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Evaluation of Existing Diesel Particulate Matter Sampling and Analysis Methods at a High Sulphide Ore Mine

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EXECUTIVE SUMMARY

This study evaluated three methods for measuring worker exposure to diesel particulate matter (dpm) in high sulphide mines. These were the Respirable Combustible Dust (RCD), the Size-Selective (SS) and the Thermal-Optical methods. Previous sampling in Canadian mines had uncovered cases where RCD samples had to be rejected because of suspected interference. This led to the suspicion that oxidation of sulphide minerals on the filter caused the sample to gain in mass during the ashing process involved in RCD analysis. The first goal of the study was to investigate the impact of the presence of respirable sulphides on the RCD sampling method. The second goal was to compare and evaluate the three sampling methods under high dpm, and mixed dpm/sulphide mineral dust conditions.

Present results show that oxidation of respirable sulphide materials on samples does not cause significant mass increases during the RCD process. Oxidation of these minerals as well as the combustion of sulphur-bearing compounds from the fuel will, however, result in the production of SO_2 gas. Laboratory testing using Thermogravimetric and Differential Thermal Analysis did show the SO_2 and its subsequent interaction with the silver from the filter membrane is a probable cause of mass increase. These data show that one very probable source of interference in the temperature range used in RCD analysis are organo-sulphates in the fuel. The results indicate that the performance of the RCD method can be enhanced by making use of a small pore-size silver membrane filter and using low-sulphur fuel in diesel applications underground. Smaller pore sizes help keep sulphur bearing minerals on the surface of the filter and away from the silver matrix, while lower sulphur fuel produces dpm with lower levels of organic sulphur, which can produce SO_2 upon ashing during the RCD analysis.

For this work, the Total Carbon (TC) concentration as measured by the Thermal-Optical method (NIOSH #5040) was used to compare and evaluate the RCD and SS gravimetric methods. During Week 1 of the study (dpm only) the RCD method overestimated by about 12% and the SS method by 13%. During Week 2 (dpm/mineral dust) RCD underestimated by 10% and SS overestimated by 8%.

Even in a sulphide ore environment, the three methods tested performed very well. It is believed that for the present and as long as the limits of exposure are at or above 0.60 milligram per cubic metre (mg/m^3), the gravimetric methods appear to be adequate in sulphide ore mines. Below these levels, alternatives such as the Thermal-Optical methods should be considered.

For mines where mineral interference is not a problem and/or in applications where dpm is the main source of airborne respirable dust, the RCD method could be used at even lower concentrations. This should be kept in mind in view of the fact that this method is compatible with silica analysis and as such, increases the amount of exposure data collected.

BACKGROUND INFORMATION

General considerations

Diesel exhaust contaminants, including dpm, and the associated health effects have become a very important issue. This is an area of concern for the Canadian mining industry, which depends heavily on production equipment powered by diesel engines. These concerns have already led to regulation limiting the exposure to dpm in Canada and elsewhere in the world. On May 23rd, 1995 the American Conference of Governmental Industrial Hygienists (ACGIH) listed diesel exhaust particulate on their Notice of Intended Changes, with a TLV-TWA® of 0.15 mg/m^3 (1).

In order to assess compliance with dpm limits or guidelines, it is critical to have the means and the tools necessary to accurately measure mine worker exposure. The sampling and analysis of dpm is complicated by its physical nature and its chemical composition. Furthermore, the chemical and physical properties of the mineral components of the respirable dust found in the mining workplace can interfere with some sampling and analytical procedures.

Sulphide components in the airborne dust are thought to interfere with the Respirable Combustible Dust (RCD) method commonly used in Canada. In this method, ashing of the sample filter (heating in a furnace at 400°C) is meant to result in an overall mass decrease that is indicative of the presence of dpm on the sample. When sulphide ores are ashed along with dpm during the RCD analysis, the sulphides may oxidize to sulphates, thereby causing the overall mass of the sample to increase. This phenomenon could then either mask or overwhelm the mass loss expected from the ashing of RCDs. At the very least, this would have a serious impact on the results obtained since worker exposure would be underestimated.

It is important to assess the impact of the mineralogy on our ability to measure dpm, since massive sulphide ore bodies are common in Canada. Analyses in Canadian mines have shown that samples may experience noticeable mass increases. The exact processes that caused these mass increases are not fully understood and the potential solutions not obvious at this point.

This paper reports the results of a study which makes use of mineralogy assessment technology in order to identify the mineral components or mechanisms that may interfere with the analytical process used in the RCD method in a massive sulphide ore mine. Furthermore, the RCD method will be compared with two other methods that can be used to measure dpm.

Sampling and analysis methods – diesel particulate matter

Respirable Combustible Dust (RCD) sampling method

Respirable combustible dust samples are obtained using the approach described by the ACGIH (1). A 10-mm nylon cyclone removes the non-respirable portion of the airborne dust. This separation process is made possible when dust and air are passed through the cyclone at a set flow rate of 1.7 litres per minute (L/min.). The centrifugal force produced by the air vortex causes the removal of the larger, non-respirable portion of the dust, while the smaller respirable dust particles are entrained by the air stream to the filtration stage. The filter used in this study is a 0.8 μm pore-size silver membrane filter.

This method for measuring the exposure of personnel to dpm was developed for use in mines and is based on the principle of ashing or “burning” of the combustible, carbon-based components of the airborne respirable dust, which is collected on a silver membrane filter. Complete ashing of the dpm takes place at a temperature of 400ºC with the catalyzing effect of the silver membrane filter. The method was designed to be compatible with existing sampling procedures used for sampling respirable dust and respirable silica in the mining workplace.

Figure 1. Silver membrane filters being placed in the muffle furnace for RCD analysis.

A disadvantage of this method is that oxidation of some species of respirable minerals collected as part of the sample are thought to interfere in the analysis, to the point where significant discrepancies may result. This analytical process which had previously been used by the mining industry was refined under the sponsorship of the Canadian ad hoc Diesel Committee and CANMET in a two-phase approach described elsewhere (2,3,4,5). The actual analytical procedure is outlined in a CANMET report (6). The RCD samples collected as part of this study were analyzed at the CANMET laboratory in Sudbury.

Size-Selective sampling method

This sampling technique and the associated apparatus were developed as a result of cooperative efforts between the USBM (7,8) and the University of Minnesota's Particle Technology Laboratory (9). The sampler was developed using size-selective criteria to specifically target the mass concentration of diesel particulate in underground coal mines. The design criteria and in-field evaluation of the sampler are reported elsewhere (10). For simplicity, this sampling technique will be referred to as the size-selective (SS) method.

As with the RCD method, the SS method makes use of sampling pumps and cyclones. The respirable portion of the dust then passes through a single-stage impactor. The impactor jets and flow rate were designed and chosen to provide a cut-size of 0.8 µm. This means that particles greater than 0.8 µm in size (coal dust portion) would, for the most part, be removed from the air stream by impaction on the substrate. Particles less than 0.8 µm in diameter pass the impactor portion and are captured by an MSA™ filter cassette. The mass of dpm is determined by weighing the filter.

The SS sampling method is also fairly simple and inexpensive. Whereas interference due to the thermal oxidation of the mineral dust portion is not a problem, the final mass collected will be affected by any type of airborne dust small enough to penetrate the impactor stage and reach the filter.

For this study, the sampling material (filters and impaction discs) were supplied by the University of Minnesota. After the study, samples were sent back to the University of Minnesota for analysis.

Thermal-Optical method

This method allows quantification of organic carbon (OC) and elemental carbon (EC) at low levels (11), typically down to 5 micrograms (µg). The sampling train used for collecting the field samples consists of a 37-mm cassette preceded by a 10-mm nylon cyclone through which air is drawn at a flow rate of 1.7 L/min using a self-regulated sampling pump. A 37-mm diameter quartz filter is used. This filter has a 99.97% efficiency based on a 0.3 micrometer (µm) D.O.P. aerosol test.

Figure 2. Sample filter cut-out being inserted into the oven for Thermal-Optical analysis.

In the Thermal-Optical method, speciation of OC, carbonates and EC is accomplished through temperature and atmosphere control. A helium-neon (He-Ne) laser and a photo-diode receptor are used to correct for any pyrolytically generated EC or "char" that is formed during the analysis of some materials.

Once the analysis is started, the initial laser transmittance is calculated. Organic carbon and carbonates are evolved in an inert, oxygen-free He atmosphere as temperature is raised in four incremental steps to 900°C. Evolved carbon is catalytically oxidized to carbon dioxide (CO_2) in a bed of granular manganese dioxide (MnO_2) at a temperature of 870°C. Carbon dioxide is reduced to methane (CH_4) in a nickel/firebrick methanator at a temperature of 500°C. A flame ionization detector (FID) quantifies the CH_4. Any "char" which is produced reduces the laser transmittance through the sample and is corrected for during the next phase of the analysis.

The oven temperature is then reduced to 525°C, an oxygen-helium mixture (2% O_2, He balance) is introduced into the sample oven, and temperature is again increased in four steps to 900°C. As oxygen enters the oven, EC is oxidized thereby increasing the filter transmittance. The point at which the filter transmittance reaches its initial value is defined as the "split" between EC and OC. Carbon evolved prior to the split is considered OC, which includes any carbonates that may be present. Carbon volatilized after the split is considered to be EC. As in the first step, CO_2 is reduced to methane, which is then quantified by the FID. Total carbon (TC) is the sum of OC and EC.

After each sample is analysed, an internal calibration is performed by injecting a known volume of methane into the sample oven.

This method provides a more direct approach than the two gravimetric methods used for assessing dpm. It allows quantification of OC and EC at low levels, typically down to 5μg. This method is also less susceptible to interference by other combustible or mineral sources. The analysis for this work was performed at CANMET's Sudbury facility.

PREVIOUS WORK

Work highlighting the results of side by side sampling involving the three methods is scarce and none of these mention or adequately assess the impact of interfering substances on the RCD method. For example, recent work performed for Inco Ltd. in

Sudbury (12) showed no statistically significant differences between the SS and the RCD method when the latter was using 0.8 μm pore size silver membrane filters. Further, the total carbon concentrations as measured by the EC method were highly correlated to the two other methods. Other work performed at Noranda's Brunswick Mining Division in Bathurst (13) demonstrated good agreement between the SS and the RCD method when the airborne dust consists mainly of dpm. The level of agreement is lower, however, when mineral dust is present.

Personnel and area sampling using the RCD method was also performed under the auspices of the New Brunswick Mineral Development Agreement (14). In this work, some negative RCD values were obtained and no information was supplied to explain these occurrences.

OBJECTIVES

This study evaluated the three methods described earlier for measuring the exposure of mine workers to dpm in a high-sulphide ore mining operation. The first objective was to study the impact of the presence of respirable sulphides on the RCD sampling method. The second goal was to compare and evaluate the three sampling methods under high dpm, and mixed dpm/mineral dust conditions.

The results will confirm whether or not the mineral dust components significantly interfere with the RCD assessment in this type of ore body. In addition, side-by-side testing of the three methods will provide an assessment of their relative performance. This will provide information to assist in the selection of a dpm sampling method. Finally, this work will provide additional dpm exposure data for Brunswick Mining Division.

TEST PARAMETERS

Mine site and daily test schedule

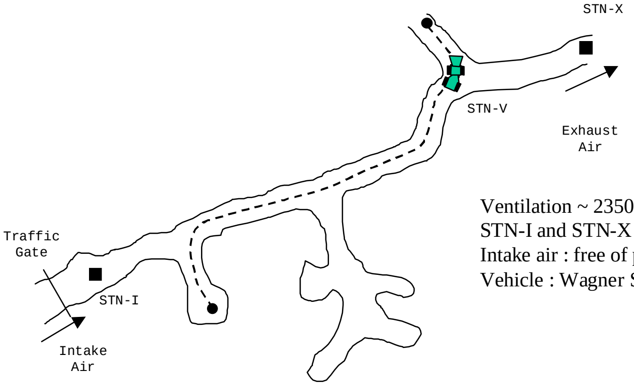
General mine information

The study took place in Bathurst, New Brunswick during a two-week survey at Noranda's Brunswick Mining Division. This is a lead-zinc mine operating in a massive sulphide ore body, the exact composition of which varies with depth and horizontal location. Two sites were selected, the 725-2 and the 1125-5 sub-level. The 725-2 sub-level was selected to compare the three methods in diesel atmospheres during the first week of study. The second week of the study was conducted at the 1125-2 sub-level location in a mixed diesel/mineral atmosphere, in order to evaluate the impact of respirable sulphide dust.

Diesel contaminated atmosphere – Week 1

The first portion of the survey was conducted on the 725-2 sub-level. This area had been used in the past for similar work and was familiar to the investigators. It is a non-productive area and it afforded a lot of control over test parameters. The Week 1 tests were conducted in such a way as to produce airborne dust that was composed mainly of dpm. This was achieved by having the scooptram adopt a duty cycle that closely resembles its regular production duties. The operator was asked to travel between points X and I as shown in Figure 3. In order to reduce airborne mineral dust concentration, the operator also kept the muck in the scooptram bucket for the duration of the sampling period. Re-entrained dust from the roadway was controlled with water or calcium chloride. This first part of the study was designed to evaluate and compare the three sampling and analysis methods under more or less pure dpm conditions. It also provided baseline data in order to quantify the impact of mineral dust on the effectiveness of the RCD and other methods.

Field Layout 725-2 Sub-Level - Week 1



Ventilation ~ 23500 cfm, flow through
STN-I and STN-X ~ 1500 ft apart
Intake air : free of production pollutants
Vehicle : Wagner ST8B scooptram, 7 yard bucket

Figure 3. Schematic plan view of the 725-2 sub-level area.

A schematic plan view of the 725-2 sub-level is shown in Figure 3. Station I (intake) and Station X (exhaust) monitored the intake and exhaust concentration of dpm and gases, respectively. Similar instrumentation was installed at both sampling stations to assess the vehicle's contribution. Sampling was also performed on the vehicle. The distance between the intake and exhaust stations was approximately 500 metres (m). This meant a duty cycle of about 9 to 10 minutes including a 30 second period of torque converter stall condition at both ends of the cycle to simulate bucket loading and unloading. Flow through ventilation in the area was set at 23,500 cubic feet per minute (cfm) and regulated by Brunswick ventilation engineers downwind from the exhaust sampling location.

Five complete sampling days were obtained during Week 1. Sampling was started at 08:00 hrs. and was completed by 14:00 hrs., for an average uninterrupted sampling time of 350 minutes.

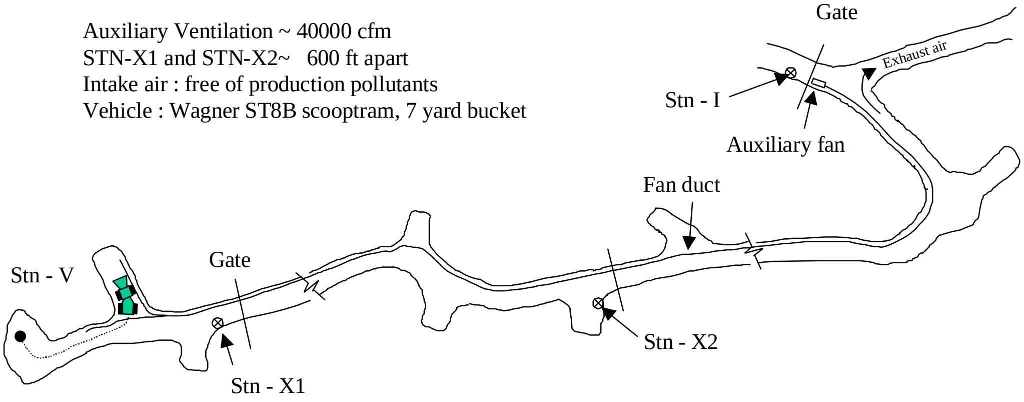
Diesel/mineral contaminated atmosphere – Week 2

The objective during Week 2 was to produce airborne mineral dust that contained sulphide material on a background of dpm produced by the same vehicle and operator as for Week 1.

The 1125-5 sub-level was an actual production area where sulphide-bearing ore had been stored ahead of the study. Additionally, rounds were being drilled and blasted on afternoon shift. These materials were being hauled back and forth using the same scooptram and operator on the "graveyard" or night shift when the study was being performed. No attempts were made to wet the roadway upwind of the two exhaust sampling stations and the operator was asked to use his judgement to try to produce a significant amount of airborne mineral dust. The operator was also asked to wear a dust mask during the test period.

Week 2 tests were designed to observe the impact, if any, of respirable sulphide mineral dust on the dpm sampling methods. The 1125-5 sub-level ore typically contains varying amounts of massive sulphide Pb/Zn ores with pyrite/pyrrhotite minerals. The ore composition in this area was such that sulphide to sulphate conversion would be expected to produce a measurable impact on the RCD method results, if this process indeed causes interference.

A schematic plan view of the 1125-5 sub-level is shown in Figure 4. Station I (intake) monitored the intake concentration of dpm and gases. There were two exhaust sampling stations located approximately 200m apart. Instrumentation was located at all three sampling locations as well as on the vehicle. The duty cycle in this case was a lot shorter than the first week cycle. The vehicle was confined to the dead end area past the X1 sampling station. Ventilation in the area was quite different from the 725-2 sub-level in that it was supplied by an auxiliary system as opposed to a flow through system. The volumes measured throughout the week were around 40000 cfm. During Week 2, sampling started at around 03:00 hrs. and was completed by 08:00 hrs., for an average continuous sampling time of 310 minutes.



Field Layout 1125-5 Sub-Level - Week 2

Auxiliary Ventilation ~ 40000 cfm
STN-X1 and STN-X2~ 600 ft apart
Intake air : free of production pollutants
Vehicle : Wagner ST8B scooptram, 7 yard bucket

Figure 4. Schematic plan view of the 1125-5 sub-level area.

Test vehicle

The test vehicle was a Wagner model ST8B scooptram (Brunswick fleet #VL213) powered by a Detroit Diesel Series 60, DDEC III engine, which had just received regular preventive maintenance (5328 hours). The last preventive maintenance had been performed at 4954 hours. No major repairs had ever been performed on this engine. The vehicle was fitted with an ECS 12DM catalytic converter that had as many operating hours as the engine. Both the engine and the hydraulic oil were Irving, IDO UNIV30-34300014. Irving also supplied the diesel fuel that complied with the Canadian Standard (CGSB–3.517-3 Type B). The fuel sulphur content was 0.044 wt%.

When used with this particular fuel, the engine requires 73 cfm/bhp according to the CSA certification standard. The engine is rated at 325 h.p., which means that 23725 cfm (11.2 m^3/s) of air are required to operate the vehicle according to the certification documents.

Samples collected and data analysis

Diesel particulate matter sampling

Diesel particulate matter concentration was measured in triplicate at all stations using the three methods described earlier (nine samplers in total). In addition, six more samples were collected at each station in order to provide three samples for oil mist analysis and three more for Variable-Pressure Scanning Electron Microscopy (VP-SEM) to determine the sample mineralogy. In total, 525 dpm samples were collected and analysed. The sample breakdown is shown in Table 1. Samples that were deployed in the drifts at the intake and exhaust sampling locations were hung on a screen with 10 cm openings. This screen was attached to a swing gate that was anchored to hinges drilled into the rock wall. Gas sampling monitors and other instrumentation were installed as shown in Figure 5.

Dpm Sampling – Number of Samples				
Week #	Location	RCD*	SS	EC/OC
1	Vehicle	45	15	15
1	Intake	45	15	15
1	Exhaust	45	15	15
2	Vehicle	45	15	15
2	Intake	45	15	15
2	Exhaust 1	45	15	15
2	Exhaust 2	45	15	15

*15 samples used for Scanning Electron Microscopy and 15 for oil mist analysis.

Table 1. Breakdown of dpm samples collected during the study.

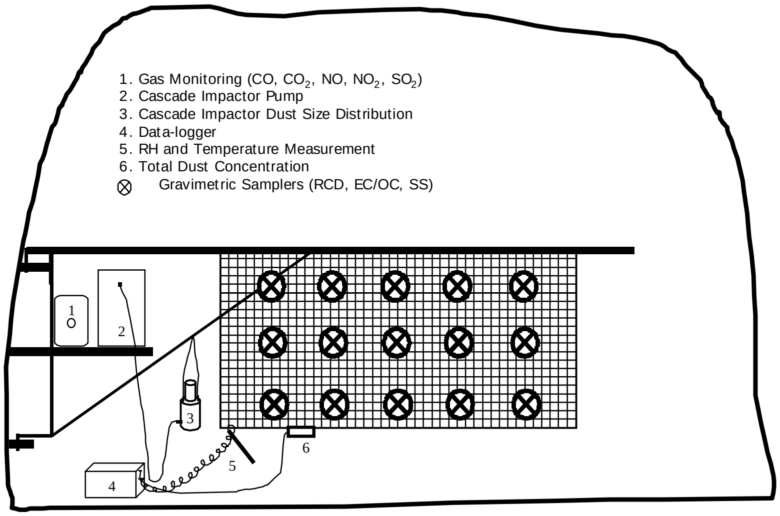


Figure 5. Drift cross-section showing instrumentation layout.

<u>Oil mist analysis</u>

The oil mist samples were sent to Inco's Central Process Technology Laboratory in Copper Cliff, Ontario for analysis by Fourier Transform Infrared Spectrometry. The Perkin-Elmer Spectrometer was calibrated using a sample of the oil that was brought back from Brunswick Mining Division. The mine uses the same oil for engine lubrication and hydraulics.

<u>Mineral analysis</u>

Variable-Pressure Scanning Electron Microscopy was used to characterize the respirable mineral dust collected on the silver membrane filters used for RCD analysis. Because VP-SEM was performed directly on a silver membrane filter substrate, the analysis is expected to yield sulphide and sulphate proportions (percentages) to an accuracy of better than 10%.

Originally the intention was to quantify the sulphide to sulphate conversion by comparing ashed and non-ashed samples. Due to background interference from the silver in the filter, ashed filters could not be analyzed accurately using VP-SEM. Instead, Thermogravimetry (TG), Differential Thermal Analysis (DTA) and Fourier Transform Infrared (FTIR) Spectroscopy were used on some bulk and airborne dust samples to detect mass changes and gases produced during the ashing process. The samples were analysed at CANMET's Mining and Mineral Sciences Laboratories facilities in Ottawa.

Size distribution

The size distribution of airborne dust was measured using Anderson Series 210 cascade impactors in a 9-stage configuration. The large pressure drop across the 9th and last stage limits the sampling flow rate to a maximum of 7 L/min. At that flow rate, the cut-sizes for the last four stages are 0.95 µm, 0.54 µm, 0.32 µm and 0.16 µm. In other words, four of the impactor stages collect particulate with aerodynamic diameters less than 1.0 µm, which is important for diesel particulate characterization. The impactors were used at the intake and exhaust locations but were not installed on the vehicle. An impactor/pump assembly and a dpm sampling train are shown in Figure 6.

Gas analysis

The main diesel exhaust gases were measured at the intake and exhaust sites using SIL multi-gas analysers and Brüel & Kjær gas monitors. The SIL instruments operate on chemical cells and infrared sensor technology and were calibrated daily. The B&K monitors operate on photo-acoustic principles and were calibrated ahead of the study. These were used as back up units to the SILs. The gas analysers are shown in Figure 7.

Fuel analysis

A sample of the diesel fuel was sent to CANMET's Fuel Characterisation Laboratory and was analysed for several parameters including sulphur, using method ASTM D-2622.

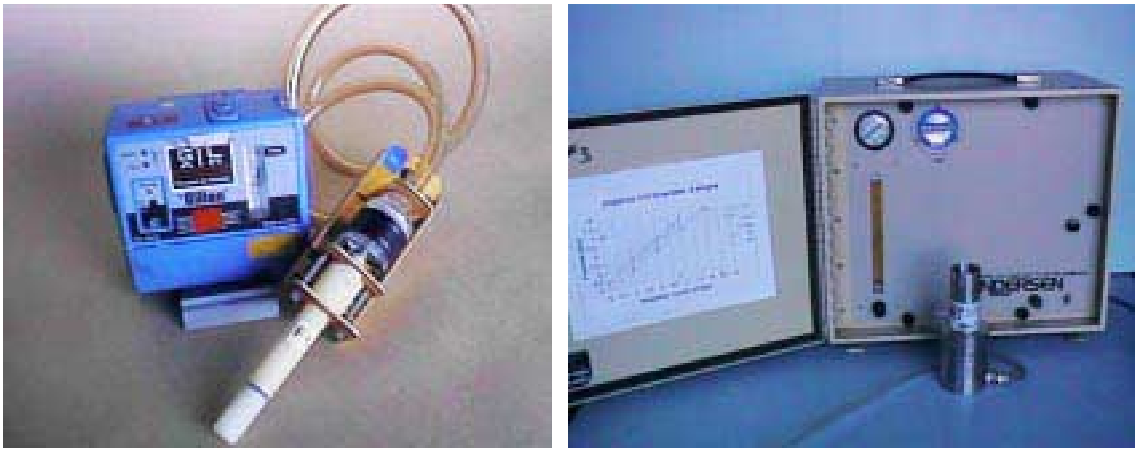


Figure 6. RCD sampling train (left) and cascade impactor/pump for particle size analysis.

Figure 7. SIL and B&K gas analysers.

RESULTS

The results discussed in this section are based in part on the dpm concentration values measured during the survey. A comprehensive listing of the average of the groups of three samplers used to measure RCD, SS and TC concentrations can be found in Appendix I along with the standard deviation associated with each value.

General characteristics of airborne dust

Information related to the airborne dust for the first week of study are shown in Table 2 and Figure 8. Table 2 lists the RCD and the total respirable dust results as well as the ratio of one to the other. Data from this table show RCD percentages ranging between 73% and 90% with an average of 83%, clearly indicating that the bulk of the airborne respirable dust is not mineral in origin. This is further supported by the size distribution data shown in Figure 8. The sub-micrometer mode (diesel particulate) has a Mass Median Aerodynamic Diameter (MMAD) of 0.1 µm and a coarser mode with an MMAD of 2.1 µm. The area under the curve associated with both modes clearly highlights the relative proportion of each type of dust.

Day	Location	RCD (mg/m^3)	Total respirable dust (mg/m^3)	% RCD
1	Exhaust	0.43	0.50	87%
2	Exhaust	0.42	0.50	85%
3	Exhaust	0.39	0.46	85%
4	Exhaust	0.39	0.48	82%
5	Exhaust	0.46	0.51	90%
1	Vehicle	0.41	0.52	80%
2	Vehicle	0.34	0.42	80%
3	Vehicle	0.30	0.37	82%
4	Vehicle	0.26	0.35	73%
5	Vehicle	0.33	0.39	84%

Table 2. Percentage RCD concentration – Week 1.

Data from Week 2 (diesel/mineral tests) are shown in Table 3 and Figure 9. In this instance, the percentage of RCD varies between 33% and 63% with an average of 46%, indicating a major contribution from mineral respirable dust. This is also apparent from size distribution data, which again shows a sub-micrometer mode at 0.1 μm and a much larger coarse mode at 6.7 μm. The relatively larger MMAD for Week 2 is indicative of mineral dust being produced by the mucking process in close proximity to the sampling stations.

Day	Location	RCD* (mg/m^3)	Total respirable dust (mg/m^3)	% RCD
1	Far Exhaust	0.49	0.80	60%
2	Far Exhaust	0.31	0.84	36%
3	Far Exhaust	0.36	0.67	54%
4	Far Exhaust	0.24	0.55	45%
5	Far Exhaust	0.23	0.52	45%
1	Near Exhaust	0.61	1.0	61%
2	Near Exhaust	0.35	0.96	36%
3	Near Exhaust	0.42	0.76	56%
4	Near Exhaust	0.27	0.63	43%
5	Near Exhaust	0.26	0.63	40%
1	Vehicle	0.87	1.39	63%
2	Vehicle	0.38	1.08	35%
3	Vehicle	0.46	0.86	54%
4	Vehicle	0.26	0.71	36%
5	Vehicle	0.27	0.82	33%

∗ The high RCD concentrations measured during Day 1 were caused by damage in the auxiliary ventilation supply system. Damages were repaired after the first day.

Table 3. Percentage RCD concentration – Week 2.

Respirable sulphide dust concentration – impact on RCD method

Table 4 contains data related to the impact of sulphide dust on the measurement of RCD concentration. It is important to remember that each data value in Table 4 is an average based on three samples. For each day and location, Table 4 lists the average percentage of sulphides in the mineral matter as computed by point counting using back-scattered electron images acquired by VP-SEM (15). Figure 10 shows the electron microscope scan of a typical dust sample collected a silver membrane filter before ashing. The minerals shown are pyrite (py) sphalerite (sp), galena (gn), quartz (qtz), dolomite (dol), siderite (sid), calcite (ca), and chlorite (chl).

Also shown in Table 4 are the average airborne sulphide concentration values computed from the data in the previous column and the mineral dust concentration. Also shown, are the ratios of RCD to Total Carbon (TC) and the error associated with this ratio as calculated from the standard deviation of the RCD and TC.

Table 4 shows a range in sulphide concentration values of 0.13 to 0.35 mg/m^3. If the conversion of sulphides to sulphates during ashing is a factor in RCD analysis, it is thought that a good indicator of this interference would be the variation of the ratio of RCD to TC as a function of the sulphide content.

Figure 11 shows the ratio of RCD to TC as a function of sulphide dust concentration. The results of linear regression analysis show a slope that is close to zero and a correlation coefficient that demonstrates the lack of a linear relationship. These data show that the presence and quantity of airborne respirable sulphides do not have a significant and direct impact on the RCD values measured. This will be developed further in the Discussion section using results from the Thermogravimetric and Differential Thermal Analysis.

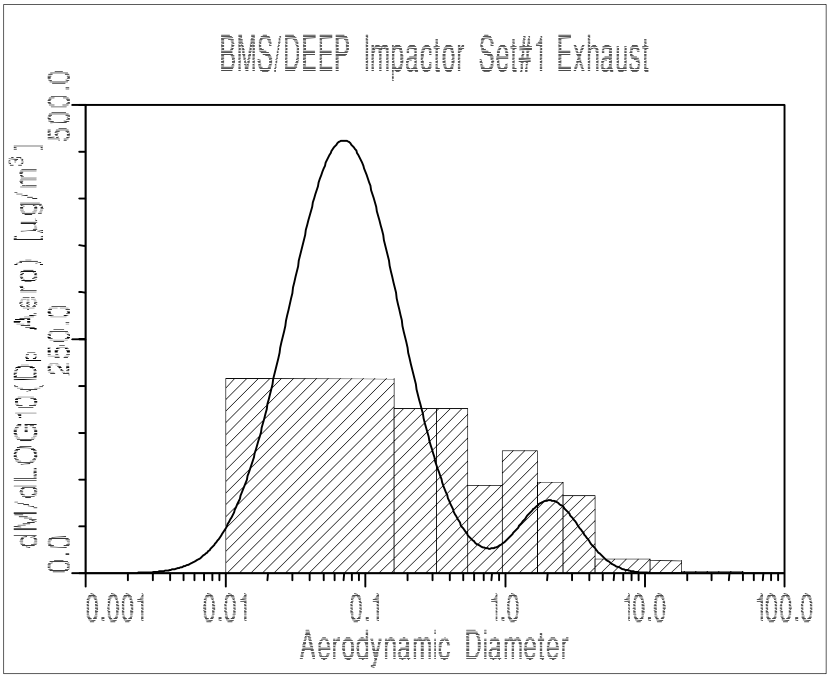


Figure 8. Size distribution of airborne dust – Week 1 - Diesel test

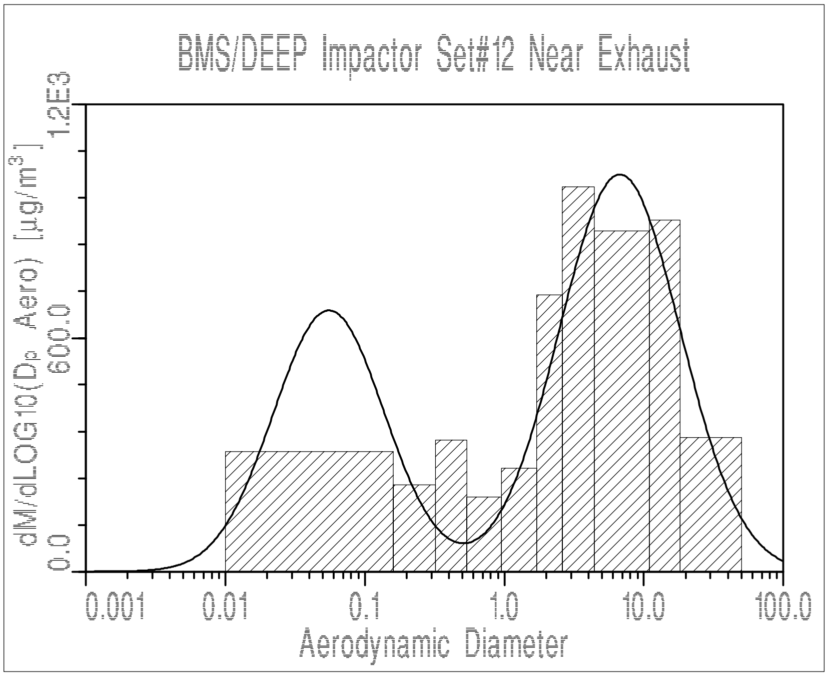


Figure 9. Size distribution of airborne dust – Week 2 – Diesel/mineral test

Date	Location	Percentage Sulphides	Sulphide conc. (mg/m3)*	Ratio of RCD/TC Concentration	Error on RCD/TC Ratio
1	Far exhaust	73%	0.19	0.91	0.05
2	Far exhaust	53%	0.25	0.86	0.07
3	Far exhaust	59%	0.15	0.89	0.10
4	Far exhaust	66%	0.17	0.85	0.06
5	Far exhaust	50%	0.13	0.88	0.10
1	Near Exhaust	72%	0.22	0.88	0.07
2	Near Exhaust	43%	0.25	0.92	0.05
3	Near Exhaust	64%	0.20	0.96	0.07
4	Near Exhaust	73%	0.22	0.85	0.11
5	Near Exhaust	67%	0.23	0.90	0.04
1	Vehicle	62%	0.30	0.96	0.14
2	Vehicle	52%	0.31	0.79	0.23
3	Vehicle	54%	0.13	0.76	0.36
4	Vehicle	70%	0.23	0.66	0.20
5	Vehicle	72%	0.35	0.80	0.44

* Total of Fe sulphides (pyrite, pyrrhotite and marcasite)
Cu sulphides (chalcopyrite, covellite), Zn sulphide (sphalerite), Pb sulphide (galena)

Table 4. VP-SEM Data (sulphide dust) and RCD/TC Ratios (Week 2).

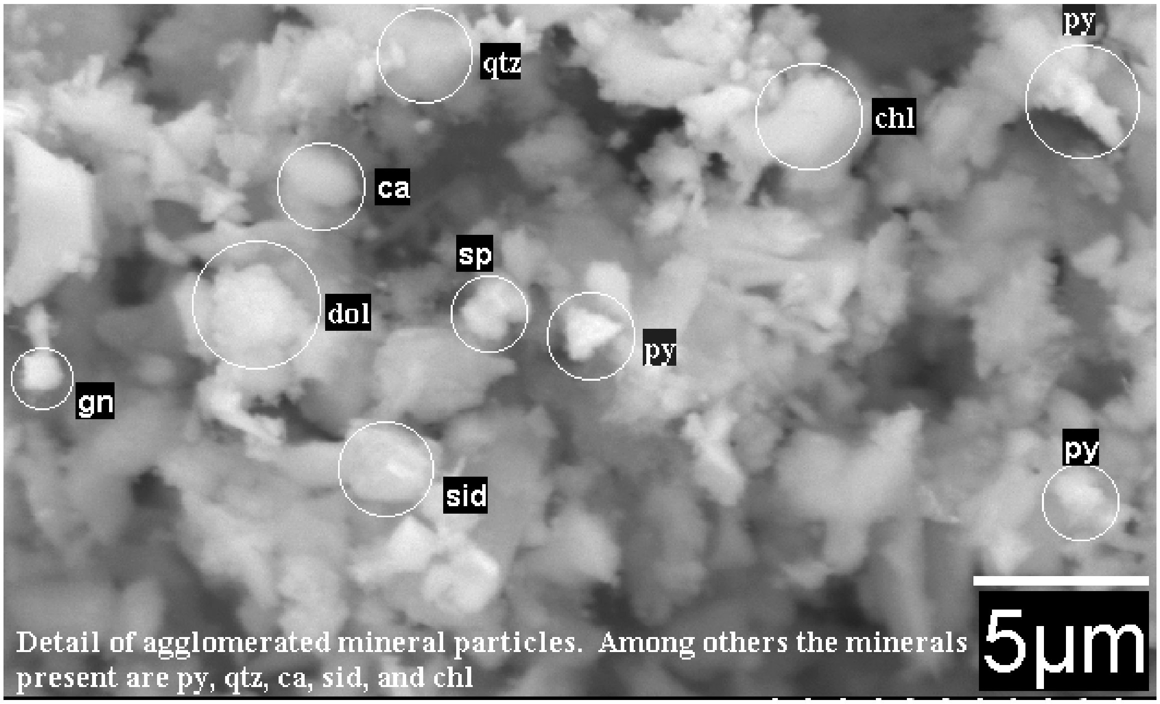


Figure 10. Scanning electron microscopy of dust sample before ashing.

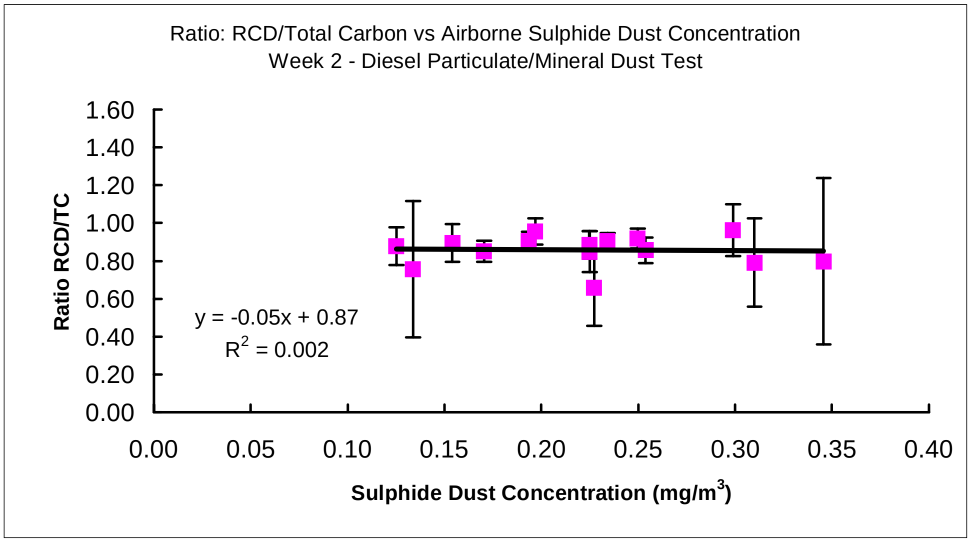


Figure 11. Relationship between the presence of sulphides and the ratio of RCD to TC.

Comparison of methods

In this section, the RCD and SS methods are being compared to the Total Carbon (TC) value as measured by the Thermal-Optical method. The TC method is used as the standard for comparison in this case since it is more precise and in most instances probably more accurate than the gravimetric methods being investigated. The National Institute for Occupational Safety and Health (NIOSH) is also evaluating the TC analytical procedure for dpm.

Two different types of statistical analyses were used to determine if the methods differ significantly, both under diesel (Week 1) and diesel/mineral (Week 2) conditions. One of the methods used is the Analysis of Variance (ANOVA) which had been used by other researchers (12). Also used here is Hotelling's T^2 test, which is thought to be better adapted to the field tests performed here. Although both methods lead to similar conclusions, the ANOVA test should not be used to make statistical inferences (16).

Table 5 shows the results of the comparison of data sets ranked in increasing order of statistical support for the null hypothesis stating that the results as measured by the pairs of methods are the same according to the Hotelling's T^2 test. A summary of the statistical analysis performed by an independent contractor is attached in Appendix I.

For data related to Week 1 (diesel atmosphere) both the ANOVA and Hotelling's test indicate that the SS method is statistically different from both the TC and the RCD methods (refer to the two first rows of Table 5). For the other pairs of measurement, the results of Hotelling's T^2 method indicate that there is weak evidence that the results of the methods differ significantly. The ANOVA approach indicates that the RCD method is statistically similar to the TC measurement during both Weeks 1 and 2. The results of the SS are also comparable to the TC method during Week 2.

In summary, except for what seems to be a statistically significant difference between the SS method and the TC method during Week 1, the SS method compares favourably with the TC measurements during Week 2 (diesel/mineral test). The RCD method compares well during the two weeks of study. These comparisons are better shown in Figures 12 and 13.

Data sets	p – values	
	Hotelling's T^2	ANOVA
Week 1 - SS vs TC	0.000*	0.000
Week 1 - SS vs RCD	0.000*	0.000
Week 1 - RCD vs TC	0.121	0.115**
Week 2 - RCD vs TC	0.194	0.338**
Week 2 - SS vs RCD	0.197	0.046
Week 2 - SS vs TC	0.490	0.22**

* Statistically different data sets according to Hotelling's T^2

** Statistically similar data sets according to ANOVA

Table 5. Statistical analysis of data sets related to the three methods used.

RCD and SS concentrations are plotted as a function of TC concentration for the diesel test and the diesel/mineral test, respectively, in Figures 12 and 13. Also shown in these figures is a dashed line that is the ideal one-to-one relationship between TC and the other methods and the results of a linear regression analysis between the data sets. It should be noted that all of these data points represent averages of three values.

Both figures show a high degree of linear correlation between data sets. For Week 1 and Week 2, the SS method shows large y-intercept values compared to the RCD method. This could cause problems at lower dpm concentrations.

The RCD method over estimates the TC method by about 12% during Week 1 and underestimates by 10% during Week 2. This would tend to indicate that while there is no measurable direct relationship between the presence of sulphides and a reduction in RCD concentration, some mechanisms might still be affecting the RCD concentrations measured.

Over most of the range of concentrations measured at the exhaust sites and on the vehicle, it can be said that both the RCD and SS methods were within 15% of the TC method. The implications of this on historical data and the potential of gravimetric methods to accurately measure lower concentrations of dpm will be discussed in the next section.

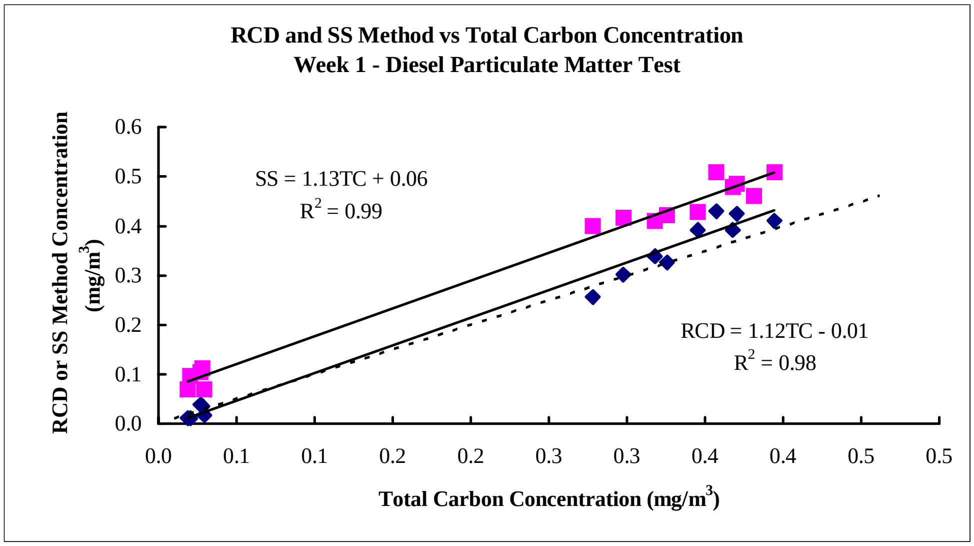


Figure 12. Linear relationship between total carbon concentrations and dpm values as measured by the RCD (◆) and SS (■) methods in a diesel environment.

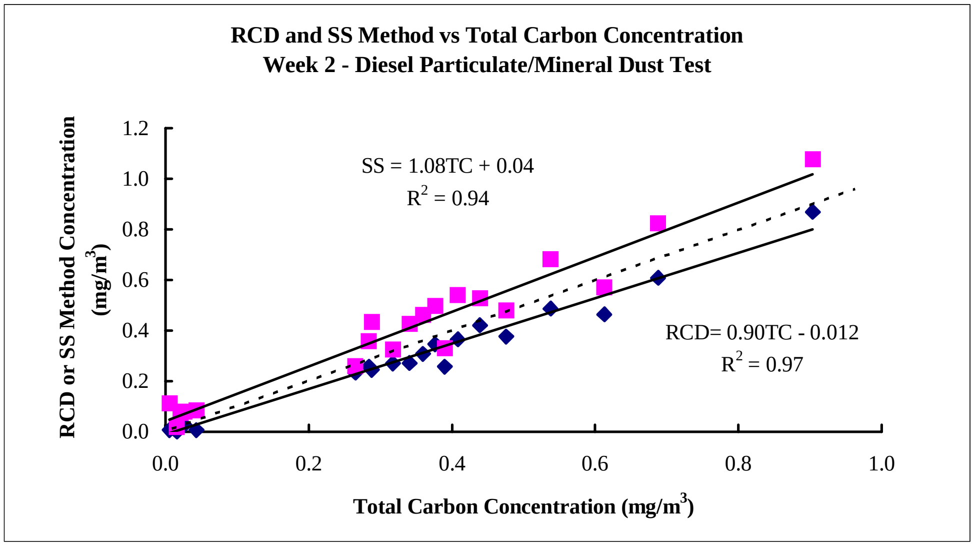


Figure 13. Linear relationship between total carbon concentrations and dpm values as measured by the RCD (◆) and SS (■) methods in a diesel/mineral environment.

The standard deviation calculated for each group of three samplers is listed in Table A1 in Appendix I. This table lists a total of 35 standard deviations for each the RCD, SS and TC methods. The standard deviation is a good measure of the intrinsic variability within a group of samplers and hence is a fairly good indicator of the precision of a particular method and its performance at lower concentrations. The precision of a method is not to be confused, however, with the accuracy or the level of agreement between the measured value and the actual concentration of a contaminant. In order to be acceptable, a method must be both accurate and precise in the range of concentrations to be measured.

The averaged standard deviations listed for the entire study are shown in Table 6. The middle column shows the average standard deviations for the three methods as computed from all of the 35 groups of samplers as listed in the Appendix. The standard deviations are 0.021 mg/m^3, 0.025 mg/m^3 and 0.056 mg/m^3 for the TC, RCD and SS methods, respectively. A significant portion of this variability can be directly attributed to variations linked to the sampling conditions on the vehicle. Because dpm is being produced close to the sampling trains, the contaminants are less well mixed and this leads to greater intersampler variability. If only the intake and exhaust sampling stations are used, the standard deviations become 0.007 mg/m^3 for the Thermal-Optical method, 0.016 mg/m^3 for the RCD and 0.055 mg/m^3 for the SS method.

Sampling Method	Average Standard Deviation (mg/m^3)	
	All Sampling Stns.	Vehicle Stns. Removed
Thermal-Optical	0.021	0.007
RCD	0.025	0.016
Size-Selective	0.056	0.055

Table 6. **Average standard deviation as a measure of sampling method variability**

Relative levels of elemental (EC) and organic (OC) carbon and oil mist issues

Table 7 contains the percentage of OC and EC concentrations as measured at the intake, vehicle and exhaust sampling stations. Intake data for both parts of the study indicate a more or less 50% split between OC and EC. It should be kept in mind that the test vehicle exhaust did not affect the intake air. Given that these conditions prevailed at both intake sampling locations over the two-week period, these data seem to be representative of low level background mine conditions. A half-and-half split is also observed at the operator or vehicle sampling station. Data collected in well mixed exhaust stations however seem to be different when taking a variability of less than 5% into account. At these locations, the EC/OC split is 65%-35% for both weeks of the study.

Oil mist contamination from the vehicle's hydraulic and lubrication system was measured. This contaminant is expected to affect all three of the dpm measurement methods tested here. This can be seen in Figure 14, where the oil mist concentration is plotted as a function of OC concentration. The linear relationship shown indicates that in this particular setting, oil mist emissions from a well-maintained production vehicle made up about 12% of the OC concentration.

Location	Ratio OC/TC	Ratio EC/TC
Week 1 – Intake	42% ± 10%	58% ± 10%
Week 1 – Exhaust	31% ± 1%	69% ± 1%
Week 1 – Vehicle	46% ± 2%	54% ± 2%
Week 2 – Intake	57% ± 7%	43% ± 7%
Week 2 – Far Exhaust	36% ± 5%	64% ± 5%
Week 2 – Near Exhaust	38% ± 5%	62% ± 5%
Week 2 – Vehicle	44% ± 8%	56% ± 8%

Table 7. Organic and elemental carbon ratios averaged by location.

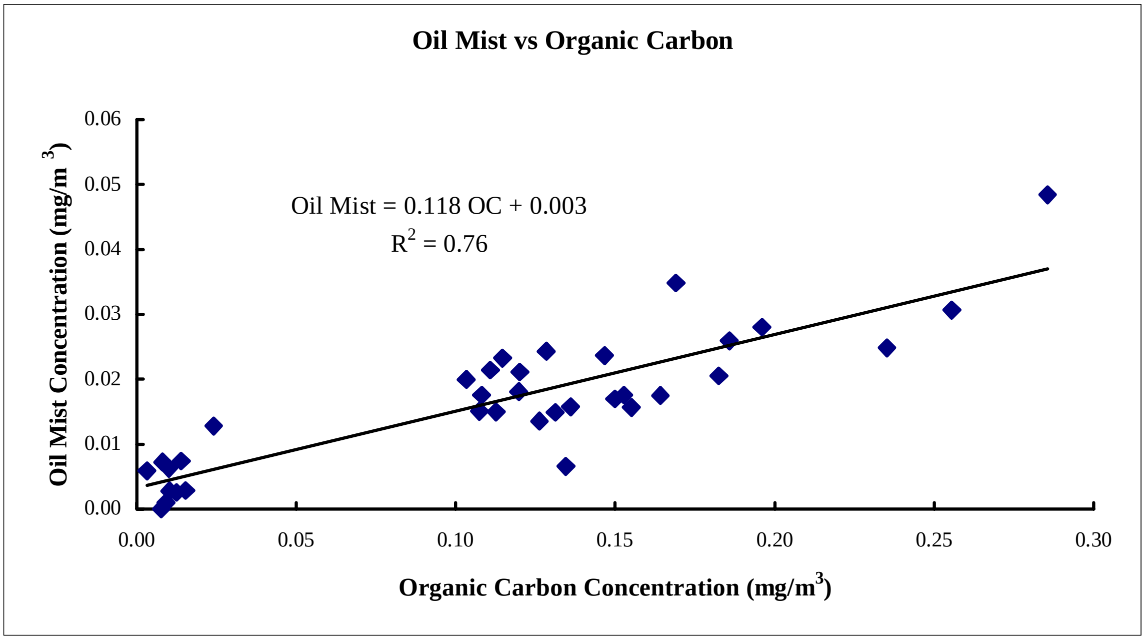


Figure 14. Oil mist concentration (lube and hydraulic oil) as a function of organic carbon concentration as measured by the Thermal-Optical method.

Gas concentration data

Table 8 lists the results of gas sampling at the exhaust stations of the test site during the first week of study. Also shown is the vehicle contribution to the contaminant levels. These values were obtained by subtracting the intake values from the exhaust concentrations.

Shown in Figure 15 is a typical daily profile of the nitric oxide (NO) concentration measured at the intake and exhaust of the work site during one day of Week 1. The exhaust trace shows a very stable concentration in which the vehicle cycles are clearly apparent. In every case, the test lasted around 5 hours and was uninterrupted.

Contaminant	TLV-TWA® or Exposure Limit	Average Gas/RCD Concentration									
		Nov. 10th		Nov. 11th		Nov. 12th		Nov. 13th		Nov. 14th	
		EX*	V**	EX*	V**	EX*	V**	EX*	V**	EX*	V**
CO2 (ppm)	5000	1786	1347	1787	1366	1761	1320	1765	1156	1930	1332
CO (ppm)	25	0.44	0.44	0.64	0.64	0.56	0.44	2.62	0.26	2.40	0.27
NO (ppm)	25	7.96	7.90	7.60	7.42	7.91	7.73	7.14	7.00	7.59	7.22
NO2 (ppm)	3	0.92	0.72	0.91	0.74	0.96	0.81	0.88	0.73	0.95	0.74
SO2 (ppm)	2	0.44	0.20	0.50	0.29	0.44	0.28	0.45	0.29	0.48	0.21
RCD (mg/m^3)	1.5	0.43	0.39	0.43	0.40	.039	0.35	0.39	0.38	0.46	0.44
AQI	3.0	1.71	1.44	1.72	1.49	1.66	1.44	1.64	1.43	1.82	1.51

EX* - Concentrations measured at the exhaust sampling station
V** - Concentrations calculated from the difference of the exhaust and intake sampling station (vehicle contribution)

Table 8. Air quality index calculations – Week 1, diesel tests.

Also shown in Table 8 are the Air Quality Index (AQI) calculations as per Equation 1. The AQI is used in the calculation of regulated air volumes for diesel engine certification according to the Canadian Standards Association (17).

These data are added for the sake of completeness and also to highlight the impact of using low sulphur content fuel. The argument for using low sulphur fuel will also be raised in the discussion section when dealing with the impact of fuel sulphur on the RCD method.

The same vehicle was tested in 1994 in the same location, under almost identical conditions. At that time the vehicle had logged 600 hours of production duty. Now at 5300 hours of production, the vehicle has the original catalytic converter and had just received regular preventive maintenance. No major repairs had been performed on the engine.

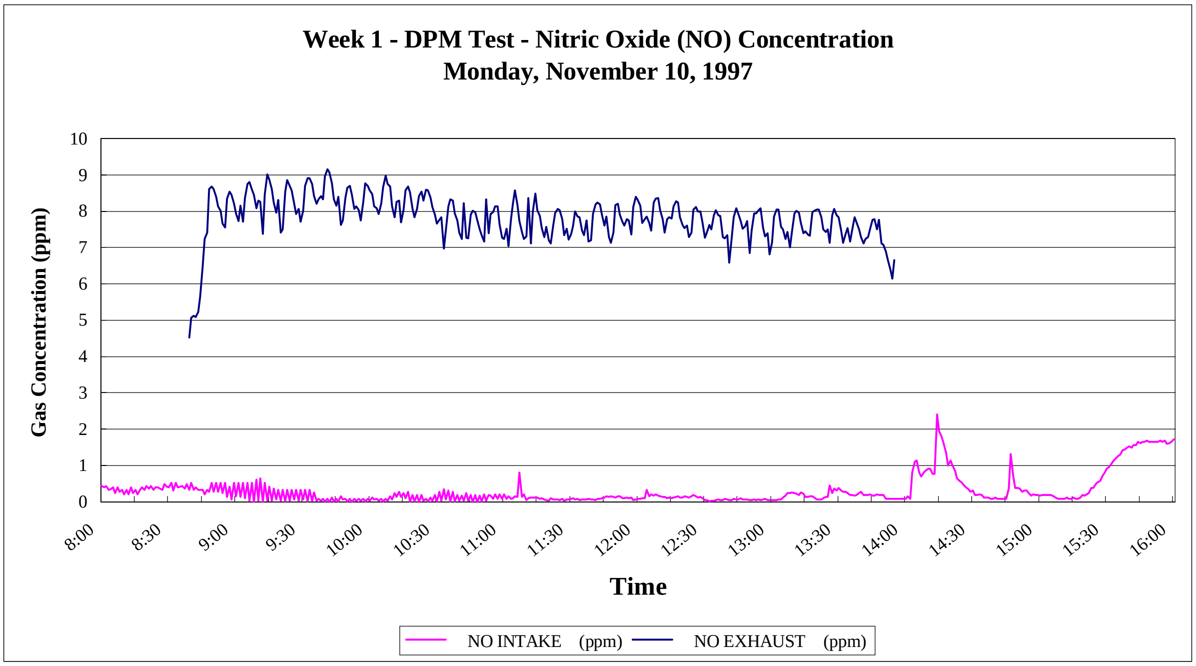


Figure 15. Nitric oxide (NO) concentration vs time – Week 1 data, November 10th.

$$AQI = \frac{CO}{50} + \frac{NO}{25} + \frac{RCD}{2} + 1.5\left\{\frac{SO_2}{3} + \frac{RCD}{2}\right\} + 1.2\left\{\frac{NO_2}{3} + \frac{RCD}{2}\right\} \qquad \text{Equation 1.}$$

At the time of the original study the AQI was measured at 1.17 with a ventilation volume of 35,000 cfm (18). If we pro-rate this value to the level of ventilation used in the present study, an AQI of 1.74 is calculated for the 1994 tests. The average AQI calculated for the present study is 1.45. Comparison of the individual contaminants reveals that most gases only changed marginally and that RCD concentrations were identical in both studies. The major difference is a three-fold decrease in the concentration of SO_2, which has a significant impact on the AQI calculation.

Several months ahead of the study, Brunswick Mining Division required low sulphur content fuel from its supplier. This fuel's sulphur content was measured at 0.044 wt%.

Results of the laboratory analysis are shown in Appendix III. This fuel is still being used at Brunswick. During the 1994 tests the vehicle was using a diesel fuel with 0.16wt% sulphur.

DISCUSSION

Impact of sulphides on the RCD method

If TC is used as a comparison, results reported in the previous section indicate that the concentration of airborne respirable sulphides is not linearly related to changes in the performance of the RCD method. This is not to say, however, that the presence of sulphides does not indirectly affect RCD results. The extent of this impact, the potential mechanisms at work and the significance of this problem will be discussed here.

The results of Thermogravimetric and Differential Thermal Analysis are reported in references 19, 20 and 21. The report dealing with the analysis of roadway dust and muckpile ore (20) found that:

- The oxidation of pyrite (common sulphide at Brunswick Mining Division) occurs at temperatures above 400°C and results in the production of iron oxides and SO_2 gas that should not cause any mass increases. In fact these reactions should lead to decreases in mass which would cause the RCD method to over-estimate the exposure to dpm.
- Blank silver membrane filters exposed to temperatures between 200°C and 600°C in artificial SO_2 atmospheres exhibited mass increases, which were not quantified but were described as substantial.
- Whereas the sulphation of certain minerals in the presence of silver (filter) could result in mass gains at temperatures of 500°C, no direct observations were made to confirm mass gains with the test samples submitted.

Whereas ashed silver membranes could not be used to quantify the different phases formed during ashing, these were qualitatively studied by VP-SEM. These analyses revealed several phases that produced energy dispersive spectra (EDS) indicating a composition of metal, sulphur and oxygen and in particular Fe-S-O. Since pyrite is the dominant sulphide in the mineral portion of the un-ashed silver membranes, then obviously the Fe-S-O phases are products of the ashing of pyrite. These Fe-S-O phases are either iron sulphates or mixtures of iron sulphides, iron sulphates, and iron oxides. Figure 16 shows the typical appearance of an ashed silver membrane, indicating that the sulphides in the mineral matter do react during the ashing of the RCD method forming sulphates or mixtures of sulphides, sulphates and oxides.

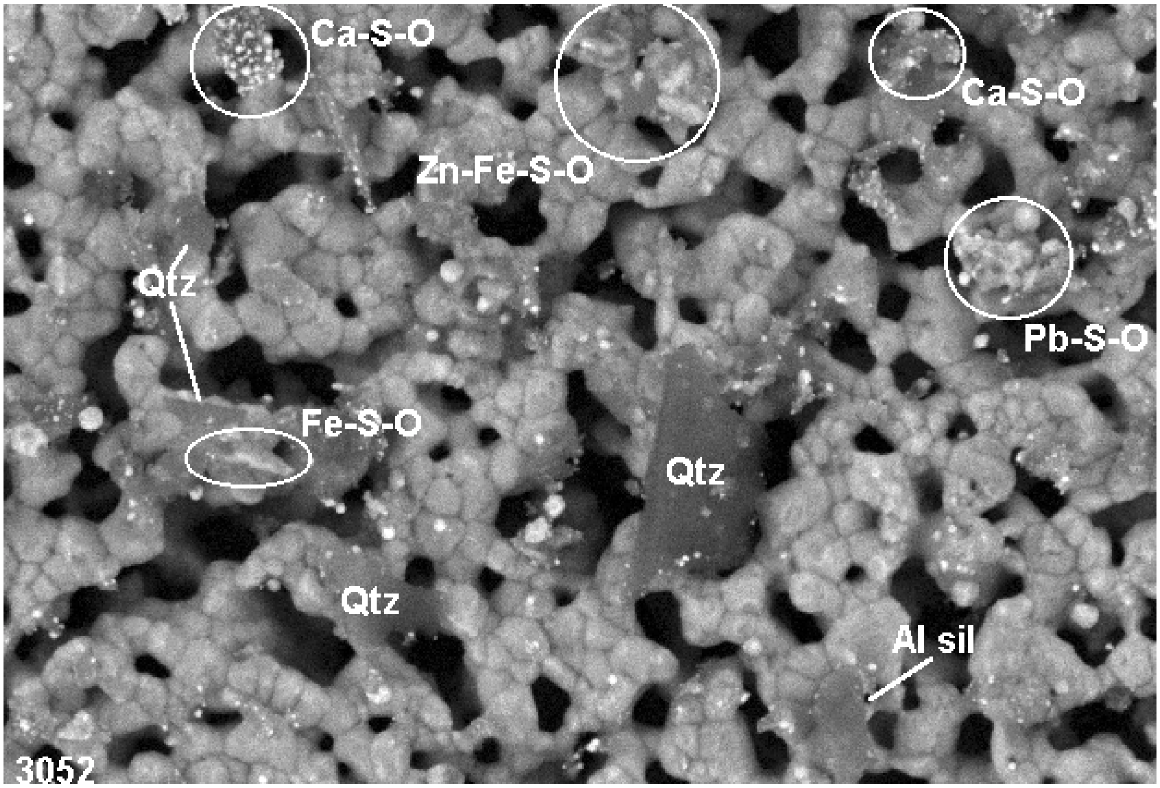


Figure 16. Scanning electron microscopy of dust sample after ashing.

Despite these observations, the statistical analysis presented in this report shows that these reactions do not significantly affect the results of RCD analysis. During the ashing process, there are mass increments from the formation of sulphates and corresponding mass decrements from the formation of oxides. It is possible that these competing mass changes result in a lesser impact on the RCD method. On the other hand, the potential mass changes due to reactions of the silver membrane could be significant. Indeed, the mass of the silver membrane is approximately 150 mg, whereas the mass of the dust sample is on the order of a milligram or less. Reactions that produce mass changes involving the silver membrane will necessarily introduce more significant errors in the results of the RCD method. The porosity of the silver membrane and the relatively high temperatures involved during ashing both favour reactions between the silver and the SO_2. Thermogravimetic analysis showed that blank silver membrane filters exposed to artificial SO_2 atmospheres between 200°C and 600°C increased significantly in mass, indicating the formation of silver sulphide. Potential problems for the RCD method arise from the sulphation of the silver membrane because of its contact with SO_2 produced from decomposition of the sulphide minerals during ashing and/or from the diesel fuel itself.

This is supported by observations describing the ashing of field samples (21) that were obtained prior to the mine using low sulphur content fuel. In this instance, SO_2 gas was being produced during ashing both in inert (N_2) and oxygen rich atmospheres between the temperatures of 250°C and 400°C. This observation indicates that the source of SO_2 were likely to be organo-sulphates in the diesel fuel.

In conclusion, the oxidation of sulphides results in the production of SO_2 and should not in itself introduce significant mass increases. Significant mass gains could result in a reaction involving the silver that is present in filter. The production of SO_2 from ore or from fuel is critical again if silver enters into the reaction. This is why keeping the mineral portion of the sample away from the silver matrix is important. This can be done by using a silver membrane filter with 0.8 µm pore size. Mineral dust being coarse compared to the filter openings will tend to remain on the surface of the sample (see Figure 17).

Diesel particulate matter is very fine (22) and can lodge within the matrix of a 0.8 µm silver membrane filter as shown schematically in Figure 17. Hence, SO_2 evolved within the silver membrane from fuel sources could cause mass increases due to the sulphation of silver. The use of a low-sulphur fuel, which is important from a health standpoint, may also prevent the interference caused by SO_2 gas in the RCD method.

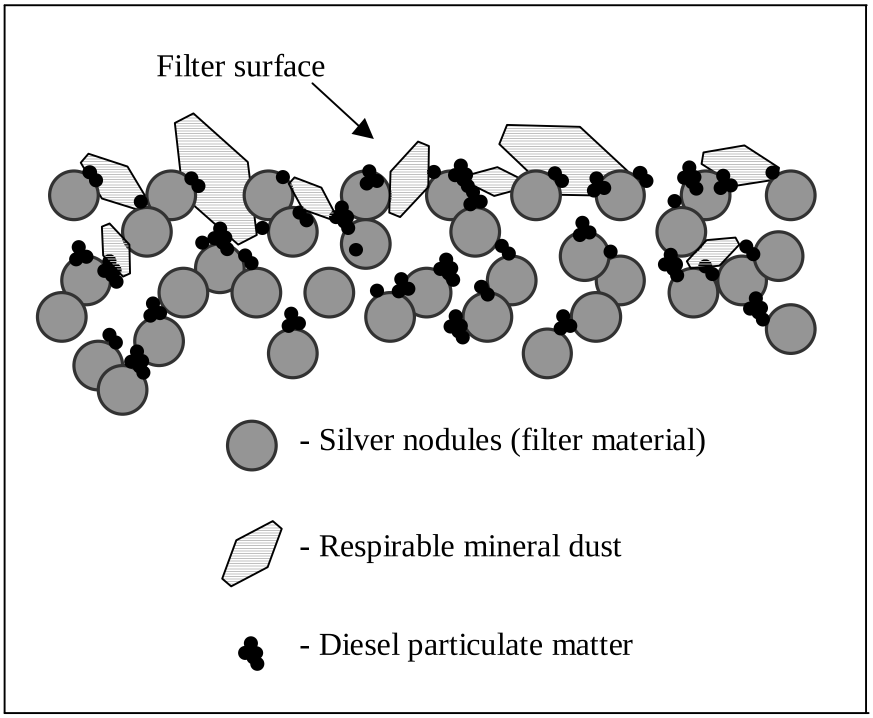


Figure 17. Filtration of dpm and mineral dust on a silver membrane filter

Comparison of methods

In spite of the fact that data analysis showed that three methods do not yield statistically similar results, linear regression analysis relating both the SS and RCD methods to the TC values show very close agreement in the higher concentration ranges. These results tend to support the fact that lower sulphur fuel and the use of a 0.8 μm silver membrane can limit the impact of sulphation of the silver membrane in the presence of SO_2 gas.

Precision

Data in Table 6, which lists the average standard deviations associated with the various sampler groups, is a good indicator of the repeatability of each method. By far the lowest average standard deviation is associated with the total carbon measurement. In a well-mixed atmosphere, the standard deviation associated with the TC results is 0.007 mg/m^3. This compares very well with European tests performed on field blanks that show standard deviations of 0.006 mg/m^3 (23, 24). The RCD sample results also displayed very low standard deviation values at 0.016 mg/m^3. This is due in large part to the well mixed dust profile in the sampling cross-section and the fact that silver membrane filters are very sturdy and not affected significantly by variations in temperature and humidity. The calculated standard deviation for the SS method was higher still at 0.055 mg/m^3. The MSA™ filter used is apparently very sensitive to fluctuations in relative humidity. Between the pre- and post-weighing sessions, the relative humidity dropped by about 7%, from 53% to 46%. This may have caused the group of analytical blanks to display an average mass difference (decrease) of 0.052 mg with a standard deviation of 0.024 mg. If we use an average sampling time of 350 minutes to convert the standard deviation (0.024 mg) in the blank SS filters to milligrams per cubic meters we obtain 0.040 mg/m^3. Further adding the variability associated with the RCD method, which is much less susceptible to relative humidity problems, a value of 0.056 mg/m^3 is obtained, which is derived independently, but still compares very well to the experimentally obtained value of 0.055 mg/m^3 for the SS method.

The standard deviation measured for the three methods tested varied between 0.007 and 0.055 mg/m^3. The higher value in that range represents 37% of the proposed ACGIH TLV-TWA® of 0.15 mg/m^3 (1) and is therefore significant.

Accuracy

This section deals with the closeness of agreement between the RCD and SS methods and the dpm concentration as measured by the TC method. Whether or not TC is a good measure of dpm concentration is not within the scope of this work. It is nonetheless the method that has the lowest variability, that does not use a gravimetric approach and that is not likely to be significantly affected by this mine's mineralogy.

Data from Figure 13 was used to calculate the discrepancy or percentage difference between the gravimetric methods and TC for the second week of work (diesel/mineral dust). When these linear regression equations are used to compare RCD and SS to the total carbon values, percentage differences between the gravimetric methods and TC can be computed and plotted in order to assess the performance of each method at low concentration levels. These plots are shown in Figure 18.

Figure 18 shows that below 0.2 mg/m^3 both gravimetric methods quickly become inaccurate. In many instances, the industry sets action levels at half of the exposure limit. Using this as a rule of thumb and setting this value at 0.3 mg/m^3 to gain a safety margin, it could be argued that for high sulphide ore bodies, the gravimetric approaches are adequate as long as the exposure limit for dpm is set at 0.6 mg/m^3 or above. For lower exposure limits, data collected here show that a gravimetric method may not be precise and/or accurate enough to assess exposure.

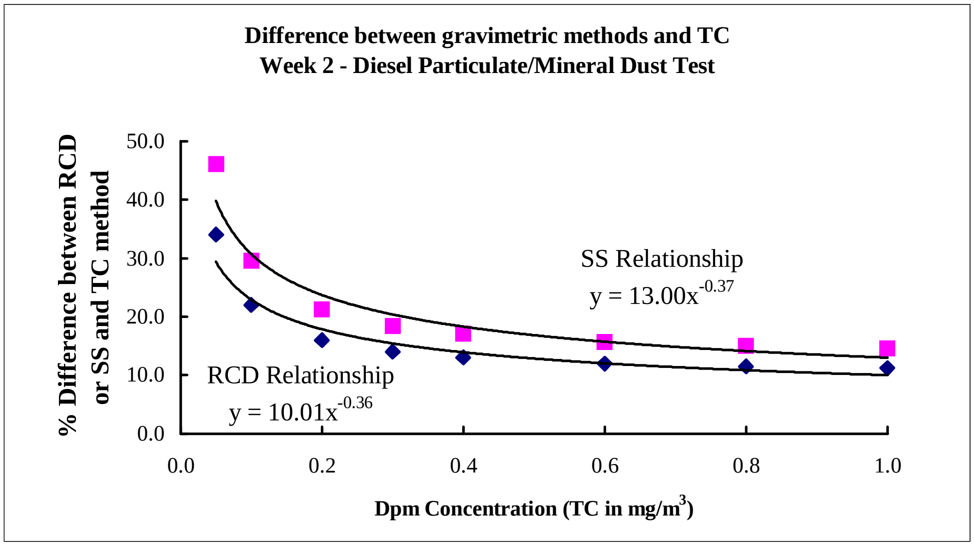


Figure 18. Difference between the TC method and the gravimetric methods – Week 2 RCD (◆) and the SS (■)

The same process was carried out for Week 1 data (more or less pure dpm environment). The results are shown in Figure 19. Results are significantly different in this case and are believed to be representative of situations where airborne dust is made up mostly of dpm or where sulphides are not present. Results for the SS method are more or less similar to those shown above for Week 2. Results for the RCD method show a 13% or better agreement with the TC method down to 0.10 mg/m^3.

The closeness of agreement between the RCD and TC method for Week 1 are due to the gravimetric stability of the silver membrane filter and the lack of interference in this particular atmosphere. Results of work performed earlier at Creighton Mine does differ (12) in that the slopes of the linear relationships between the RCD and TC methods as well as the SS and TC methods are 1.37 and 1.35, respectively. Results here show slopes of 1.12 and 1.13 for data collected in the first week of study. This difference appears to be significant and cannot be explained at this time.

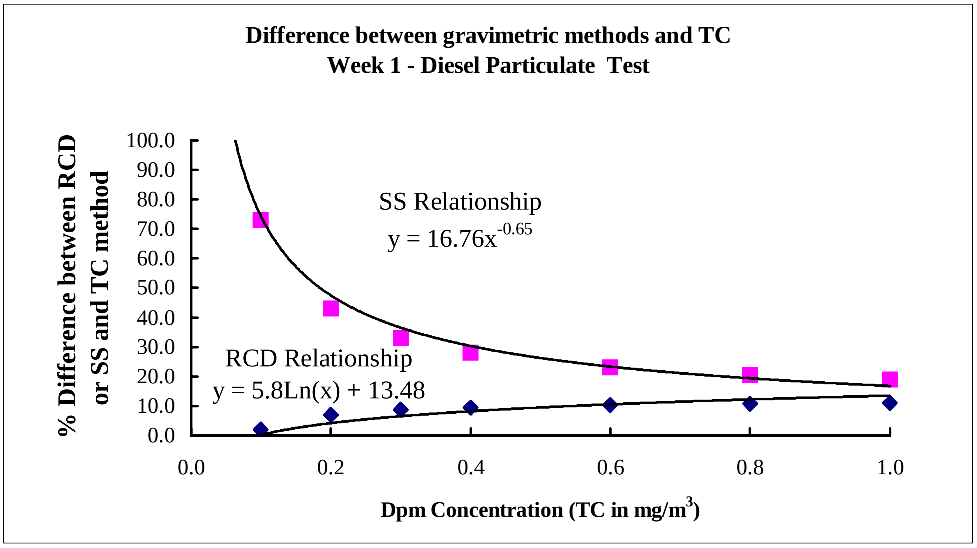


Figure 19. Difference between the TC method and the gravimetric methods – Week 1 RCD (◆) and the SS (■)

EC/OC ratios and oil mist issues

Data presented here show EC and OC in approximately equal concentrations. At intake stations and as measured on the vehicle operator the ratios are very close to 1:1. Exhaust sampling stations show comparatively higher EC concentrations.

Figure 14 shows that oil mist from the vehicle's lube and hydraulic oil make up about 12% of the airborne OC measured or only about 6% of the TC value if a 1:1 ratio of OC:EC is used. At present concentration levels and assuming that lubricating greases for drilling applications gain in popularity, the contribution of oil mists could be kept to a minimum. This is assuming that leaks of lube and hydraulic oils on vehicles are controlled.

CONCLUSIONS

This study did not find evidence directly linking the presence of sulphide minerals to interference in the RCD method. This is not to say, however, that sulphides do not have an indirect effect on the method. Oxidation of sulphides during ashing produces SO_2 gas. Thermogravimetric and Differential Thermal Analysis showed that SO_2 emanations and subsequent interaction with the silver from the membrane causes a definite mass increase of the silver membrane filter. These data also showed that another source of interference in the temperature range used in RCD analysis are organo-sulphates originating from the fuel. These results indicate that minimizing SO_2 and reducing its interaction with the silver membrane can enhance the performance of the RCD method. This can be accomplished by making use of a small pore-size silver membrane filter which reduces the amount of mineral dust that actually comes in contact with the silver. Using low sulphur fuel in underground diesel applications will also reduce SO_2 gas emissions during ashing and hence the likelihood of mass increase associated with sulphation of the silver membrane.

Even in a sulphide ore environment, the gravimetric methods and the TC analytical technique performed well. It is believed that for the present and as long as the limits of exposure are at or above 0.60 mg/m^3, the gravimetric methods appear to be adequate in sulphide ore mines. Below these levels, alternatives such as the Thermal-Optical methods should be considered.

For mines where mineral interference is not a problem and/or in applications where dpm is the main source of airborne respirable dust, the RCD method could be used at even lower concentrations. This should be kept in mind in view of the fact that this method is compatible with direct, silica analysis and, as such, increases the amount of exposure data collected.

If lubrication and hydraulic oil leaks can be minimized through maintenance practices and if lubricating greases or alternatives to rock drill oils are adopted by the mining industry, the interference from oil mists could be reduced. The data reported here show that oil mists could account for as little as little as 6% of the TC concentration. This percentage could increase as diesel emissions are controlled and reduced.

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APPENDIX I

Week/Day	Sampling Station	RCD conc. (mg/m^3) AVG.	RCD conc. (mg/m^3) ST. DEV.	SS conc. (mg/m^3) AVG.	SS conc. (mg/m^3) ST. DEV.	TC conc. (mg/m^3) AVG.	TC conc. (mg/m^3) ST. DEV.
1 - 1	Intake	0.036	0.018	0.113	0.021	0.028	0.006
	Exhaust	0.430	0.010	0.508	0.051	0.357	0.012
	Vehicle	0.411	0.044	0.509	0.070	0.394	0.031
1 - 2	Intake	0.012	0.010	0.069	0.035	0.019	0.007
	Exhaust	0.425	0.019	0.486	0.051	0.370	0.010
	Vehicle	0.339	0.054	0.411	0.042	0.318	0.021
1 - 3	Intake	0.039	0.010	0.105	0.010	0.027	0.000
	Exhaust	0.392	0.033	0.479	0.019	0.368	0.014
	Vehicle	0.302	0.010	0.417	0.019	0.298	0.006
1 - 4	Intake	0.011	0.019	0.097	0.028	0.020	0.002
	Exhaust	0.392	0.018	0.429	0.032	0.345	0.009
	Vehicle	0.256	0.032	0.401	0.058	0.278	0.012
1 - 5	Intake	0.018	0.018	0.070	0.063	0.029	0.001
	Exhaust	0.461	0.010	0.461	0.061	0.381	0.010
	Vehicle	0.327	0.010	0.423	0.017	0.326	0.010
2 - 1	Intake	0.026	0.011	0.078	0.052	0.026	0.003
	Far Exhaust	0.487	0.020	0.683	0.152	0.538	0.006
	Near Exhaust	0.608	0.020	0.824	0.052	0.688	0.034
	Vehicle	0.869	0.049	1.078	0.085	0.903	0.077
2 - 2	Intake	0.007	0.012	0.113	0.012	0.006	0.001
	Far Exhaust	0.308	0.023	0.462	0.088	0.360	0.002
	Near Exhaust	0.346	0.012	0.499	0.069	0.376	0.008
	Vehicle	0.377	0.049	0.480	0.045	0.476	0.079
2 - 3	Intake	0.007	0.011	0.085	0.056	0.043	0.003
	Far Exhaust	0.365	0.035	0.541	0.065	0.408	0.007
	Near Exhaust	0.420	0.020	0.527	0.114	0.439	0.011
	Vehicle	0.463	0.040	0.571	0.000	0.613	0.240
2 - 4	Intake	0.054	0.012	0.074	0.065	0.022	0.002
	Far Exhaust	0.245	0.012	0.434	0.024	0.288	0.005
	Near Exhaust	0.270	0.024	0.326	0.075	0.318	0.012
	Vehicle	0.257	0.042	0.331	0.155	0.390	0.057
2 - 5	Intake	0.000	0.000	0.018	0.032	0.016	0.000
	Far Exhaust	0.233	0.023	0.259	0.091	0.265	0.004
	Near Exhaust	0.257	0.010	0.359	0.054	0.284	0.002
	Vehicle	0.272	0.134	0.425	0.081	0.341	0.020
Average			0.025		0.056		0.021

Table A1. Averages and standard deviations for sampler groups – Weeks 1 & 2

APPENDIX II

Statistical Comparison of Two Methods for Measuring Airborne Diesel Particulate Concentrations

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1. Introduction

The purpose of this analysis is to develop statistical methodology for comparing two methods of measuring airborne diesel particulate concentrations and to apply this methodology to data.

Ten data sets were provided for analysis. The first nine data sets consist of 2 measurements (using different methods) of diesel particulate concentrations at 3 or 4 different workplaces on consecutive days. Data sets #1 to #8 were collected by CANMET over 5 consecutive days; diesel particulate concentrations were measured at 3 workplaces for data sets #1 to #4 and 4 workplaces for data sets #5 to #8. Most of the measurements were the average of 3 separate side-by-side measurements; however, due to sampler failure, some measurements are an average of 2 side-by-side measurements. Standard deviations are also available but are not used in the analyses that follow. Data set #9 (not collected by CANMET) was collected over 7 consecutive days. As with data sets #1 to #8, most of the measurements are the average of 3 separate side-by-side measurements but some are the average of only two. For each of data set #1 to #9, the goal is to determine whether there is a systematic difference between the two methods of measuring airborne diesel particulate concentrations.

Another data set (data set #10) consists of measurements of two variables: airborne concentration of sulphide dust and the ratio of two measurements (of airborne diesel particulate concentration). For this data set, the goal is to determine if there is a relationship between these two variables.

2. Statistical Methodology

In this section, we will develop appropriate statistical methodology for analyzing data sets #1 to #9, in particular, to determine whether there is a systematic difference between the two methods of measuring airborne diesel particulate concentrations.

Let x_{ijk} be the measurement using method i (i= 1, 2) at workplace j (j= 1,…, s, where s is 3 or 4) on day k (k = 1,…, d where d is 5 or 7 in the data sets provided). Since we are interested in determining whether the two methods are different, we will look at the difference between the two measurements

$$\Delta_{jk} = x_{1jk} - x_{2jk}$$

(Alternatively, we could define Δ_{jk} as log (x_{1jk} / x_{2jk}) that is, the logarithm of the ratio of the two measurements; for data set #2, a problem arises since there are two measurements of 0.000 as well as two negative measurements.) If no systematic difference exists, Δ_{jk} should be 0 on average or centered around 0; otherwise, the differences will tend to be either more positive or more negative.

A reasonable statistical model for Δ_{jk} is

$$\Delta_{jk} = \mu_j + \varepsilon_{jk} \tag{1}$$

where μ_j represents the systematic bias of method 1 relative to method 2 at workplace *j* and ε_{jk} represents random noise whose mean is 0. If the 2 methods are identical, we should have $\mu_1 = \ldots = \mu_s = 0$; that is, the difference between the measurements is simply random noise and there is no systematic bias. In order to test the hypothesis that $\mu_1 = \ldots = \mu_s = 0$, we need to specify the dependence structure of the noise ε_{jk}.

The simplest possible model for the ε_{jk}'s would be to assume mutual independence. While it does seem reasonable to assume between days (that is, ε_{jk} is independent of $\varepsilon_{j'k'}$), it may not be reasonable to assume independence within each day (that is, ε_{jk} need not be independent of $\varepsilon_{j'k}$). A possible explanation for any dependence (or correlation) might be the presence of some factor in the environment causing measurements to be biased in the same (or perhaps) opposite direction. In any event, it is very common for data collected in close proximity to be correlated to some extent.

Under the assumption of independence between days but not within days, we essentially have a multivariate model for the differences Δ_{jk}. More precisely, we will re-write the model (1) as

$$\begin{pmatrix} \Delta_{1k} \\ \vdots \\ \Delta_{sk} \end{pmatrix} = \begin{pmatrix} \mu_1 \\ \vdots \\ \mu_s \end{pmatrix} + \begin{pmatrix} \varepsilon_{1k} \\ \vdots \\ \varepsilon_{sk} \end{pmatrix} \tag{2}$$

and assume that the vectors of errors are independently distributed with a multivariate normal distribution. Assuming this distribution for the errors may seem a rather strong assumption; however, the results obtained by assuming this model should be fairly insensitive (or robust) to small deviations from the model.

Under the assumptions stated above, the standard test of the hypothesis of no bias (that is, $\mu_1 = \ldots = \mu_s = 0$) *is Hotelling's* T^2 *test*. This test is essentially a multivariate extension of the well-known (univariate) *Student's t test*. Student's *t* test compares a sample mean to an hypothesized population mean by comparing the difference in means (sample mean - population mean) to an estimate of the standard error of the sample mean. Hotelling's T^2 test extends this approach to the comparison of multivariate means. A description of Hotelling's T^2 test can be found in textbooks on multivariate statistical methods, for example, Johnson and Wichern [1]. Details on the calculation of the test statistic for Hotelling's T^2 test can be found in Appendix 1.

A more simple test of the hypothesis that $\mu_1 = \ldots = \mu_s = 0$ is available if we can assume that the Δ_{jk}'s are mutually independent. This test is called the *sign test*. This test is based on the number of positive Δ_{jk}'s in the data set. If $\mu_1 = \ldots = \mu_s = 0$ then it follows from model (1) that $\Delta_{jk} > 0$ with probability 1/2 (and therefore $\Delta_{jk} < 0$ with probability 1/2); thus approximately 50% of the Δ_{jk}'s should be positive when $\mu_1 = \ldots = \mu_s = 0$. Details on the calculation of the sign test are given in Appendix 1; more details can be found in Lehmann [2] as well as Moore and McCabe [3]. The sign test is a competitor of the more commonly used paired *t* test. While the sign test assumes only that the differences Δ_{jk} are positive and negative with equal probability, the *t* test also requires that the variance of the differences be constant; for data sets #1 to #9, this latter assumption does not seem to hold. (The variance of the differences does seem to depend on the workplace at which the measurements were made.)

Two points are worth noting at this stage:

1. In order to use Hotelling's T^2 test, the number of workplaces (*s*) *must* be less than the number of measurement days (*d*).

2. The sign test assumes mutual independence of the Δ_{jk}'s whereas Hotelling's T^2 test does not.

For the data sets considered here, the condition in point 1 always holds (*s* is at most 4 while *d* is at least 5) while the mutual independence required in point 2 is not automatic for reasons described above.

3. Analyses

3.1 Data sets #1- #9

For each of data sets #1 to #9, we assume a multivariate normal model (2) for the differences in measurement between methods 1 and 2; this model appears reasonable (based on some diagnostic plots) for these data.

For each data set, we carry out 3 hypothesis tests:

1. Hotelling's T^2 test as described in Appendix 1.

2. The sign test as described in Appendix 1.

3. A test of independence of the differences in measurement between the *s* workplaces; this test allows us to determine whether or not the sign test could be used in place of Hotelling's T^2 test.

The p-values for these 3 tests are given in Table 1 below.

		p-values for tests	
Data set	T^2 test	Sign test	Independence test
2	0.000	0.000	0.012
4	0.001	0.000	0.088
3	0.049	0.000	0.439
9	0.071	0.000	0.125
8	0.079	0.041	0.044
1	0.121	0.118	0.717
5	0.194	0.000	0.915
7	0.197	0.000	0.482
6	0.490	0.003	0.859

Table 1 P-values from 3 hypothesis tests ranked according to the p-value for Hotelling's T^2 test. Any p-value less than 0.0005 is indicated by 0.000.

To illustrate the computations, we will use data set #1 where $d = 5$ and $s = 3$. First, we carry out Hotelling's T^2 test of the hypothesis that $\mu_1 = \mu_2 = \mu_3 = 0$. Using the estimates

$$\begin{pmatrix} \overline{\Delta}_1 \\ \overline{\Delta}_2 \\ \overline{\Delta}_3 \end{pmatrix} = \begin{pmatrix} -0.9914 \\ 0.0558 \\ 0.0042 \end{pmatrix}$$

$$S = \begin{pmatrix} 1.1230 & -1.0635 & 0.6335 \\ -1.0535 & 4.9270 & 0.9155 \\ 0.6335 & 0.9155 & 2.8570 \end{pmatrix} \times 10^{-4}$$

(as defined in Appendix 1), we obtain $T^2 = 44.686$; based on the appropriate *F* distribution, the p-value for the hypothesis is 0.121. This p-value can be interpreted as moderate but not overwhelming evidence against the hypothesis
that $\mu_1 = \mu_2 = \mu_3 = 0$.

(Roughly speaking, the p-value is a measure of evidence against the hypothesis being tested; the smaller the p-value, the more evidence we have that the hypothesis is false. In many disciplines, a p-value that is less that 0.05 (or 5%) is considered to represent *statistical significance* and the hypothesis is rejected.)

In order to use the sign test, we must have independence of the differences Δ_{jk}. Again assuming the multivariate normal model (2), it is possible to do a test of independence of the differences Δ_{jk}; this test is based on the covariance matrix *S*. For the hypothesis of independence, we obtain a p-value of 0.72 which indicated that we do not have any strong evidence to reject independence of the differences. (However, given the very small sample size, this test may not have sufficient power to detect dependence between the differences.)

Assuming independence (which seems plausible given the p-value from the previous test), we can carry out the sign test as outlined in Appendix 1. Of the 15 differences, 11 are positive and 4 are negative. The p-value for the sign test is 0.118 (essentially the same as that obtained for Hotelling's T^2 test). Again this indicates moderate but not overwhelming evidence against the hypothesis that $\mu_1 = \mu_2 = \mu_3 = 0$.

How can we interpret the p-values for Hotelling's T^2 test in Table 1? Using the traditional 5% as a cut-off for “statistical significant” only 3 of the 9 data sets show a statistically significant difference between the 2 methods of measurement. However, it is worth noting that all 9 p-values are less than 0.50; if there were no overall differences, we would expect the p-values to fall more-or-less uniformly between 0 and 1.

The largest p-values are generally for the data sets where measurements were made at 4 workplaces. From a statistical point of view, this is not surprising since the *power* (that is, the ability of the test to detect significant differences) of Hotelling's T^2 test generally increases as (d-s) increases (if all other parameters are held constant).

Eight of the 9 p-values for the sign test are less than 5%. However, as mentioned above, use of the sign test depends on an assumption of independence of the differences Δ_{jk}; given the p-values for the test of independence, this assumption may always not be well-founded.

3.2 Data set #10

In this data set, we are given 15 measurements of two variables: the airborne concentration of sulphide dust (DUST) and the ratio of method 1 to method 2 measurements (RATIO). The goal in this analysis is to determine if there is any evidence of a relationship (linear or otherwise) between these two variables. *** The linear regression plot is shown in Figure 11 of the main report, Michel Grenier***

We start by looking for a linear relationship. A simple measure of linear dependence between two variables is the so-*called Pearson product moment correlation coefficient* (commonly called the correlation coefficient). For these data, the correlation coefficient is -0.060. Correlations close to 0 indicate little or no linear dependence while correlations close to ±1 indicate strong linear dependence.

The significance of this correlation can be tested by assuming a simple linear regression model

$$RATIO_i = \beta_0 + \beta_1 \, DUST_i + \varepsilon_i \quad for\ i = 1, \cdots, 15$$

(where $\varepsilon_1, \ldots, \varepsilon_{15}$ are independent normally distributed noise variables). Using the method of least squares, we obtain the estimates (with standard errors in parentheses)

$$\hat{\beta}_0 = 0.8749 \ (0.0785) \ and \ \hat{\beta}_1 = -0.0731 \, (0.3403)$$

Using the estimate of β_1, we can test the hypothesis that $\beta_1 = 0$ (no relationship between DUST and RATIO) using *a* either *t* or F test (there are equivalent); the resulting p-value is 0.8331 which indicates little evidence of a non-constant linear relationship between the two variables. (The test of β1 = 0 is equivalent to a test of 0 correlation.)

An alternative test for dependence between DUST and RATIO is the Spearman rank correlation test. Essentially, this test replaces the observations for each variable by their rank (from 1 to 15) and then computes the standard (Pearson) correlation coefficient of these ranks. This correlation can be converted into a test statistic of the hypothesis of independence and a p-value computed. This test is described in Lehmann [2].

From these data, we obtain a Spearman correlation r = -0.040. The corresponding p-value is 0.884 confirming the conclusion of the linear regression analysis.

4. Conclusions and Comments

1. Hotelling's T^2 test assuming the multivariate normal model (2) seems to provide the most appropriate methodology for the analysis of data sets #1 to #9. This test takes into account the possible within-day dependence in the measurements between different workplaces. However, if independence of the differences were a reasonable assumption, the sign test would be a reasonable and, in most situations, a more powerful test.

2. For most data sets, there does seem to be moderate to strong evidence that the two methods of measuring diesel particulate concentrations are different. This difference is not always statistically significant in the traditional sense (p-value ≤ 0.05) perhaps due to the relatively small sample sizes involved.

3. The sample sizes for data sets #1 to #9 are quite small. There are several consequences of this. First, the ability of Hotelling's T^2 test to detect deviations from the hypothesis being tested may be quite low particularly when the number of workplaces is nearly equal to the number of measurement days. Second, any conclusions made based on these data may not apply in general if the underlying system is ”non-stationary”. For example, there may be a strong dependence in the data on the time of year; if measurements are made at a different time of year, the conclusions may be quite different.

4. There appears to be no evidence of dependence between the two variables given in data set #10. However, as the sample size is quite small (15 pairs of observations), there may not be sufficient power in the tests used to detect a weak relationship between the two variables.

References

[1] Johnson, R.A. and Wichern, D.W. (1992) *Applied Multivariate Statistical Analysis* (3rd edition). Prentice-Hall.

[2] Lehmann, E.L. (1975) *Nonparametrics: Statistical Methods based on Ranks*. Holden-Day.

[3] Moore, D.S. and McCabe, G.P. (1993*) Introduction to the Practice of Statistics* (2nd edition). W.L. Freeman.

Appendix 1: Calculation of test statistics

Hotelling's T^2 test

Given the data, we define sample means

$$\overline{\Delta}_j = \frac{1}{d}\sum_{k=1}^{d}\Delta_{jk} \quad \mathit{for}\ j = 1,\cdots,s$$

And the vector of sample means

$$\overline{\Delta} = \begin{pmatrix} \overline{\Delta}_1 \\ \vdots \\ \overline{\Delta}_s \end{pmatrix}$$

Also define the sample variance-covariance matrix

$$S = \begin{pmatrix} s_{11} & \cdots & s_{1s} \\ s_{21} & \cdots & s_{2s} \\ \vdots & \ddots & \vdots \\ s_{s1} & \cdots & s_{ss} \end{pmatrix}$$

where

$$s_{ij} = \frac{1}{d-1} \sum_{k=1}^{d} (\Delta_{ik} - \overline{\Delta})\,(\Delta_{jk} - \overline{\Delta}_j)$$

Then given $\overline{\Delta}$ and *S*, we define Hotelling's T^2 statistic (using matrix notation) by

$$T^2 = d\overline{\Delta}^T S^{-1} \overline{\Delta}$$

Under the assumption that the errors are multivariate normal (as given in section 2), (d-s) T^2 [s (d-1)] has an *F* distribution with *s* and (d - s) degrees of freedom when $\mu_1 = \ldots = \mu_s$.= 0. We can use this *F* distribution to compute a p-value for the test of the hypothesis that. $\mu_1 = \ldots = \mu_s$.= 0. Most statistical packages will calculate both the test statistic and p-value .

Sign test

As mentioned in section 2, use of the sign test assumes that the Δ_{jk}'s are mutually independent.

The sign test uses a test statistic that counts the number of positive Δ_{jk}'s. Define

$$p_{jk} = \begin{cases} 1 \;\; if\, \Delta_{jk} > 0 \\ 0 \quad otherwise \end{cases}$$

and

$$T = \sum_{j=1}^{s} \sum_{k=1}^{d} p_{jk}$$

Assuming that the Δ_{jk}'s are independent and symmetrically distributed around 0, T has a *Binomial distribution* with parameters s x d and ½ (see Moore and McCabe [3] for details); that is,

$$P(T=x) = \frac{(sd)!}{x!(sd-x)!}\left(\frac{1}{2}\right)^{sd} \quad for \quad x = 0,1,\cdots,sd$$

Where 0!=1 and k! = 1 x 2 x … x k for k ≥ 1.

Given $T = t$, we can compute a p-value for the sign test as follows. Let u=min (t , s d - t)

Then

$$p-value = 2\sum_{x=0}^{u}\left[\frac{(sd)!}{x!(sd-x)!}\left(\frac{1}{2}\right)^{sd}\right]$$

There are also approximations for the p-value (using the normal distribution)

that are useful when $s\ d$ is large (say, greater than 20).

APPENDIX III

From:	Hobbs, Donna-Kaye	
Sent:	Monday, December 08, 1997 8:27AM	
To:	Gangal, Mahe	
Subject:	Analysis Report	

Mahe,

Listed below are the results for your two mining diesels. The original will follow in the mail.

Your ID	BMS-2350	BMS-3200
Lab ID	as970632	as970633
Carbon (wt%)	87.3	87.0
Hydrogen (wt%)	12.9	12.9
Sulphur (wt%)	0.044	0.044

Methods
Carbon & Hydrogen ASTM D-5291
Sulphur ASTM D-2622

If you have any questions please call.
Thanks

Donna Kaye Hobbs
Characterization Laboratory