

# The Diesel Exhaust in Miners Study: III. Interrelations between Respirable Elemental Carbon and Gaseous and Particulate Components of Diesel Exhaust derived from Area Sampling in Underground Non-metal Mining Facilities

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Diesel exhaust (DE) has been implicated as a potential lung carcinogen. However, the exact components of DE that might be involved have not been clearly identified. In the past, nitrogen oxides (NO<sub>x</sub>) and carbon oxides (CO<sub>x</sub>) were measured most frequently to estimate DE, but since the 1990s, the most commonly accepted surrogate for DE has been elemental carbon (EC). We developed quantitative estimates of historical exposure levels of respirable elemental carbon (REC) for an epidemiologic study of mortality, particularly lung cancer, among diesel-exposed miners by back-extrapolating 1998–2001 REC exposure levels using historical measurements of carbon monoxide (CO). The choice of CO was based on the availability of historical measurement data. Here, we evaluated the relationship of REC with CO and other current and historical components of DE from side-by-side area measurements taken in underground operations of seven non-metal mining facilities. The Pearson correlation coefficient of the natural log-transformed (Ln)REC measurements with the Ln(CO) measurements was 0.4. The correlation of REC with the other gaseous, organic carbon (OC), and particulate measurements ranged from 0.3 to 0.8. Factor analyses indicated that the gaseous components, including CO, together with REC, loaded most strongly on a presumed 'Diesel exhaust' factor, while the OC and particulate agents loaded predominantly on other factors. In addition, the relationship between Ln(REC) and Ln(CO) was approximately linear over a wide range of REC concentrations. The fact that CO correlated with REC, loaded on the same factor, and increased linearly in log–log space supported the use of CO in estimating historical exposure levels to DE.

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## INTRODUCTION

Diesel exhaust (DE) is a complex mixture of gases, vapors, and particulates generated under high pressure and temperature during the engine combustion cycle. Diesel particulate matter (DPM) has a carbonaceous core [defined as elemental carbon (EC)] with adsorbed organic compounds [described as organic carbon (OC)] and small amounts of sulfates, metals, and other compounds. The gaseous constituents include carbon oxides ( $\text{CO}_x$ ), nitrogen oxides ( $\text{NO}_x$ ), aldehydes, and low-molecular weight hydrocarbons.

In response to health concerns with long-term exposure to DE, in particular lung cancer, the US National Cancer Institute (NCI) and the US National Institute for Occupational Safety and Health (NIOSH) initiated an epidemiologic study of DE among non-metal miners, known as the Diesel Exhaust in Miners Study (DEMS) (NCI/NIOSH, 1997). The study has two epidemiologic components: a cohort mortality study and a nested case-control study of lung cancer. The third component of the study is the development of quantitative estimates of DE exposure using respirable elemental carbon (REC) as the primary indicator of DE. Details of the exposure assessment process can be found elsewhere (Coble *et al.*, 2010; Stewart *et al.*, 2010; Vermeulen *et al.*, 2010).

A major challenge in the exposure assessment process was the limited number of historical measurements of EC [currently regarded as the best surrogate of DE (Birch and Cary, 1996; Birch and Noll, 2004)] because the analytical technique to measure EC (NIOSH method 5040) was developed only in the mid-1990s (Birch and Cary, 1996). To meet this challenge we measured REC in the study facilities in 1998–2001 and back-extrapolated REC levels to the first year of diesel use in the underground operations using predictive models derived from historical area measurements of carbon monoxide (CO). Historically, CO was one of the most frequently measured DE components in our study facilities and it had fewer non-detectable measurements compared to nitrogen dioxide ( $\text{NO}_2$ ), which was also measured frequently (Stewart *et al.*, 2010; Vermeulen *et al.*, 2010). The fewer number of  $\text{NO}_2$  measurements and the larger percentage with non-detectable values, particularly in three facilities, meant that  $\text{NO}_2$  could not be used to estimate historical exposures for all facilities. Carbon dioxide ( $\text{CO}_2$ ) data were not used due to the limited amount of high-quality data (Vermeulen *et al.*, 2010).

The purpose of this paper is to describe the area measurements collected from underground locations during the monitoring surveys conducted at the study mining facilities and to investigate the interrelationships between REC and CO and other measured components of DE.

## METHODS

Nine underground non-metal mining facilities participated in the monitoring surveys (herein called the DEMS surveys). These included a limestone facility in Missouri (A), three potash facilities in New Mexico (B, C, and D), two rock salt facilities in Ohio and Louisiana (E and F), and three trona (trisodium hydrogen dicarbonate dihydrate) facilities in Wyoming (G, H, and I). Seven of these facilities (the limestone, two potash, the Ohio salt, and the three trona facilities) were included in the epidemiologic study [the eighth facility in the study, a potash facility (J), closed prior to the monitoring surveys]. Measurements from the other two facilities (C and F) are not included in the present report as the facilities were excluded from the epidemiologic study for reasons unrelated to the monitoring. Area measurement data from the surface operations of the facilities are not presented here because they were not used in the modeling of historical underground DE exposures (Coble *et al.*, 2010). Personal measurements of REC, ROC, and  $\text{NO}_x$  are described elsewhere (Coble *et al.*, 2010).

### *Sampling strategy*

We collected underground area samples for four to five consecutive days at each of the facilities in 1998–2001. Sample locations were chosen to reflect the full range of DE concentrations within the underground operations, with emphasis on the potentially higher exposed areas (i.e. the face) to facilitate the estimation of correlations between DE components. Underground areas typically selected were the maintenance shop and office area (10% of all measurements), the haulage and travel ways (20% of all measurements), and the face (70% of all measurements). The shop/office areas were expected to have the lowest DE air concentrations because these areas generally received fresh air directly from the ventilation intake shaft. Despite often high airflow rates to and from the rest of the underground operations, haulage and travel ways typically had higher DE concentrations than the shop and office areas due to more intensive

usage of diesel equipment. Face areas typically had higher DE concentrations than the haulage and travel ways because of the frequent use of heavier diesel equipment and often lower airflow. At the time of the measurement surveys, underground crushers were present at three underground operations: one was located in the exhaust air and the other two were in fresh air.

#### *Sample and analytic methods*

Baskets held area samplers for total, respirable, submicron, and submicron combustible dust; total elemental carbon (TEC), REC, and submicron elemental carbon (SEC); total organic carbon (TOC), respirable organic carbon (ROC), and submicron organic carbon (SOC); and  $\text{NO}_x$  and  $\text{CO}_x$ . Pumps were calibrated prior to sampling, and standard quality control procedures were followed. Samples were collected over the work shift, for a median measurement duration of 372 min. Details of the industrial hygiene methods and the strategy employed in the monitoring survey are in the industrial hygiene operations manual for the study (Stanevich, 1997).

**EC and OC.** TEC and TOC were collected at a flow rate of  $2.0 \text{ l min}^{-1}$  on a single, open-faced quartz membrane filter (NIOSH Analytical Method 0500: Particulates Not Otherwise Regulated, Total) (Schlecht and O'Connor, 2003). REC and ROC were collected using a single 10-mm Dorr-Oliver nylon cyclone (50% cut point of  $3.5 \mu\text{m}$ ) and quartz filter at a flow rate of  $1.7 \text{ l min}^{-1}$  (NIOSH Analytical Method 0600: Particulates Not Otherwise Regulated: Respirable) (Schlecht and O'Connor, 2003). SEC and SOC were collected on a single quartz filter using a four-hole impactor developed by the University of Minnesota (Cantrell and Rubow, 1991). The impactor was designed to collect particles  $<0.8 \mu\text{m}$  in aerodynamic diameter at a flow rate of  $1.7 \text{ l min}^{-1}$ . To prevent overloading of the impactors and cassettes from the expected high concentration of particulates in the mining environment, the flow rate was reduced to  $1.0 \text{ l min}^{-1}$ , thereby increasing the cut point of the aerodynamic diameter of the collected particles to  $1.1 \mu\text{m}$ . For simplicity of presentation, we refer to this dust fraction as 'submicron' even though some of the particulates would be expected to be  $>1 \mu\text{m}$  in aerodynamic diameter. Size-specific (total, respirable, and submicron) EC and OC were analyzed using NIOSH Method 5040 (Schlecht and O'Connor, 2003). Because trona dust was found to interfere with the determination of EC, samples from the trona facilities were first treated with acid. OC measurements from the limestone facility were corrected for the carbonate content of the samples

by:  $\text{OC (in micrograms)} \times ((100 - \% \text{carbonate}) / 100)$  (Birch, 2002).

**Other particulates.** Total dust (TD) was collected using an open-faced polyvinyl chloride (PVC) membrane filter at a flow rate of  $2.0 \text{ l min}^{-1}$  according to NIOSH Analytical Method 0500: Particulates Not Otherwise Regulated, Total (Schlecht and O'Connor, 2003). Respirable dust (RD) was collected using a 10-mm Dorr-Oliver nylon cyclone (50% cut point of  $3.5 \mu\text{m}$ ) and PVC membrane filter at a flow rate of  $1.7 \text{ l min}^{-1}$  (NIOSH Analytical Method 0600: Particulates Not Otherwise Regulated: Respirable) (Schlecht and O'Connor, 2003). Submicron dust (SMD) was collected on a silver membrane filter using a four-hole impactor designed by the University of Minnesota (Cantrell and Rubow, 1991). For the determination of submicrometer combustible dust (SCD), the silver membrane filters were preconditioned by baking in a muffle furnace at  $400^\circ\text{C}$  for 1 h. After the dust samples were collected, the silver membrane filters were weighed to determine the SMD concentrations and then heated again to a temperature of  $400^\circ\text{C}$  for a minimum of 1 h. After baking, the silver membrane filters were re-weighed to determine the SCD concentrations. All particulates were gravimetrically analyzed in an environmentally controlled room on a microbalance with a  $1\text{-}\mu\text{g}$  accuracy. For three facilities the SMD filters were not re-weighed before the SCD analysis and therefore SMD is missing for Facilities D, G, and I.

**CO and  $\text{CO}_2$ .** Draeger long-term colorimetric tubes were used with a pump adjusted to a flow rate of  $0.02 \text{ l min}^{-1}$  to measure CO and  $\text{CO}_2$ . Time-weighted average concentrations in parts per million (ppm) were determined by estimating the length of stain reading on the tubes calibrated in microliters and dividing the stain length by the volume of air drawn through the sampler. In addition, passive samplers were used, but due to the higher limit of detection (LOD) than the active methods, which resulted in an increased number of measurements below the LOD, these data are not included in this report.

**NO and  $\text{NO}_2$ .** Oxides of nitrogen were collected on triethanolamine-treated sorbent tubes (TEA tubes), as described in NIOSH Method 6014 (Schlecht and O'Connor, 2003) at a flow rate of  $0.025 \text{ l min}^{-1}$ . After collection, the solid sorbent was removed from the tubes for spectrophotometric analysis. In addition, passive samplers were used, but due to the higher LOD than the active methods, which resulted in an increased number of measurements below the LOD, these data are not included in this report.

### Statistical analysis

The average of the field blanks from each facility was used to adjust the corresponding sample results. All non-detectable results were imputed based on a maximum likelihood estimation procedure (Lubin *et al.*, 2004). Median analytical LODs were as follows: EC, 1.2 µg; OC, 2.6 µg; nitric oxide (NO), 0.29 µg; NO<sub>2</sub>, 0.50 µg; CO, 0.3 ppm; CO<sub>2</sub>, 250 ppm; TD, 10 µg; RD, 10 µg; SMD, 0.75 µg; and SCD, 0.75 µg.

We used a natural log transformation (Ln) of the measurement data for most summary statistics and in all statistical analyses because the measurement data were approximately log-normally distributed. Standard measures of central tendency (i.e. the arithmetic mean and geometric mean) and of variation [i.e. the range (10th and 90th percentile) and geometric standard deviation (GSD)] were calculated. Between-facility ( $_{\text{bf}}S_y^2$ ) and within-facility ( $_{\text{wf}}S_y^2$ ) components of variance of the logarithms of the measured DE components were estimated by restricted maximum likelihood. To quantify the relationship between the different components of DE, the Spearman ( $r_{\text{sp}}$ ) and Pearson ( $r_{\text{p}}$ ) correlations were calculated between REC and the other DE components.

We also evaluated multivariate relationships among the DE components by conducting a factor analysis. Factor analysis allows the identification of groups of agents that are correlated through a common source (i.e. factor) that cannot be directly observed (Fisher and van Belle, 1993; Vermeulen *et al.*, 2004). The eigenvalues (EVs) extracted from the factor analysis represent the variances of the factors, with the sum of the EVs of all factors totaling the number of original variables (i.e. the agents). Only factors with an EV >1.0 were retained, as these factors explained more variance than contained in an average variable. We applied a Varimax orthogonal rotation. This rotation attempts to find a linear combination of the retained factors, such that each variable loads predominantly on a single factor. The correlation between individual DE components and each retained factor was assessed by factor loadings. SMD was not included in these analyses as this agent was missing for three facilities (D, G, and I).

Although there was good external evidence that a relative change in historical CO concentrations can be directly translated to an identical change in REC (Yanowitz *et al.*, 2000), for a full understanding and evaluation of the methods we investigated the relationship of REC and CO using linear regression of the form:  $E[\text{Ln}(\text{REC})_i] = \alpha + \beta \times \text{Ln}(\text{CO}_i)$ , where  $i$  indexes the measurements and  $E[\text{Ln}(\text{REC})_i]$  is the mean or expected value of  $\text{Ln}(\text{REC})_i$ . We refer to the slope-

parameter  $\beta$  in this model as the 'overall slope'. The implications of this evaluation for historical extrapolation were, however, limited by the cross-sectional nature of the survey data. Mixed-effects models were used to assess the consistency of this relationship across the underground operations of the mining facilities by allowing for facility-specific intercepts and slopes as follows:  $E[\text{Ln}(\text{REC})_{fi}] = \alpha_f + \beta_f \times \text{Ln}(\text{CO}_{fi})$ , where  $f$  indexes the facilities and  $i$  indexes the measurements within facility. Facility-specific intercepts ( $\alpha_f$ ) were modeled as fixed effects, while facility-specific slopes ( $\beta_f$ ) were assumed to follow a normal distribution and were modeled as random effects. This model with fixed facility-specific intercepts was preferred over a model with random effects for both intercepts and slopes as it provided a much better fit to the data (AIC = 516.8 versus 532.5 and 562.6 versus 571.1 for the CO and NO<sub>2</sub> models, respectively). We refer to the mean of the distribution of (random) slopes as the 'mean slope'. Generalized additive models (GAMs) were used to explore possible non-linear relations between REC and CO (Hastie and Tibshirani, 1990). GAMs allow the mean of the dependent variable to depend on a predictor variable through an unspecified smooth function (S):  $E[\text{Ln}(\text{REC})] = S(\text{Ln}(\text{CO}))$ . In practice this function is often estimated using regression or smoothing splines. We used the mgcv package in R (2.9.0) to fit this function using penalized regression splines, allowing the smoothing parameter to be estimated by generalized cross validation.

These regression analyses were also performed to evaluate the REC and NO<sub>2</sub> relationship, as this gaseous component has been used frequently as a surrogate of DE in other studies.

Analyses used SAS® version 9.0 software (SAS Institute, Cary, NC, USA) and R version 2.9.0 (The R foundation for Statistical Computing).

## RESULTS

Table 1 shows summary statistics for the particulate and gaseous underground area air measurements. There were 179 area basket samples, resulting in 2336 observations of the 14 agents. There were generally few missing observations (<5%), except for SMD. For most agents, the percent of measurements less than or equal to LOD was <10%, except for SEC, NO, NO<sub>2</sub>, CO, and SCD.

Levels of REC varied between ( $\text{GSD}_{\text{bf}} = 2.6$ ) and within ( $\text{GSD}_{\text{wf}} = 3.4$ ) underground operations of the facilities (Table 1), with facility-wide geometric averages for REC ranging from 21 µg m<sup>-3</sup> in Facility I to 459 µg m<sup>-3</sup> in Facility A (Table 2). ROC

Table 1. Descriptive statistics of underground area air measurements for DE components in seven non-metal mining facilities

DE component	<i>n</i>	% <LOD	AM	GM	GSD	GSD <sub>bf</sub>	GSD <sub>wf</sub>	10th percentile	90th percentile
EC measurements ( $\mu\text{g m}^{-3}$ )									
TEC	177	9	171	66	5.2	2.7	3.8	5	450
REC	176	7	159	66	4.7	2.6	3.4	8	443
SEC	163	16	115	44	5.2	2.8	3.9	3	281
OC measurements ( $\mu\text{g m}^{-3}$ )									
TOC	177	2	150	125	1.9	1.2	1.9	57	274
ROC	177	2	92	78	1.8	1.3	1.8	38	165
SOC	166	1	109	90	2.0	1.5	1.8	37	187
Gaseous measurements (ppm)									
NO	179	10	1.48	0.67	4.8	2.2	4.0	0.04	3.57
NO <sub>2</sub>	179	41	0.50	0.11	7.5	5.1	3.8	0.01	1.32
CO	171	15	2.87	1.52	3.7	2.0	3.2	0.20	6.23
CO <sub>2</sub>	164	0	794	736	1.5	1.4	1.3	502	1274
Particulate measurements ( $\text{mg m}^{-3}$ )									
TD	178	1	3.37	1.41	3.9	1.4	3.7	0.29	6.58
RD	172	2	0.89	0.47	3.2	1.8	2.8	0.12	2.12
SMD <sup>a</sup>	93	5	0.32	0.18	4.6	2.0	4.2	0.06	0.60
SCD	164	27	0.17	0.04	7.7	2.0	6.9	0.002	0.35

*n* = number of measurements; % <LOD = percentage of measurements below the LOD; AM = arithmetic mean; GM = geometric mean; GSD<sub>bf</sub> = geometric standard deviation of the between-facility distribution of air concentrations; GSD<sub>wf</sub> = geometric standard deviation of the within-facility distribution of air concentrations; 10th percentile = 10th percentile of the exposure distribution; 90th percentile = 90th percentile of the exposure distribution.

<sup>a</sup>For three facilities the SMD filters were not re-weighed before the SCD analysis and therefore SMD is missing for Facilities D, G, and I.

measurements showed less variation both between and within facilities (e.g. GSD<sub>bf</sub> = 1.3 and GSD<sub>wf</sub> = 1.8). The between- and within-facility variances for NO and CO were more similar to those for REC than for ROC; however, CO<sub>2</sub> showed less total variation (GSD = 1.5), while NO<sub>2</sub> showed more variation overall, especially between facilities (GSD = 7.5 and GSD<sub>bf</sub> = 5.1, respectively). Particulate measurements (TD, RD, SMD, and SCD) varied somewhat less between facilities than did the REC measurements. In general, gaseous and particulate concentrations were highest in the limestone facility (A) and lowest in the trona facilities (G–I) (Table 2).

Figure 1 displays scatter plots of the relationship of REC with TEC and with SEC. Ln(REC) and Ln(TEC) were strongly correlated ( $r_p = 0.92$ ). REC and TEC showed strong clustering around the line of identity ( $x = y$ ) (Fig. 1, left panel) and no apparent deviation from this line for the individual facilities (median TEC/REC ratio: 1.01). The correlation between Ln(SEC) and Ln(REC) was similar to that for TEC ( $r_p = 0.94$ ), although SEC measurements were on average lower than the REC measurements (median SEC/REC ratio: 0.77) (Fig. 1, right panel).

Table 3 shows Pearson correlations on the log scale of REC with the other DE components. Spear-

man correlations were similar (data not shown). Correlations of REC with the non-EC agents were weaker than for TEC and SEC but were still high for ROC, NO, CO<sub>2</sub>, SMD, and SCD (range: 0.66–0.79). Moderate to weak correlations were found with the remaining agents (range: 0.22–0.56). Correlations between REC and the other agents tended to be highest in the limestone, potash, and salt facilities (where REC levels were higher) and lowest in the trona facilities (where REC levels were lowest).

Factor analysis using log-transformed concentrations of 132 complete sets of DE component measurements showed that the EC fractions, ROC, the gases, and SCD loaded heavily on the first factor, which we call 'Diesel exhaust' for convenience (Table 4). This is the factor that explained the most of the variance (i.e. 39%). TOC and two dust components (TD and RD) loaded heavily on the second factor, suggesting an additional 'Mine dust' factor that accounted for 21% of the variance. ROC and SOC loaded most heavily on the third factor, suggesting a separate 'Organic carbon' component that accounted for 12% of the variance.

Results of the regression of Ln(REC) on Ln(CO) for all facilities combined are displayed in Fig. 2 (upper left panel). For Ln(CO), the regression model



Table 2. Geometric means, GSDs, and numbers of measurements for underground area air measurements of selected DE components, by mining facility

Mining facility	Type	REC ( $\mu\text{g m}^{-3}$ ) GM (GSD), <i>n</i>	ROC ( $\mu\text{g m}^{-3}$ ) GM (GSD), <i>n</i>	NO (ppm) GM (GSD), <i>n</i>	NO <sub>2</sub> (ppm) GM (GSD), <i>n</i>	CO (ppm) GM (GSD), <i>n</i>	CO <sub>2</sub> (ppm) GM (GSD), <i>n</i>	SCD ( $\text{mg m}^{-3}$ ) GM (GSD), <i>n</i>	TD ( $\text{mg m}^{-3}$ ) GM (GSD), <i>n</i>
A	Limestone	459 (2.12), 26	97 (1.83), 26	1.06 (5.19), 26	0.92 (4.52), 26	2.70 (4.38), 23	1031 (1.30), 26	0.16 (11.03), 22	2.07 (2.71), 26
B	Potash	105 (3.77), 24	83 (1.48), 24	1.48 (2.96), 24	0.26 (1.71), 24	1.83 (2.93), 23	1301 (1.48), 17	0.03 (8.79), 24	1.34 (4.91), 23
D	Potash	55 (3.51), 19	62 (2.03), 20	1.15 (3.85), 20	0.49 (2.02), 20	1.72 (2.34), 20	571 (1.26), 14	0.05 (4.81), 20	0.99 (1.82), 20
E	Salt	76 (3.22), 26	100 (1.95), 26	1.61 (2.90), 26	0.59 (2.31), 26	2.71 (1.73), 26	733 (1.34), 26	0.08 (5.28), 26	1.01 (3.15), 26
G	Trona	30 (2.49), 26	54 (1.28), 26	0.20 (3.23), 26	0.10 (1.05), 26	0.44 (2.12), 23	534 (1.08), 24	0.04 (1.97), 23	2.92 (4.21), 26
H	Trona	48 (5.82), 26	107 (1.63), 26	0.57 (4.98), 27	0.08 (1.54), 27	0.96 (3.81), 26	653 (1.26), 27	0.04 (9.19), 21	1.38 (4.24), 27
I	Trona	21 (3.65), 29	58 (2.07), 29	0.26 (4.37), 30	0.10 (1.44), 30	2.29 (3.13), 30	647 (1.29), 30	0.04 (1.94), 28	0.98 (4.77), 30

GM = geometric mean; *n* = number of measurements; REC = Respirable elemental carbon; ROC = Respirable organic carbon; NO = Nitric oxide; NO<sub>2</sub> = Nitrogen dioxide; CO = Carbon monoxide; CO<sub>2</sub> = Carbon dioxide; SCD = Submicrometer combustible dust; TD = Total dust.

showed a linear association with Ln(REC) with an overall slope estimate of 0.47 [95% confidence intervals (95% CI) 0.31–0.63] (AIC = 586.6). However, there was significant heterogeneity in this relation between facilities (Fig. 2, remaining panels). A mixed-effect model allowing for facility-specific intercepts (as fixed effects) and slopes (as random effects) fitted the data significantly better (AIC = 516.8). In this model, the mean slope for all facilities was 0.58 (95% CI 0.22–0.94) with facility-specific slopes ranging from 0.13 for Facility I to 1.17 for Facility E (Fig. 2).

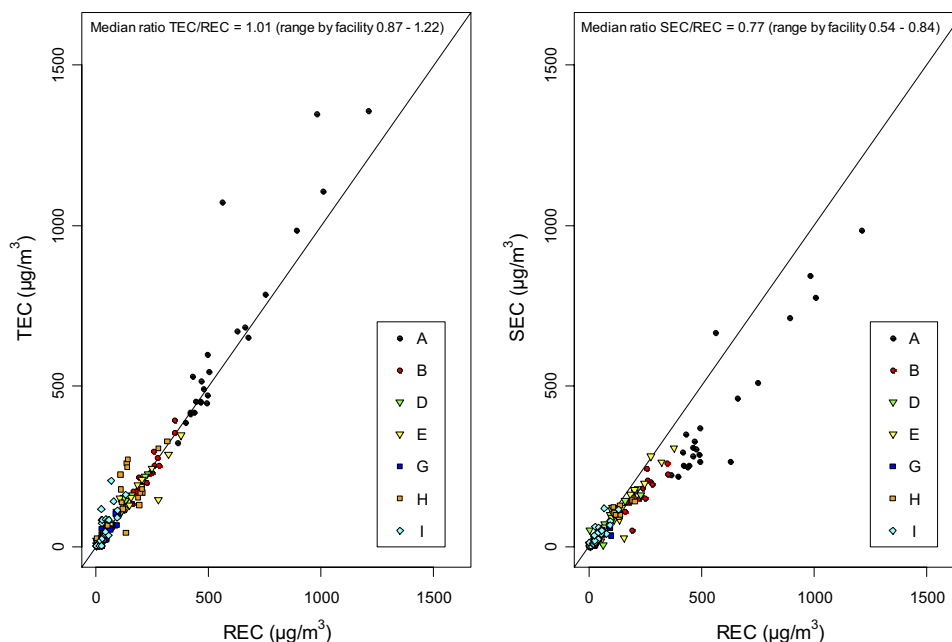
For Ln(NO<sub>2</sub>), the model including data from all facilities showed a linear association with Ln(REC), with an overall slope estimate of 0.40 (95% CI 0.30–0.49) (AIC = 600.6) (Fig. 3). Similarly to CO, a mixed-effect model with a random slope fitted the data significantly better (AIC = 562.6). The mean slope was 0.44 (95% CI 0.13–0.75) and facility-specific slopes ranged from 0.16 for Facility A to 1.04 for Facility E (Fig. 3).

Because REC and CO were associated overall and because CO was the DE component used in the back-extrapolation of REC, we further investigated whether the REC:CO relationship was approximately linear over the full range of measurement concentrations. Non-parametric regression analyses allowing for facility-specific intercepts using GAM showed that the association of REC with CO was essentially linear in log–log space (data not shown).

## DISCUSSION

In the DEMS facility/department/job-specific REC exposure levels in 1998–2001 were estimated from personal REC measurements collected during the same monitoring surveys as the area data described here (Coble *et al.*, 2010). However, almost no historical EC monitoring data were available for these facilities, limiting our ability to estimate historical EC levels directly. Instead, historical estimation of REC for underground jobs relied on back-extrapolation from the 1998–2001 REC exposure estimates to earlier time periods using predictive models based on historical measurements of CO. This evaluation was intended to explore whether this use of CO was appropriate.

Our environmental sampling was designed to include a wide range of DE concentrations both within and across the underground operations to facilitate the examination of relationships between the DE components overall and within facilities. The correlation and factor analysis showed a consistent picture, in that REC, the gases, and SCD were



**Fig. 1.** Scatter plots of REC and TEC (left panel) and of REC and SEC (right panel), by mining facility (A–I = facilities). Solid line depicts the  $x = y$  line.

correlated and loaded predominantly on a single factor. This result supported the assumption that these agents can be considered surrogates of DE. In contrast, the particulates and most OC measurements correlated only moderately with the REC measurements and loaded most heavily on separate factors, indicating probable contributions from non-DE sources within the underground operations, such as mine dust and lubricating oil.

#### EC size fractions

Three EC size components were measured: total, respirable, and submicron. The finding that almost all the EC was in the respirable size fraction ( $\sim 100\%$ ; range: 90–120%) and  $\sim 77\%$  (range 54–84%) of the REC was in the submicron size range is consistent with expectations and with the results from a study of the railroad work environment by Verma *et al.* (2003), who found a slope (or ratio) of 1.19 for TEC versus REC (i.e. TEC/REC ratio:  $\sim 119\%$ ) and of 0.75 for SEC versus REC (SEC/REC ratio:  $\sim 75\%$ ). The similarity of the two ratios from the two studies is striking because the REC concentration levels in the Verma *et al.* (2003) study, which ranged from non-detectable levels to  $\sim 20 \mu\text{g m}^{-3}$  (mean =  $6 \mu\text{g m}^{-3}$ ), were much lower than air concentrations in our study (range: non-detectable to  $452 \mu\text{g m}^{-3}$ ; mean =  $176 \mu\text{g m}^{-3}$ ). Together, the

two studies suggest that the linear relationship between the EC fractions extends over a very broad concentration range and across different environments.

#### OC size fractions

OC correlated only moderately with EC, a finding we found with the personal measurements (Coble *et al.*, 2010). The EC and the associated gases evaluated here in our underground facilities appear to have come almost exclusively from DE, whereas part of the OC in underground mining operations can come from other sources (e.g. pyrolysis products of lubricants and hydraulic oils) (Seshagiri and Burton, 2003; Noll *et al.*, 2007). The factor analyses reflected this differentiation, where agents that are more specific for DE (although measuring different aspects of it) loaded on a single factor while OC loaded most strongly on another factor (except ROC that loaded equally on the ‘Diesel exhaust’ factor and ‘Organic carbon’ factor). This finding supports the use of using EC and the gaseous components, rather than OC, for the retrospective estimation of DE.

#### Particulates

Particulate measurements, especially RD, showed an overall moderate to high correlation with REC. However, the factor analysis indicated that both RD and TD most strongly loaded on a factor other

Table 3. Pearson correlations ( $r_p$ ) between the natural logarithm of underground area air measurement results for REC and other DE components, overall and by mining facility

DE component	$r_p, n$							
	All facilities	Limestone Facility A	Potash Facility B	Facility D	Salt Facility E	Trona Facility G	Facility H	Facility I
EC measurements ( $\mu\text{g m}^{-3}$ )								
REC	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
TEC	0.92, 174	0.98, 26	0.99, 23	0.95, 19	0.94, 26	0.77, 23	0.87, 25	0.83, 29
SEC	0.94, 162	0.97, 24	0.97, 24	0.90, 18	0.93, 25	0.77, 26	0.93, 20	0.90, 28
OC measurements ( $\mu\text{g m}^{-3}$ )								
TOC	0.44, 174	0.73, 26	0.45, 23	0.58, 19	0.87, 26	0.30, 26	0.54, 25	0.67, 29
ROC	0.67, 176	0.79, 26	0.71, 24	0.95, 19	0.95, 26	0.41, 26	0.59, 26	0.59, 29
SOC	0.22, 165	0.84, 24	0.73, 24	0.52, 19	0.92, 26	-0.24, 23	0.53, 20	0.39, 29
Gaseous measurements (ppm)								
NO	0.72, 176	0.41, 26	0.78, 24	0.86, 19	0.96, 26	0.70, 26	0.91, 26	0.61, 29
NO <sub>2</sub>	0.52, 168	0.30, 26	0.50, 24	0.63, 19	0.92, 26	0.01, 26	0.28, 26	0.31, 29
CO	0.41, 168	0.49, 23	0.77, 23	0.62, 19	0.74, 26	0.44, 23	0.40, 25	0.05, 29
CO <sub>2</sub>	0.66, 162	0.70, 26	0.84, 17	0.84, 14	0.89, 26	0.46, 24	0.76, 26	0.24, 29
Particulate measurements ( $\text{mg m}^{-3}$ )								
TD	0.27, 175	0.56, 26	-0.02, 23	0.64, 19	0.68, 26	0.48, 26	0.43, 26	0.39, 29
RD	0.56, 170	0.65, 25	0.28, 24	0.79, 18	0.90, 26	0.51, 25	0.32, 25	0.36, 27
SMD <sup>a</sup>	0.79, 92	0.22, 22	0.53, 24	NA	0.48, 26	NA	0.29, 20	NA
SCD	0.69, 162	0.10, 22	0.85, 24	0.48, 19	0.86, 26	0.49, 23	0.59, 20	0.45, 28

$n$  = number of measurements; NA = not applicable.

<sup>a</sup>For three facilities the SMD filters were not re-weighed before the SCD analysis and therefore SMD is missing for Facilities D, G, and I.

than DE (i.e. 'Mine dust'). This finding was not unexpected because dust is generated during ore mining activities. In some of our study facilities, ore extraction and haulage was done using diesel-powered equipment (Facilities A, B, D, and E), while in others, it was done using electrical powered equipment [Facilities D, G, H, and I (Facility D used both types)], although some diesel equipment was used for auxiliary tasks in all the underground operations (Coble *et al.*, 2010). In the operations using diesel equipment during extraction and haulage, DE, in addition to the generated mine dust, likely contributed to the RD concentrations, whereas the percent contribution of DE to RD concentrations in operations using electrical equipment for ore extraction was likely to be lower. As such, RD loaded on a 'Mine dust' factor but also, to some extent, on the 'Diesel exhaust' factor. Based on these data, RD could not, therefore, be considered a specific surrogate for DE in underground mining operations.

#### Gaseous components

NO, NO<sub>2</sub>, CO, and CO<sub>2</sub> correlated moderately with REC, the strongest correlation being for NO

( $r_p = 0.72$ ), followed by CO<sub>2</sub> ( $r_p = 0.66$ ) and NO<sub>2</sub> ( $r_p = 0.52$ ), and the weakest for CO ( $r_p = 0.41$ ). These findings are quite similar to those of studies reporting correlations for EC and CO<sub>2</sub> of 0.51 (Wheatley and Sadhra, 2004) and for EC and NO<sub>2</sub> of 0.66 (Lewne *et al.*, 2007). Although the correlations between REC and the gases were only moderate, factor analysis showed that all four gases loaded on the same factor as the EC fractions. Interestingly, the loading factors of the individual gases (0.65–0.78) were only marginally to modestly different than those for EC (0.82–0.86). These results strongly suggest that both the EC and the gases were specific surrogates for DE in underground mining in this study. This implication is important because the historical back-extrapolation of EC exposures in our study was based on historically collected CO measurements.

Although there was good external evidence that a relative change in historical CO levels can be directly translated to an identical change in REC (Yanowitz *et al.*, 2000), for a full understanding and evaluation of the methods, we investigated the relationship of REC and CO using both non-parametric and linear regression analyses. The non-parametric regression



Table 4. Results of factor analysis of multiple correlations with Varimax rotation among components of DE (transformed by the natural logarithm)<sup>a,b</sup>

	Factor 1 Diesel exhaust	Factor 2 Mine dust	Factor 3 Organic carbon
EVs (% variance explained)	5.05 (39%)	2.75 (21%)	1.54 (12%)
EC measurements ( $\mu\text{g m}^{-3}$ )			
TEC	<b>0.82</b>	0.45	0.07
REC	<b>0.86</b>	0.40	0.06
SEC	<b>0.84</b>	0.40	0.12
OC measurements ( $\mu\text{g m}^{-3}$ )			
TOC	0.15	<b>0.73</b>	0.42
ROC	<b>0.54</b>	0.26	<b>0.55</b>
SOC	0.13	0.08	<b>0.92</b>
Gaseous measurements (ppm)			
NO	<b>0.78</b>	0.17	0.31
NO <sub>2</sub>	<b>0.75</b>	-0.23	0.15
CO	<b>0.65</b>	-0.19	0.08
CO <sub>2</sub>	<b>0.65</b>	0.21	0.06
Particulate measurements ( $\text{mg m}^{-3}$ )			
TD	-0.02	<b>0.87</b>	0.13
RD	0.36	<b>0.81</b>	-0.08
SCD	<b>0.67</b>	0.26	0.17

Factor loadings >0.5 are displayed in bold ( $n = 132$  sets of measurements).

<sup>a</sup>SMD was not included in this analysis as this agent was missing for three facilities.

<sup>b</sup>Only factors with EVs >1 were extracted.

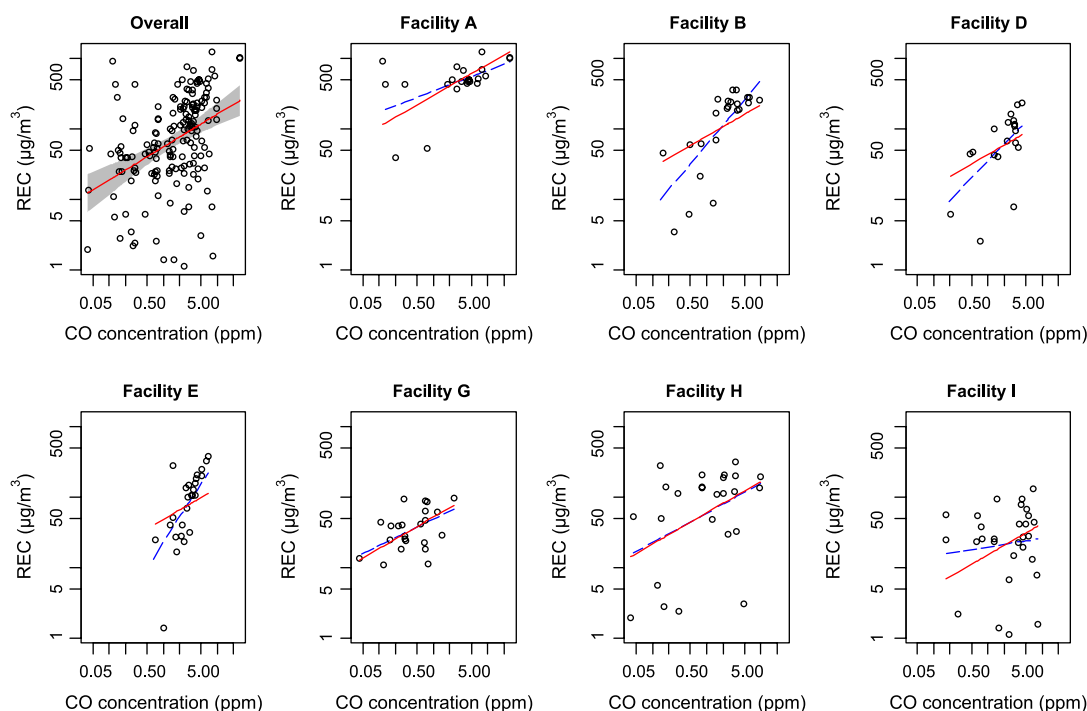
analyses showed that the association of Ln(REC) and Ln(CO) was essentially linear across a wide range of concentrations. The mean slope estimate in a linear mixed-effects model that allowed for fixed facility-specific intercepts and random facility-specific slopes was 0.58 (95% CI 0.22–0.94) for CO (a slope estimate of 1 in a log–log model indicates 1:1 proportionality in natural space). This finding suggests that REC might not increase in a 1:1 proportion with CO across the range of measurement data we observed. For NO<sub>2</sub>, similar observations were found, i.e. considerable heterogeneity in the association with REC by facility. The observed heterogeneity in the association of REC and CO and of REC and NO<sub>2</sub> was likely due to facility- and measurement location-specific circumstances, such as the type and operating conditions of equipment in the vicinity of the measurements, the distance to DE sources (and therefore, aerosol aging), and the effective ventilation. However, this level of detail was not available on an individual measurement level and we therefore were not able to explore this issue further.

#### Exposure assessment ramifications

The goal of the exposure assessment in the DEMS was to estimate DE exposure levels. The approach we took used 1998–2001 REC personal measurements to

estimate 1998–2001 exposure levels (Coble *et al.*, 2010) and back-extrapolating these estimates using predictive models derived from historical area measurements of CO (Vermeulen *et al.*, 2010). This approach was based on several assumptions. First, REC was assumed to be the best analytical surrogate for DE exposure for the study of lung cancer risk. The analyses presented here indicated that REC is highly correlated with TEC and SEC. In addition, there was essentially no difference between the REC and TEC levels, while the SEC levels were ~77% of the REC levels. Thus, there likely would have been little impact on the study if TEC or SEC had been selected as the surrogate for DE instead of REC, although the estimated exposure levels based on SEC would have been lower and therefore any estimate of relative risk, if presented per unit of exposure, would have likely been higher. REC was more specific than OC or particulates because of the likely presence of other sources of these components in underground mining. Thus, the selection of REC appeared to be appropriate.

The second assumption was that CO was related to DE and, therefore, to REC. CO correlated moderately to REC and it loaded most strongly on the factor that included EC. This finding supported our use of the CO



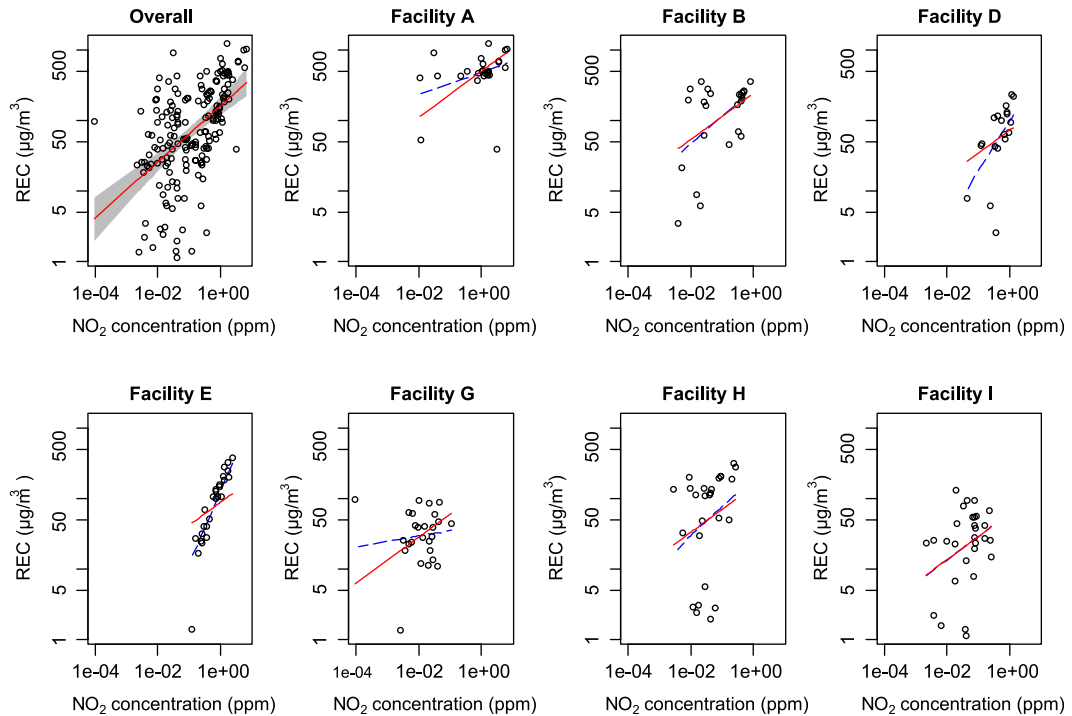
**Fig. 2.** Scatter plots and regression analyses between natural log-transformed (Ln) CO and REC measurements for all mining facilities combined (Overall) and by facility (A-I). Analysis of the data from all facilities is presented in the upper left panel where the solid line depicts the fitted regression line  $\text{Ln}(\text{REC}) = \alpha + \beta \times \text{Ln}(\text{CO})$  and the shaded area, the 95% CI. The facility-specific panels depict two models: one fixed-effects model allowing for facility-specific intercepts and a common slope (solid line) and one mixed-effects model with fixed facility-specific intercepts and facility-specific random slopes (dashed line).

measurements to estimate historical concentrations. Third, we assumed in the historical extrapolation that CO changes over time were directly proportional to temporal changes in REC levels (Vermeulen *et al.*, 2010). We found the association of REC with CO to be linear in log-log space. Further evidence supporting the historical extrapolation approach came from a study indicating that for various diesel engines with model years ranging from 1976 to the 1990s, the emissions of grams of CO per mile and grams of DPM per mile [of which a significant proportion is EC (Ramachandran and Watts, 2003; Noll *et al.*, 2007)] increased at an almost identical rate over time (Yanowitz *et al.*, 2000). This relationship was the basis for the primary models used to develop the estimates for the epidemiologic analysis.

Our own cross-sectional data presented here suggested that CO and REC might not be fully proportional, given that the findings imply a power relationship of 0.58 instead of simple 1:1 proportionality (i.e. a power relationship of 1). Given the cross-sectional nature of these data, the use of 0.58 in describing the historical relationship of REC and

CO over time might not be appropriate (Vermeulen and Kromhout, 2005) because it is likely that the observed coefficient derived from this cross-sectional study might not apply longitudinally to past conditions. Although we used the 1:1 relation in the epidemiologic analysis, to assess the sensitivity of the epidemiologic findings to our decision, we derived and examined an alternative set of estimates using the mean of the (random) facility-specific slopes (0.58) (Stewart *et al.*, 2010; Vermeulen *et al.*, 2010). Thus, using the estimates from the 0.58 parameter model we calculated cumulative exposure levels of all subjects who worked underground and correlated these levels to the cumulative exposure levels derived from the model using the 1:1 proportion for the same subjects. The Pearson correlation was quite high (0.9). It is unlikely, therefore, that using the proportion of 1:1 to develop the time trends, if the power of 0.58 is the true proportion, affected the interpretation of the exposure response relationship. It would, however, affect the risk per unit of exposure.

The results presented in this report indicate that the premise taken in the exposure assessment, i.e.



**Fig. 3.** Scatter plots and regression analyses between natural log-transformed (Ln)  $\text{NO}_2$  and REC measurements for all mining facilities combined (Overall) and by facility (A–I). Analysis of the data from all facilities is presented in the upper left panel where the solid line depicts the fitted regression line  $\text{Ln}(\text{REC}) = \alpha + \beta \times \text{Ln}(\text{NO}_2)$  and the shaded area, the 95% CI. The facility-specific panels depict two models: one fixed-effects model allowing for facility-specific intercepts and a common slope (solid line) and one mixed-effects model with fixed facility-specific intercepts and facility-specific random slopes (dashed line).

that REC and CO can be used to represent DE levels in the epidemiologic study, was generally supported by the quantitative data collected in these monitoring surveys.

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