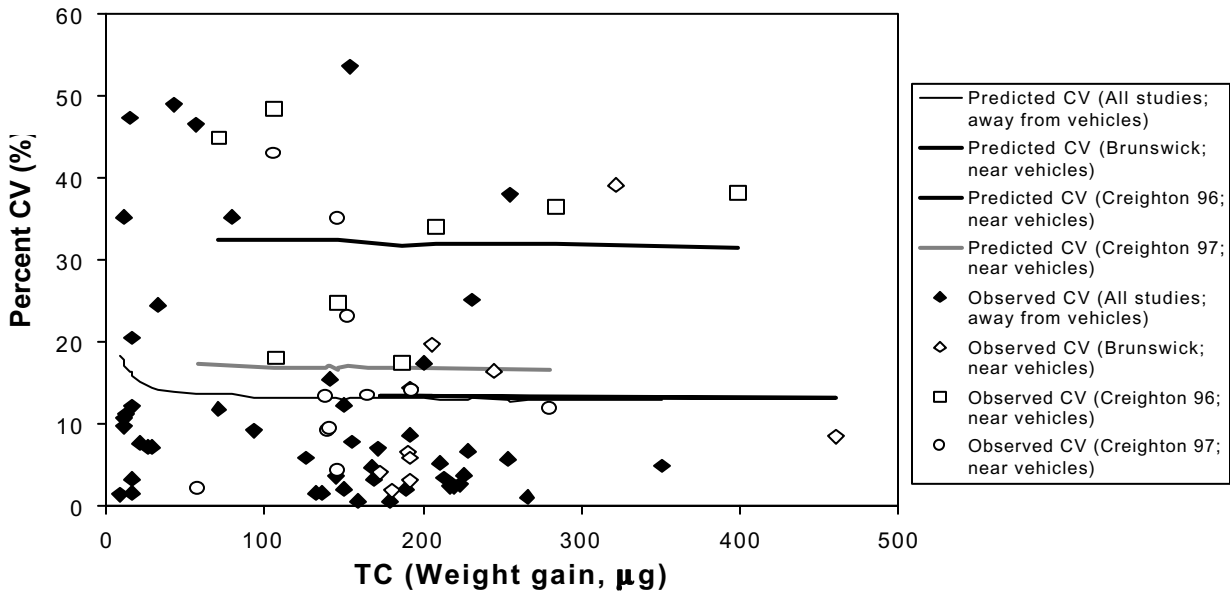


Figure 12a. Predicted and observed imprecision in TC concentration measurement as a function of weight gain. The predicted curves are stratified by sampling near or away from scoop vehicles.

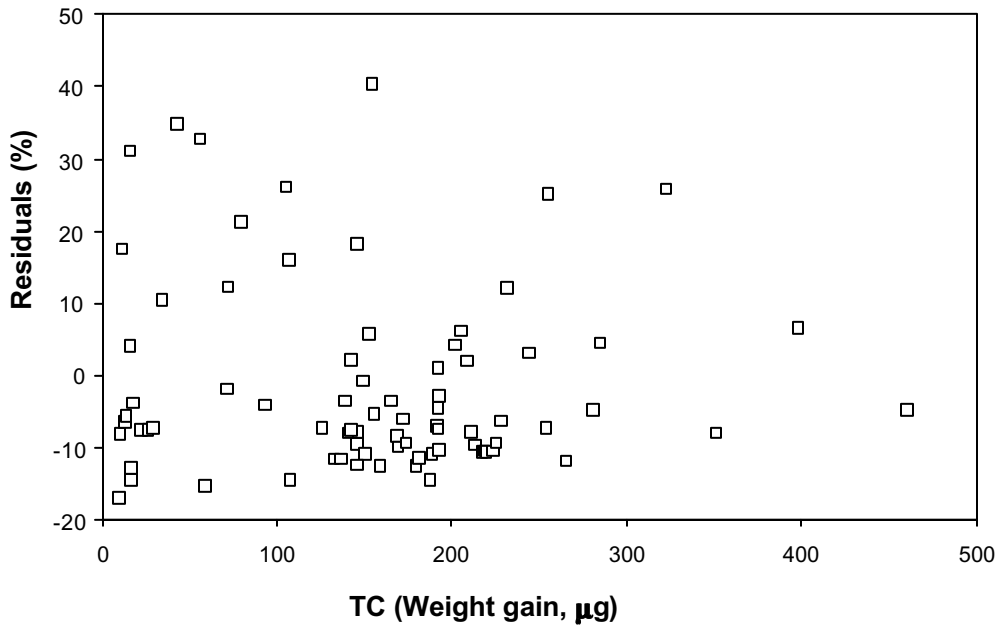


Figure 12b. Residuals between predicted as observed CV for TC measurements as a function of weight gain.

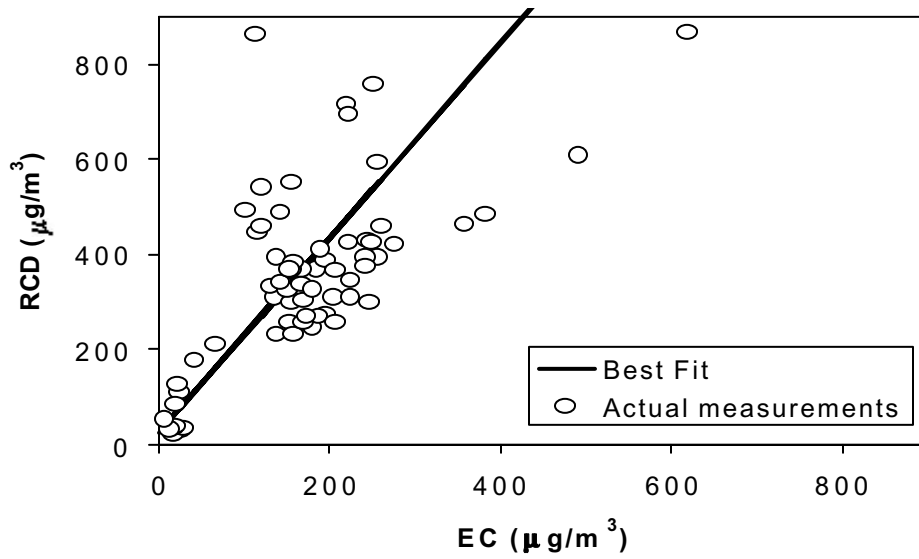


Figure 13. Calibration curve of RCD measurements vs. EC measurements.

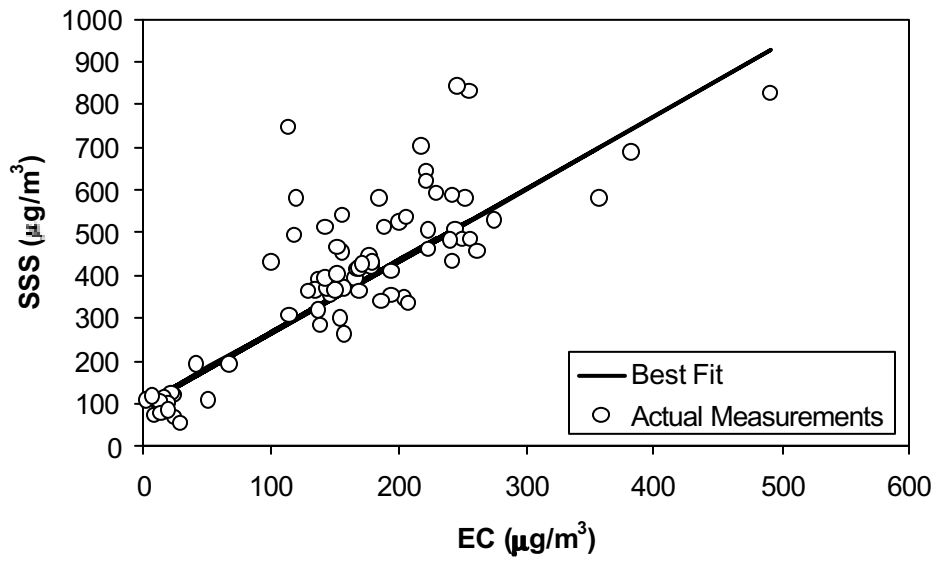


Figure 14. Calibration curve of SS measurements vs. EC measurements.

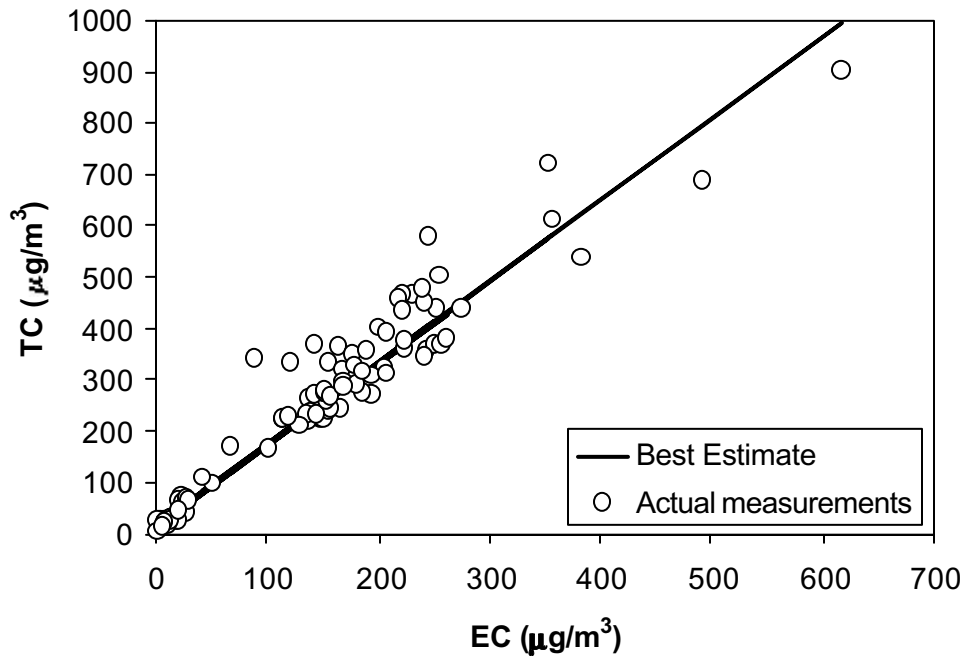


Figure 15. Calibration curve of TC measurements vs. EC measurements.

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11. APPENDICES 1,2,3,4

Appendix 1. Summary of RCD data from three studies.

Study	Day	Location	Mass (ug)	CV of mass gain (%)	N	Flow Rate (lpm)	CV of Flow Rate (%)	Conc. ($\mu\text{g}/\text{m}^3$)	CV of conc. (%)	Sampling Time (min)
Crtn '96	1	V	156.00	14.448	3	1.638	4.665	446.72	16.975	214.00
Crtn '96	2	UW	31.33	38.475	3	1.714	1.974	108.16	38.735	169.00
Crtn '96	2	V	333.33	10.536	3	1.710	2.201	1117.36	11.841	174.67
Crtn '96	2	DW	316.67	4.824	3	1.698	0.368	1187.81	4.692	157.00
Crtn '96	3	UW	100.00	10.000	3	1.714	1.974	209.47	11.814	279.00
Crtn '96	3	V	273.33	2.112	3	1.710	2.201	552.47	0.335	289.33
Crtn '96	3	DW	206.67	2.794	3	1.698	0.368	424.56	2.521	286.67
Crtn '96	4	V	606.67	3.431	3	1.690	0.876	1228.34	4.427	292.33
Crtn '96	4	DW	473.33	3.227	3	1.685	1.635	1084.75	2.434	259.00
Crtn '96	5	UW	90.00	11.111	3	1.702	0.866	176.76	12.069	299.33
Crtn '96	5	V	306.67	1.883	3	1.707	1.435	590.23	1.670	304.33
Crtn '96	5	DW	296.67	1.946	3	1.685	1.635	594.24	0.550	296.33
Crtn '96	6	UW	56.67	20.377	3	1.705	1.440	126.63	21.883	263.00
Crtn '96	6	V	336.67	4.537	3	1.705	2.385	716.95	3.510	275.33
Crtn '96	6	DW	326.00	1.623	3	1.726	2.026	694.87	3.598	272.00
Crtn '96	7	UW	40.00	35.355	2	1.712	2.045	83.81	34.061	281.00
Crtn '96	7	V	450.67	7.818	3	1.727	3.054	864.16	4.759	301.67
Crtn '96	7	DW	363.33	4.204	3	1.704	0.176	758.83	4.326	281.00
Crtn '96	8	V	154.67	9.705	3	1.727	3.054	298.16	10.510	300.67
Crtn '97	1	V	56.67	20.377	3	1.707	3.824	231.62	23.342	144.00
Crtn '97	1	DW	70.00	20.203	2	1.693	2.236	309.24	17.317	134.00
Crtn '97	2	V	206.67	22.349	3	1.707	3.824	334.29	25.315	364.00
Crtn '97	2	DW	170.00	45.943	3	1.693	2.236	273.24	44.574	365.00
Crtn '97	3	UW	20.00	0.000	3	1.677	1.917	33.33	1.927	360.33
Crtn '97	3	V	203.33	2.839	3	1.690	0.592	322.57	2.896	373.00
Crtn '97	3	DW	233.33	4.949	3	1.705	0.776	369.45	4.141	370.33
Crtn '97	4	UW	13.33	43.301	3	1.692	0.156	21.89	43.359	360.00
Crtn '97	4	V	256.67	31.492	3	1.695	2.845	395.12	29.536	382.00
Crtn '97	4	DW	223.33	2.585	3	1.673	1.244	370.38	1.943	360.33
Crtn '97	5	V	303.33	26.850	3	1.695	2.845	491.20	27.456	365.00
Crtn '97	5	DW	223.33	2.585	3	1.673	1.244	370.86	3.829	360.00

Crtn '97	6	UW	23.33	49.487	3	1.707	0.338	35.53	49.582	385.00
Crtn '97	6	V	246.67	30.428	3	1.722	1.310	383.01	29.421	373.33
Crtn '97	6	DW	240.00	4.167	3	1.623	9.268	386.47	6.478	384.00
Crtn '97	7	V	193.33	20.904	3	1.722	1.310	308.83	19.698	363.00
Crtn '97	7	DW	200.00	10.000	3	1.623	9.268	342.43	5.361	360.00
Crtn '97	8	V	193.33	10.767	3	1.733	3.841	297.25	9.138	375.00
Crtn '97	8	DW	210.00	4.762	3	1.697	0.688	334.35	4.343	370.00
Crtn '97	9	V	233.33	6.547	3	1.733	3.841	322.64	3.387	417.00
Crtn '97	9	DW	206.67	5.587	3	1.697	0.688	341.14	6.146	357.00
Crtn '97	10	V	286.67	33.155	3	1.698	2.130	459.15	31.419	366.33
Crtn '97	10	DW	230.00	7.531	3	1.727	1.672	370.39	9.107	360.00
Crtn '97	11	V	366.67	8.767	3	1.698	2.130	487.49	7.740	442.67
Crtn '97	11	DW	376.67	3.066	3	1.727	1.672	541.50	4.154	403.00
B'wick	1	Intake	20.00	50.000	3	1.700	0.000	35.65	50.000	330.00
B'wick	1	Exhaust	256.67	2.249	3	1.700	0.000	430.14	2.249	351.00
B'wick	1	Vehicle	236.67	10.634	3	1.700	0.000	410.67	10.634	339.00
B'wick	2	Exhaust	256.67	4.499	3	1.700	0.000	425.30	4.499	355.00
B'wick	2	Vehicle	203.33	15.809	3	1.700	0.000	338.83	15.809	353.00
B'wick	3	Intake	23.33	24.744	3	1.700	0.000	38.66	24.744	355.00
B'wick	3	Exhaust	240.00	8.333	3	1.700	0.000	392.16	8.333	360.00
B'wick	3	Vehicle	183.33	3.149	3	1.700	0.000	302.08	3.149	357.00
B'wick	4	Intake	20.00		3	1.700	0.000	32.32		364.00
B'wick	4	Exhaust	246.67	4.681	3	1.700	0.000	392.16	4.681	370.00
B'wick	4	Vehicle	160.00	12.500	3	1.700	0.000	256.45	12.500	367.00
B'wick	5	Exhaust	263.33	2.192	3	1.700	0.000	461.02	2.192	336.00
B'wick	5	Vehicle	193.33	2.986	3	1.700	0.000	326.80	2.986	348.00
B'wick	6	Far Exhaust	240.00	4.167	3	1.700	0.000	486.82	4.167	290.00
B'wick	6	Near Exhaust	310.00	3.226	3	1.700	0.000	607.84	3.226	300.00
B'wick	6	Vehicle	443.33	5.677	3	1.700	0.000	869.28	5.677	300.00
B'wick	7	Intake			2	1.700	0.000			295.00
B'wick	7	Far Exhaust	153.33	7.531	3	1.700	0.000	307.84	7.531	293.00
B'wick	7	Near Exhaust	173.33	3.331	3	1.700	0.000	345.63	3.331	295.00
B'wick	7	Vehicle	193.33	13.017	3	1.700	0.000	376.57	13.017	302.00
B'wick	8	Intake			3	1.700	0.000			301.00

B'wick	8	Far Exhaust	180.00	9.623	3	1.700	0.000	365.11	9.623	290.00
B'wick	8	Near Exhaust	210.00	4.762	3	1.700	0.000	420.17	4.762	294.00
B'wick	8	Vehicle	243.33	8.555	3	1.700	0.000	463.23	8.555	309.00
B'wick	9	Intake	26.67	21.651	3	1.700	0.000	54.09	21.651	290.00
B'wick	9	Far Exhaust	116.67	4.949	3	1.700	0.000	245.10	4.949	280.00
B'wick	9	Near Exhaust	123.33	12.385	3	1.700	0.000	269.63	8.894	268.67
B'wick	9	Vehicle	126.67	16.434	3	1.700	0.000	256.93	16.434	290.00
B'wick	10	Intake			0	1.700	0.000			341.00
B'wick	10	Far Exhaust	116.67	9.897	3	1.700	0.000	232.64	9.897	295.00
B'wick	10	Near Exhaust	143.33	4.028	3	1.700	0.000	257.05	4.028	328.00
B'wick	10	Vehicle	153.33	49.382	3	1.700	0.000	271.67	49.382	332.00

Abbreviations: Crtn '96 Creighton mine 1996, Crtn '97 Creighton mine 1997, B'wick Brunswick mine 1998, UW Upwind, V Vehicle, DW Downwind, N number of samples, CV Coefficient of variation, Conc. Concentration.

Appendix 2. Summary of SS data from three studies

Study	Day	Location	Mass (ug)	CV of mass gain (%)	N	Flow Rate (lpm)	CV of Flow Rate (%)	Conc. ($\mu\text{g}/\text{m}^3$)	CV of conc. (%)	Sampling Time (min)
Crtn '96	1	UW	35.67	15.943	3	1.677	0.621	105.88	15.093	200.67
Crtn '96	1	V	105.50	7.373	2	1.612	5.397	305.78	2.640	214.00
Crtn '96	1	DW	121.00	11.688	2	1.822	10.090	319.02	1.607	207.67
Crtn '96	2	UW	33.33	6.245	3	1.677	0.621	117.62	6.846	169.00
Crtn '96	2	V	146.50	28.477	2	1.612	5.397	525.38	33.234	174.67
Crtn '96	2	DW	171.50	32.572	2	1.822	10.090	592.70	22.857	157.00
Crtn '96	3	UW	88.33	8.345	3	1.677	0.621	188.71	7.855	279.00
Crtn '96	3	V	250.00	2.828	2	1.612	5.397	538.98	8.463	289.33
Crtn '96	3	DW	336.00	7.155	2	1.822	10.090	644.61	2.699	286.67
Crtn '96	4	V	274.00	4.645	2	1.683	1.555	559.82	5.713	292.33
Crtn '96	4	DW	197.50	19.692	2	1.708	0.580	445.47	19.390	259.00
Crtn '96	5	UW	97.33	2.373	3	1.703	0.189	190.98	2.370	299.33
Crtn '96	5	V	753.00	39.252	2	1.683	1.555	1468.93	40.471	304.33

Crtn '96	5	DW	420.00	6.734	2	1.708	0.580	830.49	5.679	296.33
Crtn '96	6	UW	55.50	11.467	2	1.712	0.497	123.08	10.811	263.00
Crtn '96	7	V	385.00	33.427	2	1.711	1.157	746.16	32.332	301.67
Crtn '96	7	DW	279.00	0.000	2	1.718	1.070	577.96	1.070	281.00
Crtn '96	8	UW	33.00	8.571	2	1.708	0.124	67.09	7.958	288.33
Crtn '96	8	V	433.00	5.226	2	1.711	1.157	840.56	4.070	300.67
Crtn '96	8	DW	332.00	1.704	2	1.718	1.070	585.58	0.634	329.67
Crtn '97	1	V	70.50	34.947	3	1.736	2.353	280.69	32.989	144.00
Crtn '97	1	DW	78.50	24.570	3	1.697	2.178	345.99	25.913	134.00
Crtn '97	2	V	222.17	11.047	3	1.736	2.353	351.54	10.540	364.00
Crtn '97	2	DW	219.83	3.677	3	1.697	2.178	354.78	1.890	365.00
Crtn '97	3	V	233.17	10.367	3	1.703	0.904	367.31	11.233	373.00
Crtn '97	3	DW	361.83	58.081	3	1.691	0.246	578.01	58.243	370.33
Crtn '97	4	V	252.17	2.923	3	1.697	0.681	389.03	2.254	382.00
Crtn '97	4	DW	242.50	6.937	3	1.708	1.715	393.73	5.423	360.33
Crtn '97	5	V	264.50	1.310	3	1.697	0.681	427.11	1.139	365.00
Crtn '97	5	DW	279.17	8.666	3	1.708	1.715	453.66	7.363	360.00
Crtn '97	6	UW	32.83	62.591	3	1.694	0.481	50.42	62.954	385.00
Crtn '97	6	V	233.50	11.160	3	1.696	1.476	369.13	11.977	373.33
Crtn '97	6	DW	267.83	7.655	3	1.700	1.765	410.19	7.008	384.00
Crtn '97	7	V	223.50	7.032	3	1.696	1.476	363.23	7.554	363.00
Crtn '97	7	DW	226.83	4.349	3	1.700	1.765	370.87	5.823	360.00
Crtn '97	8	V	191.17	26.828	3	1.700	1.765	299.26	25.879	375.00
Crtn '97	8	DW	233.83	10.694	3	1.748	5.038	362.80	14.056	370.00
Crtn '97	9	V	260.50	16.609	3	1.700	1.765	367.05	15.304	417.00
Crtn '97	9	DW	243.83	5.834	3	1.748	5.038	391.02	6.206	357.00
Crtn '97	10	V	305.17	4.364	3	1.697	2.657	490.78	1.649	366.33
Crtn '97	10	DW	289.50	15.398	3	1.733	3.781	462.59	11.630	360.00
Crtn '97	11	V	385.17	7.418	3	1.697	2.657	513.45	9.222	442.67
Crtn '97	11	DW	404.17	5.735	3	1.733	3.781	579.21	7.190	403.00
B'wick	1	Intake	61.67	18.082	3	1.700	0.000	109.92	18.082	330.00
B'wick	1	Exhaust	302.67	9.300	3	1.700	0.000	507.23	9.300	351.00
B'wick	1	Vehicle	294.67	14.515	3	1.700	0.000	511.31	14.515	339.00
B'wick	2	Intake	42.33	47.323	3	1.700	0.000	73.24	47.323	340.00
B'wick	2	Exhaust	293.00	11.314	3	1.700	0.000	485.50	11.314	355.00
B'wick	2	Vehicle	248.33	10.511	3	1.700	0.000	413.82	10.511	353.00
B'wick	3	Intake	60.67	8.297	3	1.700	0.000	100.52	8.297	355.00
B'wick	3	Exhaust	296.00	3.527	3	1.700	0.000	483.66	3.527	360.00

B'wick	3	Vehicle	253.00	3.087	3	1.700	0.000	416.87	3.087	357.00
B'wick	4	Intake	61.00	25.555	3	1.700	0.000	98.58	25.555	364.00
B'wick	4	Exhaust	272.33	6.794	3	1.700	0.000	432.96	6.794	370.00
B'wick	4	Vehicle	249.00	14.430	3	1.700	0.000	399.10	14.430	367.00
B'wick	5	Intake	36.67	19.869	3	1.700	0.000	104.67	19.869	340.00
B'wick	5	Exhaust	261.67	13.621	3	1.700	0.000	458.10	13.621	336.00
B'wick	5	Vehicle	250.00	4.233	3	1.700	0.000	422.58	4.233	348.00
B'wick	6	Intake	38.00	68.825	3	1.700	0.000	74.51	68.825	300.00
B'wick	6	Far Exhaust	339.33	21.778	3	1.700	0.000	688.30	21.778	290.00
B'wick	6	Near Exhaust	420.00	6.349	3	1.700	0.000	823.53	6.349	300.00
B'wick	6	Vehicle	551.00	8.191	3	1.700	0.000	1080.39	8.191	300.00
B'wick	7	Intake	54.00	6.415	3	1.700	0.000	107.68	6.415	295.00
B'wick	7	Far Exhaust	228.33	17.684	3	1.700	0.000	458.41	17.684	293.00
B'wick	7	Near Exhaust	253.00	14.036	3	1.700	0.000	504.49	14.036	295.00
B'wick	7	Vehicle	246.33	9.366	3	1.700	0.000	479.81	9.366	302.00
B'wick	8	Intake	42.33	70.326	3	1.700	0.000	82.73	70.326	301.00
B'wick	8	Far Exhaust	264.67	11.745	3	1.700	0.000	536.85	11.745	290.00
B'wick	8	Near Exhaust	263.67	21.459	3	1.700	0.000	527.54	21.459	294.00
B'wick	8	Vehicle	303.33	0.686	3	1.700	0.000	577.45	0.686	309.00
B'wick	9	Intake	57.00	19.840	3	1.700	0.000	115.62	19.849	290.00
B'wick	9	Far Exhaust	203.33	5.395	3	1.700	0.000	427.17	5.395	280.00
B'wick	9	Near Exhaust	152.67	23.729	3	1.700	0.000	337.61	29.222	268.67
B'wick	9	Vehicle	165.00	46.430	3	1.700	0.000	334.69	46.430	290.00
B'wick	10	Far Exhaust	131.67	35.965	3	1.700	0.000	262.55	35.965	295.00
B'wick	10	Near Exhaust	201.00	15.180	3	1.700	0.000	360.47	15.180	328.00
B'wick	10	Vehicle	240.67	20.635	3	1.700	0.000	426.41	20.635	332.00

Appendix 3. Summary of EC data from three studies.

Study	Day	Location	Mass (ug)	CV of mass gain (%)	N	Flow Rate (lpm)	CV of Flow Rate (%)	Conc. ($\mu\text{g}/\text{m}^3$)	CV of conc. (%)	Sampling Time (min)
Crtn '96	1	UW	17.30	29.791	3	1.656	2.204	52.17	30.462	200.67
Crtn '96	1	V	36.88	36.660	3	1.557	14.183	115.22	47.912	214.00
Crtn '96	1	DW	48.96	8.802	3	1.715	0.916	137.44	8.393	207.67
Crtn '96	2	UW	6.92		2	1.677	0.253	24.37	97.907	169.00
Crtn '96	2	V	53.62	10.273	3	1.557	14.183	200.83	20.982	174.67
Crtn '96	2	DW	62.58	2.011	2	1.721	1.027	230.95	2.590	157.50
Crtn '96	3	UW	31.08	4.330	3	1.656	2.204	67.33	6.605	279.00
Crtn '96	3	V	68.11	48.832	3	1.557	14.183	156.20	38.950	277.33
Crtn '96	3	DW	108.97	5.440	3	1.715	0.916	221.96	5.985	286.33
Crtn '96	4	UW	3.24		3	1.705	0.653	8.84		215.00
Crtn '96	4	V	84.48	19.534	3	1.767	5.583	163.62	20.437	292.67
Crtn '96	4	DW	78.57	6.938	2	1.709	0.993	177.12	6.219	259.50
Crtn '96	5	UW	21.31	45.317	3	1.705	0.653	41.76	45.308	299.33
Crtn '96	5	V	195.34	48.146	2	1.789	7.194	353.20	40.823	304.00
Crtn '96	5	DW	129.88	37.303	2	1.716	1.525	255.99	38.497	296.50
Crtn '96	6	UW	10.49	60.196	3	1.751	2.428	22.59	59.127	263.33
Crtn '96	6	V	99.39	27.860	3	1.658	6.389	218.74	30.787	276.33
Crtn '96	6	DW	102.99	19.178	3	1.700	0.893	222.97	18.338	271.33
Crtn '96	7	UW	9.81	59.251	2	1.663	6.615	20.21	59.082	281.00
Crtn '96	7	V	54.39	62.342	2	1.610	6.500	113.85	49.988	285.50
Crtn '96	7	DW	121.24	6.893	3	1.712	0.454	252.70	7.125	280.33
Crtn '96	8	UW	12.53	14.672	3	1.751	2.428	24.83	13.995	288.00
Crtn '96	8	V	121.27	27.265	3	1.647	5.944	246.14	27.493	300.00
Crtn '96	8	DW	136.25	7.896	3	1.712	0.454	241.73	8.029	329.33
Crtn '97	1	UW	6.09	48.908	4	1.705	0.295	27.38		131.50
Crtn '97	1	V	34.29	9.193	3	1.713	2.210	138.82	7.075	144.00
Crtn '97	1	DW	45.59	22.314	4	1.706	1.539	205.88	14.835	128.50
Crtn '97	2	UW	3.33	32.501	4	1.706	0.287	5.71	32.972	342.75
Crtn '97	2	V	92.23	14.966	3	1.713	2.210	147.31	12.793	364.67
Crtn '97	2	DW	120.90	4.114	4	1.706	1.539	194.36	3.262	364.50
Crtn '97	3	UW	17.51	8.755	4	1.743	3.846	27.89	4.666	360.00
Crtn '97	3	V	94.34	20.285	3	1.685	0.774	150.24	20.952	373.00
Crtn '97	3	DW	117.14	2.309	4	1.703	1.112	185.95	1.905	370.00
Crtn '97	4	UW	9.88	12.028	4	1.705	1.269	16.09	11.768	360.00
Crtn '97	4	V	92.88	8.956	3	1.757	4.196	138.29	5.972	382.00

Crtn '97	4	DW	102.23	4.443	6	1.720	3.289	166.60	3.289	356.83
Crtn '97	5	UW	8.25	43.920	4			13.48	44.331	360.25
Crtn '97	5	V	64.21	45.549	3	1.757	4.196	100.56	47.633	365.00
Crtn '97	5	DW	96.70	11.665	6	1.720	3.289	156.27	13.106	360.50
Crtn '97	6	UW	19.56	25.328	4	1.720	0.451	29.55	25.658	385.00
Crtn '97	6	V	98.90	28.918	3	1.667	2.960	157.94	26.460	373.67
Crtn '97	6	DW	122.35	8.726	6	1.695	0.651	194.54	2.365	371.17
Crtn '97	7	UW	0.79		4	1.720	0.451	1.75		360.00
Crtn '97	7	V	81.99	9.154	3	1.667	2.960	135.36	6.358	363.00
Crtn '97	7	DW	88.04	15.114	6	1.690	0.802	144.75	15.385	360.17
Crtn '97	8	V	98.58	11.502	3	1.700	4.118	154.43	12.574	376.00
Crtn '97	8	DW	75.00	42.203	6	1.610	12.838	129.97	48.275	370.17
Crtn '97	9	V	107.16	6.683	3	1.700	4.118	151.58	9.395	416.67
Crtn '97	9	DW	81.05	3.323	6	1.610	12.838	143.47	16.281	357.00
Crtn '97	10	UW	4.87		4	1.690	0.837	8.01		360.00
Crtn '97	10	V	75.58	45.369	3	1.725	1.472	119.86	46.158	366.67
Crtn '97	10	DW	92.34	4.899	6	1.694	5.778	151.82	7.811	360.00
Crtn '97	11	UW	5.27	20.276	3	1.690	0.837	7.55	19.333	412.00
Crtn '97	11	V	108.90	13.829	3	1.722	1.339	142.43	13.672	444.00
Crtn '97	11	DW	83.22	27.585	6	1.694	5.778	121.02	26.990	404.83
B'wick	1	Intake	9.99	7.649	3	1.700	0.000	17.80	7.649	330.00
B'wick	1	Exhaust	145.90	2.289	3	1.700	0.000	244.51	2.289	351.00
B'wick	1	Vehicle	108.78	18.222	3	1.700	0.000	188.75	18.222	339.00
B'wick	2	Intake	5.39	2.136	3	1.700	0.000	9.33	2.136	340.00
B'wick	2	Exhaust	150.99	3.537	3	1.700	0.000	250.18	3.537	355.00
B'wick	2	Vehicle	100.80	4.112	3	1.700	0.000	167.97	4.112	353.00
B'wick	3	Intake	11.60	3.005	3	1.700	0.000	19.23	3.005	355.00
B'wick	3	Exhaust	157.10	4.591	3	1.700	0.000	256.70	4.591	360.00
B'wick	3	Vehicle	102.70	1.726	3	1.700	0.000	169.22	1.726	357.00
B'wick	4	Intake	7.50	5.434	3	1.700	0.000	12.12	5.434	364.00
B'wick	4	Exhaust	152.22	2.800	3	1.700	0.000	242.00	2.800	370.00
B'wick	4	Vehicle	94.71	2.860	3	1.700	0.000	151.81	2.860	367.00
B'wick	5	Intake	60.50	0.921	3	1.700	0.000	13.90	0.921	340.00
B'wick	5	Exhaust	149.47	2.823	3	1.700	0.000	261.67	2.823	336.00
B'wick	5	Vehicle	105.80	4.299	3	1.700	0.000	178.83	4.299	348.00
B'wick	6	Intake	7.10	12.009	3	1.700	0.000	13.92	12.009	300.00
B'wick	6	Far Exhaust	188.63	3.264	3	1.700	0.000	382.61	3.264	290.00

B'wick	6	Near Exhaust	250.87	5.848	3	1.700	0.000	491.89	5.848	300.00
B'wick	6	Vehicle	315.07	8.541	3	1.700	0.000	617.78	8.541	300.00
B'wick	7	Intake	1.21	40.183	3	1.700	0.000	2.41	40.183	295.00
B'wick	7	Far Exhaust	111.40	1.400	3	1.700	0.000	223.66	1.400	293.00
B'wick	7	Near Exhaust	112.18	3.880	3	1.700	0.000	223.68	3.880	295.00
B'wick	7	Vehicle	123.48	17.845	3	1.700	0.000	240.52	17.845	302.00
B'wick	8	Intake	9.88	17.445	3	1.700	0.000	19.30	17.445	301.00
B'wick	8	Far Exhaust	101.93	55.921	3	1.700	0.000	206.76	55.921	290.00
B'wick	8	Near Exhaust	137.48	4.355	3	1.700	0.000	275.07	4.355	294.00
B'wick	8	Vehicle	187.70	36.738	3	1.700	0.000	357.33	36.738	309.00
B'wick	9	Intake	3.78	12.991	3	1.700	0.000	7.67	12.991	290.00
B'wick	9	Far Exhaust	85.90	2.024	3	1.700	0.000	180.47	2.024	280.00
B'wick	9	Near Exhaust	85.23	10.958	3	1.700	0.000	186.32	6.836	268.67
B'wick	9	Vehicle	102.21	16.052	3	1.700	0.000	207.33	16.052	290.00
B'wick	10	Intake	3.50	1.211	3	1.700	0.000	6.04	1.211	341.00
B'wick	10	Far Exhaust	78.87	2.834	3	1.700	0.000	157.27	2.834	295.00
B'wick	10	Near Exhaust	94.52	0.360	3	1.700	0.000	169.51	0.360	328.00
B'wick	10	Vehicle	96.90	6.629	3	1.700	0.000	171.68	6.629	332.00

Appendix 4. Summary of TC data from three studies

Study	Day	Location	Mass (ug)	CV of mass gain (%)	N	Flow Rate (lpm)	CV of Flow Rate (%)	Conc. ($\mu\text{g}/\text{m}^3$)	CV of conc. (%)	Sampling Time (min)
Crtn '96	1	UW	32.40	31.697	3	1.656	2.204	97.75	32.471	200.67
Crtn '96	1	V	71.50	33.324	3	1.557	14.183	222.91	44.956	214.00
Crtn '96	1	DW	93.10	9.566	3	1.715	0.916	261.34	9.160	207.67
Crtn '96	2	UW	13.78		2	1.677	0.253	48.55	91.371	169.00
Crtn '96	2	V	107.68	8.036	3	1.557	14.183	402.27	18.071	174.67

Crt'n '96	2	DW	125.90	5.363	2	1.721	1.027	464.71	5.940	157.50
Crt'n '96	3	UW	78.98	36.325	3	1.656	2.204	170.52	35.194	279.00
Crt'n '96	3	V	146.33	37.625	3	1.557	14.183	332.98	24.775	277.33
Crt'n '96	3	DW	228.24	6.024	3	1.715	0.916	464.96	6.777	286.33
Crt'n '96	4	UW	9.67		3	1.705	0.653	26.40		215.00
Crt'n '96	4	V	187.57	17.091	3	1.767	5.583	363.00	17.367	292.67
Crt'n '96	4	DW	155.39	8.605	2	1.709	0.993	350.29	7.887	259.50
Crt'n '96	5	UW	56.13	46.545	3	1.705	0.653	109.98	46.536	299.33
Crt'n '96	5	V	398.10	45.576	2	1.789	7.194	720.59	38.161	304.00
Crt'n '96	5	DW	254.75	36.831	2	1.716	1.525	502.07	38.028	296.50
Crt'n '96	6	UW	33.70	26.092	3	1.751	2.428	72.89	24.527	263.33
Crt'n '96	6	V	208.20	31.643	3	1.658	6.389	458.22	33.991	276.33
Crt'n '96	6	DW	201.68	18.198	3	1.700	0.893	436.67	17.352	271.33
Crt'n '96	7	UW	31.32	7.099	2	1.663	6.615	64.55	7.303	281.00
Crt'n '96	7	V	107.02	60.778	2	1.610	6.500	224.27	48.291	285.50
Crt'n '96	7	DW	210.94	5.038	3	1.712	0.454	439.65	5.244	280.33
Crt'n '96	8	UW	29.60	7.072	3	1.751	2.428	58.71	7.270	288.00
Crt'n '96	8	V	284.19	32.984	3	1.647	5.944	580.61	36.527	300.00
Crt'n '96	8	DW	253.45	5.726	3	1.712	0.454	449.62	5.741	329.33
Crt'n '97	1	UW	15.09	39.887	4	1.705	0.295	67.42		131.50
Crt'n '97	1	V	58.51	4.346	3	1.713	2.210	237.08	2.214	144.00
Crt'n '97	1	DW	71.16	19.391	4	1.706	1.539	322.23	11.824	128.50
Crt'n '97	2	UW	15.58	47.076	4	1.706	0.287	26.68	47.335	342.75
Crt'n '97	2	V	138.94	15.329	3	1.713	2.210	221.93	13.293	364.67
Crt'n '97	2	DW	168.99	4.628	4	1.706	1.539	271.64	3.314	364.50
Crt'n '97	3	UW	26.12	13.106	4	1.743	3.846	41.57	7.218	360.00
Crt'n '97	3	V	141.87	8.799	3	1.685	0.774	225.81	9.509	373.00
Crt'n '97	3	DW	172.09	6.988	4	1.703	1.112	273.20	7.003	370.00
Crt'n '97	4	UW	17.57	13.133	4	1.705	1.269	28.61	12.133	360.00
Crt'n '97	4	V	145.38	8.231	3	1.757	4.196	216.43	4.351	382.00
Crt'n '97	4	DW	150.21	2.897	6	1.720	3.289	244.84	2.168	356.83
Crt'n '97	5	UW	17.83	21.400	4			29.06	21.998	360.25
Crt'n '97	5	V	105.22	41.014	3	1.757	4.196	164.64	42.846	365.00
Crt'n '97	5	DW	149.64	10.652	6	1.720	3.289	241.87	12.396	360.50
Crt'n '97	6	UW	43.03	48.874	4	1.720	0.451	64.99	48.916	385.00
Crt'n '97	6	V	152.48	25.582	3	1.667	2.960	243.67	23.026	373.67
Crt'n '97	6	DW	192.19	9.073	6	1.695	0.651	306.51	8.688	371.17
Crt'n '97	7	UW	16.37		4	1.720	0.451	26.44		360.00

Crtn '97	7	V	140.25	11.606	3	1.667	2.960	231.47	9.176	363.00
Crtn '97	7	DW	142.10	15.191	6	1.690	0.802	233.64	15.425	360.17
Crtn '97	8	V	164.73	11.650	3	1.700	4.118	258.21	13.454	376.00
Crtn '97	8	DW	121.79	40.167	6	1.610	12.838	211.07	46.743	370.17
Crtn '97	9	V	193.09	10.129	3	1.700	4.118	273.58	14.059	416.67
Crtn '97	9	DW	152.55	3.851	6	1.610	12.838	269.26	13.736	357.00
Crtn '97	10	UW	14.43		4	1.690	0.837	23.72		360.00
Crtn '97	10	V	145.66	33.996	3	1.725	1.472	230.85	34.971	366.67
Crtn '97	10	DW	167.92	3.352	6	1.694	5.778	275.81	4.755	360.00
Crtn '97	11	UW	16.79	13.207	3	1.690	0.837			412.00
Crtn '97	11	V	280.24	11.878	3	1.722	1.339	366.59	11.916	444.00
Crtn '97	11	DW	231.55	26.963	6	1.694	5.778	336.02	25.213	404.83
B'wick	1	Intake	15.72	20.477	3	1.700	0.000	28.03	20.477	330.00
B'wick	1	Exhaust	213.15	3.372	3	1.700	0.000	357.21	3.372	351.00
B'wick	1	Vehicle	205.10	19.656	3	1.700	0.000	355.88	19.656	339.00
B'wick	2	Intake	10.75	35.160	3	1.700	0.000	18.59	35.160	340.00
B'wick	2	Exhaust	223.48	2.621	3	1.700	0.000	370.30	2.621	355.00
B'wick	2	Vehicle	190.76	6.515	3	1.700	0.000	317.89	6.515	353.00
B'wick	3	Intake	16.22	1.683	3	1.700	0.000	26.87	1.683	355.00
B'wick	3	Exhaust	224.94	3.707	3	1.700	0.000	367.56	3.707	360.00
B'wick	3	Vehicle	180.61	2.020	3	1.700	0.000	297.59	2.020	357.00
B'wick	4	Intake	12.57	10.637	3	1.700	0.000	20.31	10.637	364.00
B'wick	4	Exhaust	217.17	2.462	3	1.700	0.000	345.26	2.462	370.00
B'wick	4	Vehicle	173.46	4.149	3	1.700	0.000	278.02	4.149	367.00
B'wick	5	Intake	16.95	3.303	3	1.700	0.000	29.33	3.303	340.00
B'wick	5	Exhaust	217.84	2.697	3	1.700	0.000	381.38	2.697	336.00
B'wick	5	Vehicle	192.58	3.119	3	1.700	0.000	325.52	3.119	348.00
B'wick	6	Intake	13.42	11.234	3	1.700	0.000	26.32	11.234	300.00
B'wick	6	Far Exhaust	265.10	1.194	3	1.700	0.000	537.74	1.194	290.00
B'wick	6	Near Exhaust	350.83	5.009	3	1.700	0.000	687.91	5.009	300.00
B'wick	6	Vehicle	460.72	8.474	3	1.700	0.000	903.38	8.474	300.00
B'wick	7	Intake	2.83	14.594	3	1.700	0.000	5.63	14.594	295.00
B'wick	7	Far Exhaust	179.15	0.648	3	1.700	0.000	359.67	0.648	293.00
B'wick	7	Near Exhaust	188.79	2.217	3	1.700	0.000	376.44	2.217	295.00

B'wick	7	Vehicle	244.25	16.513	3	1.700	0.000	475.76	16.513	302.00
B'wick	8	Intake	22.25	7.786	3	1.700	0.000	43.47	7.786	301.00
B'wick	8	Far Exhaust	153.67	53.573	3	1.700	0.000	311.70	53.573	290.00
B'wick	8	Near Exhaust	219.54	2.507	3	1.700	0.000	439.25	2.507	294.00
B'wick	8	Vehicle	321.96	39.192	3	1.700	0.000	612.91	39.192	309.00
B'wick	9	Intake	10.66	9.663	3	1.700	0.000	21.62	9.663	290.00
B'wick	9	Far Exhaust	137.03	1.631	3	1.700	0.000	287.88	1.631	280.00
B'wick	9	Near Exhaust	145.06	6.785	3	1.700	0.000	317.57	6.785	268.67
B'wick	9	Vehicle	192.17	14.503	3	1.700	0.000	389.80	14.503	290.00
B'wick	10	Intake	9.31	1.482	3	1.700	0.000	16.06	1.482	341.00
B'wick	10	Far Exhaust	133.10	1.671	3	1.700	0.000	265.39	1.671	295.00
B'wick	10	Near Exhaust	158.46	0.630	3	1.700	0.000	284.18	0.630	328.00
B'wick	10	Vehicle	192.31	5.990	3	1.700	0.000	340.74	5.990	332.00

Appendix 5: Calculation of CV_C

The concentration is given by

$$C = \frac{M}{Q \times t}$$

where M is the observed mass collected on the filter, Q is the flow rate of air, and t is the time over which sampling occurs. Assuming that errors in t are negligible, but there are errors in M and Q , i.e.,

$$M = M^* + \varepsilon_M$$

$$Q = Q^* + \varepsilon_Q$$

where M^* and Q^* are the "true" mass and flow rate, and ε_M and ε_Q are measurement errors. Then

$$CV_M = \frac{\sigma_M}{M^*}$$

$$CV_Q = \frac{\sigma_Q}{Q^*}$$

Assuming that ε_Q are small compared to Q^* , we have

$$\begin{aligned} C &= \frac{M}{Q \times t} \\ &= \frac{M^* + \varepsilon_M}{(Q^* + \varepsilon_Q) \times t} = \left(\frac{M^* + \varepsilon_M}{t \times Q^*} \right) \times \left(1 - \frac{\varepsilon_Q}{Q^*} + \dots \right) \\ &\approx \frac{M^* + \varepsilon_M}{(Q^* + \varepsilon_Q) \times t} = \left(\frac{M^* + \varepsilon_M}{t \times Q^*} \right) \times \left(1 - \frac{\varepsilon_Q}{Q^*} \right) \\ &\approx \frac{M^*}{Q^* \times t} + \frac{\varepsilon_M}{Q^* \times t} - \left(\frac{M^*}{t \times Q^*} \right) \times \left(\frac{\varepsilon_Q}{Q^*} \right) \\ &\approx C^* + C^* \left(\frac{\varepsilon_M}{M^*} \right) - C^* \times \left(\frac{\varepsilon_Q}{Q^*} \right) \end{aligned}$$

where C^* is the true concentration.

Dividing both sides by C^* and noting that $CV_C^2 = \text{Var} \left(\frac{C}{C^*} \right)$, we have

$$CV_C^2 \approx \frac{\sigma_M^2}{M^{*2}} + \frac{\sigma_Q^2}{Q^{*2}} - 2 \times \left(\frac{\rho_{M,Q} \times \sigma_M \times \sigma_Q}{M^* \times Q^*} \right) = CV_M^2 + CV_Q^2 - 2\rho_{M,Q} CV_M CV_Q$$

where $\rho_{M,Q}$ is the correlation between M and Q. If M and Q are independent, then $\rho_{M,Q} = 0$.